Foundation of Quantum Theory: Relativistic Approach
Change in atomic characteristics via field interactions

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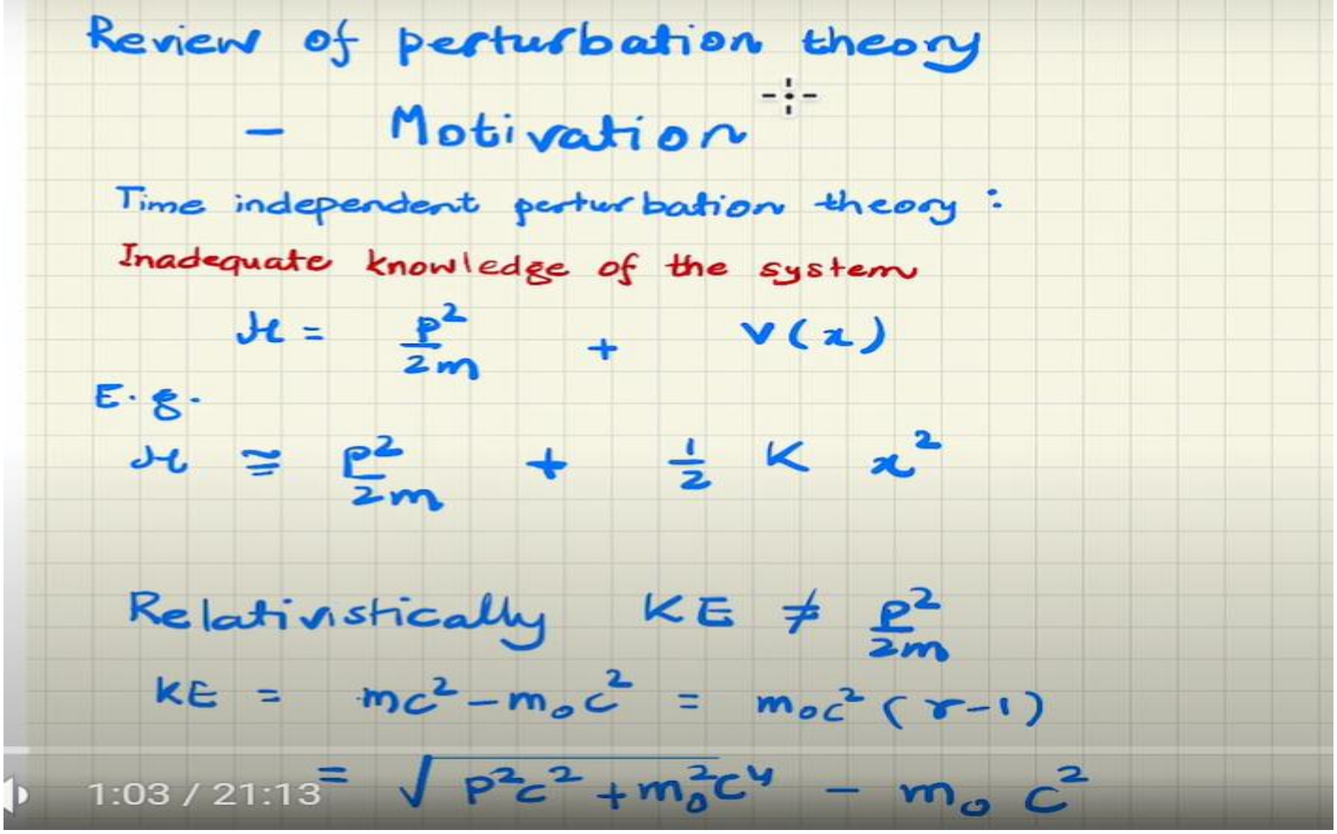
Lecture- 01

- Review and motivation of time independent perturbation theory.
- Example with hydrogen like atom

Welcome all.
So, today we will start our discussion of the course with a discussion on the review and the motivation of requirement of perturbation theory and in particular we will do our discussion today in the context of time independent perturbation theory. And we will see a couple of examples with harmonic oscillators as well as hydrogen like atoms how requirement of perturbation theory naturally arises in this kind of systems.
Let us start the discussion.



