

## Augmented Lecture, Dr. Andrew Shreve, augmented by Arezou

In general, electric and magnetic fields are vector quantities that have both magnitude and direction. The relations and variations of the electric and magnetic fields, charges, and currents associated with electromagnetic waves are governed by physical laws, which are known as Maxwell's equations. These equations were arrived at mostly through various experiments carried out by different investigators, but they were put in their final form by James Clerk Maxwell, a Scottish physicist and mathematician. These equations can be written either in differential or integral form.

In differential form, Maxwell's equations can be written as:

$$\nabla \cdot E = 0$$

$$\nabla \cdot B = 0$$

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

$$\nabla \times B = \mu_0 \epsilon_0 \frac{\partial E}{\partial t}$$

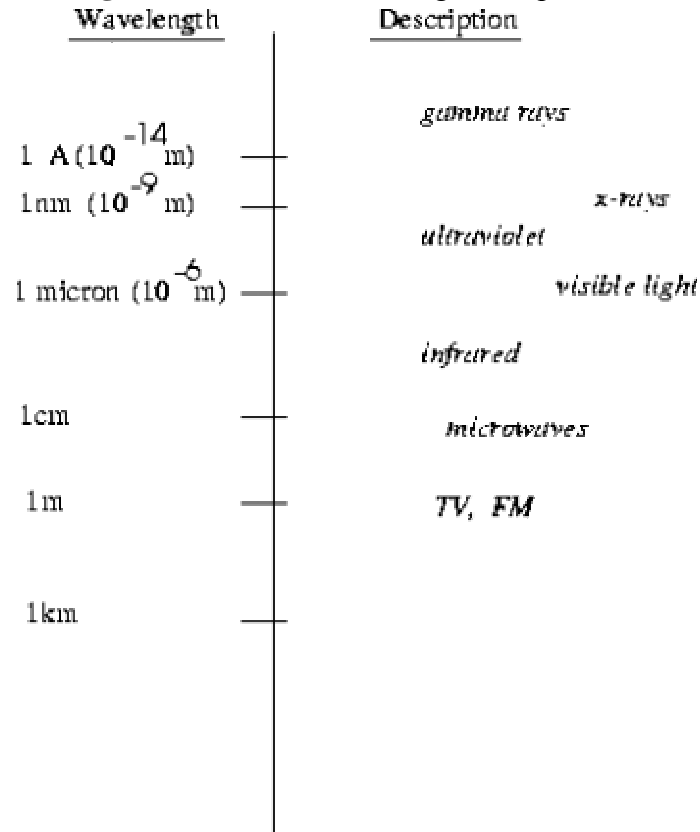
## General Properties of Light

- In vacuum light always travels at the same speed:

$$c = 3.0 \times 10^8 \text{ m/s} .$$

- Until the middle of the 1800's, the generally accepted theory of light was the particle picture. In this viewpoint, advocated by Newton, light was considered to be a stream of tiny particles. However, in the late 1800's, the particle picture was replaced by the wave theory of light. This was because certain phenomena associated with light, namely refraction, diffraction and interference, could only be explained using the wave picture.
- Visible light is just one particular type of electromagnetic radiation. Other types of electromagnetic radiation include radio waves, infrared radiation (heat), ultraviolet radiation, x-rays and  $\gamma$ -rays. The different types of radiation are distinguished by their wavelength, or frequency, as shown in the below figure.

**Figure 22.1:** The Electromagnetic Spectrum



- For example blue light has a wavelength (in vacuum) of  $434 \times 10^{-9} \text{ m} = 434$  nanometers (nm), while red light has a wavelength of 768 nm. Radiation outside the visible spectrum with wavelengths longer than red light is called infrared, while radiation with wavelength shorter than blue is called ultraviolet. The theory which accurately describes the wave-like properties of all types of electromagnetic radiation is called **Maxwell's Theory of Electromagnetism**.
- In the early 20th century, experiments revealed that there were some phenomena associated with light that could only be explained by a particle picture. Thus, light as it is now understood, has attributes of both particles and waves.

## The Curl

The curl of a vector function is the vector product of the del operator with a vector function:

$$\nabla \times \mathbf{E} = \left( \frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} \right) \mathbf{i} + \left( \frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} \right) \mathbf{j} + \left( \frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} \right) \mathbf{k}$$

where  $\mathbf{i}, \mathbf{j}, \mathbf{k}$  are unit vectors in the  $x, y, z$  directions. It can also be expressed in determinant form:

$$\begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ E_x & E_y & E_z \end{vmatrix}$$

## Faraday's Law of Induction

The line integral of the electric field around a closed loop is equal to the negative of the rate of change of the magnetic flux through the area enclosed by the loop.

This line integral is equal to the generated voltage or **emf** in the loop, so Faraday's law is the basis for electric generators. It also forms the basis for inductors and transformers.

