Approximate Methods in Quantum Chemistry
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Lecture 18
Examples of Perturbation Theory

Hello students! Welcome to this lecture. In the last lecture, we derived the expressions for energy correction and wave-function correction under perturbation theory. In this lecture, we will discuss a few applications of perturbation theory.

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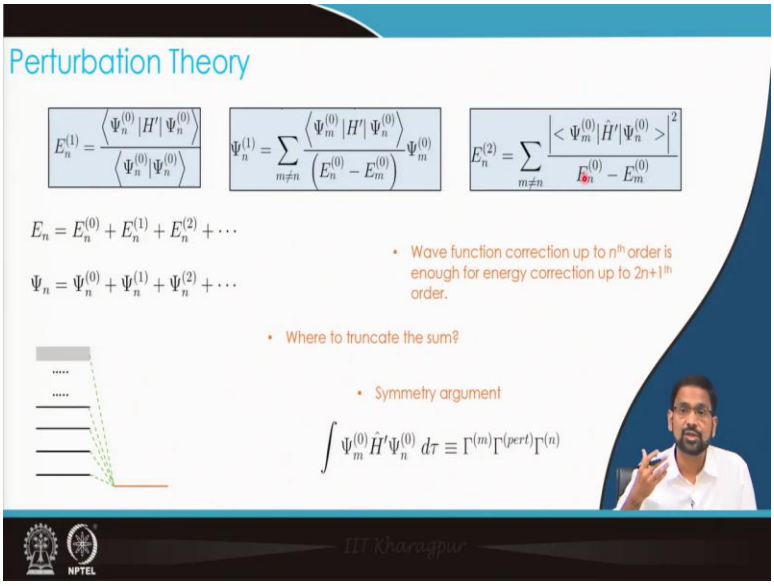

Before discussing the applications, let's review the results from perturbation theory. The perturbation theory provides a way to obtain wave function and energy of a complex system in terms the wave-function and energy of a simpler subsystem (whose solutions are already known) and some corrections (up to a certain order) arising from the remaining part of the system that is treated as a perturbation. We have already derived the expression for the first-order energy correction, the first-order wave function correction and the second-order energy correction. We discussed that if we have wave function correction up to n^{th} order, we can easily obtain energy correction up $(2n+1)$ order. We also discussed that while the first-order energy correction for the state of choice requires the evaluation of only one integral, the second-order energy correction and the first-order wave function correction require the evaluation of, in principle, an infinite number of integrals, although we can simplify the problem by considering symmetry as well as by ignoring the contributions from those unperturbed states that are farther (in energy) from the state of choice.

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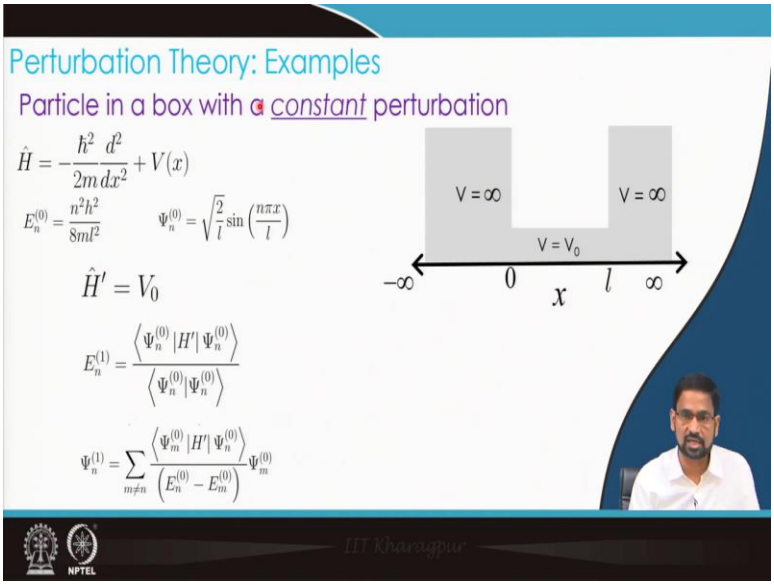

Now, let us discuss a few applications of the perturbation theory. The first example relates to the particle in a one-dimensional box, but with a different potential inside the box. In this case, instead of 0 potential energy within the box, the particle experiences a constant potential (V_0) inside the box while outside the box, $V = \infty$. We have already solved this problem when $V = 0$ (inside the box). To solve the present problem, we can use perturbation theory, where the unperturbed Hamiltonian is the standard particle-in-a-box Hamiltonian, and the perturbation Hamiltonian is $\hat{H}' = V_0$.

The known solution of the unperturbed Hamiltonian is given by,

$$E_n^{(0)} = \frac{n^2h^2}{8ml^2} \qquad \Psi_n^{(0)} = \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right)$$

The 1st order energy correction can be obtained as:

$$E_n^{(1)} = \frac{\left\langle \Psi_n^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle}$$

Since, $\hat{H}' = V_0$= a constant, $E_n^{(1)} = V_0$.

