

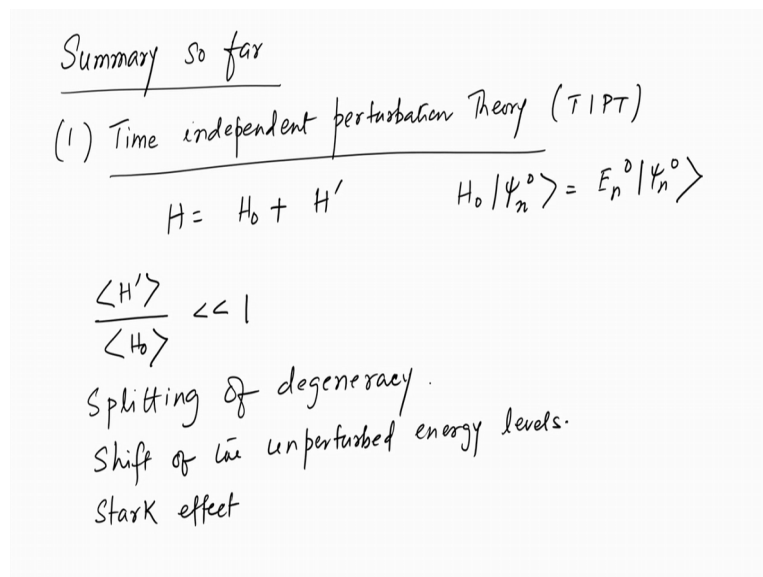
**Advanced Quantum Mechanics with Applications**  
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**Lecture - 27**

**Summary of Approximation methods, Time dependent Perturbation Theory**

Let us have a short recap on the methods of the approximation techniques, that we have learned and some of the features of that are so just small summary so far. The first approximate technique, that we have learnt is called a Time independent Perturbation Theory and in short we have called it a TIPT ok. And, the features of that are Hamiltonian is given to us, which can be split up into this two terms  $H_0$  being the unperturbed Hamiltonian which is completely known.

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So,  $H_0 \psi_n^0$  it is equal to  $E_n^0 \psi_n^0$  is known and  $H'$  is a perturbation term which is smaller or much smaller than the unperturbed Hamiltonian. By that what we mean is that the expectation value of the perturbation term, with respect to the unperturbed term is much smaller than 1. And, if you are wondering that these expectation values are calculated with respect to which states.

So, these are basically the eigenstates of the unperturbed Hamiltonian which is given here, the  $\psi_n^0$ 's that we can now see here. So, this is the condition under which we have studied the time independent perturbation theory and we have studied two variants namely the Non-

Degenerate Perturbation Theory and the Degenerate Perturbation Theory. The degenerate perturbation theory looked a little more complicated; however, it is just a finite dimensional problem and we have obtained a few salient features which are removal of degeneracy.

So, if there is a degenerate unperturbed states that in presence of the perturbation term which could be an external field, electric field or magnetic field the degeneracy gets lifted and one actually gets, sort of a closely spaced energy level which were otherwise non-degenerate otherwise degenerate in the absence of a perturbation term. So, the splitting of degeneracy and the also may be shift of the unperturbed levels. What we have seen very importantly is that, the ground state is usually non-degenerate in all these systems, that is usually under focus and other degeneracy only appears at excited states.

So, as an example we have done Stark effect in which we have calculated the first order and the second order energy correction to the ground state. And also, which of course the first order gave 0, the second order of course gave a finite correction, which is gave rise to the induced dipole moment of the hydrogen atom. The hydrogen atom, just to remind you is the simplest atom in which there is a nucleus containing a proton and there is an electron in the valance shell or the shell that is a surrounding the nucleus.

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Variational Theory

$$H \neq H_0 + H' \quad H|\psi\rangle = E|\psi\rangle.$$

(i) A variational state  $|\psi(\alpha)\rangle$  with  $\alpha$ : tunable parameter.

(ii)  $\frac{d}{d\alpha} \left[ \frac{\langle \psi(\alpha) | H | \psi(\alpha) \rangle}{\langle \psi(\alpha) | \psi(\alpha) \rangle} \right] = 0$

(iii) upper bound to the exact energy.

So, that acquires an induced dipole moment of the second order and we could also calculate the first order perturbation theory, for the first excited state of the hydrogen atom. So, these were the two main results that we have obtained in the time independent perturbation theory.

