

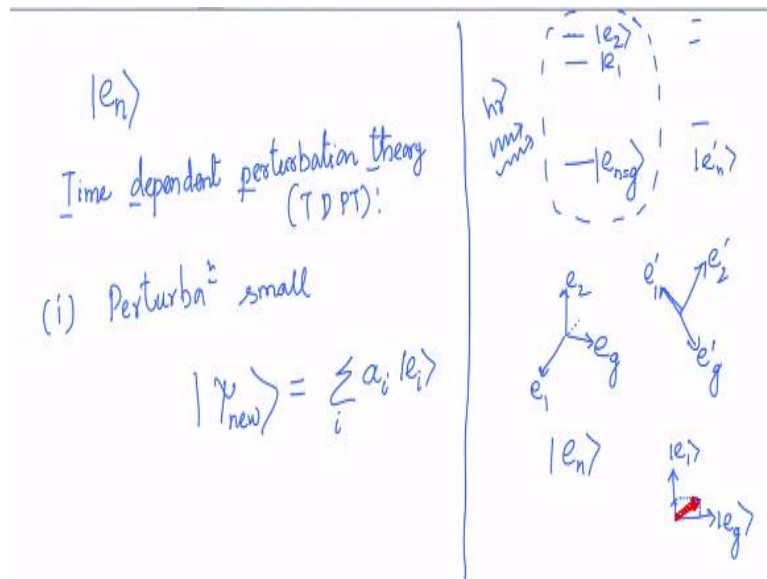
**Optical Spectroscopy and Microscopy**  
**Prof. Balaji Jayaprakash**  
**Centre for Neuroscience**  
**Indian Institute of Science – Bangalore**

**Lecture – 9**  
**Fundamentals of Optical Measurements and Instrumentation**

Alright, so far I hope that I have been able to convince you or motivate you why quantum mechanics offers a very good way of describing Dirac's formalism of quantum mechanics, most specifically offers a very good way of describing the interaction that are happening at atomic scale and why we do need these kind of descriptions to study spectroscopy and microscopy.

Now what I am going to do is I am going to use this to actually develop the framework or so to say basic description of a rate process and that would set tone for the rest of the course okay. So now, what are we after?

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The whole course is about we have matter, in the matter we have electronic states such as ground state, excited state, so let us to be general let us do this which is in general let us represent an energy eigen ket meaning these are ket vectors corresponding to an energy state, a state with an energy  $e_n$ , alright. So we could write it as  $e_n$  the ground state like that and then in general  $e_1$ ,  $e_2$ , etc., alright. So we have taken a system, an atomic system with this kind of an energy level and we are actually shining light, photons into the system.

Now, we want to ask what happens to this atomic states or these are the energy states of a system, let us not worry about atomic, molecular or what not. These are the energy states of the system, now what happens to the energy states? There are several ways to go about it. The one that we are going to follow is called as time dependent perturbation theory or called as TDPT. What it does is that it allows you to actually estimate what happens to this system or how the light interacts with the matter in terms of the original electronic states of the system itself, okay.

Let me rephrase it again. So we have a system. We have an atomic, molecular or whichever state system that you take and for that system, we have a defined energy states given by  $E_n$  in general or  $E_1, E_2$  like that eg referring the ground state. Now these are discrete states. So when you have a system, what we are asking is how are this energy states populated and upon shining this light, what happens to the states themselves? Now is there reason for us to believe that the states will undergo any change?

Yes, there are good reasons to believe that because these states themselves are obtained by assuming certain things, what have we assumed? We assumed electrostatic interaction, there is a potential energy that we have talked about right and then electrostatic interaction Coulombic interaction between the charges and using that, we have arrived at these electronic states. Now by shining this light photons, what we are actually doing is that we are disturbing that very fabric of the system.

When we are disturbing that, how does the system respond and one is to say that hey you have a new set of states okay. Let us call it as  $E'_n$  that are getting generated which takes into account the new perturbation, new energy that has put into the system and how does that actually takes into account that and then say that okay now the new possible energy states are somewhat different which is  $E'_n, E'_1$  so on and so forth, but the beauty of this is that since these the original  $E_n$  are an eigen ket of an energy operator, it is called as Hamiltonian operator.

You could describe these new states in terms of as a linear combination of the original states itself or in other words what you could ask is that we have an original energy space that is described by this basis vectors that are eg,  $E_1, E_2$ , so on and so forth. Now what all we have done is that we have generated a new  $E_n$  alright and let us represent it by new  $E_n$  and we

would like to know how do we describe this or I mean first and foremost we would like to know if we can describe this new set of  $\psi_n$ 's in terms of the old original  $\psi_n$ 's themselves, right?

The answer is as I said you could in principle do that as long as we satisfy few things. Number one we are going to make an assumption that the perturbation that we make is such that the new states that we get still can be thought of as states that are existing in the same space spanned by the original energy states, right, or in other words the perturbation is small. What do you mean by a small perturbation here?

