Time Dependent Quantum Chemistry
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Lecture: 47
Classical Description of light

Welcome to Module 8, of the course Time Dependent Quantum Chemistry. In this module, we will go over light atom interaction with the help of time dependent perturbation theory. Time dependent perturbation theory is an approximate method to get analytical solution to the TDQC and we will see how to implement that and at the same time, when we will be using time dependent perturbation theory in this module, we will introduce how to represent light classically because it is the semiclassical treatment we will be using for the presentation of this module.

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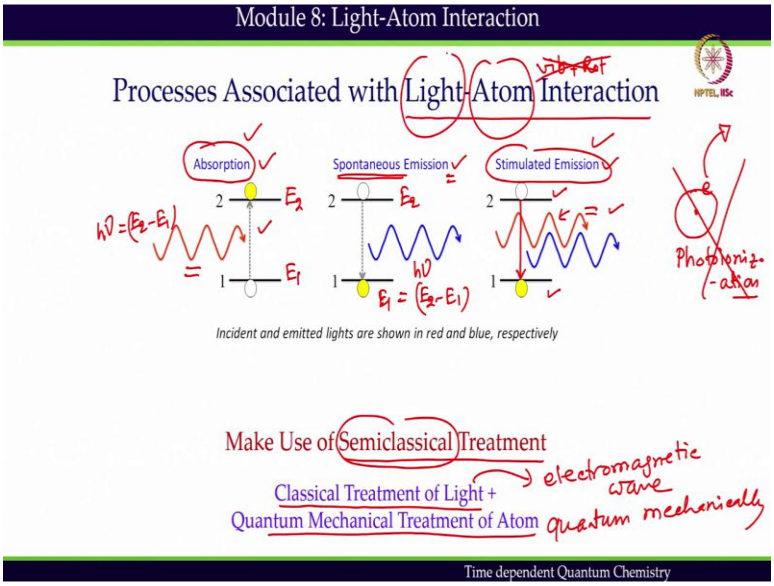

So, in the context of the interaction of light with an atom, four fundamental processes are important, Absorption, Spontaneous Emission, Stimulated Emission, and the fourth one is the photoionization which I have not shown which will remove an electron completely from an atom that is called photoionization. Photoionization will be skipped here with this discussion will not be included here. So, Photoionization will not be discussed here.

So, these are the three fundamental processes of light atom interactions can render. These three processes Absorption, Spontaneous Emission, and Stimulated Emission involve electronic transition between two states. Electronic transitions, particularly electronic transition for atom because for atom, we do not have vibration, we do not have rotation and that is why it is only electronic transition it can undergo.

For molecules, polyatomic molecules, it can have vibrational, rotational transition as well. But we will go over it later. In this module, we will just focus on the light atom interaction and which can render electronic excitation or deexcitation process in terms of Absorption, Spontaneous Emission and Stimulated Emission.

An atom can absorb a photon with an energy $(E_2 - E_1)$. So, it can absorb this photon $h\nu = E_2 - E_1$ from a beam of radiation and can undergo transition from a state of lower energy to a state of higher energy, this process is called absorption.

An atom can also undergo spontaneous transition from an excited state to a state of lower energy emitting a photon with an energy $h\nu$, which is going to be $(E_2 - E_1)$ and this process is called Spontaneous Emission. And atom can emit photon under influence of an applied radiation field while making an induced transition from an excited state to the lower energy state.

So, this transition will be stimulated by an external radiation (red color radiation depicted in the above slide) and this is called stimulated emission. These both for absorption and stimulated emission, these emission will be proportional to the intensity of the applied radiation field because in both absorption and stimulated emission you can notice here (in the slide above) this red color beam is used which is the field with which the system is interacting. The system has to interact with the external field to undergo this transition, either absorption can happen or stimulated emission can also happen. And that is why it is proportional to the intensity of the applied radiation field. This distinguishes both absorption and stimulated emission processes from spontaneous emission because the transition rate of spontaneous emission, this is a spontaneous emission where I do not have any external field which is stimulating this process or helping this process it is spontaneously done that is why it is called spontaneous emission. And that is why it is different from absorption and stimulated emission. In absorption and stimulated emission, the entire process will depend on the external field, but in spontaneous emission, it does not depend on the intensity of the applied radiation field. Here we will discuss the interaction of light with an atom using semiclassical treatment in which the incoming radiation field would be treated classically.