Review of perturbation theory

— Motivation

Time independent perturbation theory :

Inadequate knowledge of the system

$$\mathcal{H} = \frac{p^2}{2m} + V(x)$$

E.g.

$$\mathcal{H} \cong \frac{p^2}{2m} + \frac{1}{2} K x^2$$

Relativistically KE $\neq \frac{p^2}{2m}$

$$KE = mc^2 - m_0 c^2 = m_0 c^2 (\gamma - 1)$$

$$= \sqrt{p^2c^2 + m_0^2 c^4} - m_0 c^2$$

Review of perturbation theory
—Motivation
Time independent perturbation theory
Inadequate knowledge of the system

$$H=\frac{p^2}{2\mathrm{m}}+\frac{1}{2}kx^2$$

Relativistically KE $\neq \frac{p^2}{2\mathrm{m}}$

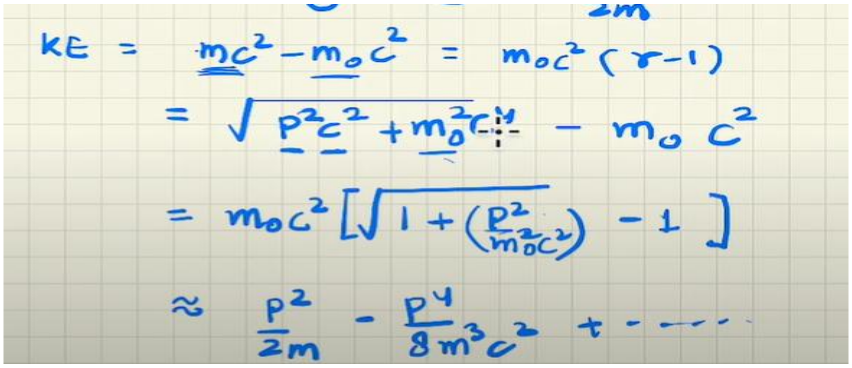
$$KE=mc^2-m_0c^2=m_0c^2=\sqrt{p^2c^2-m_0^2c^4}-m_0c^2$$

The first question which would come to our mind while going to the domain of perturbation theory that what is the requirement of having such a theory for description of system which we are looking in, in particular when we are doing the discussion today in the context of time independent perturbations one would ask why would one do time independent perturbation theory, what is the requirement of such a analysis in our description of the nature ? The answer towards that would be the inadequate knowledge of the system what we are dealing with. Most of the times we are not sure about the complete description of the system with infinite accuracy, which we try to write the system in terms of some Hamiltonian.

For example, a typical Hamiltonian of a moving particle is written as in terms of $\frac{p^2}{2\mathrm{m}}$ as a kinetic term plus some potential V(x). A case in point would be a harmonic oscillator Hamiltonian a Newtonian where the kinetic term $\frac{p^2}{2\mathrm{m}}$ is supplemented with a potential term which is also quadratic in position this time $\frac{1}{2}kx^2$, sometimes this k is written as $m\omega^2$ as well where ω is the natural oscillations frequency.

However, we know that $\frac{p^2}{2\mathrm{m}}$ is just a Newtonian description of kinetic energy. A moving particle or a moving system has to be described in more perfect sense by special relativity. And in special relativity we know for sure that kinetic energy is not just $\frac{p^2}{2\mathrm{m}}$.

This discussion we will do in coming lectures when we discuss about time, we will discuss about the special relativity in coming classes. But there we will see that the kinetic energy is just the difference between the kinetic term, kinetic energy is the difference between the total energy mc square minus its rest mass energy m_0c^2



$$\begin{aligned}KE &= \underline{mc^2}-\underline{m_0}c^2 = m_0c^2(\gamma-1)\\ &= \sqrt{\underline{p}^2\underline{c}^2+\underline{m_0}^2c^4}-m_0c^2\\ &= m_0c^2\left[\sqrt{1+\left(\frac{p^2}{m_0^2c^2}\right)}-1\right]\\ &\approx \frac{p^2}{2m}-\frac{p^4}{8m^3c^2}+\cdots\end{aligned}$$

