Advanced Measurement Techniques in Fluid Mechanics and Heat Transfer

Prof. Saptarshi Basu
Department of Mechanical Engineering
Indian Institute of Science, Bengaluru

Week – 11

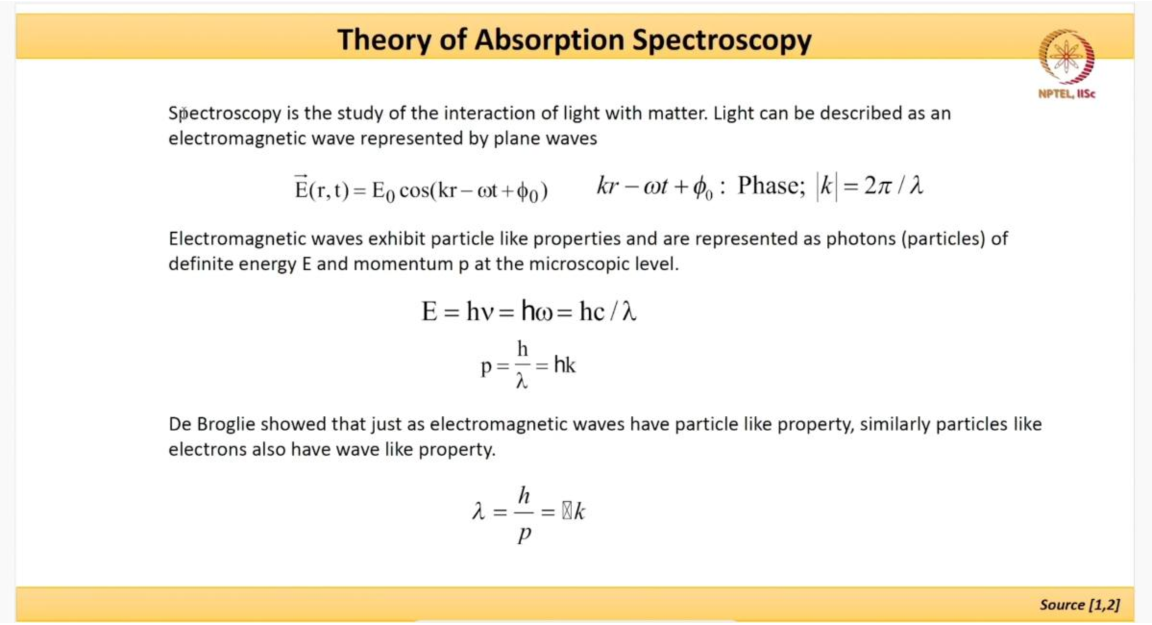
Lecture - 53

Tunable Diode Laser Absorption Spectroscopy – 1

About absorption spectroscopy, and then we will go on to infrared thermography, as we will see in due course that absorption spectroscopy is routinely used for the measurement of species concentrations and in different applications. Now, these applications can be very varied; they can be, for example, explosive detection in airports. To all the way up to water vapor concentration detection in the many channels of fuel cells, both of these things can be measured by absorption spectroscopy. Infrared thermography has a special connotation; it is usually used for the measurement of temperature. So this is very useful if you can understand what night vision goggles, etc., are.

So infrared thermography basically falls into that particular category. So in the next few lectures, we are going to cover infrared thermography and absorption spectroscopy in detail. Yeah, so let's move on and see. What we can decipher from these exercises is unclear.

So if you look at the main screen over here, you would see that this is the theory of absorption spectroscopy. Now, the theory of absorption spectroscopy is basically the interaction of light with matter, so light is basically an electromagnetic wave, which is represented by plane waves that you can see over here. So this is the electromagnetic field. Uh, okay, and this is basically the frequency and the phase. And the phase is given by that.



Theory of Absorption Spectroscopy

Spectroscopy is the study of the interaction of light with matter. Light can be described as an electromagnetic wave represented by plane waves

$$\vec{E}(r,t) = E_0 \cos(kr - \omega t + \phi_0) \qquad kr - \omega t + \phi_0 : \text{ Phase; } |k| = 2\pi / \lambda$$

Electromagnetic waves exhibit particle like properties and are represented as photons (particles) of definite energy E and momentum p at the microscopic level.

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

$$p = \frac{h}{\lambda} = hk$$

De Broglie showed that just as electromagnetic waves have particle like property, similarly particles like electrons also have wave like property.

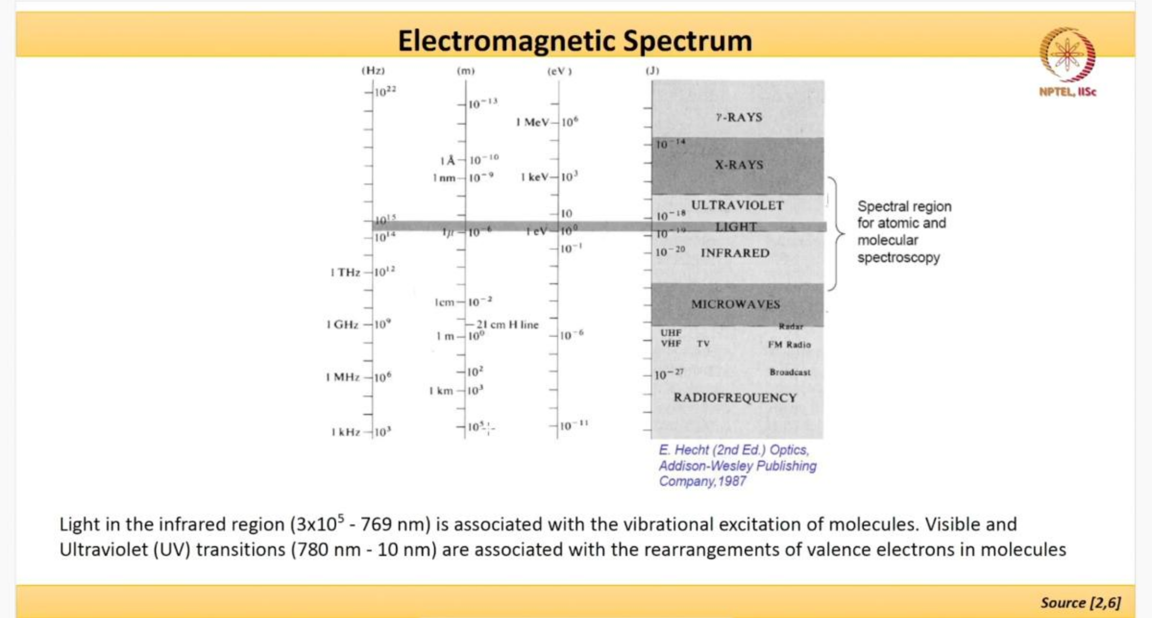
$$\lambda = \frac{h}{p} = \hbar k$$

Source [1,2]

And so when light interacts with matter, something happens, and we will see what that something is and how it can be used as a measurement principle. So electromagnetic waves exhibit particle-like properties and are represented as photons or particles of definite energy E and momentum P. at the microscopic level. So if E is the energy, it is given as $h\nu$, where $h\nu$ is written as $h\omega$, $h\omega$ is again written as hc/λ , where p is basically h/λ. So, in other words, h is nothing but Planck's constant, and this is the frequency.

Okay, so the frequency is represented in terms of the velocity of the speed of light divided by the λ, which is the wavelength. This is what the energy of the particles is. Now de Broglie showed that just as electromagnetic waves have particle-like properties, particles like electrons also have wave-like properties. And this is given as λ=h/p. So it's the other way around.

So the wavelength that is associated with the electrons is given by h over p. So, this is a very crude idea of quantum mechanics before we go on to see the theory of absorption. So, as you know, the electromagnetic spectrum is quite huge. If you look at this particular scale over here, you can see that these are the corresponding frequencies, these are the electron volts, this is the energy, and this is the wavelength. So if you go to, you know, very large wavelengths, which are basically 10^5, you know, you are going to go into the radio frequency regime.



