Time Dependent Quantum Chemistry
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Lecture 41
Nonradiative Transition Part 1

Welcome to module 7 of this course, Time Dependent Quantum Chemistry. In this module, we will go over non-radiative transition using Time Dependent Perturbation theory. In the earlier module, we have seen several approximate methods, such as Time Dependent Perturbation theory and every theory, all those approximate methods can be used to get analytical expression for a Time Dependent problem in Quantum Chemistry.

And here we will see the application of Time Dependent Perturbation theory first order Time Dependent Perturbation theory to explore this non-radiative transition, there is a particular kind of transition we will discuss. And then we will see that this application of Time Dependent Perturbation theory leads to Fermi's golden rule for non-radiative transition. And we will see the limitation of that rule which will break down and you know, to bypass that living the limitation we have to go for rigorous treatment, which is called Dissipative Quantum Dynamics, that is exactly what we will go over in this module.

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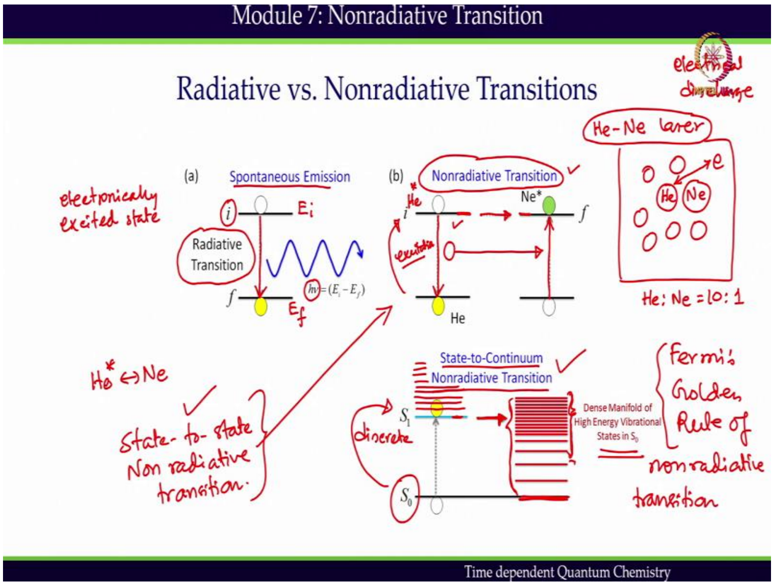

So, let us begin the discussion of this module with radiative transition radiative transition and excited Quantum system. For example, electronically excited state let us say I can have electronically excited state. Which can be prepared by light absorption a molecule can absorb light and it can be excited electronically.

And if I take such an electronically excited states, let us say it is in the i th state, that kind of system electronically excited system or vibrational excited system also is possible, they can spontaneously undergo a radiative transition from an initial state to the final state emitting a photon with an energy $h\vartheta$.

So, if the energy of the initial state is E_i and final state energy is E_f, then it can emit one photon and the system can relax back to the lower energy state and this kind of transition because it is associated with certain photon emission it is called radiative transition. Spontaneous emission is an example of radiative transition as we have shown here and excited Quantum system can also spontaneously undergo a non-radiative transition.

It can also undergo non-radiative transition and the name suggest as the name suggests, the transition will be will not be associated with any emission of photon any light. It will not accompany emission of a photon. A good example of non-radiative transition is the working principle of He-Ne laser. We have Helium Neon laser in the Helium Neon laser what happens the collision of electrons. So, we have a mixture of Helium Neon we did I guess yes mixture of Helium Neon almost 10 : 1 ratio.

Helium concentration is higher than Neon concentration and what happens we do when electrical discharge in it. So, if we in the in this case gaseous medium if we do electrical discharge, then we produce electrons energetic electrons and these electrons actually collide with this atom. So, it will because Helium concentration is high. So, Helium collision of electrons with the Helium atoms will excite the Helium atoms from its ground state.

So, initially it will be excited ground state to the excited state. So, this is the excitation process in this excitation process Helium will be excited to the ground state from ground state to the electronically excited state particular long lived electronically excited state. So, this is the excited state we have and because of a serendipitous coincidence of these Helium excited state we with the Neon excited state.

So, Helium excited state and Neon excited state they coincide with each other in energy, their energies are the same very close to each other. And that is why what happens this excited Helium then collide with ground state Neon. When it is colliding Helium excited Helium can transfer energy to the Neon and as a result, excited Helium will come back to the ground state and Neon will be as a result consequently, it will be excited to the excited state.

