Approximate Methods in Quantum Chemistry
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Lecture - 21
Molecular Response to Electric Field-II

Hello students! Welcome to this lecture. In the last lecture, we were discussing the response of molecules to electric field. We will continue our discussion in that direction in this lecture.

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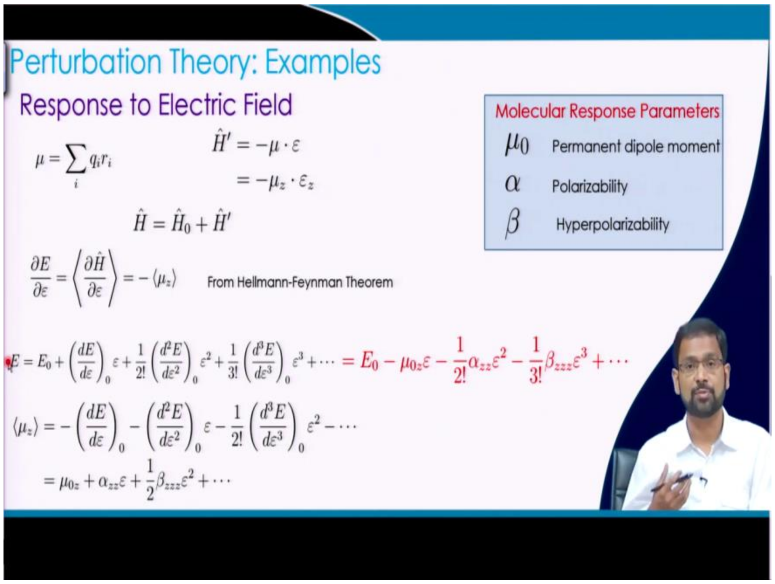

Perturbation Theory: Examples

Response to Electric Field

$$\mu = \sum_i q_i r_i \qquad \hat{H}' = -\mu \cdot \varepsilon = -\mu_z \cdot \varepsilon_z$$

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$$\frac{\partial E}{\partial \varepsilon} = \left\langle \frac{\partial \hat{H}}{\partial \varepsilon} \right\rangle = -\langle \mu_z \rangle$$

From Hellmann-Feynman Theorem

Molecular Response Parameters

μ_0 Permanent dipole moment

α Polarizability

β Hyperpolarizability

$$E = E_0 + \left(\frac{dE}{d\varepsilon}\right)_0 \varepsilon + \frac{1}{2!}\left(\frac{d^2E}{d\varepsilon^2}\right)_0 \varepsilon^2 + \frac{1}{3!}\left(\frac{d^3E}{d\varepsilon^3}\right)_0 \varepsilon^3 + \cdots = E_0 - \mu_{0z}\varepsilon - \frac{1}{2!}\alpha_{zz}\varepsilon^2 - \frac{1}{3!}\beta_{zzz}\varepsilon^3 + \cdots$$

$$\langle \mu_z \rangle = -\left(\frac{dE}{d\varepsilon}\right)_0 - \left(\frac{d^2E}{d\varepsilon^2}\right)_0 \varepsilon - \frac{1}{2!}\left(\frac{d^3E}{d\varepsilon^3}\right)_0 \varepsilon^2 - \cdots$$
$$= \mu_{0z} + \alpha_{zz}\varepsilon + \frac{1}{2}\beta_{zzz}\varepsilon^2 + \cdots$$

Just to refresh your memory, we discussed that since molecules are composed of charged particles distributed over space, they have an inherent electric dipole moment which interacts with applied electric field, thus creating a perturbation term in the original molecular Hamiltonian. We then used the Hellman-Feynman theorem (with electric field as the parameter) to obtain an expression that relates the expectation value of molecular electric dipole moment with the first derivative of molecular energy with the applied electric field.

By expressing molecular energy as a Taylor series expansion in terms of the electric field around the unperturbed energy and defining a few molecular response parameters (permanent electric dipole moment, polarizability, and hyperpolarizability), we expressed the energy of the system in terms of the molecular response parameters and electric field strength (see above in the slide).