Electromagnetic Spectrum

E. Hecht (2nd Ed.) Optics, Addison-Wesley Publishing Company, 1987

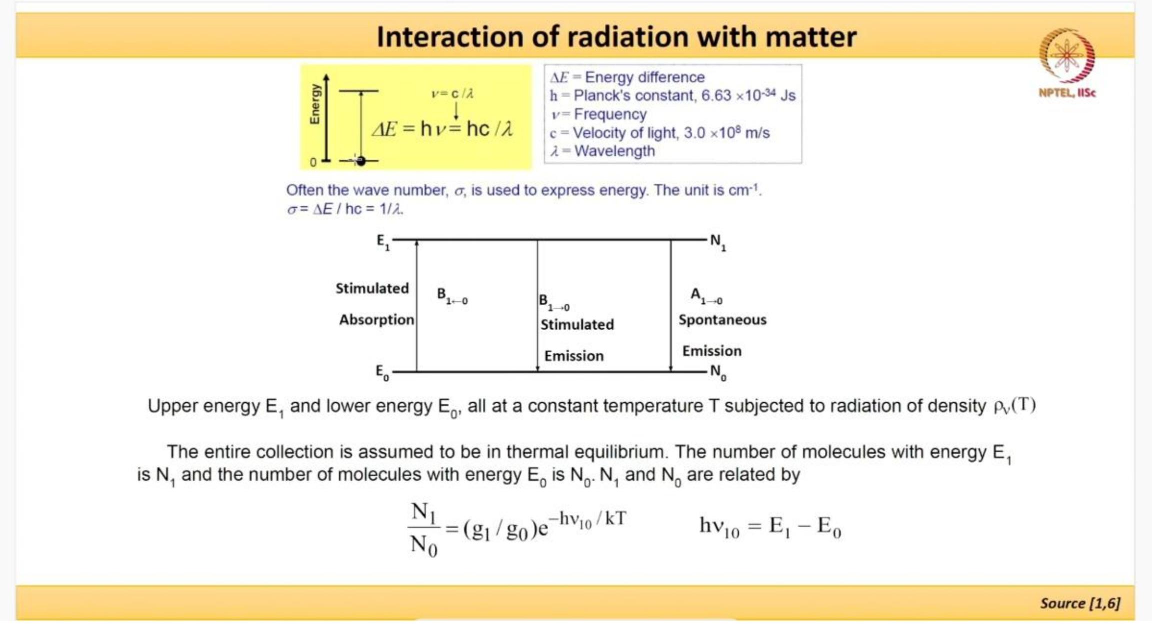
Light in the infrared region ($3x10^5$ - 769 nm) is associated with the vibrational excitation of molecules. Visible and Ultraviolet (UV) transitions (780 nm - 10 nm) are associated with the rearrangements of valence electrons in molecules

Source [2,6]

It is in the radio frequency regime where you broadcast your FM channels; if you go to a little bit lower in the wavelength domain, you reach the microwaves, and then you slowly traverse the infrared. This infrared is particularly important because our infrared thermography will also work in this particular range. Then this small band that you see over here, which is named light, is basically the area of visible light, what we can see in our day-to-day life. And then, of course, you all have heard the name of UV and how it is bad for the screen as well as for the environment. So this lies right here.

And beyond that lies the X-ray, with a very small wavelength. Now, X-rays are particularly important because they can pass through your body but not through your bones and such. So this is routinely used as a diagnostic tool in many applications, including scientific applications apart from the human body. Then you go to the gamma rays, which have very small wavelengths, so this is the spectrum we mostly work in: the UV, the visible light, and the infrared range. Sometimes people go a little bit into the microwave and sometimes a little bit into the X-rays, so this is routinely done.

You know, this is what the entire spectrum actually looks like. Okay, so the visible and ultraviolet light involves transitions that are associated with the rearrangement of the valence electrons in the molecules. And the light in the infrared region, which is this particular region, is associated with vibrational excitation of the molecules. So we'll see a little bit what those things mean in a little bit. So how does light actually interact with matter or how does radiation interact with matter? So if you look at, you know, this particular picture very carefully, this is called Einstein's two-level diagram.



Interaction of radiation with matter

NPTEL, IISc

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

ΔE = Energy difference
h = Planck's constant, 6.63×10^{-34} Js
ν = Frequency
c = Velocity of light, 3.0×10^{8} m/s
λ = Wavelength

Often the wave number, σ, is used to express energy. The unit is cm^{-1}.
$\sigma = \Delta E / hc = 1/\lambda$.

Upper energy E_1 and lower energy E_0, all at a constant temperature T subjected to radiation of density $\rho_V(T)$

The entire collection is assumed to be in thermal equilibrium. The number of molecules with energy E_1 is N_1 and the number of molecules with energy E_0 is N_0. N_1 and N_0 are related by

$$\frac{N_1}{N_0} = (g_1/g_0)e^{-h\nu_{10}/kT} \qquad h\nu_{10} = E_1 - E_0$$

Source [1,6]

What you see over here is that there is an energy level which has got E naught, and then there is an energy level E1. Okay, these are the two levels, and they have a population of n1 and n naught number of particles now. As we know, in order to have a migration of a particle from one energy level to another, you need something like a Δ E, which is given as $h\nu$, which is hc/λ, where ΔE is the energy difference, h is Planck's constant, ν is the frequency, c is the velocity of light, and λ is the wavelength. So this is also expressed as wave number, which is basically one over λ, and the unit is centimeter inverse. This is just convention; nothing more than that.

So the upper energy level E1 and the lower energy level E0 are at a constant temperature T, subject to our radiation of density rho V. So they are at a constant temperature and are subjected to a radiation density of rho V. Radiation means a flux of photons is basically impinging on this particular system, whatever the system may be. It is made of a particular material, for example. Now, if you look at these lines over here, there are three processes that are readily possible.

One is called stimulated absorption, in which what happens is that if there is a photon and this particle actually absorbs that particular photon, it migrates to the next higher level. All right, now these photons might also... Know that knocking off some particles at the higher energy level might cause them to move to the lower energy level, which is called stimulated emission, and if it happens spontaneously, the photons associated with the particles at the higher energy level migrate to the lower energy level, which is called spontaneous emission.

Each has a factor associated with it. Okay, B1 0 to 1, B1 to 0, and A1 to 0. So this basically indicates that the arrows designate the direction in which the particles move. So before we go to that, the entire collection is assumed to be in thermal equilibrium. Initially, the number of molecules with energy E1 is N1, and the number of molecules with energy E0 is N0.

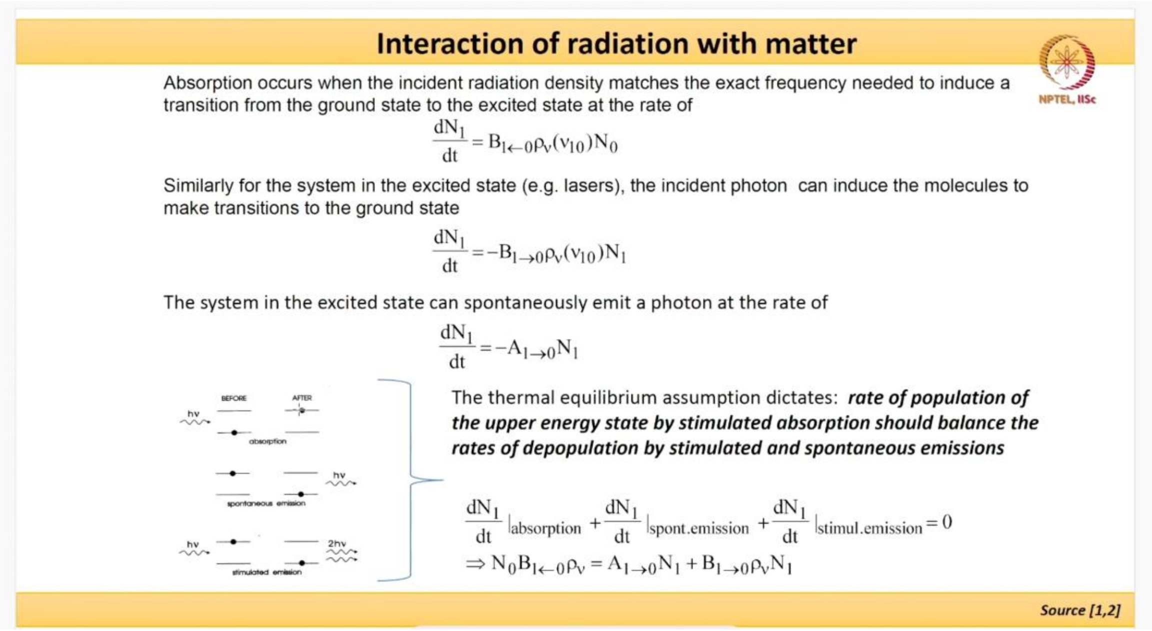
And n1 and n0 are related by this particular expression, where $h\nu$ 1 0 is basically the difference in energy levels between the two. So what it says is that g1 and g0 are basically the degeneracies associated with each particular energy level. Degeneracies essentially mean the number of energy states that are associated with a particular energy level, right? So, this is in thermal equilibrium. This particular distribution is the one that is F3. So when the interaction happens, you can see that whatever I said earlier is explained by this particular diagram.