Then we had gone ahead to discuss the variational theory and the hallmark feature of that is that one has a Hamiltonian, which of course cannot be solved exactly. But, the additional problem with this is that there is no split up of this form to be available for this case.

So, I cannot split it up; so, I do not know what is the unperturbed part and the perturbation part I just have a Hamiltonian. So, this can be very easily understood that, if we have introduced sort of a field and we are not sure that the strength of the field and in which case of course, we cannot call this  $H$  prime as a perturbation and separate it out from the unperturbed Hamiltonian which is  $H_0$ . And, we have to solve still for  $H$  and so we seek a solution of  $H\psi$  to be equal to  $E\psi$ .

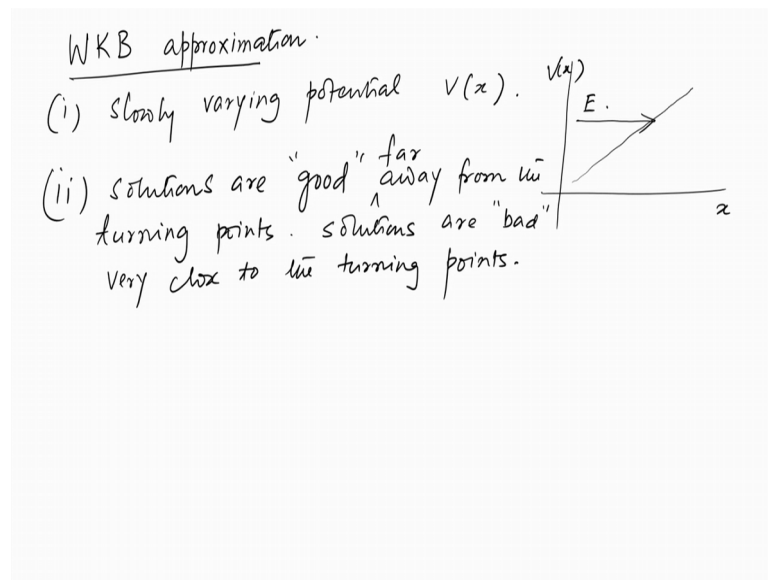
The way it is done is that, variational state is chosen with  $\alpha$  as a tuneable parameter. We have discussed that how one can actually determine  $\alpha$  by extremizing or rather minimising the energy, that is the definition of energy. And, this has to be extremized or minimised with respect to  $\alpha$  put that equal to 0, compute  $\alpha$  put that back into the wave function and that is the variational wave function. And, that wave function correspond to an energy, that energy is called as a variational energy.

Very importantly one gets upper bound to the exact energy which means that the variational energy is always above or higher than the exact energy. And, I mean what kind of a bound we have or rather how tight the bound is, upper bound is to be exact energy depends on the quality of the wave function. And, in choosing the wave function one should keep in mind about the boundary conditions.

Such as, you know particle in a box should have a wave function which should vanish at the boundaries. And, if we do not respect that then we should we still be able to do the calculation. But, the estimate of the energy say for example, we are talking about the ground state energy that we get would be quite wrong or it will be quite off from the exact energy.

In most of the situations that we have seen we have done it on the known problems I were the very well-known problems where, variational theory has been applied and with a lot of success are the hall effect, the fractional quantum hall effect by Laughlin, the wave function is a variational wave function. And, as well the BCS wave function to solve superconductivity is also has a variational parameter and the whole formalism was carried out variationally. And one obtained an expression for the superconducting transition temperature which has a good agreement with experiments.

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So, other than that we have done a third method which is called as a WKB approximation and this WKB approximation is a, it goes by the name Wentzel Kramer's and Brillouin and it is applicable for slowly varying potential. So, it is a potential that very slowly and the particle is coming from here. So, this particle has energy  $E$  and of course, the energy of the particles of this is  $V$  as a function of  $x$ . So, there is a linear variation that we have shown and of course, the region that is left to or the to the right to the straight line that is the region which is here is the region that is here is a classically forming region.

Because, here the total energy is less than the potential energy and that makes a kinetic energy to be negative which means the momentum to be imaginary which is certainly a classically forbidden region. And, we have shown that the solutions that one obtains, are asymptotically correct which means that the solutions are good far away from the, these are called turning points where a classical practical would turn back and will reverse its motion.