So, classical treatment of light will be used and classical treatment of light which means that it is nothing but the presented by electromagnetic wave and this classical light will be interacting with quantum mechanical atom. So, atom will be treated quantum mechanically and light would be treated classically that is why the name semiclassical comes in. So, we look at the nature of light first, this is something which we have to introduce here

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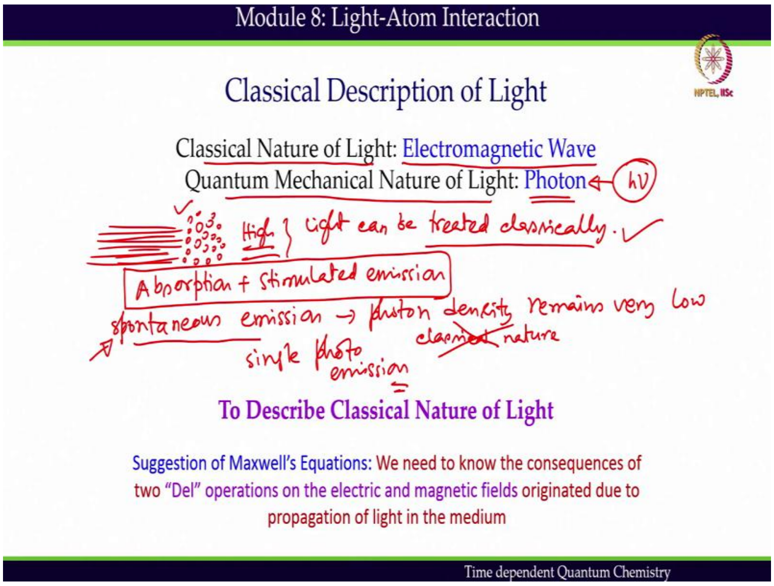

to get a complete picture of light atom interaction. Although it is not a quantum mechanics, it is classical description of light, but we have to understand the classical description of light. description of light is always difficult task. The true nature of light is unknown. Light is said to be dual in nature, certain phenomena such as interference exhibit the wave nature and in that case light possesses or it exhibits both electric and magnetic fields.

And this is the classical nature of light. So, if I say that what is the classical nature of light, it is nothing but electromagnetic wave. So, when I am describing light as electromagnetic wave, I am actually assuming that light is behaving classically. On the other hand, other phenomena associated with light such as photoelectric effect, display the particle aspect of light, which is called quantum mechanical nature of light.

So, quantum mechanical nature of light is not an wave nature anymore, it is particle nature, which is called photon. Each light particles are called photons. And each photon associated with a field of frequency ν carries an amount of energy $h\nu$. In a beam of light, if the density of photons is very high, so, let us say I have a beam of light coming in, and if the beam of light is coming, so, one can view in a particle form and this particles are $h\nu$ and what we are saying is that if the particle density or this light particle density or photon density is very high, then the light can be treated classically.

In the absorption process and stimulated emission process photon density is so high that one can treat both processes classically. But for the spontaneous emission only one photon can be emitted and as a result the photon density remains very low. And because it is low, we cannot describe spontaneous emission using classical nature of light. I have to use quantum mechanical nature. However, statistical argument can be coupled with classical nature of light to treat the spontaneous emission.

So, if I want to treat spontaneous emission semiclassically following the semiclassical description of light atom interaction, then I have to do it in an indirect way and that indirect way will come giving the statistical argument which will be coupled with the classical nature of the light to describe it, but directly using the semiclassical approach one can explore this absorption and stimulated emission particularly because in this processes photon density is so high that light can be treated classically.

So, this is something which you should remember that if the photon density is very high, then classical nature is perfectly fine and valid, but if the photon density is very very low, I can have only single photon emission then quantum mechanical nature prevails and we have to use this quantum mechanical treatment.

So, both atomic system or molecular system has to be treated quantum mechanically and light has to be treated quantum mechanically. When light with its classical nature propagates through a medium at that time, I will assume that the classical nature is valid for the description of this absorption and stimulated emission process. So, these are the two processes we will describe in this module and that is why I will say that the classical nature is valid. So, if I consider the classical nature of light, when light as a classical electromagnetic wave propagates through the medium,

