

Foundation of Quantum Theory: Relativistic Approach
Change in atomic characteristics via field interactions
Perturbation theory 1.4
Prof. Kinjalk Lochan
Department of Physical Sciences
IISER Mohali

Lecture- 04

So in this discussion session, we will move our discussion towards linear order perturbation effects to higher order effects. As we recall in the previous discussions, we have learnt about how to compute first order effects. And ultimately, let me just write down the expression for you here so that we could just reflect upon what have we learned.

Higher Order Effects
in theory 1.4

In the perturbation equation

$$\begin{aligned}
 & (\mathcal{H}_0 + \lambda \mathcal{H}_1) (|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots) \\
 & = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) (|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots)
 \end{aligned}$$

★ Comparing terms at order λ^2 :

$$\begin{aligned}
 & \mathcal{H}_0 |\psi_n^{(2)}\rangle + \mathcal{H}_1 |\psi_n^{(1)}\rangle \\
 & = E_n^{(0)} |\psi_n^{(2)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(2)} |\psi_n^{(0)}\rangle
 \end{aligned}$$

→ Taking a projection along $|\psi_n^{(0)}\rangle$

$$\begin{aligned}
 \Rightarrow & E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(0)} | \mathcal{H}_1 | \psi_n^{(1)} \rangle \\
 & = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(2)}
 \end{aligned}$$

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

We have

$$E_n^{(2)} = \langle \psi_n^{(0)} | \mathcal{H}_1 | \psi_n^{(1)} \rangle$$

7:01
Since $|\psi_n^{(1)}\rangle = \sum c_l |\psi_l^{(0)}\rangle = \sum (\mathcal{H}_1) |\psi_n^{(0)}\rangle$

Since $|\psi_n^{(1)}\rangle = \sum_{l \neq n} C_n^l |\psi_l^{(0)}\rangle = \sum_{l \neq n} \frac{(H_1)_{nl} \psi_l^{(0)}}{E_n^{(0)} - E_l^{(0)}}$

$E_n^{(2)} = \langle \psi_n^{(0)} | H_1 \sum_{l \neq n} \frac{(H_1)_{nl} \psi_l^{(0)}}{(E_n^{(0)} - E_l^{(0)})} \rangle$

$= \sum_{l \neq n} \frac{|(H_1)_{nl}|^2}{(E_n^{(0)} - E_l^{(0)})} |\psi_n^{(1)}\rangle$

$H_{1nl} = \langle \psi_l^{(0)} | H_1 | \psi_n^{(0)} \rangle$

Higher Order Effects
In the perturbation equations

$(H_0 + \lambda H_1) (|\psi_n^0\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots)$
 $= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) (|\psi_n^0\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots)$

★ Comparing terms at order $\lambda^2 \therefore$
 $H_0 |\psi_n^{(2)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(2)} |\psi_n^0\rangle$

Taking a projection along
 $|\psi_n^0\rangle$
 $\Rightarrow E_n^{(0)} \langle \psi_n^0 | \psi_n^{(2)} \rangle + E_n^{(1)} \langle \psi_n^0 | \psi_n^{(1)} \rangle + E_n^{(2)}$

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

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

Since

$$|\psi_n^0\rangle = \sum_{l \neq n} C_n^l |\psi_n^0\rangle = \frac{\sum_{l \neq n} (H_1)_{nl}}{(E_n^{(0)} - E_l^{(0)})} |\psi_n^0\rangle$$

$$= \frac{\sum_{l \neq n} |(H_1)_{nl}|^2}{(E_n^{(0)} - E_l^{(0)})}$$

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

At linear order of the perturbation parameter, at linear order of λ we have learnt that the first order correction to the energy eigenstate n-th energy eigenvalue is obtainable from taking the expectation of the perturbation Hamiltonian with respect to the unperturbed energy eigenstate. While the first order correction to the wave function of n-th eigen eigenfunction, n-th eigenfunction is obtainable from coefficient C_n^α s where α is supposed to be the n set of numbers which will describe the state n over

which we are trying to get the perturbation over and effectively the $\psi_0^{(0)}$. So this is what we have learned and these results are true at the linear order of λ that is the first order effects are these. Now in today's discussion what we will try to do is to move in the domain of higher order effects - how to compute things at second order let us say as an example and from this philosophy we will see how to obtain things for higher order effects as well. So let us get going. So, to start the story, we again rewrite the Schrodinger equation, which is the time independent Schrodinger equation, where the full Hamiltonian, the full Hamiltonian is $\mathcal{H}_0 +$ a perturbation λ , the parameter λ times the Hamiltonian \mathcal{H}_1 . This is the full change to the Hamiltonian, which is brought about by some parameter which we are calling λ as we have seen it could be it $\delta m^3 c^2$ for kinetic terms and it could be $V'''/3!$ factorial for harmonic oscillator about their minima if I try to go and try to see how the potential changes. So the λ is the scale at which Hamiltonian gets perturbed with. We do not know what function of λ the corrected eigenvalues and corrected eigenfunctions are. So, therefore, we write in terms of power series. λ order effect, λ^2 order effect because we do not know the wave function remains the same or it changes or if it changes then it changes with what function of λ . It could be any function of λ which satisfy the new differential equations. We do not know.