Integral Form

$$\oint \vec{\mathbf{E}} \cdot d\vec{\mathbf{s}} = - \frac{d\Phi_{\mathbf{B}}}{dt}$$

Differential Form

$$\nabla \times \mathbf{E} = - \frac{\partial \mathbf{B}}{\partial t}$$

## Ampere's Law

In the case of static electric field, the line integral of the magnetic field around a closed loop is proportional to the electric current flowing through the loop. This is useful for the calculation of magnetic field for simple geometries.

$$k = \frac{1}{4\pi\epsilon_0} \quad c = \frac{1}{\sqrt{\mu_0\epsilon_0}}$$

Integral form

$$\oint \mathbf{B} \cdot d\mathbf{s} = \mu_0 i + \frac{1}{c^2} \frac{\partial}{\partial t} \int \mathbf{E} \cdot d\mathbf{A}$$

Differential form

$$\nabla \times \mathbf{B} = \frac{4\pi k}{c^2} \mathbf{J} + \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t}$$

$$\nabla \times \mathbf{B} = \frac{\mathbf{J}}{\epsilon_0 c^2} + \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t}$$

## The Wave Equation

Maxwell's Equations contain the wave equation for electromagnetic waves. One approach to obtaining the wave equation:

1. Take the curl of Faraday's law:

$$\nabla \times (\nabla \times \mathbf{E}) = -\frac{\partial(\nabla \times \mathbf{B})}{\partial t}$$

2. Substitute Ampere's law for a charge and current-free region:

$$\nabla \times (\nabla \times \mathbf{E}) = -\frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2}$$

This is the three-dimensional wave equation in vector form. It is hard to visualize in this form. It looks more familiar when reduced a plane wave with field in the x-direction only:

$$\frac{\partial^2 E_x}{\partial y^2} + \frac{\partial^2 E_x}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 E_x}{\partial t^2}$$

Since the electric field is in the x-direction only, the propagation is perpendicular to the x-axis and can be in any direction in the yz plane, depending upon the values of the derivatives. This equation is in the general form of the two-dimensional wave equation.

## Interaction of Light with Matter

### Velocity of Light and Refractive Index

The energy of light is related to its frequency and velocity as follows:

$$E = h\nu = hc/\lambda$$

where E = energy

h = Planck's constant,  $6.62517 \times 10^{-27}$  erg·sec

$\nu$  = frequency

C = velocity of light =  $2.99793 \times 10^{10}$  cm/sec

$\lambda$  = wavelength

The velocity of light, C, in a vacuum is  $2.99793 \times 10^{10}$  cm/sec. Light cannot travel faster than this, but if it travels through a substance, its velocity will decrease. Note that from the equation given above-

$$C = \nu\lambda$$

The frequency of vibration,  $\nu$ , remains constant when the light passes through a substance. Thus, if the velocity, C, is reduced on passage through a substance, the wavelength,  $\lambda$ , must also decrease.

We here define *refractive index*, n, of a material or substance as the ratio of the speed of light in a vacuum, C, to the speed of light in a material through which it passes,  $C_m$ .

$$n = C/C_m$$

Note that the value of refractive index will always be greater than 1.0, since  $C_m$  can never be greater than  $C$ . In general,  $C_m$  depends on the density of the material, with  $C_m$  decreasing with increasing density. Thus, higher density materials will have higher refractive indices.

The refractive index of any material depends on the wavelength of light because different wavelengths are interfered with to different extents by the atoms that make up the material. In general refractive index varies linearly with wavelength.

Materials can be divided into 2 classes based on how the velocity of light of a particular wavelength varies in the material.

### **Electron Oscillator Model (Complex Permittivity)**

When bounded electrons or lattice interact with electromagnetic field, they generally oscillate around their equilibrium position. In a quantum mechanical picture, these changes of energy mean that system transits between one energy state to another. Classically, we could approximate the oscillation by a damped oscillator. A damping force exists because various collision processes (electron-electron interaction, electron lattice interaction, etc.) extract energy.

We can write down various force acting on the oscillator as

$$\text{Driving force} = -eE_x = -eE_0 e^{-i\omega t}$$

$$\text{Spring force} = -k_s x$$

$$\text{Damping force} = -\beta v = -\beta x'$$

where  $E_x$  is the local electrical field,  $v$  the oscillator speed, and a negative sign has been added in front of the electron charge.

The Newton's second law gives us

$$m x'' = -\beta x' - k_s x - e E_x$$

Since the electrical field is harmonic,  $E_x = E_0 \exp(-i\omega t)$ , we can rewrite the above equation as

$$x'' + \gamma x' + \omega_0^2 x = -e E_0 e^{-i\omega t} / m$$

where  $\beta = \gamma m$ , and  $k_s = \omega_0^2 m$ .  $\omega_0$  is the natural frequency, and  $\gamma$  is the damping factor. To find the solution, we assume

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

Substituting (1.3) into (1.2), and solve for A, we get

$$A = -\frac{eE_0}{m} \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

and

$$x(t) = \frac{eE_0}{m} \frac{e^{-i\omega t}}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

Recall that  $e x$  is the polarization of one oscillator. The total polarization per unit volume is thus

$$P = N_0 e x = \frac{N_0 e^2 E_0}{m} \frac{e^{-i\omega t}}{\omega_0^2 - \omega^2 - i\gamma\omega} = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \epsilon_0 E$$

Where,

$$\omega_p^2 = \frac{N_0 e^2}{m \epsilon_0}$$

The polarization is related to the electrical field through the electrical permittivity,

$$P = \chi \epsilon_0 E$$

So we have

$$\chi = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

The relative dielectric constant ( $\epsilon = \epsilon_0 \epsilon_r$ ) is:

$$\epsilon_r = 1 + \chi = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} = \epsilon_r' + i\epsilon_r''$$

where the real and the imaginary parts are

$$\epsilon_r = 1 + \frac{\omega_p^2(\omega_o^2 - \omega^2)}{(\omega_o^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

$$\epsilon_i = \frac{\omega_p^2 \gamma \omega}{(\omega_o^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