As long as we are not going to destroy the molecule, we are not going to ionize the molecule and change the things to a very great extent or break the bonds of the molecule and so on and so forth, you can think of that as a reasonable limit within which you could use this formalism, but we will qualify that bit more when we actually work out the theory, right. Now the acid test to that is very simple. Our new state of the system you can write it as  $\psi_{\text{new}}$ , you could still be able to write it as a linear combination of all states okay.

Conceptually, it is easier to think in terms of 2-level system and if you want to what you are actually asking is if it is a 2 level basically there are 2 energy states which means it is a 2-dimensional space, so let us say this corresponds to the ground state and this I eigen ket were to correspond to the, so each one of them is an eigen ket here and then this is the next excited state. Then what we are asking is that when the light interacts with this system, it is going to take the system from dominantly ground state and leave it somewhere out here okay.

So, let us say that is the superposition state we are talking about after the light interaction system or during the interaction. Now what we are asking or what we are interested in knowing is that if you have to describe this new state in terms of the old and we can actually get the projection of this new state onto even the excited state and the ground state you as you will see initially that when it is all aligned to the ground state, the projection will be close to 0.

However, now because of this rotation, this will be some non-zero value right and that non-zero value would represent the probability that you would see the system in the excited state. So, that is the go, that is the bottom line. So now, how do we do this?

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$$\hat{H}_{\text{new}} = \hat{H}_0 + \hat{H}'$$

Hamiltonian

$$|\psi\rangle = \sum_{n=0}^{\infty} a_n |e_n^0\rangle \rightarrow$$

$$\hat{H}_0 |e_n^0\rangle = i\hbar \frac{\partial}{\partial t} |e_n^0\rangle \quad (\text{Sch. Eq.})$$

$$\hat{H}_0 |\psi\rangle = i\hbar \frac{\partial}{\partial t} |\psi\rangle$$

time dependent part.

$$|\psi\rangle = \sum_n a_n |e_n^0\rangle \cdot e^{-iE_n t/\hbar}$$

spatial part of the eigen ket

What we are going to realize is that first things the operator that we are going to be interested in is going to be the Hamiltonian operator and what we are going to do is that we are going to write down the Hamiltonian operator in terms of the new Hamiltonian right. So we are going to write down the new Hamiltonian as the original and perturbed Hamiltonian plus, perturbation Hamiltonian, now this is an important a statement here right, I need to be able to write down like this.

Whatever the interaction that I am studying, I need to be able to write down that interaction to be in terms of this, the each one of them are an operator. So if I am not able to do this, then I cannot use the rules that I obtained from here, right, and then go ahead and verify with an experiment. So, this is extremely important that we need to be able to write down the new Hamiltonian as the unperturbed plus the perturbation itself.

So, the advantage of doing that is that I already told you that the new state, let us say new state psi can be thought of as the linear combination of the original unperturbed eigen kets okay, but the point here is that since they are of original eigen kets that imposes a functional form to this, it demands a functional form because we know the  $H_0$ , the Hamiltonian operator here, this is the Hamiltonian of the energy operator okay.

Now the Hamiltonian needs to satisfy, I mean this eigen kets need to satisfy this relationship which is  $i\hbar \frac{\partial}{\partial t} |e_n^0\rangle$ , this is Schrodinger equation which would mean that the form of the solutions, it fixes the mathematical form that this ens can take and so in

general what we can actually do is that actually we can write the superposition states directly itself. So, we could extend this because it is an unperturbed Hamiltonian, so this superposition state should also satisfy the Schrodinger equation.

So we could write it as  $\psi$  or in other words the  $\psi$  itself we have written it as a linear combination of the states as superposition states, so if it has to have a solution of this kind, then the  $\psi$  it imposes a functional form as I am telling all along. So the functional form will have a spatial component and a time dependent component in  $\psi$  by  $\hbar$  cross alright. So what we have done is that we have written this  $\psi$  okay, I am going to drop this not here okay, so again this basically can be thought of as having only the spatial part of the eigen ket and this is a corresponding time dependent.

I mean it looks like I have just written down an expression directly here. The restriction that mean how do I even know that it has to be of this form that goes back to this idea, so this equation the time dependent Schrodinger equation need to be obeyed by a system that is evolving in time because so that is the premise of this entire analysis. So if we demand that this is a time dependent Schrodinger equation and then the superposition state that we have described where to describe our system smoothly from all the way from no perturbation to the perturbation.

Then it should be one of the solutions to mean they should satisfy this equation, right. I mean we should be able to plug in that state and then we should be able to write okay  $H_0 \psi = i\hbar \frac{d\psi}{dt}$ . If you were to be able to write this, then the  $\psi$  can take only few functional forms, one of them being this where we can distinctly separate the space and the time part and the time part assumes a functional form of  $e^{-iEt/\hbar}$ , the complex number  $iE$  by  $\hbar$  cross, alright.