So, this efficient transfer of excitation energy from Helium to Neon, this occurs through the collision and this is a non-radiative energy transfer process non-radiative energy transfer process because this amount of energy is transferred to Neon system without any emission of photon. So, this is a non-radiative transition and if we see that non-radiative transition here one State to another state so, it is called state to state non-radiative transition.

Initially Helium is excited and then that excited Helium will be colliding with ground state Neon to produce this excited Neon. So, this is called state to state non-radiative transition and where one state is coupled with another state discrete state is coupled with another discrete state.

Another variety of non-radiative transition includes state to continuum non-radiative transition, where I have a discrete state here which is now transferring energy non-radiatively to a highly dense continuum or quasi–continuum states. This kind of state to continuum transition is particularly common in Photochemistry and photo physics of polyatomic molecules.

Following electric excitation of a polyatomic molecule let us say we are exciting a polyatomic molecule from its ground state which is a singlet state that is why he is not state let us say it is excited to the excited state is one excited state it is excited and then following electronic excitation excited state species can undergo a non-radiative transition back to ground electronic states.

So, this is this this entire manifold is in the ground electronic reserve vibrational manifold of the ground electronic state excited electronic state has also vibrational manifold it is here it should be somewhere here like this. But this part is associated with the entire vibrational manifold is associated with the ground vibrational state, of ground electronic state.

So, this excited species can actually undergo non-radiative transition back to the ground electronic state. As shown here with the help of this Jablonski diagram. this is a typical Jablonski diagram we use in Photochemistry to explain Photochemistry and Photo physics. In this case, non-radiative transition occurs from ground vibrational state of S_1 here to the dense vibrational manifold, very high energy vibrational states, which are very closely so closely spaced that we can say that it is a Continuum or quasi-Continuum almost continuum like.

So, this example represents a state to continuum transition, non-radiative transition. So, non-radiative transition, it is transferring that entire energy to another state either on to another state or to continue to a number of states. That is the way it is transferring the energy. We will go over in this module, we will go over the Quantum dynamics of this either both state to state non radiative transition and state to Continuum non radiative transition, which will lead to well-known Fermi's golden rule.

We will get Fermi's golden rule a rule of non-radiative transition and, and then we will see what is the limitation of Fermi's Golden Rule has and will try to overcome that limitation with the help of a rigorous treatment of Quantum Dissipative dynamics Quantum decaying dynamics.

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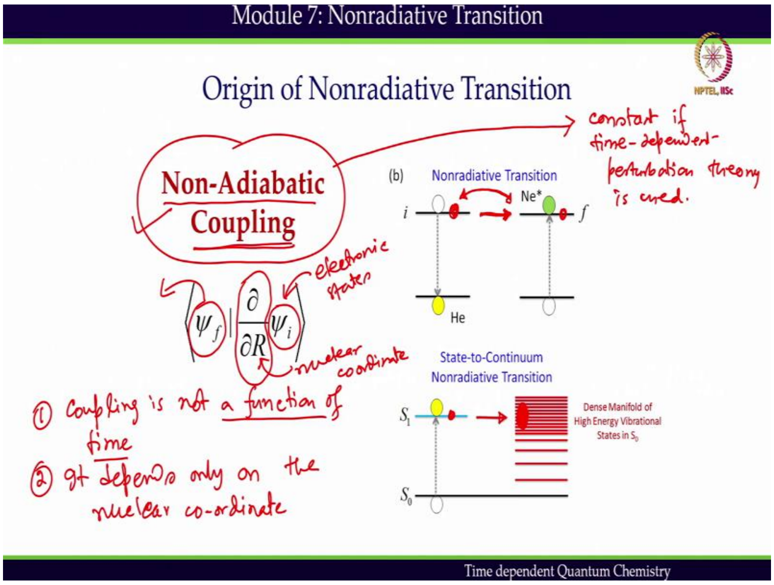