Similarly, we do not know what energy eigenvalues do. How do they change? All we know is that they will change with the introduction of a new Hamiltonian term λ . But what function of λ is unknown to us. So, therefore, again the energy also we would expand in a power series about those parameter λ . So ultimately, we have this equation where the full Hamiltonian acts upon the full wave function and results in full eigenvalue multiplying the full wave function. And now we try to collect things order by order. At zeroth order of λ , the unperturbed equations came about. At the linear order of λ , the previous two equations which we just saw got arrived. And now we want to know what happens at order λ^2 . So, again from the left hand side and the right hand side, we will try to find out what are order λ^2 effects. So, I will try to collect things which are order λ^2 . So, order λ^2 term in the left hand side can come from the following ways. If \mathcal{H}_0 goes and hits the order λ^2 term over here, then I will get order λ^2 term. So, that is one potential possibility which is this \mathcal{H}_0 hitting the $\psi_n^{(2)}$ over here.

Fine.

One more possibility is that this λ times \mathcal{H}_1 goes and hits this. So then again, I will get a λ^2 with \mathcal{H}_1 acting on $\psi_n^{(2)}$ term. So again, we can see that on the left hand side, these are the two possibilities. Either \mathcal{H}_0 acts on $\psi_n^{(2)}$ or \mathcal{H}_1 acts on $\psi_n^{(1)}$. So order λ^2 term can be generated in this way only from the left hand side. From the right hand side again the same story. This number $E_n^{(0)}$ which is free of λ can go and combine with the second order correction term to the wave function. So therefore I can have $E_n^{(0)}$ multiplying on $\psi_n^{(2)}$. One more possibility over here is that first order correction to eigenvalue goes and talks to the first order correction to the wave function itself. So, $E_n^{(1)}$ talks to $\psi_n^{(1)}$ that is also order λ^2 . And lastly, order λ^2 correction in the energy eigenvalue. Unlike Hamiltonian where I know what is the total correction, I do not know what happens to energy eigenvalues. They can be a higher function of λ . So, there is a λ^2 possibility or higher powers of λ possibility in energy eigenvalue. So therefore $\lambda^2 E_n^{(2)}$ goes and hits the λ independent term in the wave function which is $E_n^{(2)}$ multiplying the $\psi_n^{(0)}$.

So all these three terms are possible in the right hand side which are at order λ^2 and only two terms are allowed in the left hand side which are these two. So this is the story for, this is the driving equation for the second order corrections. From here, we will try to find out two quantities $E_n^{(2)}$ and $\psi_n^{(2)}$. Just like from first order story, we got to know about $E_n^{(1)}$ and $\psi_n^{(1)}$.

All right.

Now, how could we compute $E_n^{(2)}$? We just took the projection of this equation with respect to $\psi_n^{(0)}$.

So, that is what I will do again. I will take the $\langle \psi_0^{(n)} |$ from left hand side. Take the inner product of the

whole equation. So, if I take a $\langle \psi_0^{(n)} |$ from the left hand side, this operator \mathcal{H}_0 acting on this $\psi_n^{(0)}$ will give me energy eigenvalue $E_n^{(0)}$ and then $\psi_n^{(0)}$ will go and hit the $\psi_n^{(2)}$. So, that will be this term. Now, the second term here The \mathcal{H}_1 will get squeezed between $\psi_n^{(1)}$ and $\psi_n^{(0)}$. This $\psi_n^{(0)}$ is not an eigenfunction of \mathcal{H}_1 . So I will not get something like this. Here $E_n^{(0)}$ came about because the unperturbed Hamiltonian was the $\psi_n^{(0)}$ $\psi_n^{(0)}$ was coming from the left is an eigenfunction of \mathcal{H}_0 . It is not an eigenfunction of \mathcal{H}_1 . So I cannot do anything about it. I only have to keep it this way. Okay, so far so good. Let us see what happens in the right hand side. These are numbers in the right hand side. Here these were operators. So when I take $\psi_n^{(0)}$, numbers will not do anything. They will just come out like before and $\psi_n^{(0)}$ will go and hit the $\psi_n^{(2)}$. Alright, then across second term again the same thing. The number will not do anything. It will just come out and $\psi_n^{(0)}$ will go and hit the $\psi_n^{(1)}$. So I will get this term and lastly the third term $E_n^{(2)}$ also is a number it will not do anything $\psi_n^{(0)}$ coming from the left will hit this $\psi_n^{(0)}$ so here the $\psi_n^{(0)}$ coming from the left and $\psi_n^{(0)}$ already present in the right hand side here they will just overlap and give me one because it is a normalized eigenfunction so I will just get $E_n^{(2)}$ so the first term is $E_n^{(0)}$ $\psi_n^{(0)}$ inner product with $\psi_n^{(2)}$ the second term is $E_n^{(1)}$ $\psi_n^{(0)}$ inner product with $\psi_n^{(1)}$ so two things you again see the first term on the left and the first term on the right they are the same thing so they will get cancelled the second term in the right hand side which involves an inner product between first order correction of n-th eigenfunction with the unperturbed n-th eigenfunction and that we have discussed that first order correction is orthogonal to the unperturbed eigen direction. So, this is 0 they are orthogonal the $\psi_n^{(1)}$ and $\psi_n^{(0)}$ are orthogonal. So, all I am left with in the right hand side is just $E_n^{(2)}$ And left hand side only one term survives which is \mathcal{H}_1 . This time it gets squeezed between $\psi_n^{(1)}$ from the right and $\psi_n^{(0)}$ from the left.