So you see that an $h\nu$ photon comes in. It knocks a particle. This is before. This is after. So the particle absorbs energy and moves to a higher state.

Then the photon hits, and you know the particle; you know, if it is a spontaneous emission, that the particle migrates spontaneously and releases a photon in the process. If the photon goes and hits the particle and knocks it to a lower level, you basically get two H nu particles. That means two photons are basically emitted. So this is stimulated emission. This is spontaneous emission.

This is absorption. So absorption absorbs light. So there was a photon that was coming in. It is no longer there because it is utilized in migrating or in providing the energy to migrate the particle from the lower energy level to the higher energy level. In spontaneous emission, of course, this is spontaneous migration. So these particles are always in the excited state.

So they came down. To the ground state, and in the process, this process of, you know, going to a lower energy level releases a photon or releases energy, and this is what you get. When you actually have a photon that knocks off a particular particle from the higher energy level to the lower energy level, basically, you have two photons that come out in the process. So stimulated emission gives out two photons, whereas spontaneous emission gives out one photon. All right. So absorption occurs when the incident intensity and incident radiation density match the exact frequency that is needed to make this transition from the ground state to the excited state.



Interaction of radiation with matter

Absorption occurs when the incident radiation density matches the exact frequency needed to induce a transition from the ground state to the excited state at the rate of

$$\frac{dN_1}{dt} = B_{1\leftarrow 0}\rho_\nu(\nu_{10})N_0$$

Similarly for the system in the excited state (e.g. lasers), the incident photon can induce the molecules to make transitions to the ground state

$$\frac{dN_1}{dt} = -B_{1\rightarrow 0}\rho_\nu(\nu_{10})N_1$$

The system in the excited state can spontaneously emit a photon at the rate of

$$\frac{dN_1}{dt} = -A_{1\rightarrow 0}N_1$$

The thermal equilibrium assumption dictates: ***rate of population of the upper energy state by stimulated absorption should balance the rates of depopulation by stimulated and spontaneous emissions***

$$\frac{dN_1}{dt}\Big|_{\text{absorption}} + \frac{dN_1}{dt}\Big|_{\text{spont.emission}} + \frac{dN_1}{dt}\Big|_{\text{stimul.emission}} = 0$$

$$\Rightarrow N_0 B_{1\leftarrow 0}\rho_\nu = A_{1\rightarrow 0}N_1 + B_{1\rightarrow 0}\rho_\nu N_1$$

Source [1,2]

As we know in quantum mechanics, any type of energy, or even a lower frequency, will not do anything if you supply a ton of photons. It's not going to lead to a change in energy state. What happens exactly if this frequency is tuned exactly, with the energy that is needed for the transition? Then you have a change given by this, which is the number of changes, because this is absorption, and the particle from n naught, or basically e naught, is going to e1, so tn1 by dt is given by the. The absorption coefficient is basically okay, which is like stimulated absorption, and this is the radiation density, and this is the number of particles in a lower energy state. Similarly, for a system in the excited state, exactly what happens in lasers is that the incident photon can induce molecules to transition to the lower state or states, the ground state.

In that particular case, you get a minus over here, and then you get a depletion of the number of particles in the higher energy state, and this is given by this. The n1 is the initial number density at any particular time instant. So the system in the excited state can now spontaneously emit a photon, and this is given as a spontaneous emission coefficient, which is multiplied by N1. So if a system is in thermal equilibrium, it states that the rate of population of the upper energy state by stimulated absorption should balance the rates of depopulation by stimulated and spontaneous processes. So there is a rate of population increase due to the stimulated absorption, and this should match exactly whatever is taken out of that particular energy level.

by the stimulated and the spontaneous. So in other words, the sum total of all these rates should be equal to zero. Or, in other words, this is the equation because if you just substitute these numbers here now, this is what you are going to get. That

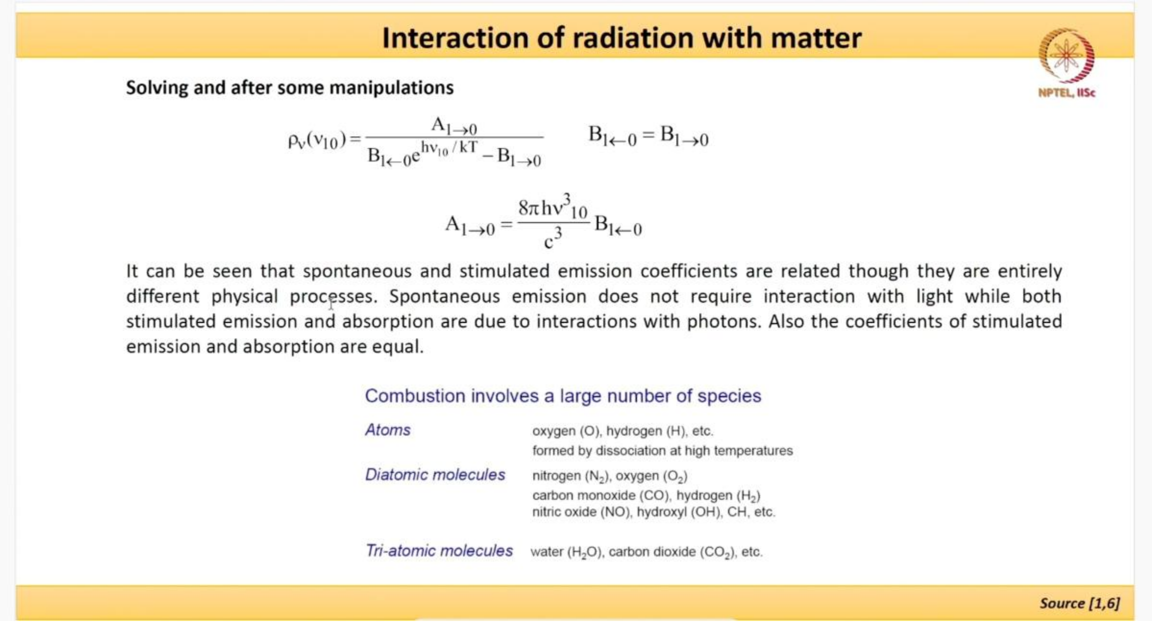
$N_0B_1\rho V_{a10}N_1 + B_1C_0\rho VN_1$. So this is what you get in the process.

Okay, so after some manipulations—I'm not going to go into the details—and assuming that stimulated absorption and stimulated emission have the same b's, you get that the radiation density required is given by something like this. That the spontaneous emission is related to the stimulated emission by this particular expression. So we can see that the spontaneous and stimulated emission coefficients are related, though they are entirely different physical processes. They are not the same process. So spontaneous emission does not require interaction with light.

It actually gives off light, while both stimulated emission and absorption are due to interaction with photons. Also, the coefficients of stimulated emission and absorption are equal, which is what we get here, right? So, typically, you see if combustion—if you do this kind of measurement, as you can see—one can, for example, in a combusting system, combustion being one example of a system, measure here atoms like hydrogen and oxygen. At high temperatures, you have diatomic molecules like nitrogen, oxygen, carbon monoxide, hydrogen, nitric oxide, and hydroxyl radicals; then we have triatomic molecules like water and carbon dioxide, etc. In an interacting box, you have so many species that one needs to consider when doing this kind of analysis. This kind of analysis, to cut a long story short, basically shows the key relationships that you see here, and this is what we are going to move forward with.

