Approximate Methods in Quantum Chemistry
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Lecture - 19
Examples of Perturbation Theory - II

Hello students! Welcome to this lecture. In the last lecture, we started our discussion on a few applications of perturbation theory. We will take up a few more examples of perturbation theory in this lecture.

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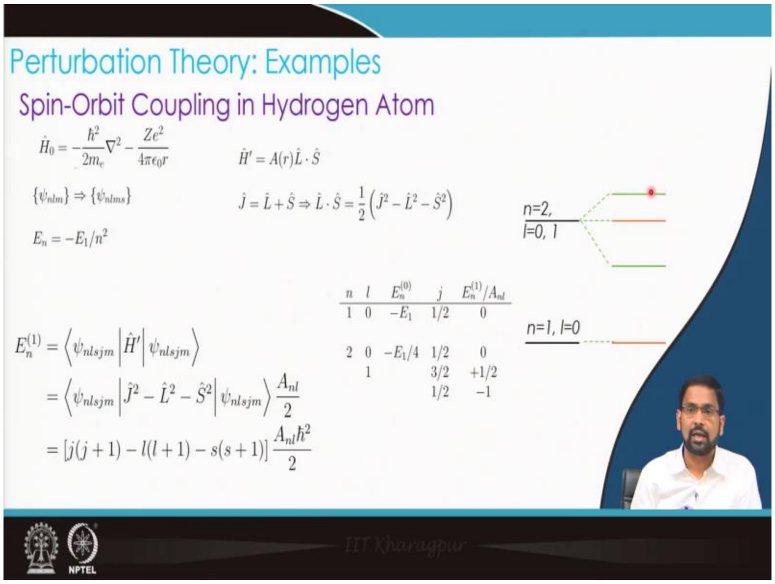


Perturbation Theory: Examples

Spin-Orbit Coupling in Hydrogen Atom

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \qquad \hat{H}' = A(r)\hat{L}\cdot\hat{S}$$

$$\{\psi_{nlm}\} \Rightarrow \{\psi_{nlms}\} \qquad \hat{J} = \hat{L} + \hat{S} \Rightarrow \hat{L}\cdot\hat{S} = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)$$

$$E_n = -E_1/n^2$$

$$E_n^{(1)} = \left\langle \psi_{nlsjm} \middle| \hat{H}' \middle| \psi_{nlsjm} \right\rangle$$
$$= \left\langle \psi_{nlsjm} \middle| \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \middle| \psi_{nlsjm} \right\rangle \frac{A_{nl}}{2}$$
$$= [j(j+1) - l(l+1) - s(s+1)]\frac{A_{nl}\hbar^2}{2}$$

n	l	$E_n^{(0)}$	j	$E_n^{(1)}/A_{nl}$
1	0	$-E_1$	1/2	0
2	0	$-E_1/4$	1/2	0
	1		3/2	+1/2
			1/2	−1

The first example in this lecture relates to the hydrogen atom. In the previous example (last class), we considered an external magnetic field to the hydrogen atom as a perturbation. In this example, we will explore a perturbation that does not come from outside, rather arises within the system. When we solved the H-atom problem, we included the spin of the electron after solving the spatial part. But spin is inherent property of the electron that can interact with its orbital motion via the so-called spin-orbit interaction.

In this example, we will consider spin-orbit coupling as a perturbation in the hydrogen atom. The unperturbed system is the Hamiltonian of H-atom

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

whose exact solutions are already known as following

$$\{\psi_{nlm}\} \Rightarrow \{\psi_{nlms}\}$$

$$E_n = -E_1/n^2$$

Here ψ_{nlms} form the complete set of energy eigenstates of H-atom, with *n*, *l*, *m* as the spatial and *s* as the spin quantum number. E_1 is the ground state energy (-0.5 au).