So, solutions are good away from the turning points or far away rather far away from the turning points and which means that solutions are bad very close to the turning points. And, we have arrived at what are called as the connection formula by matching the boundary conditions asymptotically. And, these connection formula they are found to be unidirectional which means that some solutions can be from the left, can be matched with those of right. But, the same solutions cannot be matched at the turning points from right to left and there some other solutions which can be from the left to the right, can be matched from left to the

right which cannot be matched from the right to the left and so on.

So, from these a connection formula we have obtained what are called as the Bohr Sommerfeld Quantisation condition, which is just the closed integral of a pdq which is equal to some  $n h$ . And this  $h$  is of course, the Plank's constant and this was instrumental in deriving a lot of conditions or rather quantisation conditions. One of them we have seen is that the Bohr's, formula of that the angular momentum is quantized in multiples of  $h$  over  $2\pi$ , that could be derived where  $p$  and  $q$  are of course, the generalised momentum and the coordinates respectively. And so, these are some of the features of the WKB connection formulas.

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Time dependent perturbation Theory

$$H_0 |\phi_n\rangle = E_n^0 |\phi_n\rangle \quad (0) |\phi_n\rangle : \text{unperturbed eigenstate.}$$

$$H = H_0 + H'(t) \quad (1) E_n^0 : \text{unperturbed energies.}$$

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = [H_0 + H'(t)] \psi(\vec{r}, t) \quad (2)$$

$$\text{Let } \psi(\vec{r}, t) = \phi_n(\vec{r}) g(t). \quad (3)$$

$$\text{Put } H'(t) = 0. \quad (4)$$

$$\text{Putting (3), (4) in (2).}$$

$$i\hbar \frac{\partial}{\partial t} (\phi_n(\vec{r}) g(t)) = H_0 (\phi_n(\vec{r}) g(t)) \quad (5)$$

Let us now talk about time dependent perturbation theory and the reason that we need to do this after the time independent perturbation theory is, it is one of the approximation methods in which we will see transitions of a particles or transition of say electrons or photons from one level to another, maybe from a ground state to an excited state or decay from an excited state to a ground state. And these are very important in the context of lasers in which we will learn how to calculate the Einstein's a b coefficient and so on.

So, just to make this point clear once again in time independent perturbation theory we had no transitions. We had so, those transitions are forbidden and it is only shifting of energy levels or the unperturbed eigenstates and the eigen energies, that could occur. Here there will be transitions from one level to another in presence of a time dependent perturbation.

So, once again just to make things clear, that we have this problem to be completely well known, let us write it as  $\psi_n$  and it is a  $E_n \psi_n$ ; understand that  $\psi_n$  is the unperturbed eigenstates and  $E_n$  are the unperturbed energies ok. And, we have to solve problem in which I have the full Hamiltonian looking like this, but now this  $H'$  depends on time. So, as if there is a sinusoidal field that we are driving the system with so,  $H'$  is a time dependent quantity.

So, we have to solve now an equation which is  $i\hbar \frac{\partial \psi}{\partial t}$  and we have a  $H_0$  plus a  $H'(t)$  and a  $\psi(t)$ . So, let  $\psi(t)$  be so, let us make this an such that  $\psi(t)$  is like can be split into or rather it is a function of both  $r$  and  $t$ . So, this is not only  $t$  but it is a function of  $r$  and  $t$ . So, make it very clear, this  $r$  is in general of vector we are we could write it as a vector  $r$ . So, this is a vector and  $t$  are the time and  $r$  could be  $x, y, z$ , the vector  $r$  could be consisting of three Cartesian coordinates or three spherical polar coordinates such as  $r, \theta$  and  $\phi$  and so on.

So, this certainly can be split into a term which is  $\psi(r)$  and a  $g(t)$ , because the space and time would not mix. So, we can write this as that now if you put  $H'(t)$  equal to 0 just to find out, what the time evolution of the unperturbed eigenstates are. So, we put this equal to 0 and then put this into so, let us call this as equation may be 1, equation 2 and 3. So, putting 3 in and if you call it a 4, putting 3 and 4 that is also making  $H'$  to be equal to 0 in to one gets an equation which is fairly simple, it is  $i\hbar \frac{\partial \psi}{\partial t}$  of a  $\psi(r)$ , we could write here  $\psi_n(r)$ .