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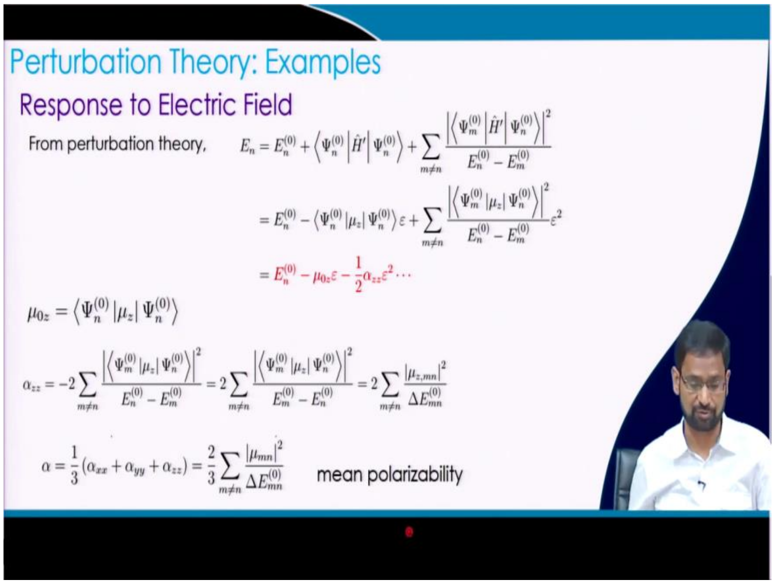

Perturbation Theory: Examples

Response to Electric Field

From perturbation theory,
$$E_n = E_n^{(0)} + \left\langle \Psi_n^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle + \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}$$
$$= E_n^{(0)} - \left\langle \Psi_n^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle \varepsilon + \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} \varepsilon^2$$
$$= E_n^{(0)} - \mu_{0z}\varepsilon - \frac{1}{2}\alpha_{zz}\varepsilon^2 \cdots$$

$$\mu_{0z} = \left\langle \Psi_n^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle$$

$$\alpha_{zz} = -2 \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} = 2 \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle \right|^2}{E_m^{(0)} - E_n^{(0)}} = 2 \sum_{m \neq n} \frac{\left| \mu_{z,mn} \right|^2}{\Delta E_{mn}^{(0)}}$$

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = \frac{2}{3} \sum_{m \neq n} \frac{\left| \mu_{mn} \right|^2}{\Delta E_{mn}^{(0)}}$$ mean polarizability

By comparing the above expression of energy (in terms of response parameters) with that of the energy expression from perturbation theory, we obtained the following two relations for the molecular response parameters:

$$\mu_{0z} = \left\langle \Psi_n^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle$$

$$\alpha_{zz} = -2 \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} = 2 \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle \right|^2}{E_m^{(0)} - E_n^{(0)}} = 2 \sum_{m \neq n} \frac{\left| \mu_{z,mn} \right|^2}{\Delta E_{mn}^{(0)}}$$

μ_{0z} and α_{zz} are the z-component of the permanent dipole moment and the zz-component of the polarizability tensor, respectively. If the molecule experiences an isotropic electric field, we can evaluate α_{xx} *and* α_{yy} and express the mean polarizability as the arithmetic mean of the three polarizability components (as shown in the slide). The mean polarizability depends on the matrix elements of dipole moment matrix in the basis of the unperturbed states of the system. Here we are restricting our discussion to 2nd order perturbation correction and hence we have dropped our discussion on the hyperpolarizability.

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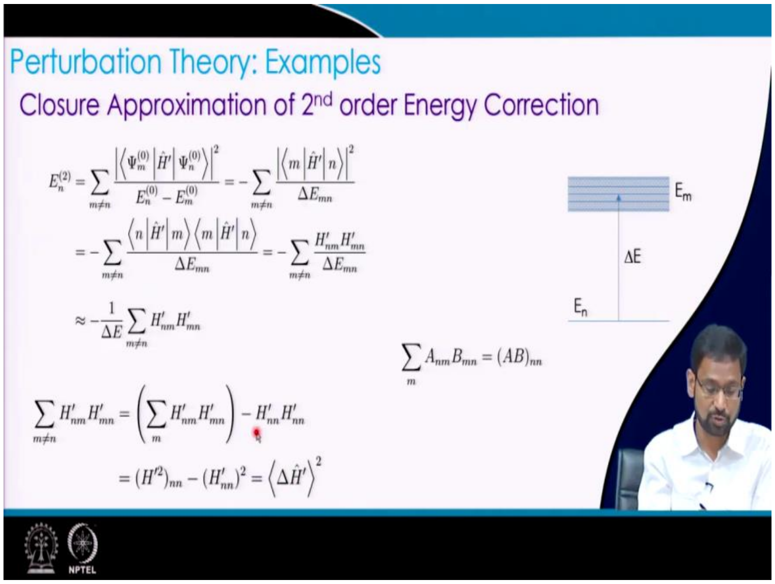