The complex refractive index is calculated from  $\epsilon_r$  as

$$N = \sqrt{\epsilon_r}$$

or,

$$n^2 - k^2 = \epsilon_r'$$

$$2nk = \epsilon_r''$$

Classically,  $\omega_o$  is the resonance frequency of the simple harmonic oscillator. Quantum mechanically, the  $\omega_o$  is the energy difference between the final and the initial states. If we have multiple oscillator, the Lorentz model can be written as

$$\epsilon_r = 1 + \sum_j \frac{\omega_{pj}^2}{\omega_{oj}^2 - \omega^2 - i\gamma_j \omega}$$

### Drude Model

For metals, there is no spring to connect free electrons to ions, so  $\omega_o=0$ . From the Lorentz model, we get

$$\epsilon_r = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$$

The real and the imaginary parts are

$$\epsilon_r' = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2}$$

and

$$\epsilon_r'' = \frac{\omega_p^2 \gamma}{\omega(\omega^2 + \gamma^2)}$$

These results are called Drude model. Generally,  $\omega_p > \gamma$ . If  $\omega > \omega_p$ , we can see that  $\epsilon_r'' \rightarrow 0$ , which means that  $\kappa \rightarrow 0$ . At high frequency, there is no absorption. A metal becomes transparent! The reason is that at this frequency, the electrons in the metal cannot react fast to the incident electrical field.

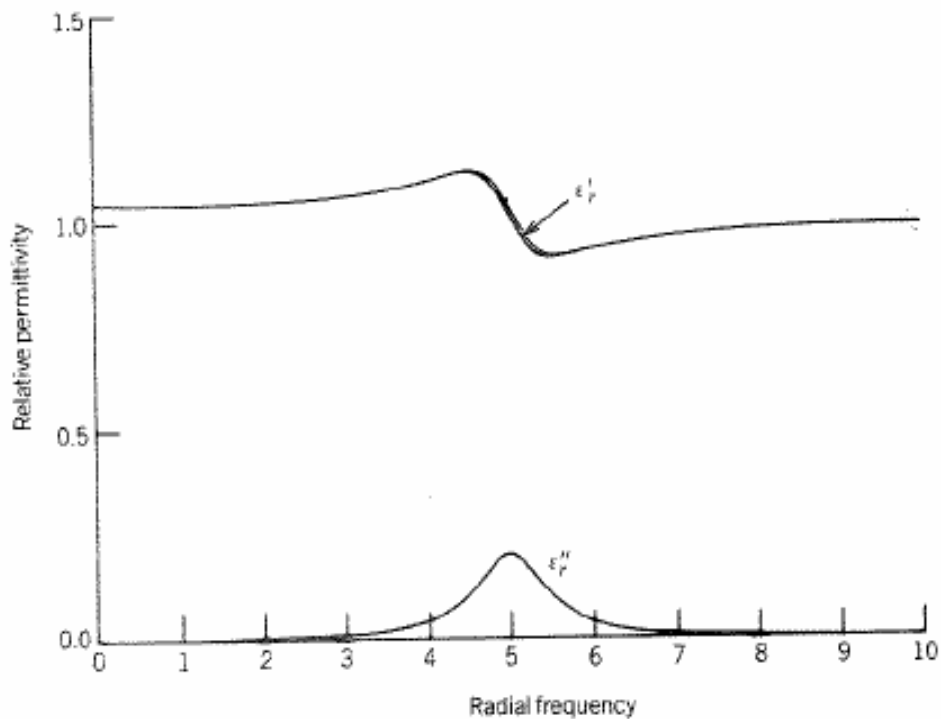
Example: Self-Extinction of a Laser-Induced Plasma

In laser material processing, the ablated and/or evaporated materials are often ionized. An ionized gas is called plasma. If the laser frequency is smaller than the plasma frequency, there will be high reflection of the laser beam and the laser energy cannot reach the target. We always want to operate in the transparent region,

$$\omega > \omega_p = \sqrt{\frac{N_o e^2}{m \epsilon_o}}$$

This leaves an upper limit for the total number of the ionized particles in the plume

$$N_o < \frac{\omega^2 m \epsilon_o}{e^2}$$



$$N_e Q^2 / \epsilon_0 m = 1, d/m = 1, \alpha/\omega_0 = 1/10, \omega_0 = 5.$$

## NUCLEAR MOTION COUPLED TO ELECTRONIC TRANSITION

The following is a presentation of a widely used model for the coupling of nuclear motions to an electronic transition, which has many applications. We will look at the specific example of electronic absorption experiments, which leads to insight into the vibronic structure in absorption spectra. Spectroscopically it is also used to describe wavepacket dynamics; coupling of electronic states to intramolecular vibrations or solvent; coupling of electronic excitation/excitons in solids/semiconductors to phonons. Also, the same type of model can be used to describe fundamental chemical rate processes. We will develop extensions to Förster Theory for electronic energy transfer and Marcus Theory for non-adiabatic electron transfer.