$$K.E.=\sqrt{p^2c^2+m_0^2c^4}-m_0c^2$$

$$= m_0 c^2[\sqrt{1+\frac{p^2}{m_0^2 c^2}}-1]$$

$$\approx \frac{p^2}{2\text{m}}-\frac{p^4}{8\text{m}^3 c^2} + \ldots$$

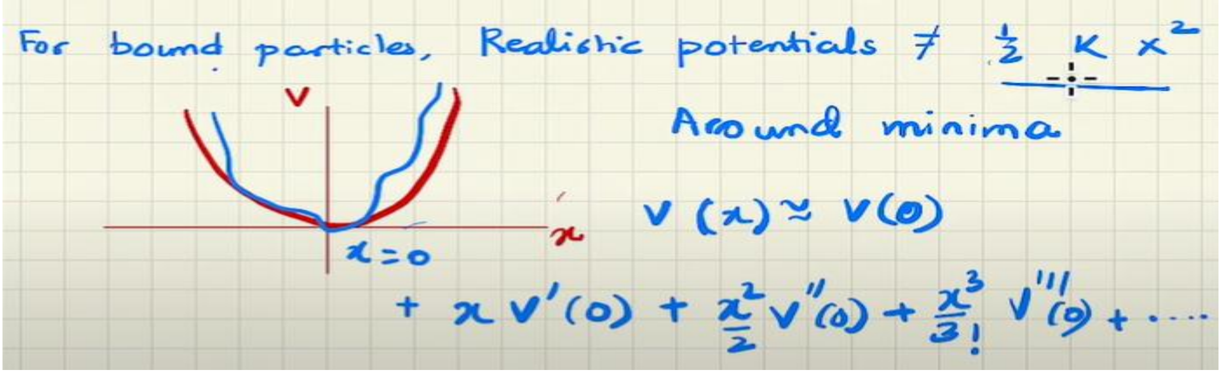
The total energy of the system can be written in terms of $p^2 c^2$ plus $m_0^2 c^4$ and then a square root. . This is the total energy of a special relativistic system minus its rest mass energy should be the kinetic energy of the system.

And for particles with large rest mass energy compared to their kinetic energy, which is this kinetic momentum driven energy. I can pull out $m_0 c^2$ as a common term in both of these such that I would have a structure like $m_0 c^2$ times square root of a quantity which is $[\sqrt{1+(\frac{p^2}{m_0^2 c^4})}-1]$

Now in the limit where $m_0 c^2$ is much, much greater than p^2, I can tailor expand this around 1, the central value that will cancel the 1 over here and I will be left with the leading order term which is $\frac{p^2}{2\text{m}_0}$. And then there will be a higher order term which is coming from the expansion of this root under 1+ x. For small x, $\sqrt{1+x}$ can be tailor expanded as $\frac{1+x}{2}$ plus higher order terms and those kind of things. So, ultimately we see the correct description of kinetic energy according to special relativity comes with $\frac{p^2}{2\text{m}_0}$ which we had written over here where m is to be treated as the left mark energy - $\frac{p^4}{8\text{m}^3 c^2}$ and in principle then there is higher order term something times p^6 and something else times p^8 as well. So all these terms are potentially present in the kinetic energy. We just write the leading order term in the kinetic part. So this $\frac{p^2}{2\text{m}_0}$ sits in our description of harmonic oscillator.

But again, this is not a most perfect description. Because if I obtain certain answer corresponding to only this term, $\frac{p^2}{2\text{m}_0}$ plus the potential, then I know I am ignoring these terms which are legitimately eligible for sitting in the habit.

However, we have made this approximation that its rest mass energy is much larger than its momentum driven term pc. All these terms are much smaller compared to the leading order term $\frac{p^2}{2\text{m}_0}$. So, $\frac{p^2}{2\text{m}_0}$ is the most dominant term in this expansion, all other terms are subdominant that means if it is contributing at first decimal place, this will be contributing at fifth decimal place, this would be contributing at eighth decimal place and so on. If I want to know the description of my harmonic oscillator up to leading order, this term is good enough. But suppose I want to increase my accuracy and talk about the harmonic oscillator up to sixth or seventh decimal place, then I should include this second order term in my Hamiltonian as well.