The perturbation Hamiltonian is given by the spin-orbit interaction,

$$\hat{H}' = A(r)\hat{L}\cdot\hat{S}$$

$$\hat{J} = \hat{L} + \hat{S} \Rightarrow \hat{L}\cdot\hat{S} = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)$$

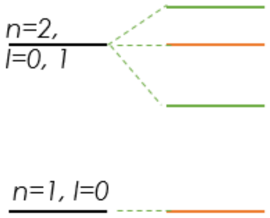
Where, *J* is the total angular momentum operator (orbital + spin) and *A* is the spin-orbit coupling constant (that depends on the principal and azimuthal quantum numbers). Using the unperturbed eigenstates ψ_{nlms} and the perturbation Hamiltonian, the 1st order energy correction can be obtained as,

$$\begin{aligned} E_n^{(1)} &= \left\langle \psi_{nlsjm} \middle| \hat{H}' \middle| \psi_{nlsjm} \right\rangle \\ &= \left\langle \psi_{nlsjm} \middle| \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \middle| \psi_{nlsjm} \right\rangle \frac{A_{nl}}{2} \\ &= [j(j+1) - l(l+1) - s(s+1)]\,\frac{A_{nl}\hbar^2}{2} \end{aligned}$$

Here *j* represents the good quantum number of the system (when spin-orbit interactions are included). For *n* =1 and 2, possible values of *j*, as well as the 1st order energy corrections, are given below:

n	l	$E_n^{(0)}$	j	$E_n^{(1)}/A_{nl}$
1	0	$-E_1$	$1/2$	0
2	0	$-E_1/4$	$1/2$	0
	1		$3/2$	$+1/2$
			$1/2$	-1

As can be seen, the lowest energy state does not show any change due to spin-orbit coupling since the orbital angular momentum is 0 here. For a similar reason, $n = 2$, $l = 0$ state also does not change its energy. However, $n = 2$, $l = 1$, leads to two possible j values ($j = l + s$, $l - s = 3/2, 1/2$). Here, the energy of $j = 3/2$ increases by $A_{nl}/2$ (in the atomic unit where $\hbar = 1$), while that of $j = 1/2$ decreases by A_{nl}. Please keep in mind that the spin-orbit coupling constant would depend (both sign and magnitude) on the nucleus of the atoms, the number of electrons in the atom, apart from the principal and orbital angular momentum quantum numbers.



A qualitative view of the splitting of the degenerate states is shown above (orange: $j = ½$ and green $j = 3/2$). Each split state is $(2j+1)$-fold degenerate ($m_j = -j, -j + 1, \dots, j - 1, j$). This degeneracy can be lifted in the presence of an external magnetic field based on their j and m_j quantum numbers.

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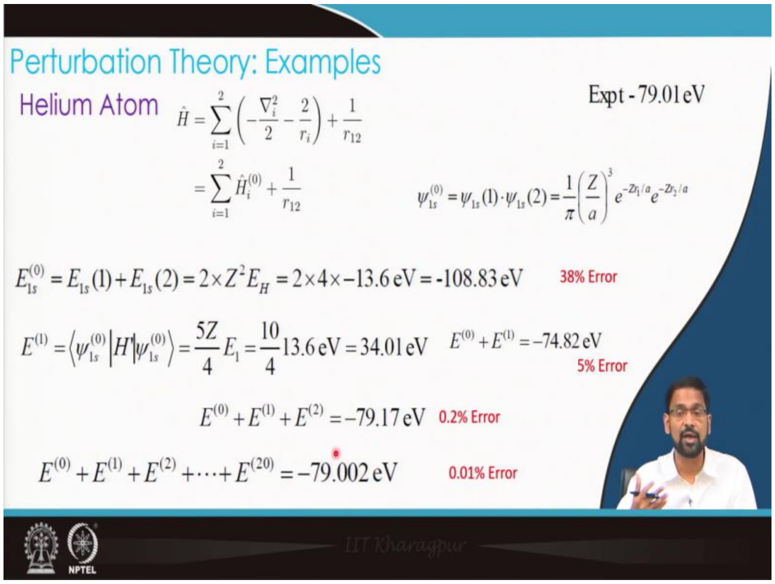