Remember $E_n^{(1)}$ was what? $E_n^{(1)}$ was \mathcal{H}_1 squeezed between $\psi_n^{(0)}$ $\psi_n^{(0)}$. This time there is a subtle difference. It is not squeezed between $\psi_n^{(0)}$ and $\psi_n^{(0)}$ or it is not squeezed between $\psi_n^{(1)}$ and $\psi_n^{(1)}$. On one side it is $\psi_n^{(0)}$ unperturbed one. On the right hand side there is a perturbed one $\psi_n^{(1)}$. The correction that gives me the second order effect. And from first order perturbation theory I know everything about $\psi_n^{(1)}$. That means $\psi_n^{(1)}$ $\psi_n^{(1)}$ has to be written in the basis of unperturbed eigenstates like this. So, just a second. So, this is $\psi_0^{(ln)}$. So, or better to write this is ψ , this C_n 's are the off diagonal elements of the perturbation Hamiltonian squeezed between n and l from left and right and the energy difference in the denominator. So, I know everything about $\psi_n^{(1)}$ from first order perturbation theory. So, I feed that information of $\psi_n^{(1)}$ into the expression of $E_n^{(2)}$. So, this whole thing over here is nothing but $\psi_n^{(1)}$ which we had derived in the previous class. So, now you see there is a \mathcal{H}_1 which is operator, there is this $(\mathcal{H}_1)_{nl}$ which is a number. This is a operator squeezed between two states. Remember $(\mathcal{H}_1)_{nl}$ meant $\psi_n^{(0)}$, $\psi_0^{(l)}$, \mathcal{H}_1 , $\psi_n^{(0)}$. So this is already a complex number. So this number will not do anything, it will just remain like that. So ultimately this \mathcal{H}_1 operator will get squeezed between $\psi_n^{(0)}$ and $\psi_0^{(l)}$.

So I will get, so there was \mathcal{H}_1 already present in the expression and from this operator, left hand side vector and right hand side vector, I will get another term which is $\psi_n^{(0)}$, \mathcal{H}_1 ψ_{nl0} which is nothing but \mathcal{H}_1 ln . So you see this is \mathcal{H}_1 ln and already there is a $(\mathcal{H}_1)_{nl}$ the off diagonal terms of row and columns reversed and since Hamiltonian is a Hermitian operator Their off-diagonal elements are complex conjugate of each other. They are just complex conjugate of each other. Therefore, you will get a mod square of one of them, $|(\mathcal{H}_1)_{nl}|^2$. So, therefore, we can again see, if I just clean up here, we can again see

that feeding the information of the first order expression, gives me the second order correction in the energy eigenvalue. $E_n^{(2)}$ is obtainable from $\psi_n^{(1)}$ and that $\psi_n^{(1)}$ information gives me what is the second order energy correction. Similar game you can play in order to know what is $\psi_n^{(2)}$. $\psi_n^{(2)}$ should be some superposition of $l \neq n$, C_n let us say 2, 2 means second order effect and $\psi_0^{(1)}$, the same game what we played for the first order field. In this case also how to obtain C_n^{2l} will be then in the same spirit what we computed from where we computed the first order correction in the same way you have to do that. So from here we can find out, I am not going to show the expression because for our discussions of future sessions, this information is not really required. So this you can take as a homework exercise for you that how to obtain C_n^{2l} and similarly how to obtain the third order correction, third order energy eigenvalue shift and those kind of things. You will see a recurring feature. What is the recurring feature? The recurring feature, it will be this. That first you obtain the first order correction to the wave function $\psi_n^{(1)}$. From there you get the second order correction to the energy eigenvalue. Now if you get the second order correction to the wave function $\psi_n^{(2)}$ that will tell you about the third order correction to the energy eigenvalue and so on. So it builds up. So, ultimately one wave functions correction tells you higher order energy eigenvalue shift and so on. But in this way they get related in some way that $E_n^{(2)}$ depends on certain feature of $\psi_n^{(1)}$. This $E_n^{(0)} - E_l^{(0)}$ has appeared in the second order correction because the same quantity appeared in the denominator of the first order correction to the wave function. And you can see if you try to build upon higher order corrections, it will keep appearing at here and there. So in C_n^l s, this denominator came. In $E_n^{(2)}$, the denominator comes. In $E_n^{(3)}$, $E_n^{(4)}$, $\psi_n^{(2)}$, all these things, this factor will come in the denominator. So setting up this is just algebraic steps starting from this equation you can now collect order 3, λ^3 order term λ^4 order term and keep using the previous information and you will set up for the higher order direction. So this is the mechanism or the machinery with which you can proceed along the higher order effects which is technical but nothing more conceptual than that but for the feature which you should pay attention to. For that, I should again write down what is $\psi_n^{(1)}$. Once again, I am just rewriting this equation cleanly here. $\psi_n^{(1)}$ is nothing but summation over l , where l is a marker for all states which are different from n . And then $(\mathcal{H})_{nl}$, which I had missed over here, $(\mathcal{H})_{nl}$ it should be, divided by $E_n^{(0)} - E_l^{(0)}$ and then $\psi_0^{(1)}$. So this is my first order correction to the wave function and while this expression is the second order correction to the energy eigenvalue. Both of these come with denominator $E_n^{(0)} - E_l^{(0)}$ where is being summed over on all other states which are there in the system. Not necessarily only first few states. All the states have to be summed over. Now l cannot be n that I should not include the wave function for which I am trying to get the correction. But in certain systems it can so happen that there is a different eigenfunction which has the same eigenvalue. So accidentally despite $\psi_0^{(1)}$ not being equal to $\psi_n^{(0)}$. Still it is possible that you will have $E_n^{(0)} = E_l^{(0)}$. We have seen examples like that. For example, in hydrogen atom we know the ground state is $|1\ 0\ 0\rangle$ and it has a single state. But first excited state $n = 2$, actually there are four states there, $|2\ 0\ 0\rangle$, $|2\ 1\ 0\rangle$, $|2\ 1\ 1\rangle$ and $|2\ 1\ -1\rangle$. So they have same n values but they have different l values and m values. It so happens that energy eigenvalue computation does not depend on l or m . Energy eigenvalue for hydrogen atom is only a function of n - $13.6\ eV/n^2$. So it is only a function of n . It does not care about l or m . So therefore these states are different from each other. But they have same n . So therefore they will have same energy.

