

Foundation of Quantum Theory: Relativistic Approach
Change in atomic characteristics via field interactions
Perturbation theory 1.3
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Lecture- 03

So let us resume our discussion in the time independent perturbation theory regime where in the previous class we learned about if there is a perturbation Hamiltonian which is correcting the correct description of the Hamiltonian which we are discussing about, then both the eigenvalues as well as the eigenfunctions do change as a function of the parameter which comes with the Hamiltonian. So with the λ parameter which appears as a correction, the wave function as well as the eigenvalue of the energy gets corrected as a function of λ and we expanded these corrections in a power series of λ . So I would have unperturbed wave function plus first order correction coming with parameter λ , second order correction to that coming with parameter λ^2 and so on and similarly in the energy as well the same game will happen that it would have unperturbed energy and then first order correction coming with λ then the second order correction to energy with order λ^2 and so on our job was to find out what are these correction functions in the eigen function and in the energy eigenvalue as well.

Order λ^0 : $H_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$

Order λ^1 : $H_0 \psi_n^{(1)} + H_1 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}$

$\langle \psi_n^{(0)} |$ projection gives

$\langle \psi_n^{(0)} | H_1 | \psi_n^{(0)} \rangle = E_n^{(1)}$

$\langle \psi_l^{(0)} |$ projection with $l \neq n$

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$\langle \psi_n^{(0)} | H_0 | \psi_n^{(0)} \rangle = E_n^{(0)}$

$\langle \psi_l^{(0)} |$ is a projection with $l \neq n$

$E_l^{(0)} \langle \psi_l^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_l^{(0)} | H_1 | \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_l^{(0)} | \psi_n^{(1)} \rangle$

$\Rightarrow \langle \psi_l^{(0)} | \psi_n^{(1)} \rangle = \frac{\langle \psi_l^{(0)} | H_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_l^{(0)})}$

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So we ended up getting these results that if I have a perturbation Hamiltonian \mathcal{H} , that brings out this as the first order correction in the eigenvalue $E_n^{(1)}$. This is the first order correction which is just the expectation of the perturbation Hamiltonian between the states of n-th eigen energy level of unperturbed Hamiltonian.

Similarly, we found out that the first order correction to the wave function $\psi_n^{(1)}$ is an expansion over the basis of the unperturbed Hamiltonian. Just one term is missing, which is the eigenfunction itself over which the correction is being found out. And these corrections $\psi_n^{(1)}$ are totally characterized by the coefficient C_n^m s which are coming here so if I know what are the C_n^m s I know what is the correction first order correction to the wave function and we found out that these C_n^m s are also to be obtained from the matrix element of the Hamiltonian. So, we obtain that these C_n^m s or C_n^l s. I have written over here are nothing but the matrix element of the perturbation Hamiltonian \mathcal{A} , squeezed between ψ_n of the unperturbed state from the right and ψ_l , the unperturbed l^{th} eigen energy, energy eigen state from the left. So, on the numerator, I have an n^{th} matrix element of the perturbation Hamiltonian \mathcal{A} , and that gets divided by the energy difference between the unperturbed Eigen functions, Eigen states $E_n^{(0)}$ and $E_l^{(0)}$. So we computed those things for harmonic oscillator with a Hamiltonian, which is relativistic correction to the kinetic energy. And we found out what is the first order correction to the energy eigenvalue $E_n^{(1)}$. And we also found out what are the corrections to the first order correction to the energy eigenstate C_n^l . In particular, I wanted to know how much the ground states get changed. So we learned that the ground state becomes the unperturbed ground state plus first order correction is C_0^2 coming with the second excited state, the second correction which is still at order λ . All these things are at order λ itself. They are coming with coefficient C_0^2, C_0^4 and so on. C_0^1 for example is 0 as we computed, C_0^3 is also 0 and you are left out, you were given a task of finding out what is C_0^2 . The computation is simple all right so now let us cement this notion with one more computation one more example where we will be discussing an atom talking to externally applied field. I'm taking this example because throughout the course, when we develop it further, one idea of the course is to discuss matter field interaction. As we evolve in the course, we will see more and more examples of this where we not only try to learn about what happens to atom, but we also invoke quantum features to the externally applied field as well. It is a good idea to start with the classical field as an externally applied agent.

So what we talk about?