For bound particles, Realistic potentials ≠ $\frac{1}{2} K x^2$

Around minima

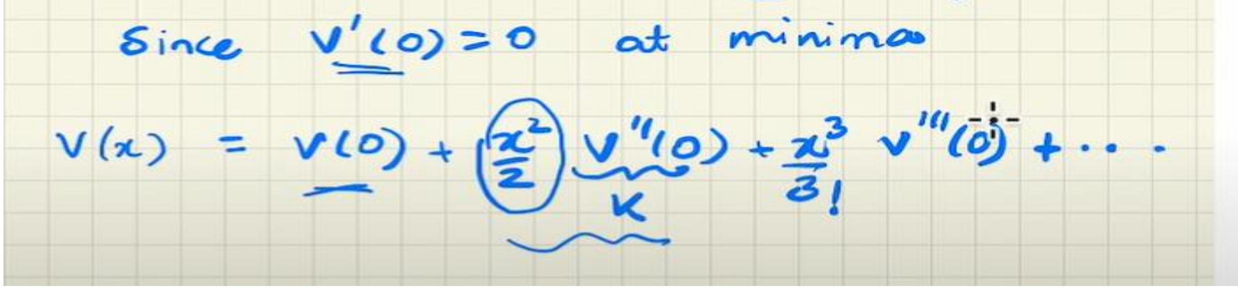
$$V(x) \simeq V(0) + x V'(0) + \frac{x^2}{2} V''(0) + \frac{x^3}{3!} V'''(0) + \cdots$$

This is as far as the correct description of kinetic energy is concerned. Even the potential term which we have written $\frac{1}{2}kx^2$ is not the most realistic potential which we come across to, in lab settings or day to day settings as well. $\frac{1}{2}kx^2$ is a quadratic potential which is very smooth. So, something drawn by this red curve over here $\frac{1}{2}kx^2$. However, most of the realistic system do not live in a simple potential like $\frac{1}{2}kx^2$. But they live in more complicated potentials like the blue one over here.

They are more stable system. The potential indeed has an extrema, it has a minima actually at the bottom of its pit. However, they do not rise from the minima as a quadratic structure, but they have more complicated.

However, if we are concerned about small oscillations around the minima, that means I do not go much high in energy or displacement, then I can Taylor expand the potential around its minimal point. So, V(x) can be written as a Taylor expand around its point of minima, which I am just choosing x is equal to 0, if you could have chosen any x, call it x*. It would be the potential at the location x*, or and then the Taylor expansion which will be taking the derivative of the potential at the point of minima which I have depicted by 0, you can call it x* as well, times the first order deviation term $x+\frac{x^2}{2}$, the second derivative at the point of minima, the third derivative at the point of minima supplemented with the x cube term and so on so forth. So, I can Taylor expand around this point of minima. These terms become more and more important if I increase my axis more and more. So I will start seeing the structure of the potential with more accuracy if I go further away from the point of minima.

However, since at this location at 0 or x* whatever the notation you are using, the potential has a minima that means its first derivative is 0 at that point.



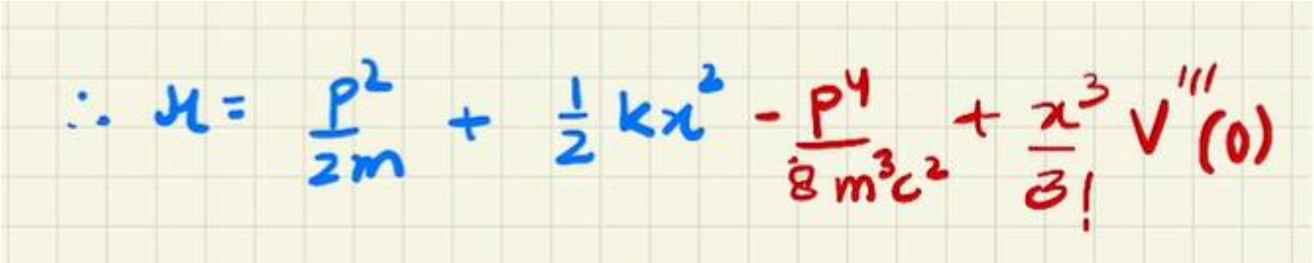
Since $\underline{V'(0)} = 0$ at minima

$$V(x) = \underline{V(0)} + \underbrace{\boxed{\frac{x^2}{2}} \underbrace{V''(0)}_{K}} + \frac{x^3}{3!} V'''(0) + \cdots$$