So, that is those eigenstates that we have talked about and  $g(t)$ . So,  $g(t)$  is the temporal part which takes into account the time dependence and  $\psi_n(r)$ , takes into account the special dependence and this is equal to  $E_n \psi_n(r)$  and  $g(t)$ . For the moment, I am doing way without the with the ket notation, but simply writing it as an algebraic quantity here. So, that is my 5, that is equation 5 and we of course know that so this would give me a  $\psi_n(r)$  and  $i\hbar \frac{d}{dt} g(t)$  it is equal to  $E_n$ .

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$$\begin{aligned} \phi_n(\vec{r}) i\hbar \dot{g}(t) &= E_n^0 \phi_n(\vec{r}) g(t) \\ i\hbar \frac{\dot{g}(t)}{g(t)} &= E_n^0 \Rightarrow g(t) = e^{-iE_n^0 t/\hbar} \end{aligned} \quad (5)$$

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-iE_n^0 t/\hbar} |\phi_n\rangle$$

Putting (5) into (2).

$$\begin{aligned} \sum_n \left[ i\hbar \dot{c}_n(t) e^{-iE_n^0 t/\hbar} + E_n^0 c_n(t) \right] \phi_n(\vec{r}) &= \sum_n \left[ H_0 + H'(t) \right] c_n(t) e^{-iE_n^0 t/\hbar} \phi_n(\vec{r}) \\ i\hbar \sum_n \dot{c}_n(t) e^{-iE_n^0 t/\hbar} &= \sum_n H'(t) c_n(t) e^{-iE_n^0 t/\hbar} \end{aligned} \quad (6)$$

So, that is let us not write it with the bracket,  $E_n^0 \phi_n(\vec{r})$  and the  $g(t)$  and since  $\phi_n$  and 0 is not equal to 0. So, we can write this as  $i\hbar \dot{g}(t) = E_n^0 g(t)$  which is equal to  $E_n^0$  that gives us a solution  $g(t)$  equal to exponential minus  $i E_n^0 t$  by  $\hbar$  cross. So, that immediately brings us to the  $\psi$  of  $t$ , which is the full wave function, this is equal to a sum over  $n$   $C_n(t)$ , exponential minus  $E_n^0 t$  over  $\hbar$  cross and a  $\phi_n$  sorry  $\phi_n$ , because we have written it as  $\phi_n^0$ . If you want to put the ket here, they mean the same thing. So, this is the important part that for a Hamiltonian, that is independent of time. The time evolution of the eigenstates can be expressed like this.

So, there is a sum over  $n$  and  $C_n(t)$ 's are the coefficients which depend only on time and the basis vectors or rather the  $\phi_n$ 's they do not depend upon time. And, there is a stationary state evolution that is the mod  $\psi$  square is independent of time for all time, when the Hamiltonian does not depend upon time. So, the probability density is independent of time and these are called as stationary states and if of course, our  $H'$  of  $t$  remains 0 at all times.

Now, we are going to bring in the  $H'$  of  $t$ , if  $H'$  of  $t$  is 0 for all times then  $C_n(t)$  is independent of  $t$ . However, this thing now can be put into so, let us call this as equation 5 and we are going to put it in 2. So, equation 5 and putting a 5 into 2, one gets summation over  $n$   $i\hbar \dot{C}_n(t)$  with a dot, just mind these dots carefully because this dots maybe sometimes invisible; let us just show me show you once. So, there is a dot here there is a dot here  $g(t)$ .

And so, is a dot here  $C_n$ , dot  $t$  so, this and exponential minus  $i E_n^0 t$  over  $\hbar$  cross equal to sum over  $n$   $H_{0n}$  plus  $H'$  prime  $t$  and  $C_n t$ . And, so there is the term that we have missed here should not miss that. So, there is a  $E_n^0 C_n$  of  $t$  because, you have to differentiate this, keeping this as constant which is the first term and differentiate this, keeping this as the constant which is the second term. So, that is the those are the two terms that will be there.