This is a hydrogen atom whose Hamiltonian is kinetic energy - the Coulomb potential which is the unperturbed Hamiltonian \mathcal{H}_0 as we know. And then there is a correction term which is coming from application of an externally applied electric field. The electron for which we are trying to write down this Hamiltonian will see the electric field present and would therefore feel a electric potential which is the amount of electric field which is constant in time. I am assuming this that it is constant in time because we are doing time independent perturbation theory.

For that constant electric field the electric potential is E times z if I have applied the electric field in the z direction, this is the potential I would be getting, potential energy of the electron put in the electromagnetic electric potential ϕ .

Now, you can see that the electric field is the - of the gradient of the potential. Therefore, with the potential being - e times E being the electric field magnitude times z then it becomes just its gradient just becomes constant electric field in the z direction. Now in spherical polar coordinate system the coordinate z can be written as $r \cos\theta$ as you are familiar with. This is the z axis this is the x -axis and this is the y -axis and the angle which it makes with the z -axis is the angle θ .

Now, perturbation Hamiltonian is known to us which is $E r \cos\theta$, the position operator r is the parameter which is coming in as an operator. So, we will work in the position representation of the system. In any case, the first order correction to let us say the ground state, ground state of hydrogen atom is n is equal to 1. Remember unperturbed energy eigenstates of hydrogen atom was was - $13.6 \text{ eV} / n^2$. . Therefore, n is equal to 1 is the ground state. If I want to know what is the first order correction to the ground state. So, I will compute E_1^1 n being 1 and this 1 upstairs is the first order correction. That would be the

perturbation Hamiltonian squeezed between the ground states. So, this exercise we have to do. So, I have \mathcal{H} , which is known to me which is nothing but e times electric field and times $r \cos \theta$ which is z .

And this has to be squeezed between the ground state that means in position representation I have to integrate the perturbation Hamiltonian with $\psi_n^{(1)*}(r)$ from the left and $\psi_n^{(1)}(r)$ from the right, the ground state wave function. And we know in hydrogen atom the ground state wave function is this exponential - r upon a_0 with a constant factor which is coming outside, where a_0 is the Bohr radius as we understand.

Example 2: Hydrogen atom in electric field

$\mathcal{H} = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} - eEz$ (Constant in time assumed)

$\mathcal{H}_0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$

$V = eEz$

$\mathcal{H}_1 = qEz = E \hat{r} \cos \theta$

$E = -\nabla \phi$

$E_1^{(1)} = \langle \psi_1^{(0)} | \mathcal{H}_1 | \psi_1^{(0)} \rangle$

$= -eE \int d^3r \psi_1^{(0)*}(r) r \cos \theta \psi_1^{(0)}(r)$

$\psi_1(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$

$= -eE \int d\phi \int d\cos \theta \int dr r^2 \frac{1}{\pi a_0^3} e^{-2r/a_0} r \cos \theta$

Example 2: Hydrogen atom in electric field.

$$H = \frac{\vec{p}^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} - eEz \quad \text{Constant in time}$$

$$H_1 = qEz = Ercos\theta$$

$$E_1^{(1)} = \langle \psi_1^{(0)} | \mathcal{H}_1 | \psi_1^{(0)} \rangle$$

$$= -eE \int d^3r \psi^*(r) r \cos \theta \psi_1(r)$$

$$\psi_1(r) = \frac{1}{\sqrt{\pi a^3/2_0}} e^{-\frac{r}{a}}$$

$$= -eE \int_0^{2\pi} d\phi \int_{-1}^1 d\cos \theta \int_0^\infty dr r^2 \frac{1}{\pi a_0^3} e^{-2r/a_0} r \cos \theta$$

So, we can do this computation, we can evaluate this integral by just putting $\psi_n^{(1)}$ here and $\psi_n^{(1)}$ star here and you will get an integration of this kind. You will see that the exponential will get doubled

$dr r^2 \frac{1}{\pi a_0^3} e^{-2r/a_0} r \cos \theta$ will come from the square of these quantities because $\psi_n^{(1)*}(r)$ and $\psi_n^{(1)}(r)$ are coming from, coming about. Now, the measure the d^3r can be written as $d\phi$ integral, $\sin d\theta$ integral

which can be compactly written as $d\cos\theta$ integral. In $\sin\theta d\theta$ case, the angle would run from 0 to π . But if I use $d\cos\theta$, the $\cos\theta$ will run from -1 to 1. Then in this case, the radial parts measure will be $dr r^2$. So this is just d^3r written in their respective limits. And this overall is the $|\psi_1|^2$, which is coming from $\psi_n^{(1)}(r)$ here and $\psi_n^{(1)*}(r)$ here and this object $-eE\cos\theta$ is just the Hamiltonian of perturbation. So, ultimately I have to do this integration, ϕ integral is simple to do because the ϕ integration is simple to do because there is no ϕ dependence in the expression.