Now, a little bit of a primer on quantum mechanics: the interaction of electromagnetic radiation with matter is governed by the time-independent Schrödinger equation, which is given as this. The first equation that you see shows the molecules as a conglomeration of nuclei and electrons at different positions, Ri, and with charges Qi. This is obvious because the electrons are all at different spatial locations, and the vectors that separate them are basically Ri and charges Qi. The system, due to this charge distribution, may have what we call a net dipole moment, provided that the random distribution is coupled with the molecular structure and does not cancel out. So sometimes this might cancel out, especially with homonuclear diatomics.

This might actually cancel out. But in other words, we are going to get three dipole moments, μx, μy, and μz, and they are given by the separation distance, ξ, the sum total of all the separation distances multiplied by the individual charges, and the summation of them in a particular direction. So this is in a particular direction; this is in the y direction, and this is the z direction. Okay. So now, once this is done, the interaction of radiation with matter, which is given by a time-dependent Hamiltonian perturbation, is given by this.



Interaction of radiation with matter

NPTEL, IISc

Solving and after some manipulations

$$\rho_V(\nu_{10}) = \frac{A_{1\rightarrow 0}}{B_{1\leftarrow 0}e^{h\nu_{10}/kT} - B_{1\rightarrow 0}} \qquad B_{1\leftarrow 0} = B_{1\rightarrow 0}$$

$$A_{1\rightarrow 0} = \frac{8\pi h\nu^3_{10}}{c^3} B_{1\leftarrow 0}$$

It can be seen that spontaneous and stimulated emission coefficients are related though they are entirely different physical processes. Spontaneous emission does not require interaction with light while both stimulated emission and absorption are due to interactions with photons. Also the coefficients of stimulated emission and absorption are equal.

Combustion involves a large number of species

Atoms	oxygen (O), hydrogen (H), etc. formed by dissociation at high temperatures
Diatomic molecules	nitrogen (N_2), oxygen (O_2) carbon monoxide (CO), hydrogen (H_2) nitric oxide (NO), hydroxyl (OH), CH, etc.
Tri-atomic molecules	water (H_2O), carbon dioxide (CO_2), etc.

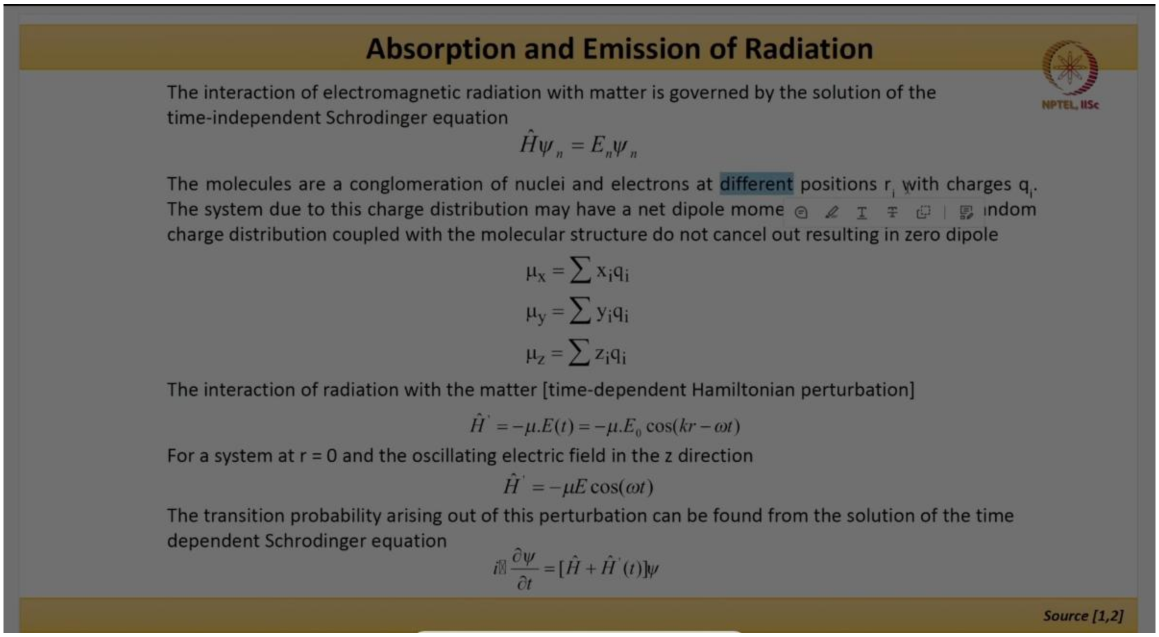
Source [1,6]

For a system at r equal to zero, the oscillating electric field in the z direction becomes, $\mu e^{\cos(\omega t)}$." Therefore, the transition probability arising from this perturbation can be found from the solution of the time-dependent Schrödinger's equation, which is given as this. There is an H hat over here that is not readable, but this is what it is. So, this is the transition probability. Why are these important? Because it tells you the probability of the transitions of these particles.

So now, what happens here is that the system is subjected to no radiation; that is, the perturbation Hamiltonian is absent. Then the two time-dependent solutions become like this. Okay, this is ψ_0 and ψ_1 , you see? For a perturbed wave function, it is given by the linear combination of two wave functions. These are time-dependent coefficients. Okay, and the total solution becomes something like this.

Right. So manipulating and integrating it over the entire space gives rise to two coupled differential equations. All right. So these are not necessarily the most important learnings coming out of this particular course, you know. But I mean, these are just for completeness. OK, so, you know, to cut a very long story short, that's because the symbols are coming out a little off.

So what we show over here is that these were the constants that you did not see because of some software problem. So, this is $\overline{H}$, okay? So this is the transition probability, if we remember. And these were the two solutions, okay? Two time-dependent solutions exist. One was ψ_0, and one was ψ_1, as you can see over here. For a perturbed system, the wave function is given by a linear combination of these two wave functions.



Absorption and Emission of Radiation

The interaction of electromagnetic radiation with matter is governed by the solution of the time-independent Schrodinger equation

$$\hat{H}\psi_n = E_n\psi_n$$

The molecules are a conglomeration of nuclei and electrons at different positions r_i with charges q_i. The system due to this charge distribution may have a net dipole mome ndom charge distribution coupled with the molecular structure do not cancel out resulting in zero dipole

$$\mu_x = \sum x_i q_i$$

$$\mu_y = \sum y_i q_i$$

$$\mu_z = \sum z_i q_i$$

The interaction of radiation with the matter [time-dependent Hamiltonian perturbation]

$$\hat{H}' = -\mu.E(t) = -\mu.E_0 \cos(kr - \omega t)$$

For a system at r = 0 and the oscillating electric field in the z direction

$$\hat{H}' = -\mu E \cos(\omega t)$$

The transition probability arising out of this perturbation can be found from the solution of the time dependent Schrodinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = [\hat{H} + \hat{H}'(t)]\psi$$

Source [1,2]

These are the time-dependent coefficients. And the total solution, therefore, becomes this, all right? And this is manipulating, and when you integrate it over the entire space, it leads to two coupled differential equations. Okay, and the integrals are odd functions, so these are kind of, you know, more of quantum mechanics, so to say. So when we simplify the results, this is given in these two forms, where m01 is called the transition dipole moment, and it plays a pivotal role. So m_{01}=m_{01}, and it is given by this expression. Okay, and this ωr that you see over here, which is the transition dipole moment divided by $\overline{H}$, is called the Rabi frequency, and the time-dependent coefficients are given by $\dot{a}_0$ and $\dot{a}_1$ and these are given by these two.