**Two-Electronic Level System: Displaced harmonic oscillators** ( $T=0^\circ$ )

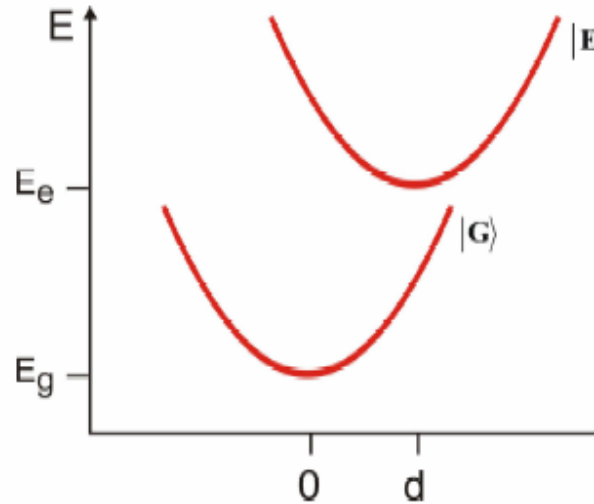
We will calculate the electronic absorption spectrum using T.C.F.

$$H = H_0 + V(t)$$

$$H_0 = |G\rangle H_G \langle G| + |E\rangle H_E \langle E|$$

$$H_G = T(Q) + W_g(Q) + E_g$$

$$H_E = T(Q) + W_e(Q) + E_e$$



$$T(Q): \text{ Nuclear kinetic energy} \longrightarrow p^2 / 2m$$

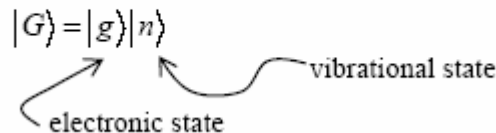
$$W_g(Q) / W_e(Q): \text{ Potential energy} \begin{cases} \longrightarrow \frac{1}{2} m \omega_0^2 Q^2 \\ \longrightarrow \frac{1}{2} m \omega_0^2 (Q-d)^2 \end{cases}$$

$$E_e - E_g: \text{ Electronic energy gap}$$

$$H_E = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 (Q-d)^2 + E_e = H_e + E_e$$

$$H_G = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 Q^2 = H_g + E_g$$

1) **Born-Oppenheimer Approximation**



2) **Condon Approximation**

No  $Q$  dependence to  $\bar{\mu}$  – The dipole operator is an operator only in the electronic states.

$$V(t) = -\bar{\mu} \cdot E(t)$$

$$\bar{\mu} = |g\rangle \mu_{ge} \langle e| + |e\rangle \mu_{eg} \langle g|$$

Now let's calculate an absorption lineshape. Write dipole correlation function:

$$\begin{aligned} \langle \bar{\mu}(t) \bar{\mu}(0) \rangle &= \sum_n p_n \langle n | \bar{\mu}(t) \bar{\mu}(0) | n \rangle \\ &= \langle g, 0 | e^{iH_0 t / \hbar} \bar{\mu} e^{-iH_0 t / \hbar} \bar{\mu} | g, 0 \rangle \quad \text{since at low T all population in } |g, 0\rangle \end{aligned}$$

By substituting

$$e^{-iH_0 t / \hbar} = |G\rangle e^{-i(H_g + E_g)t / \hbar} \langle G| + |E\rangle e^{-i(H_e + E_e)t / \hbar} \langle E|$$

and dipole operator  $\bar{\mu}$  we find:

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 \underbrace{\langle 0 | e^{iH_g t / \hbar} e^{-iH_e t / \hbar} | 0 \rangle}_{F(t)} e^{-i(E_e - E_g)t / \hbar} e^{-i\omega_{eg} t}$$

Note we can write our correlation function as  $C(t) = \sum_n p_n |V_{mn}|^2 e^{-i\omega_{mn}t - g(t)}$  where  $g(t)$  is our lineshape function. Let's concentrate on  $F(t) = \exp(-g(t))$ , sometimes known as the dephasing function:

$$F(t) = \langle 0 | e^{iH_g t / \hbar} e^{-iH_g t / \hbar} | 0 \rangle$$

$$= \langle 0 | U_g^\dagger U_g | 0 \rangle$$

Using the displacement operator:

$$e^{i\alpha p} Q e^{-i\alpha p} = Q + \alpha \hbar$$

$$\therefore H_g = e^{-idp/\hbar} H_g e^{idp/\hbar} \quad \text{and} \quad e^{-iH_g t/\hbar} = e^{-idp/\hbar} e^{-iH_g t/\hbar} e^{idp/\hbar}$$

$$F(t) = \langle 0 | \underbrace{e^{iH_g t/\hbar} e^{-idp/\hbar} e^{-iH_g t/\hbar} e^{idp/\hbar}}_{U_g^\dagger \quad U_g} | 0 \rangle$$

$$= \langle 0 | e^{-idp(t)/\hbar} e^{idp(0)/\hbar} | 0 \rangle \quad \text{since } p(t) = U_g^\dagger p(0) U_g$$

Now,  $H_g = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 Q^2 = \hbar \omega_0 \left( a^\dagger a + \frac{1}{2} \right)$   $a^\dagger a = n$

$$p = \frac{i}{\sqrt{2}} (a^\dagger - a) \sqrt{m\hbar\omega_0} \quad Q = \frac{1}{\sqrt{2}} (a + a^\dagger) \sqrt{\frac{m\omega_0}{\hbar}}$$

Note:  $U_g^\dagger a U_g = e^{in\omega_0 t} a e^{-in\omega_0 t} = a e^{i(n-1)\omega_0 t} e^{-in\omega_0 t} = a e^{-i\omega_0 t}$

$$U_g^\dagger a^\dagger U_g = a^\dagger e^{+i\omega_0 t}$$

So:  $p(t) = i\sqrt{\frac{m\hbar\omega_0}{2}}(a^\dagger e^{i\omega_0 t} - a e^{-i\omega_0 t})$

$$F(t) = \left\langle 0 \left| \exp\left[\tilde{d}(a^\dagger e^{i\omega_0 t} - a e^{-i\omega_0 t})\right] \exp\left[-\tilde{d}(a^\dagger - a)\right] \right| 0 \right\rangle \quad \text{with } \tilde{d} = d\sqrt{\frac{m\omega_0}{2\hbar}}$$