Okay so let us move to another example to see these things in action so we will consider a hydrogen atom electron in that is interacting with high electric field which is applied externally so we will be dealing with these examples more and more. Because in the event of this course and during discussions of course, one idea is to develop the understanding of matter field interaction.

So, therefore, we will see these kind of examples very frequently.

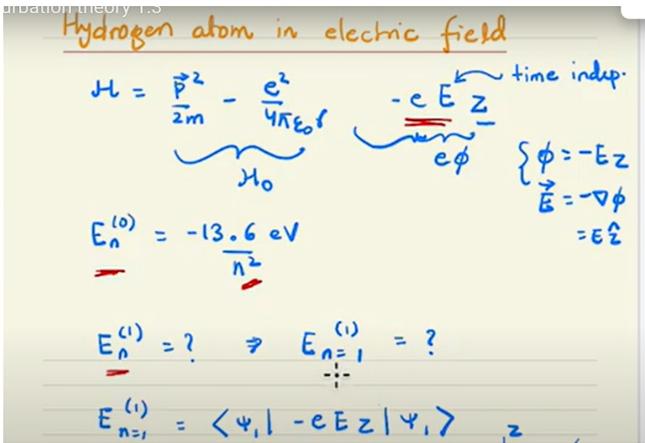
So, it is good idea to build things start from the very beginnings, starting with classical electric field, which is time independent. A constant electric field is applied in a direction z such that the electron in the hydrogen atom which was already living under unperturbed Hamiltonian which was kinetic term plus Coulomb potential, so that was the unperturbed Hamiltonian \mathcal{H}_0 . And now due to application of the externally applied electric field there is another term which is electric charge times the potential of the electric field $e\phi$, ϕ happens to be $-Ez$ where ϕ is $-Ez$. That means the electric field is $-\nabla\phi$ which is equal to E along the z direction.

So, this is how the Hamiltonian of such a system is written. We know that unperturbed system which is the ordinary hydrogen atom, the electrons live in energy eigenstates with eigenvalues given by this expression over here. $E_n^{(0)}$ on part of the eigenstates are $-13.6eV/n^2$ where n denotes which eigenstate we are talking about ground state is n is equal to 1, first excited state is n is equal to 2, second excited state is n is equal to 3 and so on.

So, I hope these things are familiar to you through your discussions or your exposure to quantum mechanics.

Now, we want to know under the action of the external electric field, this Hamiltonian, what happens to the ground state energy? Does it remain $-13.6eV/n^2$ where n is equal to 1 or 2 or 3 depending upon which state we are talking about. So, we want to know what happens to any general eigenstates energy, whether it shift and if it shifts by how much amount.

For a particular case, I am interested in knowing what is the first order correction in the energy eigenvalue of the ground state. That means I want to know how much change at the leading order λ is brought about by the perturbation of this Hamiltonian. So \mathcal{H}_1 is $E\phi$. Okay?



Hydrogen atom in electric field

$$H = \frac{\vec{p}^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} - eEz$$

$$e\phi \quad \left\{ \begin{array}{l} \phi = -Ez \\ \vec{E} = -\nabla\phi = E\hat{z} \end{array} \right.$$

$$E_n^{(1)} = ? \quad E_{n=1}^{(0)} = ?$$

$$E_{n=1}^{(0)} = \langle \psi_1 | -eEz | \psi_1 \rangle$$

So in order to compute the first order correction, what I have to do I have to take the Hamiltonian which is $e\phi$ and since ϕ is $-E$ times z , the Hamiltonian therefore becomes $-e$ times capital E which is electric field times z and squeeze it between the ground state n and is equal to 1. So, that would be the first order correction to the energy eigenvalue of the ground state. In order to do so I have to compute this object. One easier way of computing this is going to the position representation.

For harmonic oscillator it was more convenient to work with bra-ket notations and in this case it is more convenient to work in the position representation. So I will just evaluate this thing in position basis. For that, I need to know how does the wave function, ground state wave function $\psi_n^{(1)}$ looks like in the position representation. We all know the answer. It looks like an exponentially decaying function, e^{-r/a_0} with a normalization dictated by $\frac{1}{\sqrt{\pi a^3/2}} e^{-r/a}$, where this a_0 is the Bohr radius. So, this is about the wave function.