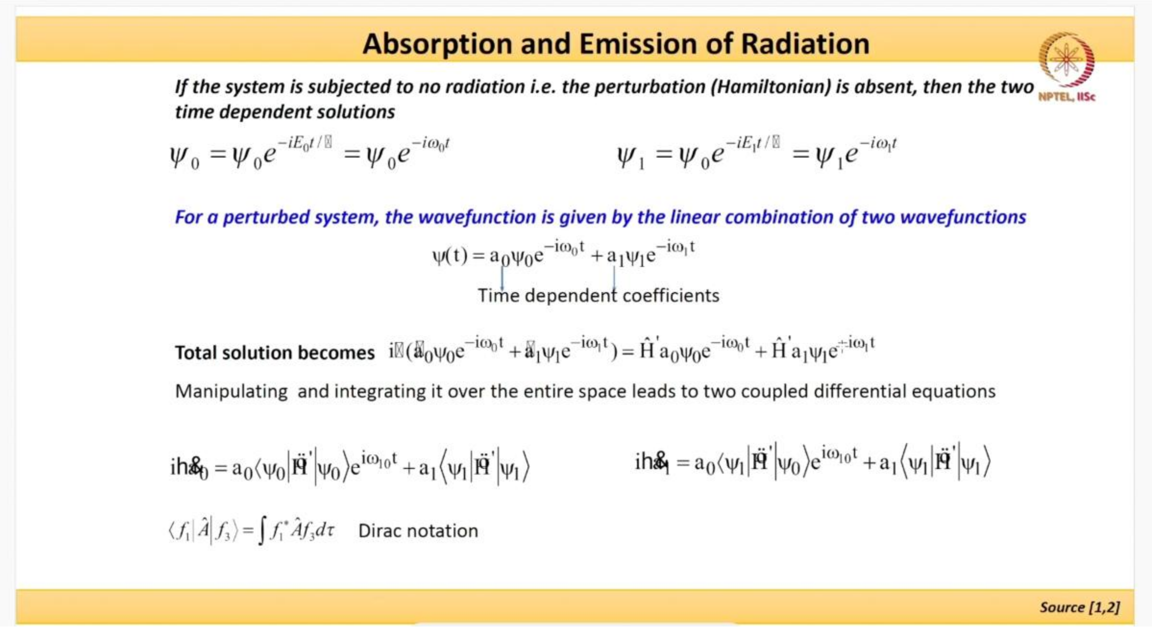
So, uh, when you assume that ω_{10} which is basically the... We neglect the resonant higher-order terms and set them equal to ω .

This is what you do. And this Δ, which is the difference between omega and omega naught, is called the detuning frequency. It tells you how far the electromagnetic radiation frequency is detuned from the resonant frequency. Therefore, the time-dependent coefficients become something like this. For a system that is initially in the ground state, $a_0 = 1$ *and* $a_{10} = 0$, so these are the two expressions that we have, where

$\Omega = [\omega_R^2 + \Delta^2]^{0.5}$. The time-dependent probability of finding the system in an excited state is given by this. while the corresponding time-dependent probability of finding a system in the ground state is given by that. The at-resonance condition occurs when Δ is equal to zero, and knowing that $\Omega = \omega_R$, you get

$$|a_1(t)|^2 = sin^2(\frac{\omega_R t}{2})$$

So this essentially translates to: if you look at this diagram carefully, this plots $|a_1|^2$, and these are for different detuning levels. When the detuning is zero, the probability of finding a system between two levels is shown by these three states.



Absorption and Emission of Radiation

If the system is subjected to no radiation i.e. the perturbation (Hamiltonian) is absent, then the two time dependent solutions

$$\psi_0 = \psi_0 e^{-iE_0 t/\hbar} = \psi_0 e^{-i\omega_0 t} \qquad \psi_1 = \psi_0 e^{-iE_1 t/\hbar} = \psi_1 e^{-i\omega_1 t}$$

For a perturbed system, the wavefunction is given by the linear combination of two wavefunctions

$$\psi(t) = a_0 \psi_0 e^{-i\omega_0 t} + a_1 \psi_1 e^{-i\omega_1 t}$$

Time dependent coefficients

Total solution becomes $i\hbar(\dot{a}_0 \psi_0 e^{-i\omega_0 t} + \dot{a}_1 \psi_1 e^{-i\omega_1 t}) = \hat{H}' a_0 \psi_0 e^{-i\omega_0 t} + \hat{H}' a_1 \psi_1 e^{-i\omega_1 t}$

Manipulating and integrating it over the entire space leads to two coupled differential equations

$$i\hbar \dot{a}_0 = a_0 \langle \psi_0 | \hat{H}' | \psi_0 \rangle e^{i\omega_{10} t} + a_1 \langle \psi_1 | \hat{H}' | \psi_1 \rangle \qquad i\hbar \dot{a}_1 = a_0 \langle \psi_1 | \hat{H}' | \psi_0 \rangle e^{i\omega_{10} t} + a_1 \langle \psi_1 | \hat{H}' | \psi_1 \rangle$$

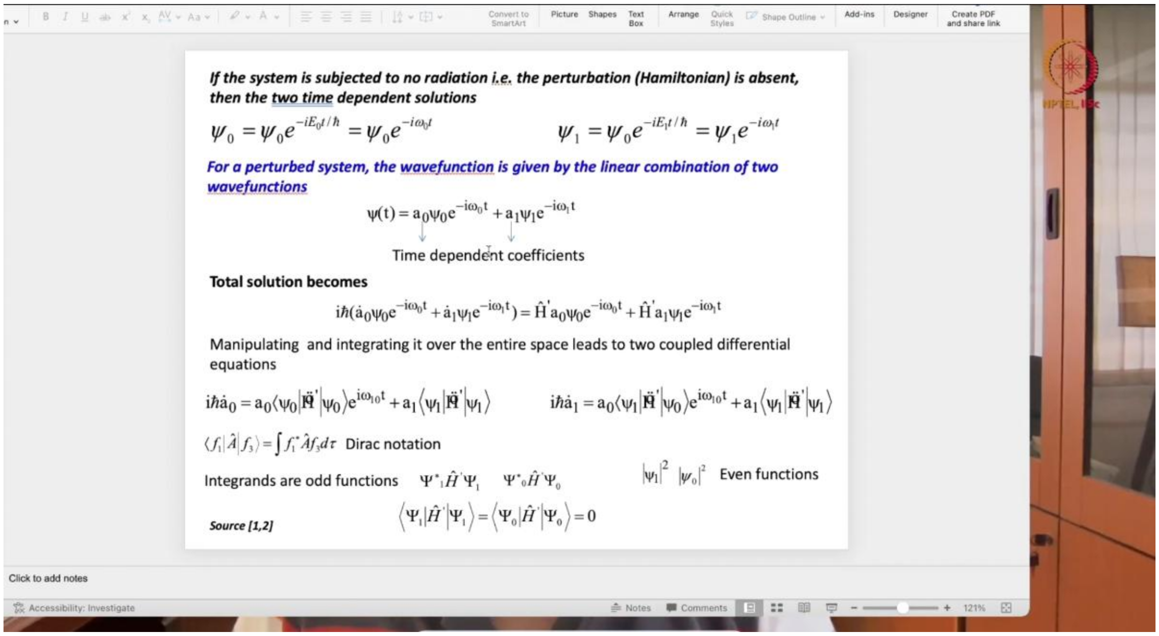
$\langle f_1 | \hat{A} | f_3 \rangle = \int f_1^* \hat{A} f_3 d\tau$ Dirac notation

Source [1,2]

This is like a probability, if you recall, so it goes up to a maximum of one, and $|a_1|^2$ is the probability. Thus, the system undergoes coherent cycling between the ground state and the excited state. By the electromagnetic radiation, you can see that it goes up, then it comes down, then it goes up again, and then it comes down. Okay, so this probability of cycling actually goes on reducing as we increase the extent of detuning, where ω_R, if you remember, is the resonance. So this is a little bit of a primer on quantum mechanics, which shows that when electromagnetic radiation interacts with matter, there are a few things that actually determine it.

One is basically the transition dipole moment. And the other one comes from the solution of the Schrödinger wave equation. And this gives you the ultimate probability that how cycling works. Okay, so $2\pi/\omega_R$ is a resonant timescale. So at resonance, the system is at a state of complete inversion. That means all the particles are driven to the upper excited state.

While away from resonance, the probability of finding the particle in the excited state is greatly reduced, as you can see. It cycles down. So there is no damping in this coherent cycling, remember, because all the system goes up and then it comes down. So there is no damping as such. The scenario is idealistic because effects like spontaneous emission and non-radiative decay processes, like collisions, have not been considered.