$$\begin{aligned}
 \checkmark |\Psi_n^{(1)}\rangle &= \sum_{l \neq n} \frac{(H_1)_{nl}}{(E_n^{(0)} - E_l^{(0)})} |\Psi_l^{(0)}\rangle \quad \xrightarrow{E_n^{(0)} = E_l^{(0)}} \infty \\
 |\Psi_l^{(0)}\rangle &\neq |\Psi_n^{(0)}\rangle \quad \Rightarrow \quad E_n^{(2)} = E_l^{(0)}
 \end{aligned}$$

$$|\psi_n^0\rangle = \sum_{l \neq n} C_n^l |\psi_n^0\rangle = \frac{\sum_{l \neq n} (H_1)_{nl}}{(E_n^{(0)} - E_l^{(0)})} |\psi_n^0\rangle \rightarrow \infty$$

$$|\psi_l^0\rangle \neq |\psi_n^0\rangle \xrightarrow{E_n^{(2)} = E_l^{(0)}} E_n^{(0)}$$

So therefore in hydrogen atom, a system like hydrogen atom, you can see that such a possibility arises that despite I am talking about different state, I will end up getting a term in the denominator which is zero and therefore this will blow up first order correction will blow up if $E_n^{(0)}$ is E_l^0 if the first order correction blows up second order energy eigenvalue also blows up third order energy eigenvalue also blows up second or third order country second order wave function correction also blows up because as we discussed there was a recurring theme one thing sets the other.

So if that happens, no longer I can say these corrections are small. This, this, if things start blowing up, $\psi_n^{(1)}$ blows up, $E_n^{(2)}$ blows up, I can no longer trust this perturbation expansion. So therefore, the robustness of the perturbation theory is under question. So the perturbation theory will break down if such a thing happens. So I cannot use this perturbation theory machinery which we have developed if it so happens that I am talking about a system where two states have the same energy despite being different states altogether like hydrogen atom. And this gives rise to aspect or the approach of a degenerate perturbation theory.

ion theory 1.4.2
 $C_n^{(1)}$ or $E_n^{(2)}$ will diverge if
 $E_n^{(0)} = E_l^{(0)}$ for any $n \neq l$!
 Thus, perturbation theory will break down
Degenerate perturbation theory
 ▷ In order to keep things in check we need to diagonalize \mathcal{H}_1 in n, l subspace

$$\mathcal{H}_1 = \begin{matrix} \langle n | & \langle l | \\ \begin{pmatrix} (\mathcal{H}_1)_{nn} & (\mathcal{H}_1)_{nl} \\ (\mathcal{H}_1)_{ln} & (\mathcal{H}_1)_{ll} \end{pmatrix} \\ \langle l | \end{matrix}$$

 If $|l\rangle$ is replaced by $|l'\rangle = \alpha|n\rangle + \beta|l\rangle$
 $|n\rangle$ and $|l'\rangle$ will still be degenerate but
 $(\mathcal{H}_1)_{e'n} = \langle n | \mathcal{H}_1 | l' \rangle = \langle n | \mathcal{H}_1 (\alpha|n\rangle + \beta|l\rangle)$

$C_n^{(1)}$ or $E_n^{(2)}$ will change if
 $E_n^{(0)} \neq E_l^{(0)}$ for any $n \neq l$!

Thus perturbation theory will break down

Degenerate Perturbation Theory

In order to keep things in check we need to diagonalize \mathcal{H}_1 in n, l subspaces.

$$\mathcal{H}_1 = \begin{matrix} \langle n | & \langle l | \\ \begin{pmatrix} (\mathcal{H}_1)_{nn} & (\mathcal{H}_1)_{nl} \\ (\mathcal{H}_1)_{ln} & (\mathcal{H}_1)_{ll} \end{pmatrix} \\ \langle l | \end{matrix}$$

If $|l\rangle$ is replaced by $|l'\rangle = \alpha|n\rangle + \beta|l\rangle$, $|n\rangle$ and $|l'\rangle$ will still be degenerate but

$$(\mathcal{H}_1)_{e'n} = \langle n | \mathcal{H}_1 | l' \rangle = \langle n | \mathcal{H}_1 (\alpha|n\rangle + \beta|l\rangle)$$

$$= \alpha(\mathcal{H}_1)_{nn} + \beta(\mathcal{H}_1)_{nl} = 0$$

For $\frac{\alpha}{\beta} = -\frac{(\mathcal{H}_1)_{nl}}{(\mathcal{H}_1)_{nn}} \Rightarrow (\mathcal{H}_1)_{e'n} = 0$

Thus $C_n^{(1)}$ or $E_n^{(2)}$ will be finite.

$$(\mathcal{H}_1)_{l'n} = \langle n | \mathcal{H}_1 | l' \rangle$$

$$= \langle n | \mathcal{H}_1 (\alpha|n\rangle + \beta|l\rangle) | l' \rangle$$

$$= \alpha(\mathcal{H}_1)_{nn} + \beta(\mathcal{H}_1)_{ln} = 0$$

For $\frac{\alpha}{\beta} = \frac{-(\mathcal{H}_1)_{ln}}{(\mathcal{H}_1)_{nn}} \Rightarrow (\mathcal{H}_1)_{l'n} = 0$

Thus $C_n^{(1)}$ or $E_n^{(2)}$ will be finite.