Perturbation Theory: Examples

Helium Atom

$$\hat{H} = \sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \frac{2}{r_i}\right) + \frac{1}{r_{12}}$$

$$= \sum_{i=1}^{2}\hat{H}_i^{(0)} + \frac{1}{r_{12}}$$

Expt - 79.01 eV

$$\psi_{1s}^{(0)} = \psi_{1s}(1)\cdot\psi_{1s}(2) = \frac{1}{\pi}\left(\frac{Z}{a}\right)^3 e^{-Zr_1/a}e^{-Zr_2/a}$$

$$E_{1s}^{(0)} = E_{1s}(1) + E_{1s}(2) = 2\times Z^2 E_H = 2\times 4\times -13.6\,\text{eV} = -108.83\,\text{eV}$$ 38% Error

$$E^{(1)} = \left\langle \psi_{1s}^{(0)} \middle| H' \middle| \psi_{1s}^{(0)} \right\rangle = \frac{5Z}{4}E_1 = \frac{10}{4}13.6\,\text{eV} = 34.01\,\text{eV}$$

$$E^{(0)} + E^{(1)} = -74.82\,\text{eV}$$ 5% Error

$$E^{(0)} + E^{(1)} + E^{(2)} = -79.17\,\text{eV}$$ 0.2% Error

$$E^{(0)} + E^{(1)} + E^{(2)} + \cdots + E^{(20)} = -79.002\,\text{eV}$$ 0.01% Error

We will now discuss another example, where we would study two-body interaction. Let us consider the helium atom, whose Hamiltonian is given by (within Born-Oppenheimer approximation):

$$\begin{aligned}\hat{H} &= \sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \frac{2}{r_i}\right) + \frac{1}{r_{12}} \\ &= \sum_{i=1}^{2}\hat{H}_i^{(0)} + \frac{1}{r_{12}}\end{aligned}$$

The first term is the sum of two one-electron operators (electron kinetic energy and electron-nuclear potential energy), and the second term is the two-electron operator. The exact solution is possible for the 1-electron part (two independent 1-electron systems), which constitutes the unperturbed system. The wave function of the unperturbed system can be written as the product of eigenstates of two H-like atoms (with electron coordinates r_1 and r_2 and nuclear charge Z=2):

$$\psi_{1s}^{(0)} = \psi_{1s}(1)\cdot\psi_{1s}(2) = \frac{1}{\pi}\left(\frac{Z}{a}\right)^3 e^{-Zr_1/a}e^{-Zr_2/a}$$

The unperturbed energy is given by the sum of the energy of two H-like atoms,

$$E_{1s}^{(0)} = E_{1s}(1) + E_{1s}(2) = 2\times Z^2 E_H = 2\times 4\times -13.6\text{ eV} = \text{-}108.83\text{ eV}$$

Where E_H is the energy of H-atom (-0.5 au = -13.6 eV). The unperturbed energy of -108.83 eV is about 38% overestimation of the true (experimental) energy of He atom (-79.01 eV).

The two-electron operator ($1/r_{12}$) constitutes the perturbation Hamiltonian. The 1st order energy correction is calculated as

$$E^{(1)} = \left\langle \psi_{1s}^{(0)} \middle| H' \middle| \psi_{1s}^{(0)} \right\rangle = \frac{5Z}{4}E_1 = \frac{10}{4}13.6\text{ eV} = 34.01\text{ eV}$$

After including the 1st order energy correction, the energy of He atom becomes -74.82 eV (5% error). This error reduces to 0.2% when 2nd order energy corrections are included and it reduces to

0.01% when perturbation correction up to 20th order is included! It shows that the true solution is in principle, achievable, but it may take several higher-order terms. In this example, we actually did not explicitly evaluate the integrals, but we looked at how the energies converge towards the experimental value or the true energy. Since the energy converges to its true value, the wave function is also expected to converge to its true value, which can be verified by evaluating other properties of the system from this wave function.