Using the identity  $e^{\lambda+\hat{B}} = e^\lambda e^{\hat{B}} e^{-\frac{1}{2}[\lambda, \hat{B}]}$  with  $[a^\dagger, a] = -1$

$$e^{\lambda a^\dagger + \mu a} = e^{\lambda a^\dagger} e^{\mu a} e^{\frac{1}{2}\lambda\mu}$$

So . . .

$$F(t) = \left\langle 0 \left| \exp\left[\tilde{d} a^\dagger e^{i\omega_0 t}\right] \exp\left[-\tilde{d} a e^{-i\omega_0 t}\right] \exp\left[-\frac{1}{2}\tilde{d}^2\right] \right. \right. \\ \left. \left. \times \exp\left[-\tilde{d} a^\dagger\right] \exp\left[\tilde{d} a\right] \exp\left[-\frac{1}{2}\tilde{d}^2\right] \right| 0 \right\rangle$$

since  $a|0\rangle = 0$ ;  $\langle 0|a^\dagger = 0$

$$F(t) = e^{-\tilde{d}^2} \left\langle 0 \left| \exp\left[-\tilde{d} a e^{-i\omega_0 t}\right] \exp\left[-\tilde{d} a^\dagger\right] \right| 0 \right\rangle$$

Note that the operator defined through expansion! So this is a bit tough to evaluate, as is. To help evaluate, we note that  $e^{-za}|0\rangle = 1$ ;  $\langle 0|e^{za^\dagger} = 1$ . This would make evaluation of expression easier if we exchange order of operators. Since  $e^{\hat{A}}e^{\hat{B}} = e^{\hat{B}}e^{\hat{A}}e^{-[\hat{B},\hat{A}]}$ .

$$F(t) = e^{-\tilde{d}^2} \left\langle 0 \left| \exp\left[-\tilde{d} a^\dagger\right] \exp\left[\tilde{d} a e^{-i\omega_0 t}\right] \exp\left[\tilde{d}^2 e^{-i\omega_0 t}\right] \right| 0 \right\rangle$$

$$= \exp\left[\tilde{d}^2 (e^{-i\omega_0 t} - 1)\right]$$

$$\equiv e^{-g(t)}$$

(where  $g(t) = -\tilde{d}^2 (e^{-i\omega_0 t} - 1)$   
is the lineshape function)

So we have the dipole correlation function:

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 \exp[-i\omega_{eg}t + D(e^{-i\omega_0 t} - 1)]$$

Where  $D = d^2 = \frac{d^2 m \omega_0}{2 \hbar}$  Huang-Rhys parameter

This is a dimensionless factor related to the mean square displacement. It represents the strength of coupling to the nuclear degrees of freedom.

Absorption Lineshape:

$$\begin{aligned} \sigma_{abs}(\omega) &= \int_{-\infty}^{+\infty} dt e^{i\omega t} |\mu_{eg}|^2 \underbrace{e^{-i\omega_{eg}t} \exp[D(e^{-i\omega_0 t} - 1)]}_{\text{expand exponential}} \\ &\quad \downarrow \text{(specifically: expand } e^{[D \exp(-i\omega_0 t)]}) \\ &= |\mu_{eg}|^2 \sum_{j=0}^{\infty} e^{-D} \frac{1}{j!} D^j \delta(\omega - \omega_{eg} - j\omega_0) \end{aligned}$$

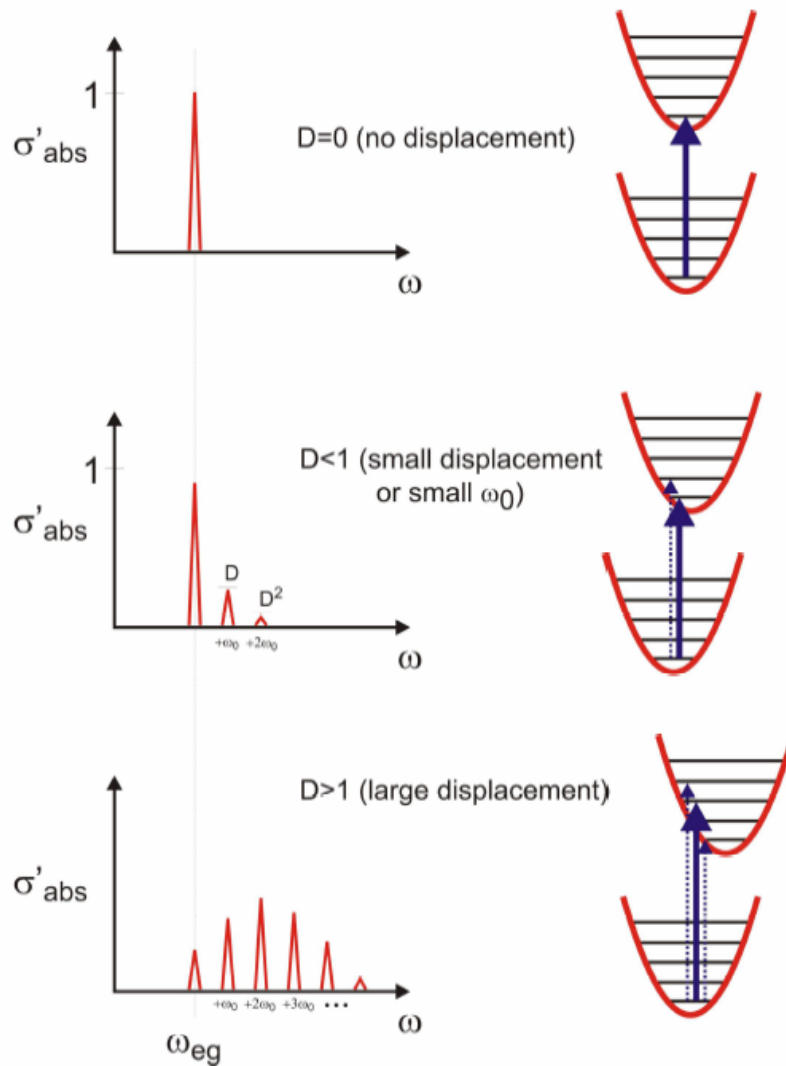
Spectrum is a progression of absorption peaks separated by  $\omega_0$  with a Poisson distribution of intensities  $\rightarrow$  vibrational progression!