The approach what we discussed will work fine for all the systems where one state has a unique Eigen energy. There are not two different states with the same energy. If that happens, your system is safe. You can do the perturbation theory. But if you have system where degenerate Eigen states are there, then you have to be careful. You cannot use this formulae because these formulae are not made to come to terms with different states of same energy. So therefore we go to the domain of a degenerate perturbation theory.

So degenerate perturbation theory will be a theory again in which let us say two states or more states in principle have the same energy and the problem was the theory will become perturbatively problematic because these terms which are supposed to be small start becoming very large so I do not have a technique to keep them small in order to make the sense of perturbation theory otherwise I have to give up on perturbation theory so one way people thought about that fine the denominators are going to zero and these things will blow up. But it will blow up only when the numerators are finite. Then only some finite upon 0 will blow up. But suppose the numerator also goes to 0. In that case, then I have no issue because if that goes to 0, I will come back to the story where we started from, from here. If that goes to 0, then it is 0 by 0, which is not necessarily infinity. It can be small number or finite. And therefore, things could be under control. And if I go back to the genesis of how did we compute the $E_n^{(2)}$ and what not. So, $E_n^{(2)}$ was made up from $\psi_1^{(n)}$ and $\psi_1^{(n)}$ involved this $(\mathcal{H}_1)_{nl}$. If $(\mathcal{H}_1)_{nl}$ is 0, then $\psi_1^{(n)}$ will also become 0, at least for those subsector.

So the idea is that we will not panic just on seeing the degenerate states. We will first check and see if

$(\mathcal{H}_1)_{nl}$ is 0 or not for those states which are degenerate. So I will take n , state n and state l which have the same energy corresponding to \mathcal{H}_0 . But I will try to write down the perturbation Hamiltonian in this subsector across n and l subsector. So, in this two-dimensional subspace, the perturbation Hamiltonian's diagonal terms will be \mathcal{H}_1 , \mathcal{H}_1 and off diagonal terms will be $(\mathcal{H}_1)_{nl}$ and \mathcal{H}_1 . Now, if it so happens that these terms are non-zero, they are finite, then I know we are in a problem that perturbation theory will be problematic.

However, a remedy to this is already available. The statement is, suppose these terms are non-zero. Can I do something to make them to go to zero? The answer turns out to be yes, we can do that. Actually, what we can do, we can change l , the state l to something called l' , which is a linear combination of the two degenerate states, n and l . Some coefficients times αn + some coefficient β . The new l' you can verify it has the same energy like E_l^0 , E_l^0 call it E_l^0 with l' as well. So, not only n and l have the same energy, even l' also has the same energy as far as the unperturbed Hamiltonian is concerned. You can verify that if this is eigenstate of Hamiltonian with energy $E_n^{(0)}$ and this is also eigenstate of Hamiltonian with energy $E_n^{(0)}$, then this combination is also an eigenstate of the Hamiltonian with the same energy. So when I do, I go from l to l' , I have not done any energetic changes as far as \mathcal{H}_0 is concerned. \mathcal{H}_0 does not see at different states. However, while doing so, I can carefully select some α and β such that $(\mathcal{H}_1)_{nl'}$ and the off diagonal term in the new wave function basis is 0. That means I want this to be zero. $(\mathcal{H}_1)_{l'n}$ is zero.

So I compute what is $(\mathcal{H}_1)_{l'n}$. That will be \mathcal{H}_1 squeezed between l' and n . That means this is the l' and this is the n from the left and I want this to be zero, which I can open up this term is nothing but $(\mathcal{H}_1)_{ln}$ and the second term is nothing but $(\mathcal{H}_1)_{ln}$. In because l' comes from the left \mathcal{H}_1 is in the middle n is from the right the other way l' is on the right \mathcal{H}_1 is in the middle n comes from the left so I get a $(\mathcal{H}_1)_{ln}$ this I want to be 0 if this is 0 then the coefficient α and β should be related like this the value which was there which was not 0, I will just take the ratio of this and the ratio of the eigenfunction, the ratio of the diagonal element to off diagonal element that will tell me what should be the ratio of α and β . And therefore, that will make the Hamiltonian, perturbation Hamiltonian not \mathcal{H}_0 , the perturbation Hamiltonian diagonal in this new basis. So therefore, in this new basis, $(\mathcal{H}_1)_{l'n}$ or $(\mathcal{H}_1^*)_{n'l'}$, these orthogonal matrix elements will be 0.

Therefore, this term will go to 0 and the risk of the denominator going to 0 will not hit us anymore. So the idea is you should, whenever you have degenerate states.

You should check the Hamiltonian of perturbation first and see if the off diagonal terms are 0 or not.