Since V'(0) = 0 at the minima

$$V(x)=V(0)+\frac{x^2}{2}V''(0)+\frac{x^3}{3!}V'''(0)$$

Therefore, this term goes out from the expansion and we have a constant term which is the value of the potential at the point of minima V at 0 or V at x* term plus the second term will start with $x^2 \times V''$ the potentials double derivative at the location of minima. This has to be supplemented with $\frac{x^2}{2}$. This is the $\frac{1}{2}kx^2$ term which we typically write. But we know this is not the end of the story.



$$\therefore \mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}kx^2 - \frac{p^4}{8m^3c^2} + \frac{x^3}{3!}V'''(0)$$

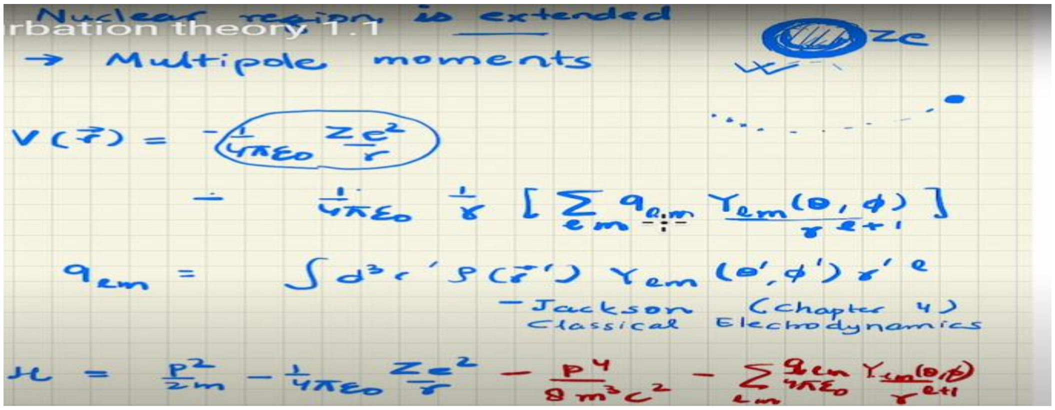
$$So\,H=\frac{p^2}{2\text{m}}+\frac{1}{kx^2}-\frac{p^4}{8m^3c^2}+\frac{x^3}{3!}V'''(0)$$

There is a third order term which is supposed to come here, which comes with a third derivative as well. Therefore, you can see that more accurate description of the potential also comes up with higher and higher order effect, just like more accurate description of the kinetic energy came up with higher and higher order terms in the kinetic part. For instance, the next sub leading order correction term to harmonic oscillator would be $\frac{p^4}{8m^3c^2}$

This is coming from the kinetic energy's more accurate description. And in addition to the potential half Px square, there can be this term as well which is coming from more accurate description of the two potential the particles are living here. There can be other higher order terms coming from this as well.

The momentum side can also contribute with higher p powers, p^6 to p^8 and the potential side can also come up with higher order x^4 or x^5 coming from their respective aspects.

In hydrogen-like atom



Nuclear region is extended

→ Multipole moments

$V(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$

$- \frac{1}{4\pi\varepsilon_0}\frac{1}{r}\left[\sum_{lm} q_{lm} \frac{Y_{lm}(\theta,\phi)}{r^{l+1}}\right]$

$q_{lm} = \int d^3r'\rho(\vec{r}')Y_{lm}(\theta',\phi')r'^{l}$

– Jackson (Chapter 4) Classical Electrodynamics

$\mathcal{H} = \frac{p^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} - \frac{p^4}{8m^3c^2} - \sum_{lm}\frac{q_{lm}}{4\pi\varepsilon_0}\frac{Y_{lm}(\theta,\phi)}{r^{l+1}}$

$$V(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} - \frac{1}{4\pi\varepsilon_0}\left[\sum_{lm} q_{lm}\frac{Y_{lm}(\theta,\phi)}{r^{(l+1)}}\right]q_{lm}$$

$$q_{lm} = \int d^3r'\rho(\vec{r}')Y_{lm}(\theta',\phi')r'^{l}$$

- Jackson (Chapter 4)
Classical Electrodynamics

$$H = \frac{\vec{p}^2}{2\mathrm{m}} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} - \frac{p^4}{8\mathrm{m}^3c^2} - \frac{1}{4\pi\varepsilon_0}\left[\sum_{lm} q_{lm}\frac{Y_{lm}(\theta,\phi)}{r^{(l+1)}}\right]$$