Perturbation Theory: Examples

Closure Approximation of 2nd order Energy Correction

$$E_n^{(2)} = \sum_{m\neq n} \frac{\left|\left\langle \Psi_m^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}} = -\sum_{m\neq n} \frac{\left|\left\langle m \middle| \hat{H}' \middle| n \right\rangle\right|^2}{\Delta E_{mn}}$$

$$= -\sum_{m\neq n} \frac{\left\langle n \middle| \hat{H}' \middle| m \right\rangle \left\langle m \middle| \hat{H}' \middle| n \right\rangle}{\Delta E_{mn}} = -\sum_{m\neq n} \frac{H'_{nm} H'_{mn}}{\Delta E_{mn}}$$

$$\approx -\frac{1}{\Delta E} \sum_{m\neq n} H'_{nm} H'_{mn}$$

$$\sum_m A_{nm} B_{mn} = (AB)_{nn}$$

$$\sum_{m\neq n} H'_{nm} H'_{mn} = \left(\sum_m H'_{nm} H'_{mn} \right) - H'_{nn} H'_{nn}$$

$$= (H'^2)_{nn} - (H'_{nn})^2 = \left\langle \Delta \hat{H}' \right\rangle^2$$

Before we start using the results obtained thus far, let us discuss the closure approximation of the 2nd order energy correction that will help us in our future discussion.

From 2nd order perturbation theory we know,

$$E_n^{(2)} = \sum_{m\neq n} \frac{\left|\left\langle \Psi_m^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}} = -\sum_{m\neq n} \frac{\left|\left\langle m \middle| \hat{H}' \middle| n \right\rangle\right|^2}{\Delta E_{mn}}$$

$$= -\sum_{m\neq n} \frac{\left\langle n \middle| \hat{H}' \middle| m \right\rangle \left\langle m \middle| \hat{H}' \middle| n \right\rangle}{\Delta E_{mn}} = -\sum_{m\neq n} \frac{H'_{nm} H'_{mn}}{\Delta E_{mn}}$$

where, the states $\left|\psi_n^{(0)}\right\rangle$ are defined in short-hand notation $|n\rangle$ and the square of the integral is expressed as a product of two matrix elements (H'_{nm}). The summation in the last term is for all $m \neq n$. If our state of interest is the ground state, m accounts for all the excited states. It is often the case that the ground state is well separated from the excited states. In other words, the energy difference between any two excited states is negligible compared to the energy difference between the ground state and any excited state. Hence, ΔE_{mn} can be treated as a constant (since it does not change that much for different values of *m*) and be brought out of the summation, resulting in $E_n^{(2)}$

$$\approx -\frac{1}{\Delta E}\sum_{m\neq n} H'_{nm}H'_{mn}$$

The above approximation goes by the name of closure approximation.

We can express the terms within the summation sign as following

$$\sum_{m\neq n} H'_{nm}H'_{mn} = \left(\sum_{m} H'_{nm}H'_{mn}\right) - H'_{nn}H'_{nn}$$

Which can be expressed as

$$= (H'^2)_{nn} - (H'_{nn})^2 = \left\langle \Delta\hat{H}' \right\rangle^2$$

The first term is the element of the square of the matrix, while the second term is the square of that matrix element. The difference between the two is the mean squared deviation or fluctuation. The delta symbol indicates the uncertainty in the measurement of *H'*.

Combining the closure approximation and above relation, we obtain a very useful relation

$$E_n^{(2)} = -\frac{\left\langle \Delta\widehat{H'} \right\rangle^2}{\Delta E}$$

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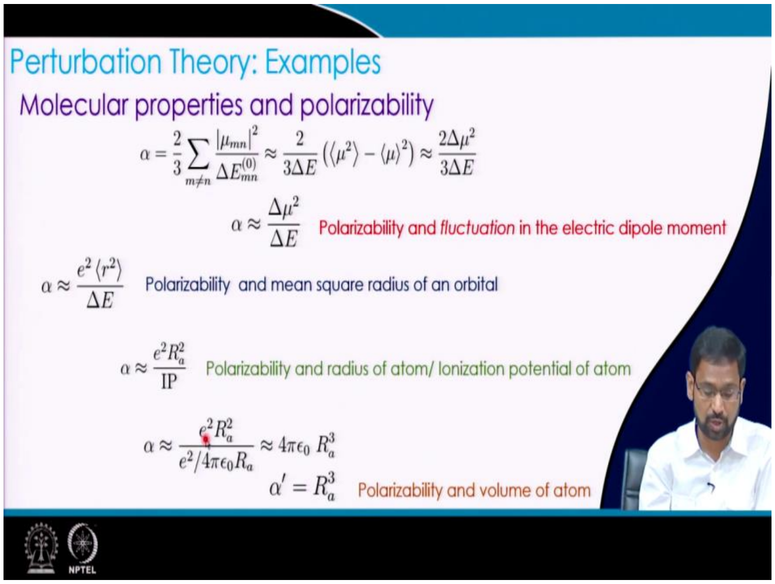