If they are 0 to begin with, you do not have to worry about because despite the energy eigenvalues being the same, the 0 in the numerator saves you. If they happen to be non-zero, then you should try to find a new basis in the degenerate subspace. Degenerate subspace meaning all those states which have the same energy corresponding to \mathcal{H}_0 . You write down the perturbation Hamiltonian in that basis and try to see if this is diagonal or not. If they are not diagonal, do something about it. Try to diagonalize it. While you try to diagonalize it, you are just linearly superposing n and l . This does not change anything corresponding to unperturbed Hamiltonian. So the idea is we will always write down the perturbation Hamiltonian in a diagonal degenerate basis. Let us see one example and to get the point.

For example if we want to know the change in wavefunction for $|200\rangle$ state of H-atom

$|210\rangle, |21-1\rangle, |211\rangle$ have the same energy as $|200\rangle$

$$H_1 = \begin{pmatrix} \langle 200 | & \langle 210 | & \langle 211 | & \langle 21-1 | \\ 0 & -3eEa_0 & 0 & 0 \\ -3eEa_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

Hydrogen atom in electric field

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

time indep.

$$E_n^{(0)} = -13.6 \frac{\text{eV}}{n^2}$$

$$H_1 = e\phi = -eEz$$

$$\begin{cases} \phi = -Ez \\ \vec{E} = -\nabla\phi \\ = E\hat{z} \end{cases}$$

$$E_n^{(1)} = ?$$

$$\Rightarrow E_{n=1}^{(1)} = ?$$

$$\int_{-1}^1 dy y = 0$$

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

where $\vec{J} = \vec{L} + \vec{S}$

Eigenstates of $\vec{J}, \vec{L}, \vec{S}$ will be the eigenstate of H_1

H_1 is diagonal in the $|n, j, l, s, m_j\rangle$ basis

$$\therefore E_n^{(1)} = \langle n, j, l, s, m_j | \frac{\alpha}{2r^3} (J^2 - L^2 - S^2) | n, j, l, s, m_j \rangle$$

$$= \frac{\alpha}{2} \langle n, l | \frac{1}{r^3} | n, l \rangle [j(j+1) - l(l+1) - s(s+1)] \frac{\hbar^2}{2}$$

Hydrogen atom in electric field

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

$$H_1 = qEz = Ercos\theta$$

$$E_1^{(1)} = \langle \psi_1^{(0)} | H_1 | \psi_1^{(0)} \rangle$$

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

$$\psi_1^{(0)}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

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

where $\vec{J} = \vec{L} + \vec{S}$

Eigen states if $\vec{J}, \vec{L}, \vec{S}$ will be eigen state of \mathcal{H}_1

\mathcal{H}_1 is diagonal in the $|n, j, l, s, m_j\rangle$ basis

$$\therefore E_n^{(1)} = \langle n_j l s m_j | \frac{\alpha}{2r^2} (J^2 - L^2 - S^2) | n_j l s m_j \rangle$$

$$= \alpha/2 \langle n l | 1/r^3 | n l \rangle [j(j+1) - l(l+1) - s(s+1)] \frac{\hbar^2}{2}$$

For example, in the last discussion session, we computed the first order correction, let us say $E_n^{(1)}$ for $n = 1$ of hydrogen atom. That is what we computed. Suppose I want to know what is $E_n^{(1)}$ for $n = 2$, the first order correction to that, that exercise you can do. But here again you can compute things from the formula which we had learnt, $n = 2$ and then you have to tell which elements you are talking about. $n = 2$ and which elements you are talking about. This will be the first order correction. But if I want to know second order correction to $n = 2$, second order correction or if I want to know what is the first order correction to the wave function. So, these things are problematic here because $n = 2$ comes up with a energy $E_{n=2}^{(0)}$ which are shared by four states $|2, 1, 0\rangle, |2, 1, 1\rangle, |2, 1, -1\rangle$ and $|2, 0, 0\rangle$. All these have the same energy.

Therefore, we are talking about degenerate perturbation theory here. So, how to find out whether the perturbation theory is stable or not or if we can do something about it. So, again look back at the same problem which we computed in the previous class. I will just go back to that.

We were considering a hydrogen atom put in external electric field. The Hamiltonian was E times ϕ or compactly written as e times E times z with a $-$ sign. That was my perturbation Hamiltonian. For this Hamiltonian, I want to know what is the first order correction to the wave function for $n = 2$ and what is the second order energy eigenvalue shift for $n = 2$. So, I already know that the perturbation Hamiltonian