Its conjugate, the $\langle \psi_1 |$ would be just complex conjugation of this. The Hamiltonian itself, this would be e times E times z . z in the radial coordinate or spherically polar coordinates, z would be written as $r\cos\theta$. So, given z , given r , vector r , its projection along the z axis is $r\cos\theta$. So, now we are ready. We have the position representation of the wave function. We have the position representation of the Hamiltonian of perturbation and then we can compute the first order correction to the ground state energy. So, $E_n^{(1)}$ ground state first order correction is this integral $\int \psi_1 \psi_1^* \dots$ which is together making $|\psi_1|^2$ and the Hamiltonian. So, let us write these things nicely. The d^3r integral which is appearing over here can be broken into three pieces $d\phi$ integrals from 0 to 2π , $d\theta$ integral with a $\sin\theta$ coefficient which can collectively be written as $d\cos\theta$ running from -1 to 1 and dr integration with a major r square running from 0 to infinity. So, this whole thing the three limits integral r is just a total volume integral in spherical polar coordinates. After that I have a Hamiltonian $eE r\cos\theta$ where $r\cos\theta$ was z and ψ mod square. So, $|\psi|^2$ will be exponential with twice the argument divided by square of the denominator of the wave function. So, all these things are fine. Definitely ϕ integral is easy to do Because nothing depends on ϕ , I will just get a 2π out of this integral.

$E_n^{(1)} = \int d^3r H_1(r) \psi_1(r) ^2$ $= \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos\theta) \int_0^\infty dr r^2 \frac{-eE \cos\theta}{\pi a_0^3} e^{-2r/a_0}$ $= 0 !! \checkmark$	$E_{n=1}^{(1)} = \int d^3r H_1(r) \psi_1(r) ^2 =$ $-eE \int_0^{2\pi} d\phi \int_{-1}^1 d\cos\theta \int_0^\infty dr r^2 \frac{-eE \cos\theta}{\pi a_0^3} e^{-2r/a_0} =$ $= 0 !!$
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Only contributions will come from $\cos\theta$ integral because there is a $\cos\theta$ over here and dr integral because functions depends on r . However, before going to r integral, if we just do the $d\cos\theta$ integral, you can call $\cos\theta$ as y . So, it will search for $\cos\theta$ everywhere. So, only time $\cos\theta$ appears is here in the Hamiltonian. So, ultimately it becomes -1 to 1 dy of a y , the $\cos\theta$ integral is just coming with one $\cos\theta$ appearance. So, you know the answer -1 to 1 dy of y , an odd function under symmetric limit is 0 . So, therefore the θ integral exactly vanishes and therefore whatever be the result of the r integral. If it is finite, finite times a 0 will be 0 . Therefore, ground state energy does not change under perturbation at the leading order. That means at the order of λ it does not change. Maybe at order λ^2 it changes. $E_n^{(1)}$ happens to be 0 . That does not mean $E_n^{(2)}$ is also 0 , $E_n^{(3)}$ is also 0 . And this is true for n is equal to 1 only. If I went on to compute what is the answer for n is equal to 2 , I might not get a 0 . So, therefore, one has to be very careful. This tells me only that first order correction for the ground state is 0 . This is not a general statement. It is not a statement about any order. It is not a statement about any eigenfunction. It is only true for first order for n is equal to 1 . So we have seen the ground state does not change at the first order in eigenvalue. The eigenvalue does not change. Does it mean eigenfunction also does not change?

Let us check that and let us go downwards.