The amplitudes are the Franck-Condon coefficients:

$$|\langle 0 | v \rangle|^2 = e^{-D} \frac{1}{v!} D^v$$

The intensities of these peaks are dependent on  $D$ , which is a measure of the coupling strength between nuclear and electronic degrees of freedom.

Let's plot the normalized absorption lineshape  $\sigma'_{abs}(\omega) = \frac{\sigma_{abs}(\omega)}{e^{-D}|\mu_{eg}|^2}$  as a function of  $D$ .



## Franck-Condon Transitions

Note that for  $D < 1$  peak absorption at  $n = 0$ . For  $D \gg 1$  peak at  $n \approx D$ . Note that  $D$  is the number of quanta excited at  $Q = 0 \rightarrow$  Franck-Condon principle. The envelope for these transitions is Gaussian:

Short time expansion:

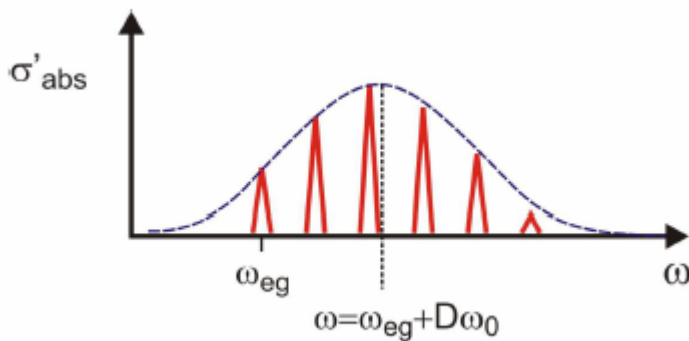
$$t < \frac{1}{\omega_0}$$

$$\begin{aligned} \sigma_{abs}(\omega) &= |\mu_{eg}|^2 \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-i\omega_{eg}t} e^{D(\exp(-i\omega_0 t) - 1)} \\ &\approx |\mu_{eg}|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg})t} e^{D[-i\omega_0 t - \frac{1}{2}\omega_0^2 t^2]} \\ &= |\mu_{eg}|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg} - D\omega_0)t} e^{-\frac{1}{2}\omega_0^2 t^2} \\ &= \sqrt{\pi} |\mu_{eg}|^2 \exp\left[-\frac{(\omega - \omega_{eg} - D\omega_0)^2}{2\omega_0^2}\right] \end{aligned}$$

Here we expand the exponential keeping the first three terms:  $1 - i\omega_0 t - \frac{1}{2}\omega_0^2 t^2$

Solve this by completing the square.

Gaussian profile centered at Franck-Condon vertical transition.

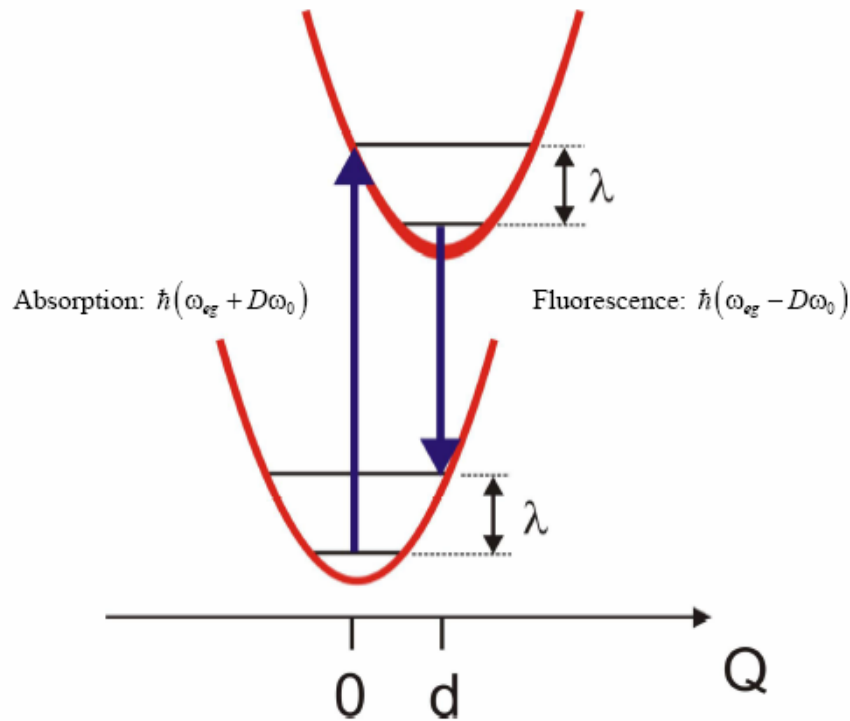


D: mean number of vibrational quanta excited in  $|E\rangle$  on absorption.