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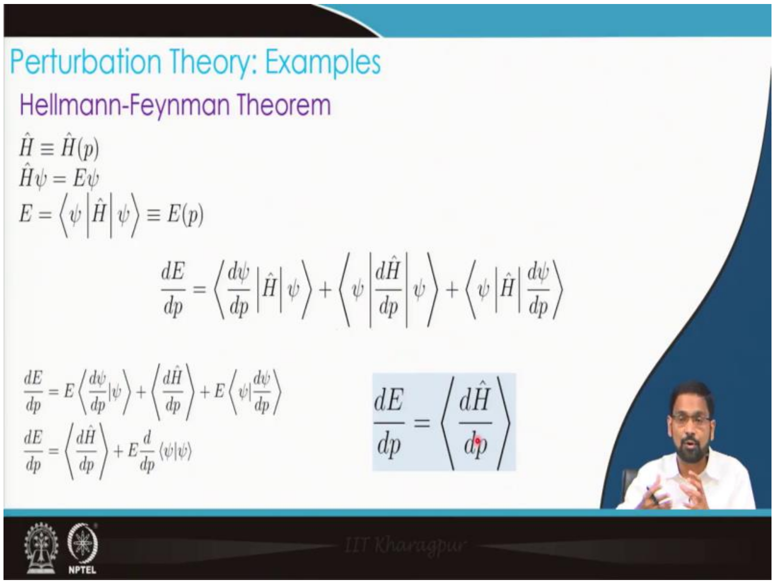

Perturbation Theory: Examples

Hellmann-Feynman Theorem

$$\hat{H} \equiv \hat{H}(p)$$
$$\hat{H}\psi = E\psi$$
$$E = \left\langle \psi \middle| \hat{H} \middle| \psi \right\rangle \equiv E(p)$$

$$\frac{dE}{dp} = \left\langle \frac{d\psi}{dp} \middle| \hat{H} \middle| \psi \right\rangle + \left\langle \psi \middle| \frac{d\hat{H}}{dp} \middle| \psi \right\rangle + \left\langle \psi \middle| \hat{H} \middle| \frac{d\psi}{dp} \right\rangle$$

$$\frac{dE}{dp} = E\left\langle \frac{d\psi}{dp} \middle| \psi \right\rangle + \left\langle \frac{d\hat{H}}{dp} \right\rangle + E\left\langle \psi \middle| \frac{d\psi}{dp} \right\rangle$$
$$\frac{dE}{dp} = \left\langle \frac{d\hat{H}}{dp} \right\rangle + E\frac{d}{dp}\langle \psi | \psi \rangle$$

$$\boxed{\frac{dE}{dp} = \left\langle \frac{d\hat{H}}{dp} \right\rangle}$$

Before we discuss any further application of perturbation theory, now, let us look at a very useful theorem that goes by the name Hellmann Feynman theorem. Hellman Feynman theorem relates to a situation where the Hamiltonian depends on some parameters (*p*) such that when this parameter is changed, the Hamiltonian changes.

Let this Hamiltonian follow the following Schrodinger equation:

$$\hat{H}\psi = E\psi$$
$$E = \left\langle \psi \middle| \hat{H} \middle| \psi \right\rangle \equiv E(p)$$

Now let us consider

$$\frac{dE}{dp} = \left\langle \frac{d\psi}{dp} \left| \hat{H} \right| \psi \right\rangle + \left\langle \psi \left| \frac{d\hat{H}}{dp} \right| \psi \right\rangle + \left\langle \psi \left| \hat{H} \right| \frac{d\psi}{dp} \right\rangle$$

The three terms above are obtained by differentiating the energy expression given in the previous equation. The above expression can be rearranged as (by considering Hermitian property of *H*)

$$\frac{dE}{dp} = E \left\langle \frac{d\psi}{dp} | \psi \right\rangle + \left\langle \frac{d\hat{H}}{dp} \right\rangle + E \left\langle \psi | \frac{d\psi}{dp} \right\rangle$$

$$\frac{dE}{dp} = \left\langle \frac{d\hat{H}}{dp} \right\rangle + E \frac{d}{dp} \langle \psi | \psi \rangle$$

Since the last term in the above expression is 0 (differentiation of a constant), we obtain the Hellman-Feynman relation

$$\frac{dE}{dp} = \left\langle \frac{d\hat{H}}{dp} \right\rangle$$

This relation tells us that if there is a parameter on which the Hamiltonian depends, the expectation value of this operator d*H*/d*p* simply is the first derivative of the energy with respect to the same parameter. We will see a few examples of the Hellmann-Feynman theorem in our next lecture.

Thank you for your attention.