If the system is subjected to no radiation i.e. the perturbation (Hamiltonian) is absent, then the two time dependent solutions

$$\psi_0 = \psi_0 e^{-iE_0 t/\hbar} = \psi_0 e^{-i\omega_0 t} \qquad \psi_1 = \psi_0 e^{-iE_1 t/\hbar} = \psi_1 e^{-i\omega_1 t}$$

For a perturbed system, the wavefunction is given by the linear combination of two wavefunctions

$$\psi(t) = \underset{\downarrow}{a_0}\psi_0 e^{-i\omega_0 t} + \underset{\downarrow}{a_1}\psi_1 e^{-i\omega_1 t}$$

Time dependent coefficients

Total solution becomes

$$i\hbar(\dot{a}_0\psi_0 e^{-i\omega_0 t} + \dot{a}_1\psi_1 e^{-i\omega_1 t}) = \hat{H}' a_0\psi_0 e^{-i\omega_0 t} + \hat{H}' a_1\psi_1 e^{-i\omega_1 t}$$

Manipulating and integrating it over the entire space leads to two coupled differential equations

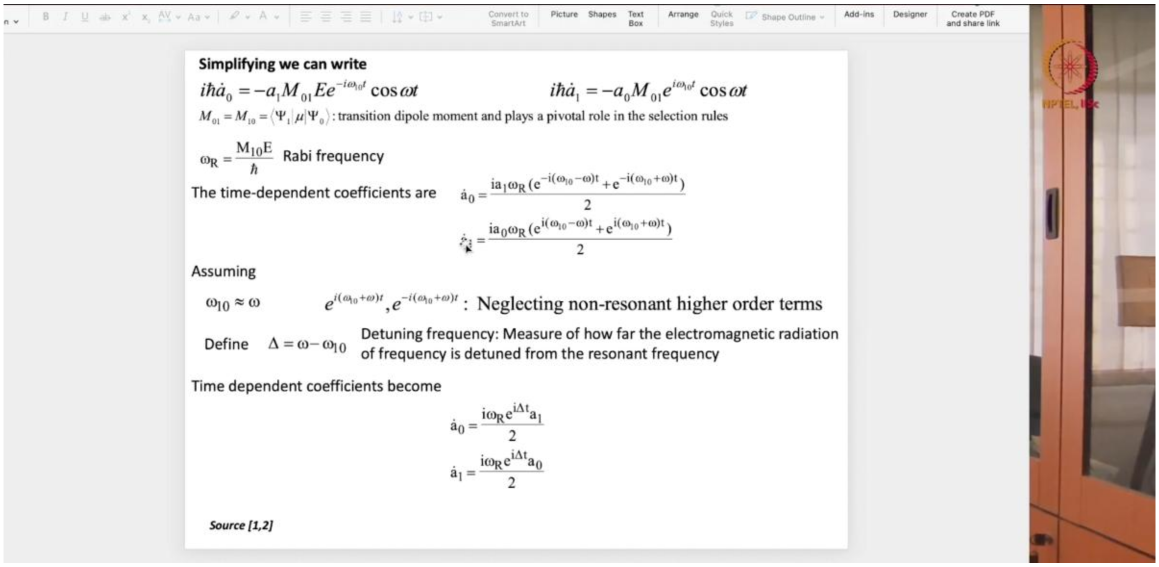
$$i\hbar\dot{a}_0 = a_0\langle\psi_0|\ddot{H}'|\psi_0\rangle e^{i\omega_{10}t} + a_1\langle\psi_1|\ddot{H}'|\psi_1\rangle \qquad i\hbar\dot{a}_1 = a_0\langle\psi_1|\ddot{H}'|\psi_0\rangle e^{i\omega_{10}t} + a_1\langle\psi_1|\ddot{H}'|\psi_1\rangle$$

$\langle f_1|\hat{A}|f_3\rangle = \int f_1^* \hat{A} f_3 d\tau$ Dirac notation

Integrands are odd functions $\Psi^*{}_1\hat{H}'\Psi_1$ $\Psi^*{}_0\hat{H}'\Psi_0$ $|\psi_1|^2$ $|\psi_0|^2$ Even functions

$$\langle\Psi_1|\hat{H}'|\Psi_1\rangle = \langle\Psi_0|\hat{H}'|\Psi_0\rangle = 0$$

Source [1,2]


Simplifying we can write

$$i\hbar\dot{a}_0 = -a_1 M_{01} E e^{-i\omega_{10}t}\cos\omega t \qquad i\hbar\dot{a}_1 = -a_0 M_{01} e^{i\omega_{10}t}\cos\omega t$$

$M_{01} = M_{10} = \langle\Psi_1|\mu|\Psi_0\rangle$: transition dipole moment and plays a pivotal role in the selection rules

$\omega_R = \frac{M_{10}E}{\hbar}$ Rabi frequency

The time-dependent coefficients are

$$\dot{a}_0 = \frac{ia_1\omega_R(e^{-i(\omega_{10}-\omega)t} + e^{-i(\omega_{10}+\omega)t})}{2}$$

$$\dot{a}_1 = \frac{ia_0\omega_R(e^{i(\omega_{10}-\omega)t} + e^{i(\omega_{10}+\omega)t})}{2}$$

Assuming

$\omega_{10} \approx \omega$ $e^{i(\omega_{10}+\omega)t}, e^{-i(\omega_{10}+\omega)t}$: Neglecting non-resonant higher order terms

Define $\Delta = \omega - \omega_{10}$ Detuning frequency: Measure of how far the electromagnetic radiation of frequency is detuned from the resonant frequency

Time dependent coefficients become

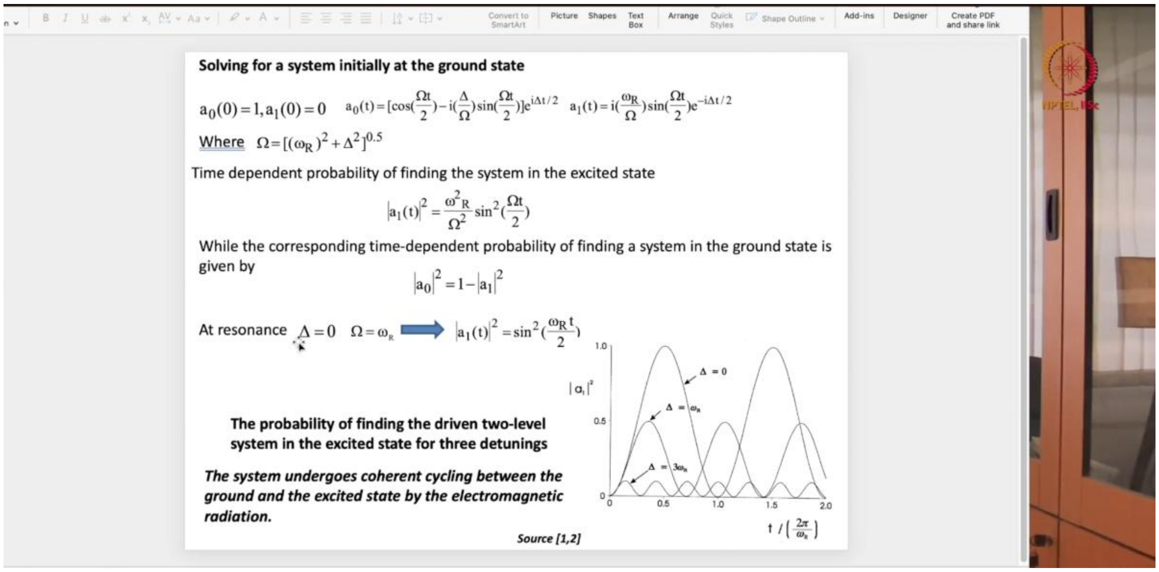
$$\dot{a}_0 = \frac{i\omega_R e^{i\Delta t} a_1}{2}$$

$$\dot{a}_1 = \frac{i\omega_R e^{i\Delta t} a_0}{2}$$

Source [1,2]

Now, what are those spontaneous emission can actually destabilize the system. So because it's spontaneous, limits don't require interaction with light. So this cycle, this coherent cycle of going up and then coming down, will be broken. The other thing that can lead to damping, if you look at this damper, is basically when there are collisions between the molecules.