So, this is and there is of course, a  $\phi_n$  of  $r$  and there is a  $C_n t$  exponential minus  $i E_n^0 t$  by  $\hbar$  cross and a  $\phi_n$  of  $r$ . So, that is the question that one has to solve and this tells us that so, if we transferred the  $C_n t$ 's into one side or do a bit of simplification by assuming that the first equation which went unnumbered. So, let us call that as equation 0. So, if you use equation 0 and simplify this this becomes equal to  $i \hbar$  cross  $C_n$  dot  $t$  exponential minus  $i E_n^0 t$  by  $\hbar$  cross. And, the  $C_n t$  is been transferred to the other side and this is equal to a  $H'$  prime of  $t C_n$  of  $t$  and exponential minus  $E_n^0 t$  over  $\hbar$  cross and then the  $\phi$  of course, cancel from both sides.

So, that is the equation that one has, let us call that as equation 6 and this equation see one thing in equation 6 is that  $C_n$  dot includes a power of  $H'$  prime, because there is a  $H'$  prime on the side. So, if  $C_n$  prime or  $C_n$  dot can be expanded in powers of  $H'$  prime. So, one will always get the same power of  $H'$  prime that is there on both sides of equation 8 or equation 6.

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Take an inner product with  $\phi_m$  and hence divide by  $e^{-i E_m^0 t / \hbar}$ . (use  $\langle \phi_n | \phi_m \rangle = \delta_{nm}$ ).

$$i \hbar \dot{c}_m(t) = \sum_n c_n(t) e^{i(E_m^0 - E_n^0)t/\hbar} \langle \phi_m | H' | \phi_n \rangle$$

At the first order

$$i \hbar \dot{c}_m^{(1)}(t) = \sum_n \delta_{nk} H'_{mn} e^{i \omega_{mk} t} \quad \omega_{mk} = \frac{E_m^0 - E_n^0}{\hbar}$$

$$H'_{mn} = \langle \phi_m | H' | \phi_n \rangle$$

$$c_m^{(1)}(t) = \frac{1}{i \hbar} H'_{mk} e^{i \omega_{mk} t}$$

$$c_m^{(1)}(t) = \frac{1}{i \hbar} \int_{-\infty}^t H'_{mk}(t') e^{i \omega_{mk} t'} dt'$$

In order to simplify this further let us take an inner product with  $\phi_n \phi_m$  and use the orthogonality relation. And then of course, again divide by exponential and hence, divide by



exponential minus  $i E_m^0 t / \hbar$  by  $\hbar$  cross one arrives at the and of course, use  $i \hbar$  cross  $C_m \dot{t}$  it is equal to sum over  $n$   $C_n t$  and exponential  $i E_m^0 - E_n^0 t / \hbar$  cross and now there is a  $\langle \phi_m | H' | \phi_n \rangle$ .

So, it is very clear that  $m$  is not equal to  $n$  here and  $m$  and  $n$  actually corresponds to two different states and that is what we are interested in that whether, this can cause a transition from one state to another. This is the matrix element which is been computed between two orthogonal states  $\phi_m$  and  $\phi_n$ . And so, we have been able to strip off the left-hand side from a summation and the summation is entirely on this on the right-hand side over  $n$ . So, the  $m$  index is free,  $m$  is coming from the energies as well as the matrix elements and so on.

Now, what could happen is that, if for some reason we take this as  $\delta_{nk}$ , will tell you just in a while that, why we are taking it as a delta function  $\delta_{nk}$ . If we take it then this is a sum over  $n$  and there is a  $\delta_{nk} \langle \phi_m | H' | \phi_n \rangle$  and exponential  $i \omega_{mk} t$ , where  $\omega_{mk}$  is equal  $E_m^0 - E_k^0$  divided by  $\hbar$  cross. And  $\langle \phi_m | H' | \phi_n \rangle$  is nothing but the matrix elements  $\langle \phi_m | H' | \phi_n \rangle$ . And so, if this is true then this is equal to your  $i \hbar$  cross  $C_m \dot{t}$  and so  $C_m \dot{t}$  is equal to. So, we are now making an approximation of at the first order where the 0th order, because as I said that if this is first order then this has to be 0th order and does not include the effect of  $H'$ , because there is already an  $H'$  that is there in this matrix element.

So, this at the first order so, this is at the first order, So, this is equal to 1 by  $i \hbar$  cross  $\langle \phi_m | H' | \phi_k \rangle$  exponential  $i \omega_{mk} t$ . So, that is your first order coefficient that or the time derivative of the coefficient. And, if I simply want the coefficient itself because that is related to the probability density, I need to integrate it. I am putting the integration limit now from minus infinity to  $t$  and make this  $\langle \phi_m | H' | \phi_k \rangle$  which was always a function of  $t$  which was not written here it is a function of  $t$ .