This result is valid for all *n*. That means the total energy of a state is the energy of the unperturbed state added plus the constant potential energy that the particle experiences.

Let us, look at the wave function correction. The first order wave function correction is given by,

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \Psi_m^{(0)}$$

Since *H'* is a constant and since $\Psi_n^{(0)}$ and $\Psi_m^{(0)}$ are orthonormal, all the terms in the above sum will be zero. That means, there is no correction to the wave function due to the constant perturbation.

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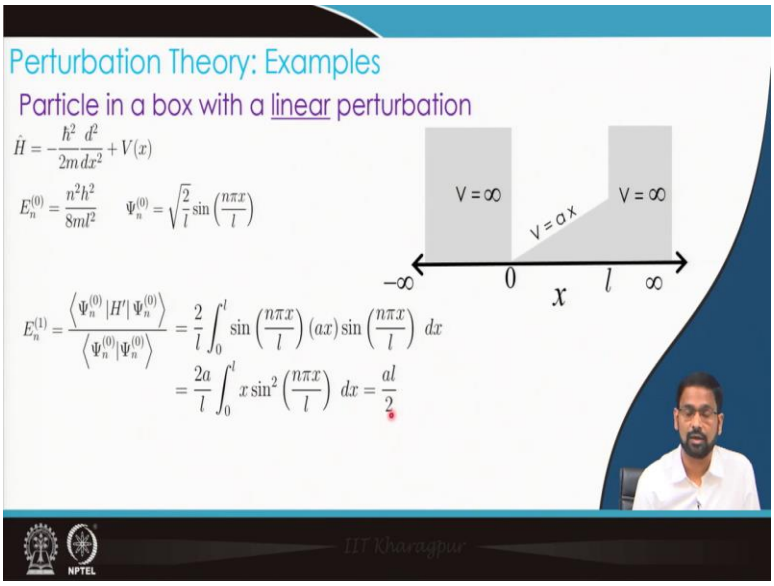

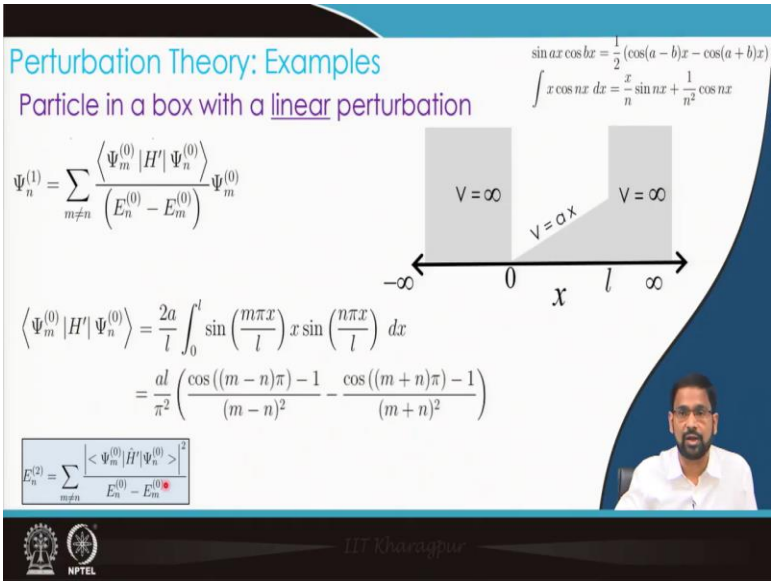

So, after looking at a rather trivial example, we will go to a slightly difficult problem. Again, we have a particle in a box. But unlike the previous example, we do not have a constant perturbation, rather a linear perturbation ($V = ax$).

We can evaluate the first order energy correction as

$$E_n^{(1)} = \frac{\left\langle \Psi_n^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} | \Psi_n^{(0)} \right\rangle} = \frac{2}{l} \int_0^l \sin\left(\frac{n\pi x}{l}\right) (ax) \sin\left(\frac{n\pi x}{l}\right) \, dx$$
$$= \frac{2a}{l} \int_0^l x \sin^2\left(\frac{n\pi x}{l}\right) \, dx = \frac{al}{2}$$

The first order correction is independent of *n*, i.e., a constant (*al*/2) for all the unperturbed energy levels. All unperturbed energy levels are shifted by a constant due to the linear perturbation.

Now, let us consider the first order wave function correction for this system.