We can similarly think of a case of hydrogen like atom where an electron revolves classically around a nucleus of charge Z times the electronic charge e. The electron has a charge e with a negative sign while the nucleus has a charge Z times e where Z is the number of protons let us say, that big number. So, the description of the Hamiltonian in this case will be

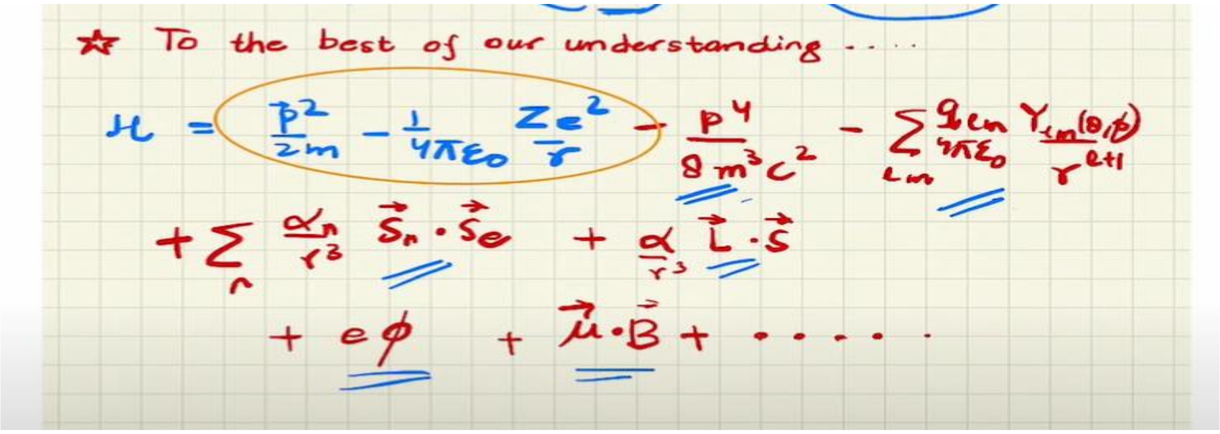
$$H_0 = \frac{p^2}{2\mathrm{m}} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

$\frac{p^2}{2\mathrm{m}}$ the kinetic term minus $\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$

.

So, this is the Coulomb interaction between the nucleus and the electron. .Ze is the charge of the nucleus, E is the charge of the electron. Effectively they are $\frac{q_1 q_2}{4\pi\varepsilon_0 r}$ with a minus sign is the potential energy of the electron in the central Coulombic potential. However, this description, this $\frac{q_1 q_2}{4\pi\varepsilon_0 r}$ is the potential energy between two point-like particles in electrodynamics. We know for sure that the nucleons, the nucleus is not just a point-like because it is made up of protons, neutrons, several of them. And therefore, the charge which we are putting Ze is not located just at a point, but we know that this charge is distributed in an extended region of some size. Therefore, I should not use the potential between two point like objects, but we should talk about the potential of an extended region which comes with total charge Ze which is distributed in some small tiny volume. This can be written if you are familiar with electrodynamics in terms of the usual potential point like potential which is $\frac{Ze^2}{R}$ in addition to the higher order terms which come from the multipole expansion of this extended object. So these q_{lm} s over here are called the multiple moments of the charge distribution. If the charges live in an extended region and not at a point, then there are higher multipole moments.