So, this is a function of  $t$  I put a  $t'$ ,  $t'$  for a dummy variable it is actually the same as  $t$ . So, that is a time and a  $dt'$  and I am putting the limit from minus infinity to  $t$ , as if the perturbation is switched on at minus infinity and it is switched off only at  $t$  ok. Let us make this discuss a little more concrete and we will also explain that why at the 0th order, we have written this  $C_n(t)$  as the  $\delta_{nk}$  which is independent of time. But, let me box this because this is one of the important working formula of this or the mod square of this is actually the working formula. A few details about the perturbation ok.

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A few details about the perturbation.

$$H'(t) = 0 \text{ for } t < 0 \text{ and } t > t_0.$$

The perturbation is switched on for time  $t_0$ .

$$C_m^{(1)}(t_0) = \frac{1}{i\hbar} \int_0^{t_0} H'_{mk}(t') e^{i\omega_{mk}t'} dt'$$
$$C_m^{(1)}(t) = C_m^{(1)}(t_0) \text{ for } t > t_0$$

So, let us make it little simpler. So,  $H'$  prime  $t$  equal to 0 for  $t$  less than 0 or I do not need so, it is  $t$  less than 0 and  $t$  greater than equal to  $t_0$ . So, it is only switched on at  $t$  equal to 0 and switched off at  $t_0$ . So, the perturbation is switched on for time  $t_0$ . So, what is then the  $C_m^{(1)}$ , this 1 as I said correspond to the first order perturbation theory  $t_0$  it is equal to 1 by  $\hbar$  cross 0 to  $t_0$   $H'$  prime  $m$   $k$   $t$  prime exponential  $i$   $\omega_{mk}$   $t$  prime  $dt$  prime. And of course,  $C_m^{(1)}$   $t$  equal to  $C_m^{(1)}$   $t_0$  for all time for  $t$  greater than  $t_0$ ; we can also make this as just  $t$  greater than  $t_0$ . So, that is so, the perturbation is of course, switched on in this time interval.

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At zeroth order.

(i) for  $t < 0$ ,  $\bar{u}$  system is assumed to be in  $|\phi_k\rangle$ .

(ii) of all the coefficients,  $C_n(t)$  only  $C_k(t)$  survives,  $C_k(t) = C_k(0)$  for all  $t$ .

(iii) At  $t=0$   $H'$  is switched and rises discontinuously to a finite value  $H'(0)$ .

(iv) Since  $H'(t)$  remains finite,  $\bar{u}$  solution of Schrödinger equation, i.e.  $\bar{u}$  eigenstates are continuous.

(v)  $C_n(t=0) = \delta_{nk}$   $C_n(0)\phi_n = \phi_k$ .

So, let us now see this  $\delta n k$  and how it comes that is the 0th order. So, at 0th order for  $t$  less than 0, the system is assumed to be in  $\phi_k$ . And so, of all the coefficients  $C_n(t)$  only  $C_k(t)$  survives and not only this survives  $C_k(t)$  is equal to  $C_k(0)$  for all  $t < 0$ . Because, that is independent of time, because your  $H'$  is equal to 0. So, this is for  $t < 0$ , at  $t = 0$  keep this in mind, at  $t = 0$  the perturbation is switched on. So, at  $t = 0$   $H'$  is switched on and rises discontinuously to a finite value, it rises discontinuously to a finite value to  $H_0$ .

So, this is  $H_0$  at time 0 and then it could have a time variation, but at least it rises discontinuously at that value at  $t = 0$ , because we said that it is switched on at  $t = 0$  and then switched off at  $t = t_0$ . Now, since  $H'$  remains finite, the solution of Schrodinger equation, that is the eigenstates are smooth, smooth means continuous. So, if the eigenstates are continuous the amplitudes the  $C_n(t)$  at  $t = 0$  has to match with the  $\phi_k$  and hence, this has to be  $\delta n k$  such that,  $C_n, \phi_n$  becomes equal to  $\phi_k$  at  $t = 0$ . So, basically  $C_n(0) \phi_n$  has to be equal to  $\phi_k$ . So, which means that this has to be equal to  $\delta n k$  and that was the reason that at 0th order we have plugged in  $\delta n k$  in place of the coefficient  $C_n$  at 0 alright.