the state which I am talking about suppose I want to know for state what is the shift in the eigenvalue at the second order and what is the first order shift in the wave function itself. In both the cases there is a problem because For $|2\ 0\ 0\rangle$, there are other states which are different from it. For example, $|2\ 1\ 0\rangle$, $|2\ 1\ 0\rangle$, $|2\ 1\ -1\rangle$ and $|2\ 1\ 1\rangle$, which have the same energy as $|2\ 0\ 0\rangle$. So, what I should do, I should first try to check whether \mathcal{H}_1 is diagonal in this degenerate subspace or not. So I compute the matrix \mathcal{H}_1 in this degenerate subspace, $|2\ 0\ 0\rangle$, $|2\ 1\ 0\rangle$, $|2\ 1\ 1\rangle$ and $|2\ 1\ -1\rangle$ and the columns, row and columns are like that. If you do this exercise, which I am just skipping, but you know how to compute, you will take \mathcal{H}_1 , what is $\langle 2\ 0\ 0 | 2\ 0\ 0 \rangle$, it will go and sit here you will find out that this number vanishes actually all diagonals vanish and not only all diagonals most of the off diagonals also vanish if you do this computation only thing survives is \mathcal{H}_1 is squeezed between $|2\ 1\ 0\rangle$ and $|2\ 0\ 0\rangle$ that survives with a value $-3eEa_0$ and its off diagonal counterpart e squeezed between So, these are just off diagonal elements. So, ultimately apart from this sub block, the perturbation Hamiltonian is already diagonal matrix, but for this small two-dimensional subs, two + two-dimensional sub block. So what we want, we can just focus on this two-dimensional subspace where the Hamiltonian, perturbation Hamiltonian looks like this. And want to know if we can diagonalize this. $|2\ 0\ 0\rangle$, $2, 0, 0$ and $2, 1, 0$ basis does not diagonalize it. So can I find a new basis ψ_A and ψ_B , let us say. Here I will get a ψ_B and ψ_A from a linear superposition of these two wave functions. Can I combine them in such a way to land up on two different states ψ_A and ψ_B such that they become diagonal. The idea is clear. You have to just combine these. While you are combining, the new state will have the same energy as each one of them because they are degenerate eigenstates. Their superposition does not change their unperturbed energy eigenvalues. Their superposition does not change their unperturbed energy eigenvalues. So you combine them and try to find out if it is possible by linear superposition of $2, 0, 0$ and $2, 1, 0$ to diagonalize this. And you will learn that indeed you can do that and you can diagonalize this Hamiltonian Actually, this 2 cross 2 dimensional Hamiltonian can be diagonalized in a new basis called $\psi_{|2a\rangle}$ and $\psi_{|2b\rangle}$. The other 2 dimensional sub basis was not needed to be changed because Hamiltonian was already diagonal in this subspace. Only where it was not diagonal is across this and across that. So therefore, I have changed those two states to $\psi_{|2a\rangle}$ and $\psi_{|2b\rangle}$. This is also $\psi_{|2a\rangle}$, this is also $\psi_{|2b\rangle}$. Other things remain as they were.

So, is indeed it is possible to diagonalize this perturbation Hamiltonian for $l = 2$ subspace and it so happens that $\psi_{|2a\rangle}$ is just addition superposition of the two state $\frac{|2\ 0\ 0\rangle + |2\ 1\ 0\rangle}{\sqrt{2}}$ and $\psi_{|2b\rangle}$ is the difference between $2\ 0\ 0$ and $-2\ 1\ 0$ with 1 by root 2 . if I declare $\psi_{|2b\rangle}$ and $\psi_{|2a\rangle}$ as my basis in, so effectively the four states of the hydrogen and which were $|2\ 0\ 0\rangle$, $|2\ 1\ 0\rangle$, $|2\ 1\ 1\rangle$, $|2\ 1\ -1\rangle$ are being replaced into $\psi_{|2a\rangle}$, $\psi_{|2b\rangle}$, $|2\ 1\ 1\rangle$ and $|2\ 1\ -1\rangle$. All these have the same energy to each other and all these have also same energy to each other, but this basis has a benefit that the perturbation Hamiltonian is also diagonal in this space.

So, therefore you can do this business carefully over there, there is no problem. The diagonal elements of the perturbation Hamiltonian therefore tells you about the first order correction. Now the perturbation theory is safe so you know due to perturbation the hamiltonian of the energy eigenvalue for $l = 2$ will change previously we had learned that for $l = 1$ it did not change but for $l = 2$ it will change it will change for two of them it will change for two of them it will not change out of these four the two of them it will change and two of them it will not change. For one of them it will go up by amount $3eEa_0$ and for one of them it will go down from by $-3 E_A^0$. So, if I draw it pictorially, let me see over

here. All of them were having the same energy. Now, it so happens after the correct application of the perturbation theory degenerate perturbation theory rather where I go to a correct basis first I go to a correct basis again which have the all the same four states has the same energy so this basis was for $|2\ 0\ 0\rangle$, $|2\ 1\ 0\rangle$, $|2\ 1\ 1\rangle$ and $|2\ 1\ -1\rangle$ while this is for $\psi_{|2a\rangle}$ and $\psi_{|2b\rangle}$, $|2\ 1\ 1\rangle$ and $|2\ 1\ -1\rangle$. All these have the same energy. There are four states here and there are four states here as well. All of them have the same energy as far as \mathcal{H}_0 is concerned. But once you apply \mathcal{H}_1 , perturbation theory on this basis is ill-defined. Perturbation theory on this basis is well defined. And here it so happens that two of the states do not change at all. So their energy remains the same.

One state goes up by energy by this much amount and one state goes down by energy $-3eEa_0$. So ultimately the four states here, two of them go here. One of them goes up and one of them goes down. And this is a result which we knew from correct usage of perturbation theory on correct basis. All right. I could not have applied perturbation theory on this because things were blowing up on this basis. So it is a good idea to go to a correct basis and then find out what happens to those terms. Okay

One more example, which is very famous example, something called the spin orbit coupling, where a new term due to the spin of the particle and its angular momentum around the nucleus, they talk to each other and they give rise to a term like this. You can look at the textbook by Griffith, Introduction to Quantum Mechanics, Chapter 6, to see the conceptual reasoning for this term. So, in this course, we are not talking about quantum mechanics from the perturbation theory approach completely, we are just reviewing it. So, therefore I will guide you to look for where does this structure come from, but ultimately it comes like this. And we know that $\vec{L} \cdot \vec{S}$ can be written as $(J^2 - L^2 - S^2)/2$ and this comes from the decomposition of the total angular momentum as orbital angular momentum + spin angular momentum. So therefore, you know that this is operator J^2 , this is operator L^2 , this is operator of S^2 . So if I take a state which is an eigenstate of j , l and s , that will be an eigenstate of full \mathcal{H}_1 . So therefore, I can choose, if I can choose the state in a basis where I have j , l and s , Then I know the Hamiltonian, this will be the eigen state of the Hamiltonian. Eigen state of the Hamiltonian meaning, Hamiltonian meaning perturbation Hamiltonian. This will be Eigen state of the perturbation Hamiltonian as well. And if it has an information of n . then it is eigen state of unperturbed hamiltonian as well so if I write things in a basis $n\ j\ l\ s$ and z component of the total angular momentum m_j then I know this is a basis in which \mathcal{H}_0 is diagonal as well as \mathcal{H}_1 is diagonal so \mathcal{H}_1 happens to be diagonal in this basis despite