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)} \Psi_m^{(0)}$$

$$\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle = \frac{2a}{l} \int_0^l \sin\left(\frac{m\pi x}{l}\right) x \sin\left(\frac{n\pi x}{l}\right) \, dx$$
$$= \frac{al}{\pi^2} \left(\frac{\cos\left((m-n)\pi\right) - 1}{(m-n)^2} - \frac{\cos\left((m+n)\pi\right) - 1}{(m+n)^2} \right)$$

When *m* and *n* are both even or both odd, $\cos((m \pm n)\,\pi) = 1$, and the above integral becomes 0 and it is non-zero when $m \pm n$ is odd. Suppose, the state of interest is *n* = 1. Only *n* = 2, 4, 6, … (i.e., when *n* is even) will contribute to the wave function correction. Of these, *n* = 4, 6, 8, … are farther from *n* = 1 state. Hence, for these states, $\left|E_n^{(0)} - E_m^{(0)}\right|$ are large and hence, the overall contribution of these states to the wave function correction will become increasingly small.

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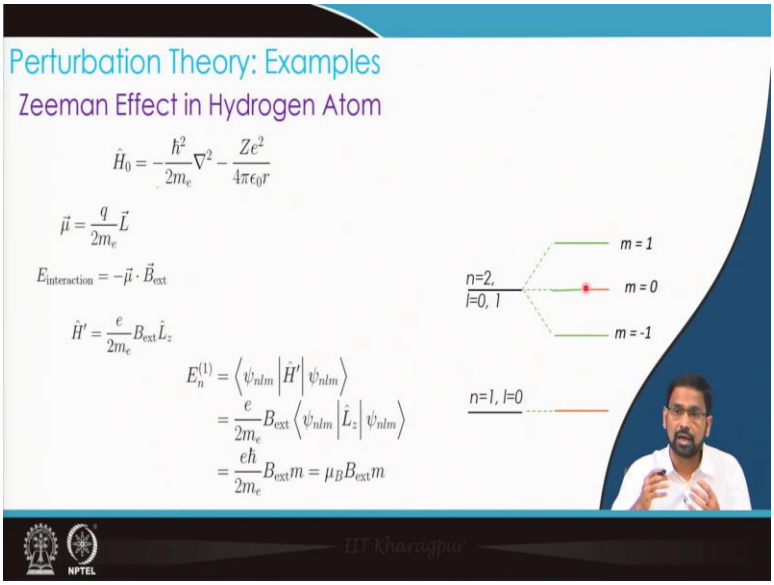


Now, let us look at another problem. This problem is related to the Zeeman effect in hydrogen atom or the effect of external magnetic field on the energy levels of the hydrogen atom. Here, we consider the external magnetic field as a perturbation to the unperturbed system (H-atom) whose solution is already known.

The unperturbed part of the Hamiltonian is

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The orbiting electron generates a dipole moment $\vec{\mu} = \frac{q}{2m_e}\vec{L}$

that interacts with the external magnetic field (B_{ext}) as, $E_{\text{interaction}} = -\vec{\mu}\cdot\vec{B}_{\text{ext}}$

If the magnetic field is applied along z-direction, the perturbation Hamiltonian is given by:

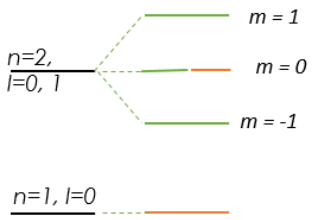
$$\hat{H}' = \frac{e}{2m_e}B_{\text{ext}}\hat{L}_z$$

The first-order energy correction can be obtained as

$$\begin{aligned} E_n^{(1)} &= \left\langle \psi_{nlm} \middle| \hat{H}' \middle| \psi_{nlm} \right\rangle \\ &= \frac{e}{2m_e}B_{\text{ext}} \left\langle \psi_{nlm} \middle| \hat{L}_z \middle| \psi_{nlm} \right\rangle \\ &= \frac{e\hbar}{2m_e}B_{\text{ext}}m = \mu_B B_{\text{ext}}m \end{aligned}$$

where, ψ_{nlm} are the eigenfunctions of H-atom with principal, azimuthal, and magnetic quantum numbers n, l, and m, respectively. L_z is the z-component of the orbital angular momentum of the electron. Here we use the fact that the energy eigenstates of H-atom are also eigenstates of L_z (with eigenvalues $m\hbar$). The constant $e\hbar/2m_e$ is known as the Bohr magneton.

Let us consider the n = 1 and 2 states of H-atom. The lowest energy eigenstate, with n = 1, l =0, m = 0, does not get affected by the external magnetic field (since the magnetic quantum number is 0). For n = 2, l = 0, 1 are degenerate (orbital degeneracy is not lifted in 1-electron system). For l =1, the m = +1, -1 states change their energy in the presence of magnetic field, while m = 0 states (from l = 0 and l = 1) remain unchanged. This differential interaction leads to the lifting of degeneracy in the presence of a magnetic field. The extent of separation of energy levels depends on the strength of the magnetic field (B_{ext}).



This lifting of degeneracy results in the appearance of additional lines in the emission spectrum of H-atom in the presence of external magnetic field. Bohr's atomic model could not explain this Zeeman effect, although it could explain the emission spectra of the hydrogen atom. Here, using perturbation theory we are able to explain the Zeeman effect.

We will continue to discuss a few more examples of perturbation theory in our next lecture.

Thank you for your attention.