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Example A H-atom in its ground state is subjected to an electric field which is switched on and off such that,

$$\vec{E}(t) = \vec{E}_0 e^{-t^2/\tau^2} \quad t \gg \tau.$$

What is the probability that the H-atom lands up in  $(210)$ ?

Ans:  $H'(t) = e E_0 z e^{-t^2/\tau^2}$

$$C_{210}(\infty) = \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt' e^{i(E_{210} - E_{100})t'/\hbar} e^{-t'^2/\tau^2} (H')_{210,100}$$

$$= \frac{e E_0}{i\hbar} \langle \phi_{210} | z | \phi_{100} \rangle \int_{-\infty}^{\infty} dt' e^{i\omega t' - t'^2/\tau^2}$$

$$\omega = \frac{E_{210} - E_{100}}{\hbar} = \frac{e E_0}{i\hbar} \langle \phi_{210} | z | \phi_{100} \rangle \tau \sqrt{\pi} e^{-\omega^2 \tau^2 / 4}$$

So, after this we will talk about the transition probability of for a time dependent perturbation. But, before that let us do one example problem is quite interesting in its own sense. It says a hydrogen atom in short I will write it as a H atom in its ground state is

subjected to an electric field which is switched on and off such that, basically the form of the or rather the time dependence of the electric field is as follows.

So, its electric field which is equal to  $E_0 \exp(-t^2/\tau^2)$  where  $t$  is much greater than  $\tau$ ; so, the question is what is the probability that the H atom so, it was initially in its ground state. So, remember that our ground state in the previous discussion was  $\psi_{100}$ . So, that is the  $\psi_{100}$  and so, this lands up in  $210$  state. So,  $210$  means  $n$  equal to 2,  $l$  equal to 1 and  $m$  equal to 0. So, that is the first excited state and so, this is the question that what is the probability the transition probability from, for the hydrogen atom or rather the electron in the hydrogen atom to make a transition from the ground state which is  $100$  to a state which is  $210$ .

So, what is the form of the perturbation here? It is  $H' = e E_0 z \exp(-t^2/\tau^2)$ . This is like the Stark effect that we have seen. So,  $z$  is equal to  $r \cos \theta$  where we simply had the  $e E_0 z$ , because the way the perturbation was time independent, here the perturbation depends on time.

Now, since  $t$  is far greater than  $\tau$  which is the denominator we can set the integration limit from minus infinity to plus infinity. So, we have to calculate a  $C_{210}$ , I am writing it as infinity it is actually  $t_0$ , but since  $t_0$  the time for which it switched on is very large. So, this is equal to  $\frac{1}{i\hbar} \int_{-\infty}^{+\infty} dt' \exp(i\omega t') \psi_{210} - \psi_{100}$  which is the known quantity of course, because this has a minus 3.4 electron volt energy and this has an energy minus 13.6 electron volt.

So, this divided by that and then  $\exp(-t'^2/\tau^2)$  and I have to calculate  $H'$  between  $210$  state and  $100$  state, which is known thing I will skip that for now and write it as simply equal to a  $\psi_{210} H'$  which is a nothing, but  $z$ . So, here it is  $z$ ,  $z$  is the  $r \cos \theta$ . So, given the wave function, this is what we have seen how to calculate this in the Stark effect picture and this is from minus infinity to plus infinity  $dt'$   $\exp(i\omega t')$ . Let us just call it as  $\omega$ , because  $t'$  and  $\exp(i\omega t')$  square by  $\tau^2$ . And so, where  $\omega$  equal to this  $E_{210} - E_{100}$  divided by  $\hbar$  cross  $\omega$  is of course, that minus 13.6 plus 3.4 electron volt by  $\hbar$  cross.

Now, this I this part I leave it to you to work out, because that is just going to be a number and this is a  $\psi_{210} z \psi_{100}$ . And, it is a  $\tau$  root over of  $\pi$  that is the integral that comes, and  $\exp(-\omega^2 \tau^2/4)$  and of course, there is bit of a

problem because it shows that, so the probability of transition is given by P equal to C 210 this infinity square.

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Probability of transition:

$$P = |C_{210}(\infty)|^2$$

When  $\tau \rightarrow \infty$ ,  $P \rightarrow 0$ .

When the perturbation is switched on adiabatically then the atom adjusts adiabatically and does not make a transition.