$C_n^{(l)} \quad \psi_n^{(1)}\rangle = \sum_{l \neq n} C_n^{(l)} \psi_l^{(0)}\rangle$ $C_1^{(l)} = \frac{eE \int \psi_l^{(0)*} r \cos \theta \psi_1^{(0)}(r) d^3r}{-13.6 \left(1 - \frac{1}{2n^2}\right)}$ <p>Thus, $C_1^{(200)} = \frac{eE}{-10.2} \int_{2\pi}^{2\pi} \int_0^\pi \int_0^\infty \psi_{200}^{(0)*} r \cos \theta \psi_{100}^{(0)}(r) d^3r$</p> $= -\frac{eE}{10.2} \int_0^\pi d\phi \int_{-1}^1 d\cos \theta \int_0^\infty dr (r \cos \theta)$	$ \psi_n^{(1)}\rangle = \sum_{l \neq n} C_n^{(l)} \psi_n^{(1)}\rangle$ $C_1^{(l)} = \frac{eE \int \psi_l^{(0)*} r \cos \theta \psi_1^{(0)}(r) d^3r}{-13.6 \left(1 - \frac{1}{r^2}\right)}$ <p>Thus $C_1^{(200)} = \frac{eE}{-10.2} \int \psi_{200}^{(0)*} r \cos \theta \psi_{100}^{(0)}(r) d^3r$</p> $= \frac{-eE}{10.2} \int_0^{2\pi} d\phi \int_{-1}^1 d\cos \theta \int_0^\infty dr (r \cos \theta)$
$C_1^{(200)} = \frac{eE}{-10.2} \int_{2\pi}^{2\pi} \int_0^\pi \int_0^\infty \psi_{200}^{(0)*} r \cos \theta \psi_{100}^{(0)}(r) d^3r$ $= -\frac{eE}{10.2} \int_0^\pi d\phi \int_{-1}^1 d\cos \theta \int_0^\infty dr (r \cos \theta)$ $\times \frac{1}{(8\pi a_0^3)^{1/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$	$= \frac{-eE}{10.2} \int \psi^{(0)} \text{star}_{200}(r) r \cos \theta \psi_{100}^{(0)}(r) d^3r$

$$\frac{-eE}{10.2} \int_0^{2\pi} d\phi \int_{-1}^1 d\cos \theta \int_0^\infty dr (r \cos \theta) \frac{1}{(8\pi a_0^3)^{1/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

In order to know that, I need to compute these coefficients $C_l^{(1)}$. If $C_l^{(1)}$ happens to be 0 for all else, then I can say that there are no changes in the ground state wave function as well remember we had learned that we have to compute c and l's because these c and l's decided for me what is the first order correction $\psi_n^{(1)}$ was supposed to be summation over l for all the states which are not n of c and l and then ψ_l of the unperturbed basis. So, we need to know what are the $C_n^{(l)}$ s. If all the $C_n^{(l)}$ s are 0, then I can say that the first order correction to the wave function is also 0. So, we have just seen that $E_n^{(1)}$ for n is equal to 1 is 0. I want to know whether $C_l^{(1)}$ is 0 or not.

So, let us do the computation.

As we have seen $C_l^{(1)}$ will be obtainable from taking the Hamiltonian, the perturbation Hamiltonian which was $-eE r \cos \theta$ squeezed between ψ_n which is n is equal to 1 from the right and ψ_l from the left. So, this integration we have to do. So $C_n^{(l)}$ has this computation. l can be any other state not n is equal to 1. In hydrogen atom I know what are the states for me. There is a ground state which in the nlm basis is given by 100. We are trying to get the correction into this. And then the first excited state 200. Actually there are three more of them at n is equal to 2. 2 1 0 is there, 2 1 1 is there and 2 1 - 1 is there. This is for n is equal to 2. This was for n is equal to 1. So, I want to know $C_{1l}^{(1)}$. l is supposed to be all other states, but not just the ground state. It cannot be the same value for which you are trying to find out the correction. We are trying to find out the correction for ground state n is equal to 1. So, l has to take all other states.

This l right now is just an indication of summation over all the states. We could have called it m as well, let us say m or some other symbol not called m or l because we are using l and m here as well. So, let us call it some α and then it has to be α . Now this α is the label of all other states. All other states

are labeled by three numbers, n, l & m . α is a collective name of n, l & m . So therefore, I cannot take α as 1, 0, 0 because that is the state, ground state which we are trying to find the perturbation for. So the next value α can take is 2, 0, 0. So C_1^{200}

So that we can compute like here. Here l , so now we are calling it α . α has to be supplied as 2 0 0. So I will supply 2 0 0 here. This is the Hamiltonian $r \cos\theta$ times $-E$ upon E . So there is a - - cancellation which I should do. And then the ψ_α which is ψ_{200} , the ground state on the right and the Hamiltonian in the middle. You can again write down the position representation of ψ_{100} which we had already written in the previous slides and you can look up any textbook on quantum mechanics of hydrogen atom. Then you will find out that ψ_{200} this state as a position representation of this kind exponential with ψ_{200} extra factor and some normalization. Okay, again the same thing you see this ψ_{200} does not depend on θ .