If the charge live in an extended region not at point then there are higher multipole moments. This is called the monopole moment. While there are legitimate higher order terms which can come up due to its extended region of charge distribution. q_{lm} s are given in terms of moment of the charge distribution. So this integral gives rise to higher order moments, dipole moments, quadrupole moments, hexadipole moments. And all these terms generate the total potential for you in which the electron lives, not just the monopole term, which we typically assume. So, you see a more accurate description of the nucleus in addition to the monopole term gives rise to the multipole expansion of the potential as well. So again, if we demand more accurate description of hydrogen atom even, Then the electron does not live in this potential and this kinetic term only, it can come up with this kinetic term correction plus higher order terms as we discussed and multiple moments expansion which is also possible like this. Again, how good is this description with the just two terms depends upon how much accuracy we are asking the hydrogen atoms analysis to be with. For instance, the first two terms for hydrogen atom gives me a ground state energy of minus 13.6 eV. While if I accounted for, if I account for these kind of terms, they will give rise to shifts in energy up to 10 to the power minus 5 eV. That either you might have seen in quantum perturbation theory or we will just do a couple of examples to settle this point out. Therefore, if I am interested about hydrogen atoms description at energy range eV, few then I can make our business with just these two terms. But if I want to be more accurate and know the transition lines or the locations of energy eigenstate up to 6th or 7th or 8th decimal place, then these higher order terms have a legitimate right to come and sit in the expansion of that Hamiltonian. So, we cannot ignore them anymore. In addition to these terms which are intrinsic to potentials description or kinetic description, there are other things which go on in the hydrogen like atom.



☆ To the best of our understanding . . . .

$$\mathcal{H} = \frac{p^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} - \frac{p^4}{8m^3c^2} - \sum_{lm}\frac{q_{lm}}{4\pi\varepsilon_0}\frac{Y_{lm}(\theta,\phi)}{r^{l+1}} + \sum_n \frac{\alpha_n}{r^3}\vec{S}_n\cdot\vec{S}_e + \frac{\alpha}{r^3}\vec{L}\cdot\vec{S} + e\phi + \vec{\mu}\cdot\vec{B} + \cdots$$

$$H=\frac{\vec{p}^2}{2\mathrm{m}}-\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}-\frac{p^4}{8\mathrm{m}^3c^2}-\frac{1}{4\pi\varepsilon_0 r}\left[\sum_{lm} q_{lm}\frac{Y_{lm}(\theta,\phi)}{r^{(l+1)}}\right]+\sum_n\frac{\alpha}{r^3}\vec{S}_n.\vec{S}_e+\frac{\alpha}{r^3}\vec{L}.\vec{S}+e\phi+\vec{\mu}.\vec{B}+\ldots$$

For example, the neutrons and the electrons both come up with spin. There is a spin-spin coupling of this sort. Similarly, there is an angular momentum of the electron due to its motion around the nucleus and it has a spin as well. So, there is a spin orbit coupling which goes by the name of LS coupling. I am assuming that you might have seen these things already in your courses on quantum second course of quantum mechanics which deals with perturbation theory. I am just reviewing it quickly and we will move on to do more analysis with more realistic setup of relativistic kind. However, as resuming our discussion, there are spin-spin interaction, spin-orbit coupling and in addition to that there can be in the lab some electric field which is present. We can never be sure up to 30th decimal place that there is no electric field. In principle whatever tiny electric field which is by accident present can also give rise to a term in the Hamiltonian which is of this sort. Similarly, a magnetic field in the lab which is present can also give rise to a shift in the Hamiltonian by this kind of terms.

So, accounting for all these things put together, our correct description to best of our understanding will become, not only the first two terms which we typically deal with, but higher order kinetic terms which are coming from more accurate description of the kinetic term, higher order potential terms which are coming from more accurate description of the potential, the interactions which we ignored between spin and spin, the spin orbit coupling, accidental electric field, accidental magnetic field in the lab and all sort of these things, all these things have legitimate right to be in the Hamiltonian. blue color and they are circled.

However, leading order description goes ahead with the first two terms which written in

blue color and they are circled. These higher order terms will become important only when we ask for more accurate description or higher order decimal places values for hydrogen atoms .

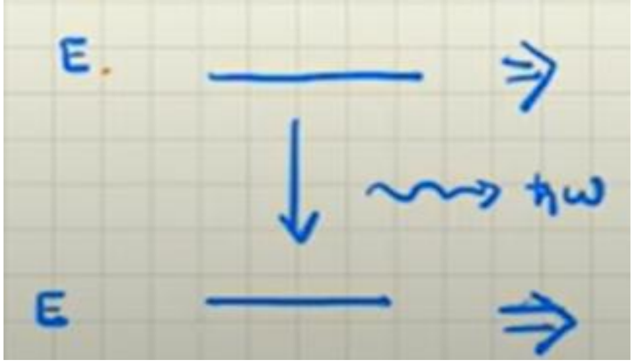
The question is how accurate is the description through the $\mathcal{H}_0$ erm, the first two terms only.