So, when tau goes to infinity that is the time constant goes to infinity P goes to 0. So, the physical meaning is that when the perturbation is switched on adiabatically, then the atom adjusts adiabatically and does not make a transition. So, this is the transition probability for such a such an event to occur.

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Application of the first order result to Fermi's Golden rule.

$$H'_{mk}(t) = A_{mk} \sin \omega t$$

$A_{mk}$  is time independent. Want to find  $C_m^{(1)}(t)$

$k = \text{ground state}$  and  $m = \text{excited state}$ .

$$C_m^{(1)}(t) = \frac{1}{i\hbar} A_{mk} \int_0^t dt' e^{i\omega_{mk}t'} \left[ \frac{e^{i\omega t'} - e^{-i\omega t'}}{2i} \right]$$

$$= \frac{A_{mk}}{-2\hbar} \int_0^t dt' \left[ e^{it'(\omega_{mk} + \omega)} - e^{it'(\omega_{mk} - \omega)} \right]$$

$$= \frac{iA_{mk}}{2\hbar} \left[ \frac{e^{it_0(\omega_{mk} + \omega)} - 1}{\omega_{mk} + \omega} - \frac{e^{it_0(\omega_{mk} - \omega)} - 1}{\omega_{mk} - \omega} \right]$$

So, let us carry on with what is called as the Fermi's golden rule and how to apply this time

dependent perturbation theory for a harmonically given system. So, let us assume that we have a harmonic perturbation of the form  $H' = H_{mk}$ . So, now just to make matters clear  $m$  is an excited state and  $k$  is the ground state just for a specific case and this is equal to  $A_{mk}$ . So, in our last problem this was like our  $A_{mk}$ . So, this is that matrix element which does not depend on time and there is a time dependence that is so, this is that  $A_{mk}$  and this is the time dependent part, here it is harmonic ok.

So, as if there is field that is switched on a harmonic field that is switched on and  $A_{mk}$  is of course, time independent and we want to find  $C_{m1}(t)$  and  $k$  is the ground state and  $m$  is the excited state ok. So, if this is the case then  $C_{m1}(t)$  it is equal to  $1$  by  $i\hbar$  cross  $A_{mk}$  and say it is switched on again from  $0$  to  $t_0$ , it is a dt prime exponential  $i t$  prime. So, this is a  $i\omega_{mk} t$  prime and the sign I am going to write it as exponential  $i\omega_{mk} t$  prime minus exponential minus  $i\omega_{mk} t$  prime divided by  $2i$ . And, so this is if you do a bit of simplification then this becomes equal to  $t_0$  and a dt prime exponential  $i t$  prime  $\omega_{mk} + \omega_{mk}$ , minus exponential  $i t$  prime  $\omega_{mk} - \omega_{mk}$  or rather  $\omega_{mk} - \omega_{mk}$  minus  $\omega_{mk}$  one should write it symmetrically.

So, let us write it symmetrically, it is a  $\omega_{mk} + \omega_{mk}$  and it is  $\omega_{mk} - \omega_{mk}$  and divide this  $2i$  has been taken into account. So, if I do this integral it comes out as just a little bit of simplification it comes out as,  $2\hbar$  cross and then exponential  $i t_0 \omega_{mk} + \omega_{mk}$  plus  $\omega_{mk} - 1$ , divided by  $\omega_{mk} + \omega_{mk}$  and exponential  $i t_0 \omega_{mk} - \omega_{mk}$  minus  $\omega_{mk} - 1$  divided by  $\omega_{mk} - \omega_{mk}$ . And, we want to stop here for now and just to mention that these terms are called as the anti-resonant term. The first one inside the square bracket is called as the anti-resonant term and the second one is called as the resonant term.

The first term is related to the absorption. So, that the perturbation actually carries away energy whereas, in the second term which is called as a resonant term which is of important to us, mainly important to us that actually pumps in energy to the system which leads to emission. So, these are emission and absorption, the spectra or the spectrum, that we are interested in they would contribute respectively to these energies. As we said that we are mostly interested in the resonant term and only one will contribute at a time, under certain circumstances which is what we are going to see. Now, if it happens that the final state falls into a continuum of energies then we cannot very sharply define the transition probability for a final state.

So, then we will have talk about the probability density and that probability will come out by integrating over the final density of states. And, this is known as the Fermi's golden rule, this is what we are going to do just immediately afterwards.