It is free of θ . It only depends on r . 100 is again free of θ . So like before $d\phi$ integral we go from 0 to 2π will give me 2π . But $d\cos\theta$ integral previously it was vanishing because of the $\cos\theta$ appearing in the Hamiltonian. Only one $\cos\theta$ was appearing that made it odd function. This time again since the wave function ψ_{200} also does not depend on θ . So, the previous argument still remains true that if I do the integration of $d\cos\theta$ from -1 to 1, it is equivalent to integration of dy of y from -1 to 1. And therefore, even this correction term will become 0. So, α_{200} is 0. So, C_n is equal to 1 and α when α takes a value 2 0 0 is 0. That tells me that the first term which comes in this summation or call it α over here, the first term which comes in this summation is 0. but still it does not tell me that all other terms are 0. What about C_1^{210} , C_1^{211} , C_1^{21-1} and further I can go down this ladder and I will have more and more states. If any of them are non-zero then I know that the wave function - ground state wave function has been modified. So, this is the computation for α equals to 210. Here, the Hamiltonian and this divided by the energy difference. Remember, in the downstairs, the energy difference is supposed to come ground state - excited state. So, 13.6 divided by $1 - 13.6$ divided by n^2 . So, this will still remain true for n is equal to 1 and α is equal to 2 1 0 or 2 1 1 or 2 1 - 1 all of them have the same energy and hence same energy difference compared to the ground state. So, this term comes about and there is a Hamiltonian's z dependency which is $r\cos\theta$ and 2 1 0. Now, there is a typo I have not corrected. Here you will see that the 2 1 0 due to the fact that it has a 1 here, remember the states are marked by n, l, m , l is equal to 0 has no θ dependency but l is equal to 1 has a θ dependency, l is equal to 1 will come with a $\cos\theta$. So the state coming over here has a $\cos\theta$ dependency and already there was a $\cos\theta$ here as well. So the two terms combined gives me $\cos^2\theta$ here and $d\cos\theta$ integral I have to do. So it is no longer an integration of a kind dy of y from -1 to 1. This is dy of y^2 and this is not 0. So, therefore, if I do this computation C_1^{210} turns out to be non-zero. So, C_1^{210} is not zero. So, in this summation at least one term is present which is non-zero. That means $\psi_n^{(1)}$ is non-zero. Therefore, despite at the leading order energy eigenvalue of the ground state did not change, the wave function changed. So wave function changed in a manner that it remained the same energy at the leading order. Again, I am saying it is only the answer at first order of λ . In true picture, there is a net change or not would be known only from computing all order effects. All λ is proportional to λ , λ^2 , λ^3 , all those coefficients need to be computed. But at least at the leading order, we have seen that the wave function changes but the ground state energy does not. So this is the input story which we need to be aware of that due to perturbation the energy eigenvalue and the energy eigenstate both may or may not change.

For energy eigenvalue we have to compute one quantity which is $E_n^{(1)}$ and check whether it is 0 or not

for energy eigen functions we have to check all the coefficients C_n^α s not one coefficient two coefficient but all of them if any of them is non-zero that means wave function has changed just like we saw the case for hydrogen atom ground state. Okay? So this is as far as the leading order effects of perturbations are considered this is the first order correction coming from the change in the hamiltonian from the exact solution which we could have obtained. Now, we know that there are other sources of extra terms present in the Hamiltonian from various reasons, be it the correct description of kinetic energy, correct description of potential or some external applications. They all tend to put some extra Hamiltonians in the game. And we need to know due to the presence of such extra terms, how exact is our knowledge of ground state, excited state, their energies and so on. In some cases, it looks like they are very weakly perturbed in the sense that ground state energy does not change much. For example, in hydrogen atom for the ground state, we just saw that first order, it does not change. Second order, it might change, but it will be very small as we will see later. But for some cases like the harmonic oscillator, we saw that even the ground state energy changed. So we need to compute these things every time and get to know what kind of changes this Hamiltonian brings at various orders. So let us stop this discussion on the leading order here.

In the next discussion session, we will discuss about higher order effects, higher order corrections to energy eigenvalues. And in that process, we will see one interesting case where something of more interest comes about if there are two different states with same energy. These are called degenerate eigenstates. So, how to do perturbation theory for higher orders as well as degenerate energy eigenstates, we will deal with in the next discussion session. So, let us stop here for today.