**Reorganization Energy**

$$\lambda = D\hbar\omega_0 = \frac{1}{2}m\omega_0^2 d^2 = \text{vibrational energy in } |E\rangle \text{ on excitation at } a = 0$$

$$= \text{vibrational energy in } |G\rangle \text{ at } Q = d$$



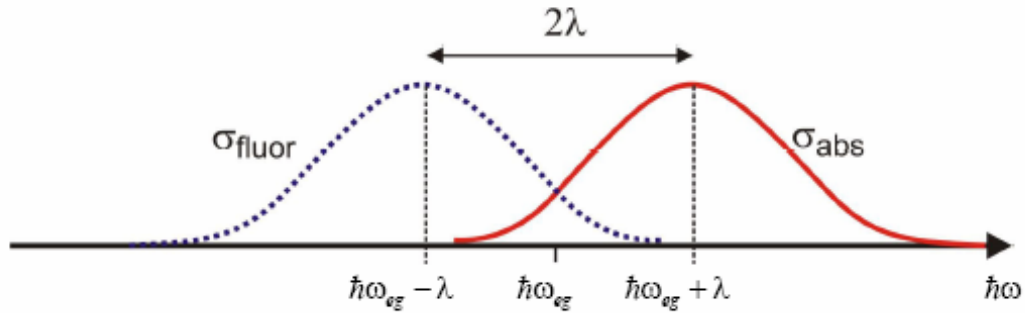
Since vibrational energy on  $|e\rangle$  is dissipated quickly, we expect fluorescence to be red-shifted by  $2\lambda$  and have mirror symmetry:

$$\sigma_{abs}(\omega) = \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg})t - g(t)}$$

$$\sigma_{fluor}(\omega) = \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg} - 2\lambda)t - g^*(t)}$$

$$g(t) = D(e^{-i\omega_0 t} - 1)$$

2λ: Stokes Shift



What if the electronic transition is coupled to many vibrational coordinates with own displacement?

Correlation function is a straightforward extension if the modes are independent. We imagine an electronic transition coupled to a set of normal modes for the molecule or lattice. Then we write

the state of the system as product states, i.e.  $|G\rangle = |g; n_1, n_2, \dots, n_i\rangle$

$$\begin{aligned}
 C_{\mu\mu}(t) &= |\mu_{e\bar{g}}|^2 e^{-i\omega_{e\bar{g}}t} \cdot F_1(t) \cdot F_2(t) \cdots F_N(t) \\
 &= |\mu_{e\bar{g}}|^2 e^{-i\omega_{e\bar{g}}t} \left[ \prod_{i=1}^N \exp\left[ D_i (e^{-i\omega_i t} - 1) \right] \right] \\
 &= |\mu_{e\bar{g}}|^2 e^{-i\omega_{e\bar{g}}t - g(t)} \\
 g(t) &= \sum_i D_i (e^{-i\omega_i t} - 1)
 \end{aligned}$$

## Raman scattering

Raman scattering or the Raman effect is the inelastic scattering of a photon. Inelastic scattering is a kind of scattering that the energy is not conserved so the incoming particle has different energy than the scattered particle.

When light is scattered from an atom or molecule, most photons are elastically scattered (Rayleigh scattering). The scattered photons have the same energy (frequency) and, therefore, wavelength, as the incident photons. However, a small fraction of light (approximately 1 in  $10^7$  photons) is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. In a gas, Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule (see energy level). Chemists are concerned primarily with the vibrational Raman effect. In 1922, Indian physicist Chandrasekhara Venkata Raman published his work on the "Molecular Diffraction of Light," the first of a series of investigations with his collaborators which ultimately led to his discovery on 28 February 1928 of the radiation effect which bears his name. The Raman effect was first reported by C. V. Raman and K. S. Krishnan, and independently by Grigory Landsberg and Leonid Mandelstam in 1928. Raman received the Nobel Prize in 1930 for his work on the scattering of light. In 1998 the Raman Effect was designated a ACS National Historical Chemical Landmark in recognition of its significance as a tool for analyzing the composition of liquids, gases, and solids

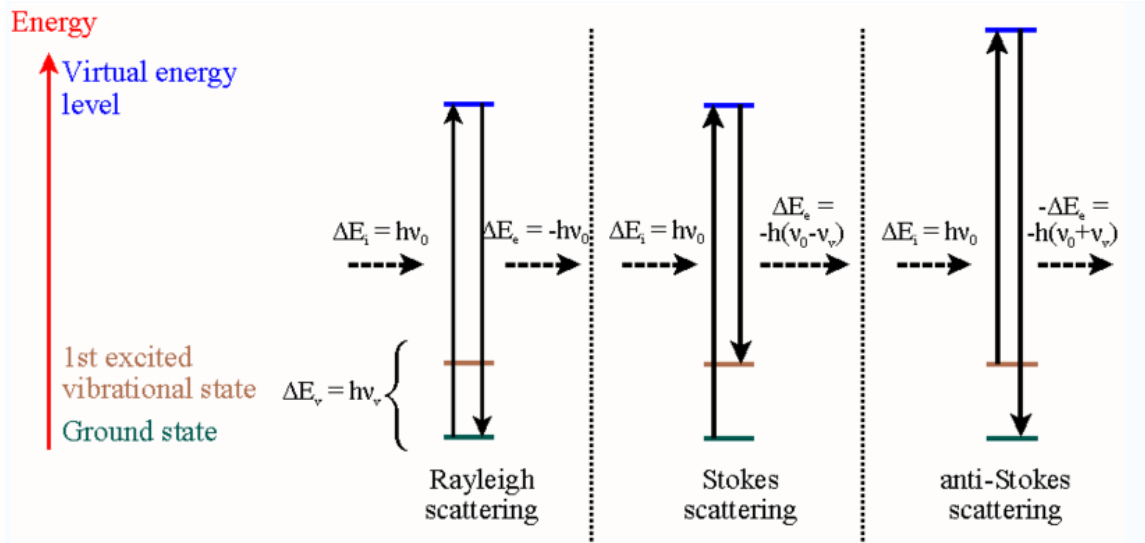
### Raman scattering: Stokes and anti-Stokes

The interaction of light with matter in a linear regime allows the absorption or simultaneous emission of light of energy precisely matching the difference in energy levels of the interacting electrons.