This being a degenerate theory that means = 1 event. I can have a J which is L and S . L for = 1 you know = 1. L can only take value 0. So L happens to be 0 for = 1. But S has a value 1 by 2 spin half electron is spin half object. Even for = 1, j can take a value half. Since s is $1/2$ $j = l + s$. So, therefore the magnitude of j is magnitude of s which is half.

In the sense of eigenvalue, it is $1/2 * 1/2 + 1$. But magnitude of \vec{J} is magnitude of $\vec{L} + \vec{S}$. And its z component is twofold. It could be + half or - half. So, there are two states even for = 1. Actually that is how this $1s^1$ and $1s^2$ come about in $s = 1$ one thing one electron up and one electron with spin down they will both have the same energy so first state ground state two electrons can live this is a degenerate perturbation theory right because $1s^1$ state and $1s^2$ state both have the same energy. Yet it so happens this particular Hamiltonian is already diagonal in this basis. So, I do not have to worry about validity of, validity of perturbation theory and I can compute my things like first order correction to the wave function which you can go ahead and compute things which are fairly straight forward. You might have done it at the quantum mechanical level as well. It is good idea to revise. So, I will just take the perturbation Hamiltonian squeezed between the energy eigen states. I do not have to worry anymore because Hamiltonian, perturbation Hamiltonian is already diagonal. So, I do not have to worry whether the perturbation theory is valid or not. Then you will see that this j^2 , this l^2 , this s^2 acting on this eigenstate gives me j into $j + 1$, l into $l + 1$ and s into $s + 1$ and then 1 over r cube which comes about gets squeezed between this n and l . Effectively this operator acting j^2 , l^2 , s^2 gives me. This j this factor

$j(j+1)$, $l(l+1)$ and $s(s+1)$ times $\frac{\hbar^2}{2}$ and the state back $|n j l s m_j\rangle$ now these are numbers so it will go

left and $1/r^3$ will get squeezed between these two states but it so happens that $1/r^3$ operator does not care about *your* j value does not care about your spin value does not care about your m_j value only things it care about is n and l so this $|n j l s m_j\rangle$ could be written as $|nl\rangle$ times $|j s m_j\rangle$ as a direct product and when I squeezed $1/r^3$ across this state the $|j s m_j\rangle$ part does not undergo any operation they will just plainly get inner product with respect to each other and gave me 1 and $1/r^3$ will come in between this and this is a good exercise if you have forgotten about quantum mechanics computation in hydrogen atom you can go back and do this you will get this as an answer so I am not telling you how to get it because in this course we are just talking about the essential feature. Hamiltonian, perturbation Hamiltonian happens to be diagonal in this basis if I choose. Otherwise, if I started from some different basis, the idea would be to do a basis transformation and land up here in this correct basis, $|n j l s m_j\rangle$ basis, which is degenerate but diagonal. So, therefore, we are safe.

So, therefore, I know in order to deal with any system, I will go to first check whether my system is degenerate corresponding to unperturbed Hamiltonian \mathcal{H}_0 . If it is, I will always try to construct a basis in the degenerate subspace where the perturbation Hamiltonian becomes diagonal. Remember, a crucial point is to remember, we are not demanding that \mathcal{H}_1 becomes completely diagonal. We are not saying that it should be diagonal completely. It is good and valid. But if it is not, I am not saying that we should diagonalize it completely. I am saying we should diagonalize it in the degenerate subspace only. For example, suppose two states have the same energy heat this and this. The Hamiltonian here should look diagonal.

Here and here here it should it could be of diagonal terms can be non-zero. So I am not demanding \mathcal{H}_1 to be completely diagonal we are just demanding that it should be diagonal in the degenerate subspace so that is the idea of perturbation theory that if I want to know my system completely through perturbation theory I should check whether we are talking about a degenerate system or a non-degenerate system non-degenerate system life is easy we can compute things as we learn degenerate systems, I should make sure that the perturbation Hamiltonian becomes diagonal in the subspace, in the limited regime of the full matrix description.

In this subsector, it is diagonal. If it is diagonal, then I can relax and my perturbation theory is safe. We can do computations like before. So, this is a review we are stopping here for the time independent perturbation theory. We learned how to take out terms on left and right side compared to various powers of λ . Then we learned about how to take projections of those equations along $\psi_n^{(0)}$ or $\psi_0^{(l)}$ and from there we got corrections to eigenvalues at different orders and correction to wave functions at different orders. We have seen a couple of examples as well for hydrogen atom and harmonic oscillator. Fine, so we stop over here and this ends the review. It is the rather quick review of a time independent perturbation theory. In the next class onwards, what we will do, we will learn about time dependent perturbation theory approach because that is more relevant for matter field interaction which we discussed about, which we will discuss about in coming lectures. So, we stop over here for today.