Therefore, the molecules collide and reset their energy. As a result of that, there is no collision. You know, emission-related or non-radiative decay processes, like collisions in which energy is exchanged between the molecules. So the spontaneous emission of photons breaks the coherence and resets the system to the ground state.



Solving for a system initially at the ground state

$a_0(0)=1, a_1(0)=0 \quad a_0(t)=[\cos(\frac{\Omega t}{2})-i(\frac{\Delta}{\Omega})\sin(\frac{\Omega t}{2})]e^{i\Delta t/2} \quad a_1(t)=i(\frac{\omega_R}{\Omega})\sin(\frac{\Omega t}{2})e^{-i\Delta t/2}$

Where $\Omega=[(\omega_R)^2+\Delta^2]^{0.5}$

Time dependent probability of finding the system in the excited state

$$|a_1(t)|^2 = \frac{\omega^2{}_R}{\Omega^2}\sin^2(\frac{\Omega t}{2})$$

While the corresponding time-dependent probability of finding a system in the ground state is given by

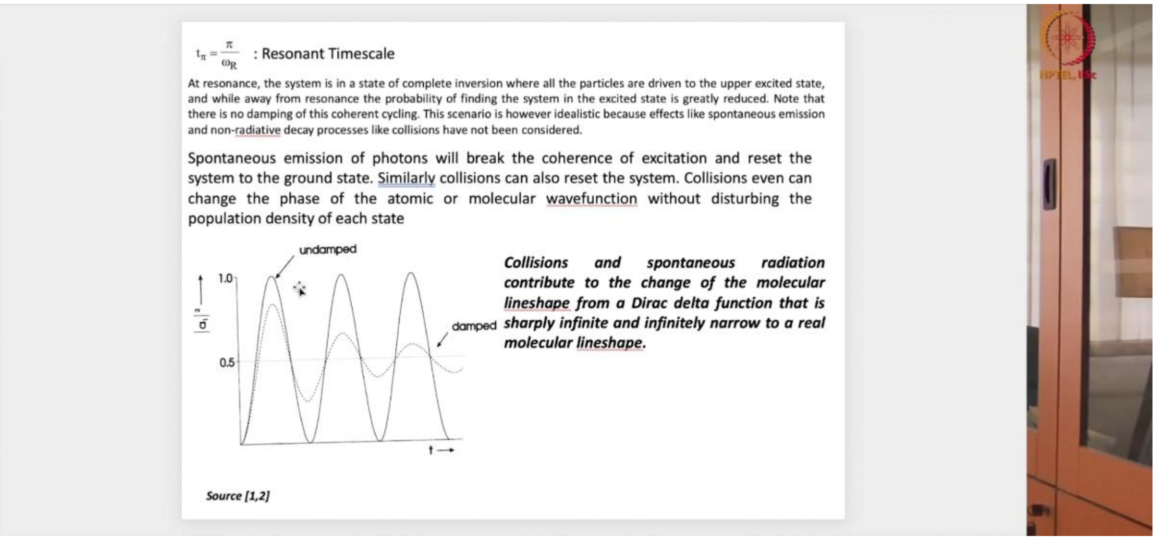
$$|a_0|^2 = 1-|a_1|^2$$

At resonance $\Delta = 0 \quad \Omega = \omega_R \Rightarrow |a_1(t)|^2 = \sin^2(\frac{\omega_R t}{2})$

The probability of finding the driven two-level system in the excited state for three detunings

The system undergoes coherent cycling between the ground and the excited state by the electromagnetic radiation.

Source [1,2]



$t_\pi = \frac{\pi}{\omega_R}$: Resonant Timescale

At resonance, the system is in a state of complete inversion where all the particles are driven to the upper excited state, and while away from resonance the probability of finding the system in the excited state is greatly reduced. Note that there is no damping of this coherent cycling. This scenario is however idealistic because effects like spontaneous emission and non-radiative decay processes like collisions have not been considered.

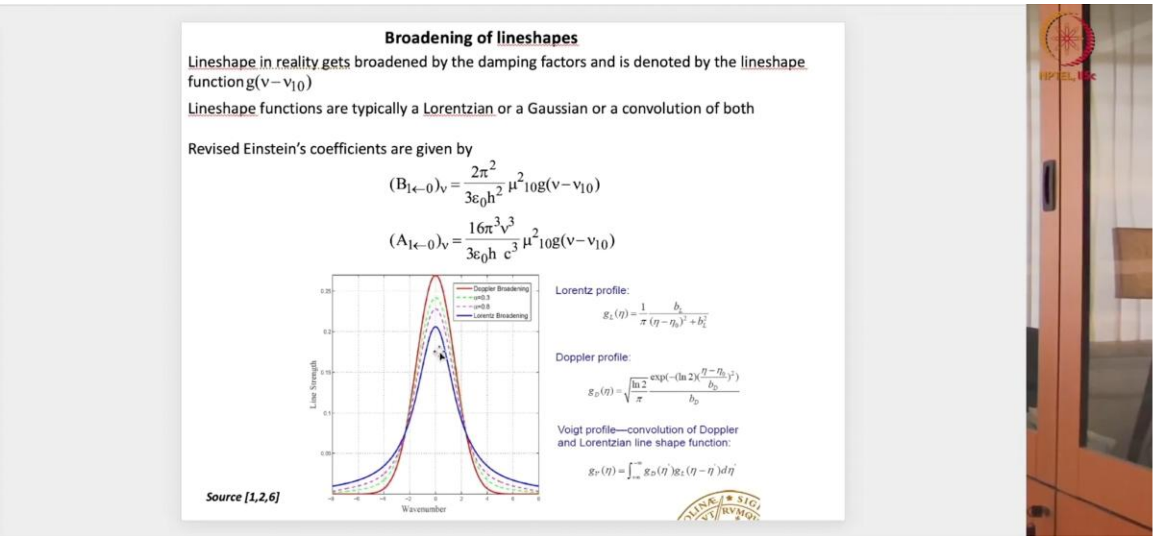
Spontaneous emission of photons will break the coherence of excitation and reset the system to the ground state. Similarly collisions can also reset the system. Collisions even can change the phase of the atomic or molecular wavefunction without disturbing the population density of each state

Collisions and spontaneous radiation contribute to the change of the molecular lineshape from a Dirac delta function that is sharply infinite and infinitely narrow to a real molecular lineshape.

Source [1,2]

That is what happens. Similarly, collisions can also reset the system. Collisions can even change the phase of the wave function without disturbing the population density. So collisions and spontaneous radiation contribute to the change in the molecular line shape from a Dirac Δ function. Because, if you remember, the molecules always had, technically, it should have the Dirac Δ. And the Dirac Δ, as you know, is sharply infinite and infinitely narrow.

to a more realistic molecular line shape. And that is exactly what happens. So the broadening of line shapes happens for several reasons. The line shape in reality gets broadened by damping factors and is denoted by the line shape function, which is given by $g(\nu - \nu_{10})$. The line shape functions are either Lorentzian, Gaussian, or a convolution of both.



Broadening of lineshapes

Lineshape in reality gets broadened by the damping factors and is denoted by the lineshape function $g(\nu - \nu_{10})$

Lineshape functions are typically a Lorentzian or a Gaussian or a convolution of both

Revised Einstein's coefficients are given by

$$(B_{1\leftarrow 0})_\nu = \frac{2\pi^2}{3\varepsilon_0 h^2}\mu^2_{10} g(\nu - \nu_{10})$$

$$(A_{1\leftarrow 0})_\nu = \frac{16\pi^3\nu^3}{3\varepsilon_0 h\ c^3}\mu^2_{10} g(\nu - \nu_{10})$$

Lorentz profile:

$$g_L(\eta) = \frac{1}{\pi}\frac{b_L}{(\eta - \eta_0)^2 + b_L^2}$$

Doppler profile:

$$g_D(\eta) = \sqrt{\frac{\ln 2}{\pi}}\frac{\exp(-(\ln 2)(\frac{\eta - \eta_0}{b_D})^2)}{b_D}$$