I am made a little bit of an error here, so this has to be  $n$  going from 0 to infinity, 0 being  $g$  okay, so this is  $n$  and which means this is  $n$  and this is  $n$ , so let me correct that. So, we have an expression, a possible solution for a  $\psi$  right. Now, the point here is, the trick here is if you have to have any more meaning of what the  $\psi$  is going to look like, we need to really know what the values of this  $a_n$ , if we know the values of  $a_n$ , then we can actually write down this whole  $\psi$  in terms of the ground state  $\psi_0$  right.

I mean the unperturbed energy states  $E_n$ , right, remember I just dropped the  $n$  because I am just going to use only this, I am not going to talk about perturbed  $E_n$  at all, I am going to only talk about perturbed  $\psi$  from now on, so I dropped the  $n$  here, but essentially what it means is that this  $\psi$ , the new  $\psi$  can be written in terms of the ground state, I mean unperturbed states eigen kets and its energies okay. The only unknown here is the  $a_n$ , the coefficients that come in the linear combination of the unperturbed eigenstates, so now how do we evaluate these coefficients?

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$$[\underline{H}_0 + \underline{H}'(t)] |\psi\rangle = i\hbar \frac{\partial}{\partial t} |\psi\rangle$$

$$|\psi\rangle = \sum_n a_n(t) \cdot e^{-iE_n t/\hbar} \cdot |e_n\rangle$$

There is a way to evaluate these coefficients and the way we do that is by taking a dot product with the complex conjugate of a particular state  $e_k$ , alright. So now that is how we are going to evaluate and the first step in doing so would be to actually be able to write down these expressions that is our the Hamiltonian, the perturbed Hamiltonian this is a time dependent part when operating on the  $\psi$  should also be equal to, so what I am doing is that I told you that you could write the superposition state, the superposition state should be a solution of the unperturbed Hamiltonian.

Now, let us take the real situation which is the Hamiltonian plus its perturbation it should also be a solution to that. So everything still remains the same, we are just going to write down the  $\psi$  themselves in terms of the linear combination, so I am going to go back and forth just,  $e$  to the power minus, I am just collecting it, the same expression here, I am just writing it here. I am just collecting the terms so that I can write it conveniently  $E_n$  by  $\hbar$  cross okay, that is our eigen ket.

Now one thing we realized is that since this whole thing is evolving with time, the mixing, the new state that you are writing, right, the  $\psi$  also that the linear combination also changes as a function of time or in other words, the  $\psi$  unlike the previous unperturbed, I mean previous state where we are actually looking at the solution for the Hamiltonian of the unperturbed state, where  $a_n$ s are basically not changing at all, they are just staying wherever they are, they do not have any time dependence, they are one fixed number.

However, here what we are actually doing is that we are introducing perturbation, this is a time dependent phenomena, as a result the state is going to evolve, the superposition is going to evolve as a function of time, remember my vectorial representation of the two state system where you have the ground state on the excited state and then the red arrow was rotating right as depending on the perturbation the red arrow is going to rotate and the degree of rotation is going to change as a function of time as it evolves in time.

As a result, the  $a_n$ s that we are writing here right where we are explicitly putting now not the perturbation itself, I mean not the unperturbed the state but the unperturbed plus the perturbation, the real Hamiltonian, and then asking oh now can we demand this  $\psi$ , the  $\psi$  that we have written previously will also be a solution for that. If I have to demand this, then what it means in turn is that the  $a_n$ s themselves become time dependent okay. So since they are becoming time dependent, now what we can actually do is that, so what I was telling is that the  $a_n$ s themselves are time dependent so how do we get the  $a_n$ s?

That will be the crux of the rest of the derivation or the framework, basically derivation that we are actually doing. So now just to give you a brief purview into what we will be seeing later what we are going to do is that we are going to first write down a way of estimating  $a_n$ s, we do that by doing something called as a dot product, we will take us some special kind of a dot product here and then when we do that and then rearrange this whole expression for  $a_n$ s, even when we do that what we will see is that it becomes messy and hard to specifically arrange for the  $a_n$ s themselves.

So what we will do is we will try to expand this whole  $a_n$ s in terms of the perturbation Hamiltonian  $H$  itself and after which we would be able to write to  $f$  zeroth order and the first order and the second order corrections to the  $a_n$  okay. Do not worry, my job is here to walk you through this entire process and on the way I would actually try to motivate, physically

what it means has a very simple 2-3 steps and for people who are not able to follow it, I want to do it as an exercise to say that it does not come out from nowhere.

There are procedures which we can follow and then be able to get this, but the key is the result that we get from here and that is going to be important and I do not want you guys to lose track of that and I will insist that we need to be able to understand the result, not necessarily the derivation but definitely the result is of paramount importance. Derivation serves the purpose of understanding this result better, okay. I will see you in the next class where we progress towards obtaining the coefficients here, bye.