How accurate is description through $\mathcal{H}_0$ analysis.

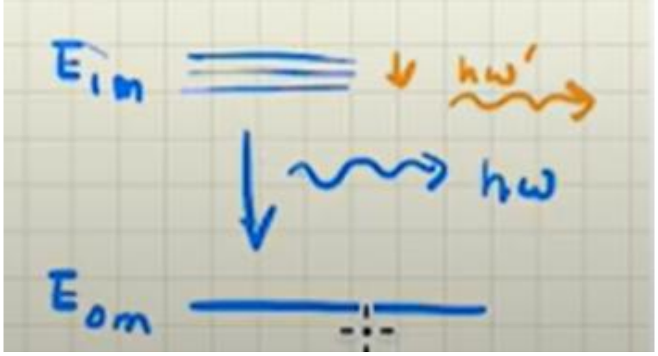
⇒ ~~For~~ some analysis good enough

⇒ ~~For~~ some processes not so much!

For instance the energy shifts marginally.



But truer description may resolve



Again as we discussed the answer would be for some analysis it is good enough description, for some analysis and some process they are not so good enough description. For instance, if I am just looking at hydrogen atoms energy eigenvalues. In unperturbed system let us say it was E_0 and E_1 . This was from the first two terms only, E_0 and E_1 .

What will happen if I accounted for more and more terms in the expansion? The E_0 will be corrected to E_0' which will be this line and E_1 will be corrected to E_1' which will be this line. So the previous gap which was between the E_0 and E_1 will now become a gap between E1' and E_0' value of the gap between the ground state and excited state roughly remains of the same order $\hbar\omega_0$. Previously it was from here

E_1 to E_0 and this time it is E_1' to E_0'. The frequency does not remain necessarily the same, but the shift in the frequency is very minor. If this was minus 13.6 eV, this would have worked as the ionization energy effectively.

In a more accurate description, it will become 13.6001, that means fifth decimal place there will be some shift.

Ballpark value remains the same. As far as if we are interested about knowing the gap, it is not much of a consequence, it changes by fifth decimal place, but not much.

However, what perturbation theory can do as we will see, it can split up certain energy levels, it does not only shift the energy by some amount, it can do is that whatever we were thinking as one energy eigenstate, it can get split up in many energies' eigenstate with a split parameter, splitting gap being much tiny and comparing to, compared to the perturbation Hamiltonian.

So, the ground state gets slightly shifted, the first excited state not only gets slightly up shifted, but it splits into three let us say. And these three things are very tiny, so that if we are interested about leading order energy, they are all the same, but if we are interested about accuracy up to sixth decimal place, we will see that some of them are different from each other by sixth decimal place. So, now here also from the three excited state the ground state transition energies are roughly of the same $\hbar\omega_0$ with difference being at the sixth order decimal places. So, not much of a difference as far as the transition gap is concerned. But now due to splitting a new process can start that an excited state can jump between these lines as well not from the E_1 to E_0, but one of the excited states which has just been generated due to perturbation to one of the new excited states as well. This will be very tiny transition line and a very a photon with a tiny frequency will be emitted. So, here while we were discussing just the transition gap I will just see that it has marginally shifted. But in this process, we have learnt that there is a possibility of a physical process in which a very tiny energy photon can be emitted by the excited atom. Here if we were not accounting for perturbation theory, we would not be knowing that such a process can happen. More accurate description of a system through perturbation theory not only shifts and updates your knowledge of exact value of energy eigenstates, that can give rise to new processes as well, new transition lines, which is important for discussions and learning about relativistic systems and quantum fields in our discussion of the course. So, those things we will see in more details in coming lectures. Here I just wanted to convey this message that not only perturbation theory is required for more and more accurate description of the system, they give rise to new processes as well and many of these new processes are of consequence as far as relativistic settings description is concerned. We stop here for the first lecture.

We will resume our discussion with more examples and we will set up the analysis how do we see the transition lines and their shifts and their degeneracy breaking in the coming lecture.

So, I stop here for the first lecture.

Thank you.