Voigt profile—convolution of Doppler and Lorentzian line shape function:

$$g_V(\eta) = \int_{-\infty}^{\infty} g_D(\eta')g_L(\eta - \eta')d\eta'$$

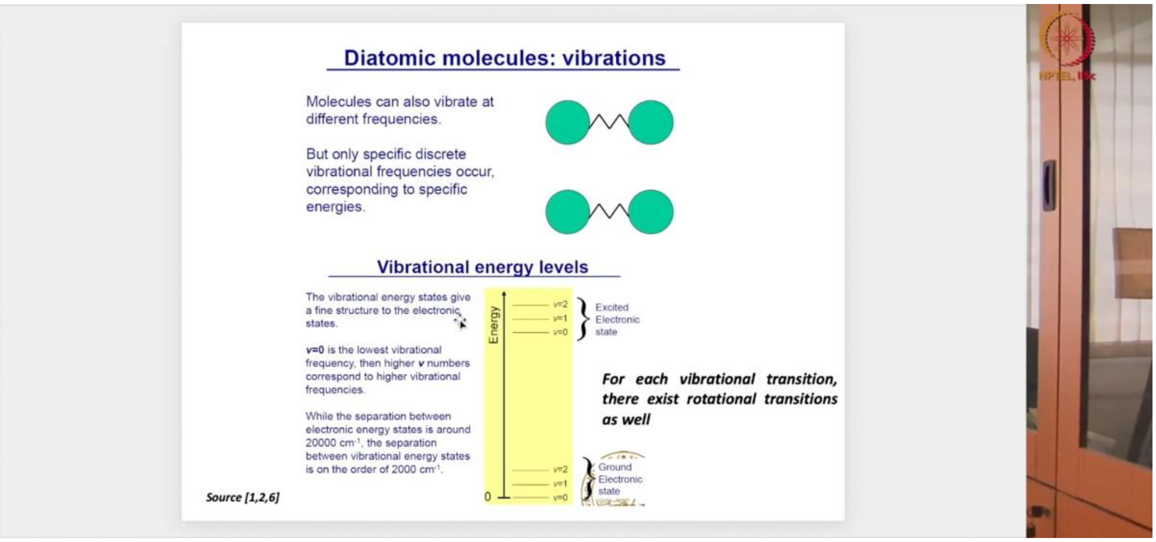
Source [1,2,6]

So the revised Einstein's coefficients are therefore given like this. So this, you know, is the same for spontaneous emission and absorption. So this is given. Now you have the line shape function, which is multiplied by it. And the same with spontaneous emission.

There is a line-shaped function that is multiplied by it. So, these are the different line shapes. So remember, the normal line shape is called a Dirac Δ. These are the broadened line shapes. Okay. So the broadened line shapes are given like this: the Lorenz profile is the one that you can see over here.

Okay, so one is Lorenz broadening; you can see this is the blue-colored line, and you can see that the peak is reduced because there are long tails in the broadening. Then there is Doppler broadening, which is basically this: the red color, which is sharper. That means the peak is higher and the tails are less spread out. Okay? Now the combination profile is given by a convolution of both the line shapes, which is basically the multiplication of both factors, the line shape functions, and it is called a void profile. So, the void profile is basically a convolution of the Lorentzian and Doppler line shapes.

So the broadening of the line shape happens mainly because of collisions, depending on the number density of the system and other factors. So you can readily understand that if the line shapes broaden because of collisions between the molecules, and if the collision is a function of the concentration of the molecules, then these techniques can theoretically be used to determine what the density of the molecules is in the first place, which is exactly the way we are going to go in the next few slides. Right? So now, a little bit of a primer on diatomic molecules and what to do: the diatomic molecules—if you look at a diatomic molecule, you can see that the two molecules are given in green, and there is some kind of spring-like thing that attaches them, so the molecules can vibrate at different frequencies. But only specific, discrete frequencies occur because of quantum mechanics. Now, for each vibrational transition, there can be a lot of rotational transitions as well.



Diatomic molecules: vibrations

Molecules can also vibrate at different frequencies.

But only specific discrete vibrational frequencies occur, corresponding to specific energies.

Vibrational energy levels

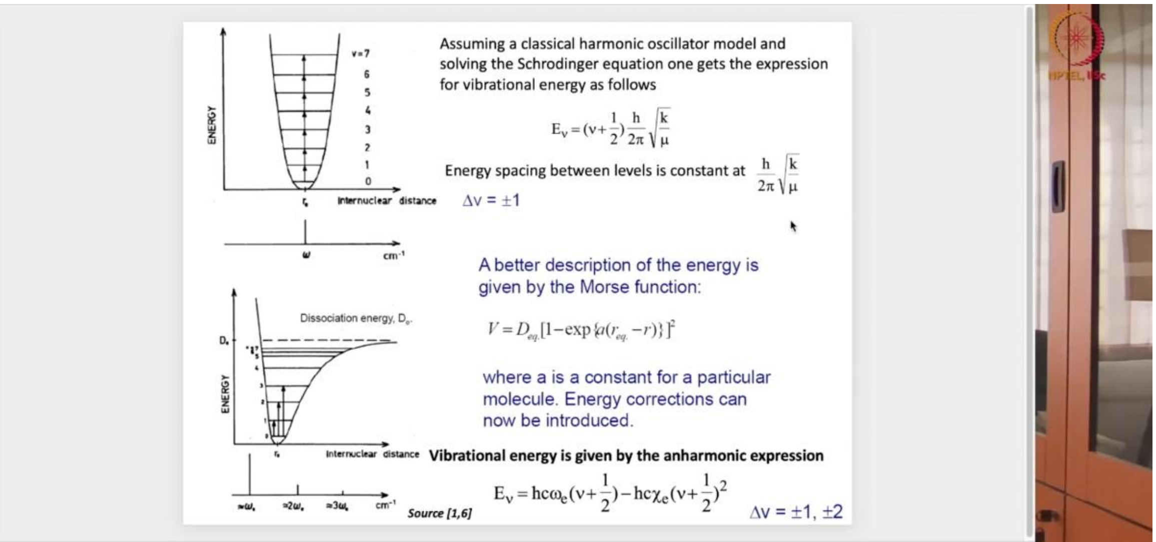
The vibrational energy states give a fine structure to the electronic states.

v=0 is the lowest vibrational frequency, then higher ***v*** numbers correspond to higher vibrational frequencies.

While the separation between electronic energy states is around 20000 cm^{-1}, the separation between vibrational energy states is on the order of 2000 cm^{-1}.

For each vibrational transition, there exist rotational transitions as well

Source [1,2,6]



Assuming a classical harmonic oscillator model and solving the Schrodinger equation one gets the expression for vibrational energy as follows

$$E_v = (v+\frac{1}{2})\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

Energy spacing between levels is constant at $\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$

$\Delta v = \pm 1$

A better description of the energy is given by the Morse function:

$$V = D_{eq.}[1-\exp\{a(r_{eq.}-r)\}]^2$$

where a is a constant for a particular molecule. Energy corrections can now be introduced.

Vibrational energy is given by the anharmonic expression

$$E_v = hc\omega_e(v+\frac{1}{2}) - hc\chi_e(v+\frac{1}{2})^2$$

Source [1,6]

$\Delta v = \pm 1, \pm 2$

The molecules can rotate and perform all those functions. This can happen. So the vibrational state gives fine structure to the electronic state. So we gain more finesse if you look at the lines of the spectroscopy. And this is more about that. Now, if you assume that it's like a classical harmonic oscillator model, this is for the vibrational part. If you assume it's a classical harmonic oscillator and solve the Schrödinger equation once again, one gets an expression for the vibrational energy, which is given by this.

But the energy spacing between the levels is constant at $(\frac{h}{2\pi})\sqrt{k/\mu}$. And, you know, the energy spacing of the levels is given by plus or minus one. A better description of the energy is given by the Morse function. Okay, this is a little bit more complicated; you know, the energy potential.

This is basically the internuclear distance. So E is here; of course, E is a constant for a particular molecule. The energy corrections can now be introduced when you actually have a Morse function. So the vibrational energy in this case is given by an anharmonic function, whereas this was not; and here, the difference in frequencies is plus or minus one, plus or minus two, etc. So these all come from the solution of the Schrödinger wave equation.

Okay, so now this is set; we know how these molecules are actually. actually respond to radiation. And we know that once they respond, their absorption line shapes can become broadened. And why they get broadened and how they get broadened will be the focus of the next class, where we are going to cover what leads to a change in the line shapes.