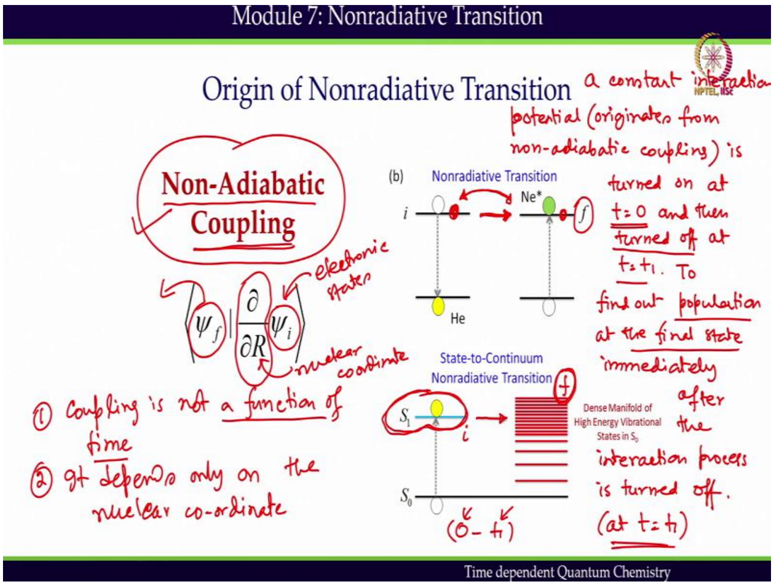

Once an excited state is populated, for example, through photoexcitation, subsequent non-radiative transition, non-radiative transition, it can be state to state or state to Continuum both are possible this non-radiative transition occurs due to one coupling. So, this state and this state these discrete states or these states and number of states here, let us say this many states they get coupled via this non-Adiabatic coupling term.

What is non-Adiabatic coupling that we will discuss in this course later, not right now, exact nature of non-Adiabatic coupling which will ultimately facilitate non radiative transition and will be discussed and also explicitly will show what is the expression mathematical expression, but in a very naive way, if we want to say what is non-Adiabatic coupling, it is nothing but one initial state and final states, they are getting coupled with the help of nuclear coordinate.

So, only thing which we will note without looking at the rigorous treatment of non-Adiabatic coupling, which we will go over later. One thing we will just note here is that non-Adiabatic coupling the this these two states are getting coupled, that is why they are transferring energy. Now, this coupling is not a function of time. That is one thing we will note here. It is a little early we are introducing non-Adiabatic coupling without looking at the exact mathematical form of non-Adiabatic coupling, which will do it later.

But if we just extract some information, which will be useful for the present module, then that is going to be two information we want to collect from the exact nature of non-Adiabatic coupling, it is not a function of time. So, it does not vary as a function of time. So, question is this coupling which is which will now lead to them this non-radiative transition. So, quite the point is that, when a system is undergoing non-radiative transition, they are basically they are getting coupled through this non-Adiabatic coupling.

And which is not a function of time and it depends only on the nuclear coordinate and that is exactly what we are showing here. This is an let us say electronic state, this is also electronic state. These are electronic states but coupled by nuclear coordinate. So, one nuclear coordinate one particular kind of nuclear coordinate is coupling these states. So, that is why it is not dependent on time and as a result of one can say that it is constant.

So, this coupling term this part can be considered to be constant if Time Dependent Perturbation theory is used. So, in the Time Dependent Perturbation theory if we want to use this coupling, which is now leading to this non-radiative transition we will say that, that is constant. So, under constant coupling potential if we try to understand the dynamics, then that is going to explore this non-radiative transition.

So, here we will as we will assume here, So, based on these facts we can actually assume describe the problem as follows a constant interaction potential interaction potential a constant interaction potential which originates from non-Adiabatic coupling is turned on at t equals 0. And then turned off at t equals t_1 time.

So, I will assume that I have a system which is electronically excited let us say I have a system which is already electronically excited this system and then at t equals 0 time I have turned on this coupling which will lead this non-Adiabatic coupling term. So, 0 to t_1 time during this interval this coupling will be acting on this system after the action after I have turned off the coupling part all I am going to check is that what is the population in the final state.

So, our task is to find out population have the final state immediately after the interaction process is turned off. So, I will repeat this one this is an important concept which needs to be adopted before we employ Time Dependent Perturbation theory. So, what is the basic idea what is the initial state initial state is the electronically excited state, let us say this is electrical excitation excited states, and then at t equals 0 time I turn on the coupling and the moment I turn on the coupling, it will start transferring the population to them final state. So, this is my initial state, this is my final states, let us say a number of it can be a number of states or it can be just a single state, both are possible.

So, at t equals 0 time, it will start the coupling which will lead the transfer of the population and at t equals t_1, I will turn off the coupling which means I have completely turn off the coupling process which will not further transfer the population anymore. And my task here is to find out the final state the population in the final state at time t, which means at t equals t_1 time I have to find out the population because that population is nothing but the probability of transfer the probability of non-Adiabatic transfer or population is nothing but the population which I have finally in the final state will assume that there was no population in the final state before the interaction process was turned on. And we have to find out the final state population with the help of Time Dependent Perturbation theory.