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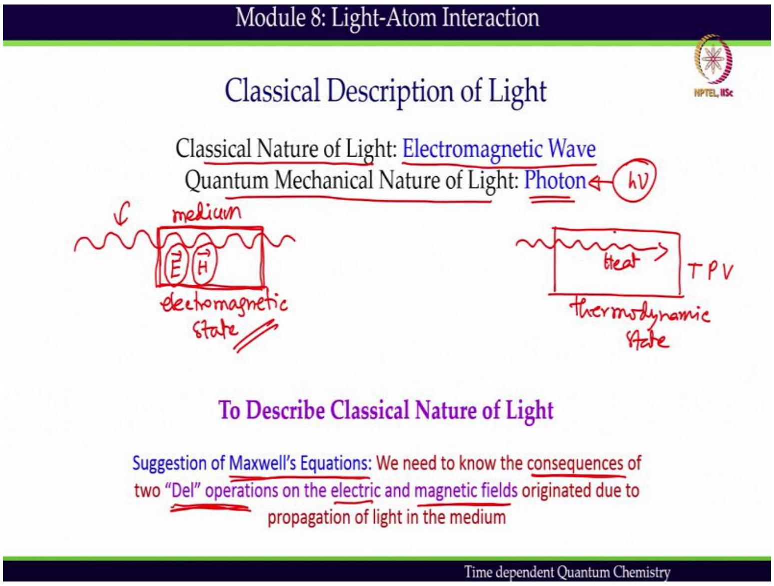

So, let us say I have a medium and light as a electromagnetic wave very soon we will see that this is just a plane wave that is why I am drawing it like this way. When light is propagating through the medium medium's electromagnetic state changes, it is just like when heat energy is propagating through the medium, it is thermodynamic state changes.

A thermodynamic state of the medium is defined by its Temperature, Pressure, Volume like these physical quantities that we know. Similarly it will follow the laws of thermodynamics to define this thermodynamics state similarly, when the light (classical light) is propagating through the medium, its electromagnetic state changes and then to describe this light,

in the medium, if we want to describe the light, how it is propagating, what is the nature of light, all we need to find out the electric and magnetic field in the medium, what is the nature of the electric and magnetic field? Because this electromagnetic state of the medium due to propagation which is prepared this kind of state is prepared due to propagation of the light through the medium.

This electromagnetic state of the medium is defined by Maxwell's Equations and Maxwell's Equations suggesting that we only need to know the consequences of a particular operation, which is called "DEL" operation, I will show what does it mean of the electric and magnetic fields in the medium due to propagation, which is originated due to propagation of light in the medium.

So, let us say in this medium or in this room light is propagating, how do I know what is propagating? I will be able to check the nature of the electric and magnetic field in the medium and if it is following certain nature, I will be able to confirm that light is propagating. And that is a way we can describe the true nature of light classically, so that is the classical nature of the light.

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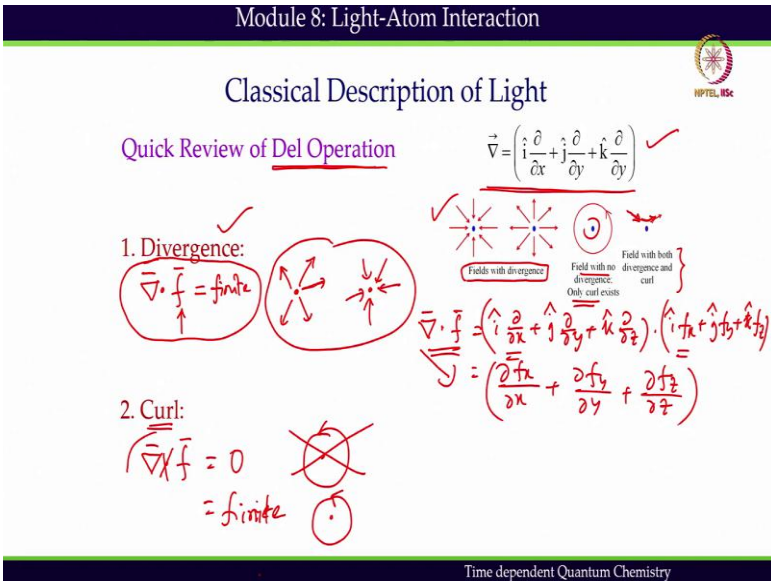

So, because we need to find out the “DEL” operation, we will just go over review it very quickly, what does it mean by these “DEL” operator. “DEL” operator is known as vector differential operator, what is the physical meaning we get when the DEL operator acts on a particular field that we will get to know.

But mathematically “DEL” operator is nothing but is a vector differential operator which is given by this differential operator. For the dot product of this operator, we have a field, field is nothing but the force is representing some kind of force.