The Raman effect corresponds, in perturbation theory, to the absorption and subsequent emission of a photon via an intermediate electron state, having a virtual energy level

There are three possibilities :

- no energy exchange between the incident photons and the molecules (and hence no Raman effect)
- energy exchanges occur between the incident photons and the molecules. The energy differences are equal to the differences of the vibrational and rotational energy-levels of the molecule. In crystals only specific phonons are allowed (solutions of the wave equations which do not cancel themselves) by the periodic structure, so Raman scattering can only appear at certain frequencies. For amorphous materials like glasses, more phonons are allowed and thereby the discrete spectral lines become broad.
- molecule absorbs energy: Stokes scattering. The resulting photon of lower energy generates a Stokes line on the red side of the incident spectrum.
- molecule loses energy: anti-Stokes scattering. Incident photons are shifted to the blue side of the spectrum, thus generating an anti-Stokes line.



These differences in energy are measured by subtracting the energy of the mono-energetic laser light from the energy of the scattered photons. The absolute value, however, doesn't depend on the process (Stokes or anti-Stokes scattering), because only the energy of the different vibrational levels is of importance. Therefore, the Raman spectrum is symmetric relative to the Rayleigh band. In addition, the intensities of the Raman bands are only dependent on the number of molecules occupying the different vibrational states, when the process began. The Boltzmann distribution teaches us that more molecules occupy the lower energy levels in most cases:

with:

$N_0$ : amount of atoms in the lower vibrational state

$N_1$ : amount of atoms in the higher vibrational state

$g_0$ : degeneration in the lower vibrational state (amount of orbitals of the same energy)

$g_1$ : degeneration in the higher vibrational state (amount of orbitals of the same energy)

$\Delta E_v$ : energy difference between these two vibrational states

$k$ : Boltzmann's constant

$T$ : temperature in kelvins

Thus the Stokes spectrum is more intense than the anti-Stokes spectrum.

## Distinction with fluorescence

The Raman effect differs from the process of fluorescence. For the latter, the incident light is completely absorbed and the system is transferred to an excited state from which it can go to various lower states only after a certain resonance lifetime. The result of both

processes is essentially the same: A photon with the frequency different from that of the incident photon is produced and the molecule is brought to a higher or lower energy level. But the major difference is that the Raman effect can take place for any frequency of the incident light. In contrast to the fluorescence effect, the Raman effect is therefore not a resonant effect.

### **Selection rules**

The distortion of a molecule in an electric field, and therefore the vibrational Raman cross section, is determined by its polarizability.

A Raman transition from one state to another, and therefore a Raman shift, can occur only when the polarizability changes during the process under consideration (that is, during the vibration or rotation). The key quantity is the derivative of the polarizability with respect to the normal mode excited during the transition.

### **Stimulated Raman scattering and Raman amplification**

Raman amplification can be obtained by using Stimulated Raman Scattering (SRS), which actually is a combination between a Raman process with stimulated emission. It is interesting for application in telecommunication fibers to amplify inside the standard material with low noise for the amplification process. However the process requires significant power and thus imposes more stringent limits on the material. The amplification band can be up to 100nm broad, depending on the availability of allowed photon states.

### **Raman spectrum generation**

For high intensity CW (continuous wave) lasers, SRS can be used to produce broad bandwidth spectra. This process can also be seen as a special case of four wave mixing, where the frequencies of the two incident photons are equal and the emitted spectra are found in two bands separated from the incident light by the phonon energies. The initial Raman spectrum is built up with spontaneous emission and is amplified later on. At high pumping levels in long fibers, higher order Raman spectra can be generated by using the Raman spectrum as a new starting point, thereby building a chain of new spectra with decreasing amplitude. The disadvantage of intrinsic noise due to the initial spontaneous process can be overcome by seeding a spectrum at the beginning, or even using a feedback loop like in a resonator to stabilize the process. Since this technology easily fits into the fast evolving fiber optic laser field and there is demand for transversal coherent high intensity light sources (i.e. broadband telecommunication, imaging applications), Raman amplification and spectrum generation might be widely used in the near future.

### **Applications**

Raman spectroscopy employs the Raman effect for materials analysis. The frequency of light scattered from a molecule may be changed based on the structural characteristics of the molecular bonds. A monochromatic light source (laser) is required for illumination, and a spectrogram of the scattered light then shows the deviations caused by state changes in the molecule.

Raman spectroscopy is also used in combustion diagnostics. Being a completely non-intrusive technique, it permits the detection of the major species and temperature distribution inside combustors and in flames without any perturbation of the (mainly fluid dynamic and reactive) processes examined.

Stimulated Raman transitions are also widely used for manipulating a trapped ion's energy levels, and thus basis qubit states, in ion trap quantum computing.