So, if we take the dot product we can have also cross product these are the two products I can have and each product has certain meaning, if we take the dot product of this field, f field which is a force, it will give me some idea about the field nature of the force, what kind of force I have. And what is the idea the physical meaning of these two products are following.

If I take the dot product, and if I have the dot product to be is 0 i.e., $\vec{\nabla}.\vec{f} = 0$, it means that the field is not diverging from a point in the medium or converging to a point, none of this happening. So, by doing this mathematical operation, we get to know what is the nature of the field or the force I have in the medium.

So, if I have dot product to be 0 i.e., $\vec{\nabla}.\vec{f} = 0$, it means that the field or the force is not, diverging from a point or converging to a point. That is the meaning of it. So, none of this is happening if it is 0, but if it is not 0, let us say some finite value I have then the field must be converging to a point or diverging from a point.

So, the field would be like this in the medium (in the referred slide), and this dot product because it is showing the divergence of that field is called the divergence relation. On the other hand, mathematically dot product is represented. So, one can calculate the dot product like this way, I have this vector differential operator and then $\vec{\nabla}.\vec{f} = \left(\hat{i}\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}\right).\left(\hat{i}f_x + jf_y + kf_z\right)$ effects plus f y plus f z.

So, if we take the dot product, we can only get this products alive, remaining part would be 0 because $\hat{i}.j = 0$, they are perpendicular to each other, in $\cos\theta$, θ would be 90°. So, they will be 0. So, finally I will get $\vec{\nabla}.\vec{f} = \left(\frac{\partial f_x}{\partial x} + \frac{\partial f_y}{\partial y} + \frac{\partial f_z}{\partial z}\right)$.That is the value we get. So, this is the mathematical derivation, but what does it mean?

After doing all these mathematical derivations if I find that this dot product is 0, it will mean that the fields are not originating from a point or diverging sorry diverging from a point or converging to a point that is the meaning it will hold. On the other hand, I can check the Curl, which is defined by the cross product of this with the Del operator and if the Curl is 0, i.e., $\vec{\nabla} \times \vec{f} = 0$ it means that the field is not rotating in nature, it is not rotating in nature like this, but if it is finite if there if the Curl exist, then the field is rotating in nature. So, what you are seeing is that Divergence and Curl these can be mathematically represented by dot and cross products respectively, but it shows that divergence of a field or curl of a field.

So, this is an example we have shown here(slide) the field with divergence would be looking like this, which means the dot product will exist, field with no divergence only curl exist because it is only rotating is not converging or diverging to a point in this field. And field with both divergence and curl you see that there is a tendency to converge to a point and then curl also exist. So, by doing these two mathematical derivations one can directly find out whether the field or the force which I am looking for in the medium, what is the nature of that force.

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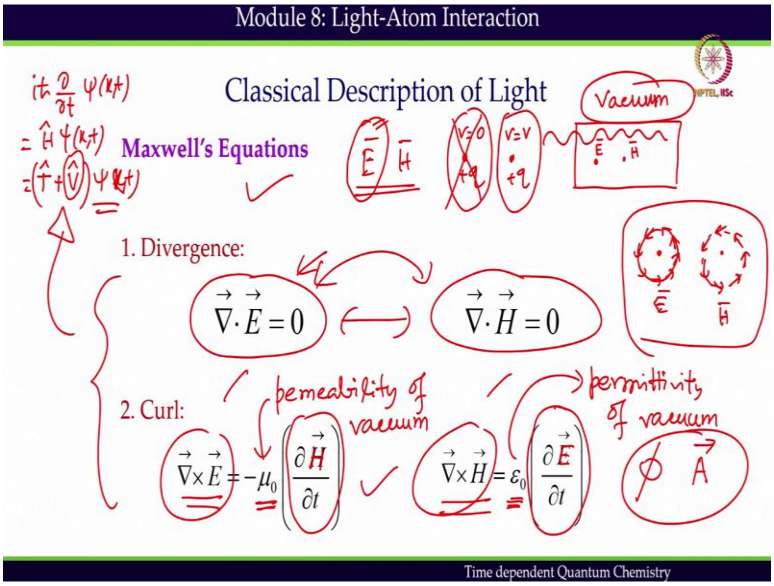

And Maxwell's equations showing that there is a particular kind of nature it will follow, if the light is going through a medium. So, medium for our problem for this module, we have considered medium to be vacuum is a free space medium, in the vacuum, light is propagating as classical nature with its classical nature, when it is propagating,

I have to define how does it look like and, to define it, what I need to do Maxwell's equations in suggesting that in different points of this medium, you find out what is the nature of electric and magnetic fields we have in the medium, and that nature will define how does the light behave in that medium.

So, in the vacuum, what you are seeing is that the electric field, if the light is propagating through the medium electric field is still divergence less it does not have divergence, magnetic field also does not have divergence. So, these are the two properties, which will show up always in the vacuum, if the light is propagating through the medium and that will define that I have light propagating through the medium.

So, divergence will be 0, in the vacuum, but its Curl exist, which means that both electric fields and magnetic field are rotating in nature. The fields there is the force, this is the electric field and magnetic field will also be in rotating in nature. So, this is the way fields are behaving.

$$\vec{\nabla}.\vec{E}=0,\vec{\nabla}.\vec{H}=0$$

$$\vec{\nabla}\times\vec{E}=-\mu_0\frac{\partial\vec{H}}{\partial t},\vec{\nabla}\times\vec{H}=\varepsilon_0\frac{\partial\vec{E}}{\partial t}$$

So, if through a medium if the light is propagating, how do I know light is propagating or not? Immediately I have to check in that medium in different points of the medium, we have to check how the electric and magnetic fields are behaving. If the electric and magnetic fields in the vacuum, if the medium is vacuum.

Then if the electric and magnetic fields are divergence less, but it curl exist, it means that there is a light which is propagating through the medium. And I have to combine these equations to get the final form of the light the Maxwell's equation of the light which will represent the nature of the light classically.

Does Maxwell's equations in vacuum suggests that the electric and magnetic fields do not diverge from a point or converge to a point. And mathematically that is described by this, Del operations dot products would be 0. Curl of the electric and magnetic fields exist. This infers that both electric and magnetic fields are rotating in nature and that is exact pictorial depiction of electric magnetic fields in the medium.

Furthermore, that time varying what we see is that this is time varying magnetic field is producing electric field time varying electric field is producing magnetic field, in this equations μ_0 is the permeability of the vacuum and ε_0 is the permittivity of vacuum, from simple point of view permittivity and permeability of vacuum features some kind of resistance against the electric and magnetic fields respectively.

So, one can imagine that there is an absolute value somewhere and in vacuum this fields which is nothing but the force what force I am experiencing is a certain fraction of certain absolute value. So, this is going as a resistance against those corresponding fields. So, ε_0 going against E, the electric field and μ_0 is going against this magnetic field. Here we note that Maxwell's equations, these are the four equations which is called Maxwell's equations is given here are presented based on the respective fields.

So, E and H are the fields this equation has been represented in terms of the fields, electric field exerts force on both stationary and moving charged particle while magnetic field exerts force only on the moving charged particle, this is something we should remember that these are the force electric field and magnetic field acting on, they will not act on the neutral particle, They will act on a charged particle +q charge I have, I have a particle with a +q charge they will act force on it. And interestingly electric field can act force on charged particle with 0 velocity which is a stationary charged particle or a charged particle with certain velocity both can be affected by the electric field.

But magnetic field if I consider magnetic field cannot exert force on a stationary charged particle it can only exert force on a moving charge particle. So, these are the two there is a primary difference between how electric field and magnetic field will behave to a charged particle. And that is the consequence of Lorentz force we will not discuss Lorentz force here.

But this is something which we should remember, as potential terms instead of this kind of field terms directly entered the time dependence Schrodinger equation remember time dependence Schrodinger equation finally, we have to solve this in order to solve explode this light atom interaction we have to get this we had to solve this time dependence Schrodinger equation which has the Hamiltonian and this Hamiltonian has kinetic energy term plus potential energy term it does not have field or force in it.

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = H\psi(x,t)$$
$$= (T+V)\psi(x,t)$$

But Maxwell's equation which is describing the light is in terms of electric and magnetic fields. So, in order to use these Maxwell's equations in the TDQC to exploit light atom interaction, which will come as a potential we have to convert all these equations in the potential form and that is called potential formulation of the Maxwell's equations.

And we will see that we can use scalar potential φ and vector potential A, these are the two potential formulations will have to represent these electric and magnetic fields. So, potential formulation of Maxwell's equations will be useful in the context of light matter interaction, because in the light matter interaction we will be using time dependent Schrodinger equation which only involves potential term. We will stop here and we will continue this module in the next session.