Perturbation Theory: Examples

Molecular properties and polarizability

$$\alpha = \frac{2}{3}\sum_{m\neq n}\frac{|\mu_{mn}|^2}{\Delta E_{mn}^{(0)}} \approx \frac{2}{3\Delta E}\left(\langle\mu^2\rangle - \langle\mu\rangle^2\right) \approx \frac{2\Delta\mu^2}{3\Delta E}$$

$$\alpha \approx \frac{\Delta\mu^2}{\Delta E}$$ Polarizability and *fluctuation* in the electric dipole moment

$$\alpha \approx \frac{e^2\langle r^2\rangle}{\Delta E}$$ Polarizability and mean square radius of an orbital

$$\alpha \approx \frac{e^2R_a^2}{\mathrm{IP}}$$ Polarizability and radius of atom/ Ionization potential of atom

$$\alpha \approx \frac{e^2R_a^2}{e^2/4\pi\epsilon_0R_a} \approx 4\pi\epsilon_0\, R_a^3$$

$$\alpha' = R_a^3$$ Polarizability and volume of atom

Now we will use the results of closure approximation in the definition of polarizability. In our case, $\hat{H}'_{mn} = \mu_{mn}$. It gives us the following

$$\alpha = \frac{2}{3}\sum_{m\neq n}\frac{|\mu_{mn}|^2}{\Delta E_{mn}^{(0)}} \approx \frac{2}{3\Delta E}\left(\langle\mu^2\rangle - \langle\mu\rangle^2\right) \approx \frac{2\Delta\mu^2}{3\Delta E}$$

$\Delta\mu$ is the fluctuation in the electric dipole moment of the molecule, and ΔE is the energy difference between the state of the interest (the ground state) and the excited states within the closure approximation. By ignoring the constant (2/3), we can write

$$\alpha \approx \frac{\Delta\mu^2}{\Delta E}$$

This expression tells us that the polarizability is proportional to the square of the fluctuation of the electric dipole moment. In other words, the more is the fluctuation in the electric dipole moment, the greater is the polarizability. The fluctuation in this electric dipole moment arises due to the movement of the electrons with respect to the nuclear positions. Hence, large fluctuation in the electric dipole moment indicates less control of the nuclei over the electrons and thereby greater degree of polarizability.

For an atom, the fluctuation in the electric dipole moment can be equated to the mean square radius of the orbital containing the electron, i.e.,

$$\alpha \approx \frac{e^2 \langle r^2 \rangle}{\Delta E}$$

A greater value of the mean square radius of an orbital indicates that the electron is found farther from the nucleus, which makes the atom easily polarizable. So, the polarizability is again related to this mean square radius. Now, let us consider a particular value of mean square radius of the orbit that defines the radius of the atom (R). For such a value of the mean squared radius, the term ΔE is essentially the ionization potential of the atom. Hence,

$$\alpha \approx \frac{e^2 R_a^2}{\mathrm{IP}}$$

The polarizability is greater for an atom with a greater atomic radius and it is inversely proportional to the ionization potential. Since the radius of the atom can be used to express the atomic volume, and the ionization potential is essentially the negative of the Coulombic interaction experienced by the electron, we can write the following

$$\alpha \approx \frac{e^2 R_a^2}{e^2/4\pi\epsilon_0 R_a} \approx 4\pi\epsilon_0 \ R_a^3$$

This expression shows how polarizability is related to the volume of the atom. It is a convention to express $\alpha' = \alpha/(4\pi\epsilon_0)$, α' is known as the polarizability of the volume of an atom.

From the above discussion, we see that polarizability relates to various other molecular properties, such as volume, the mean square radius, the ionization potential, and the fluctuation in the electric dipole moment.

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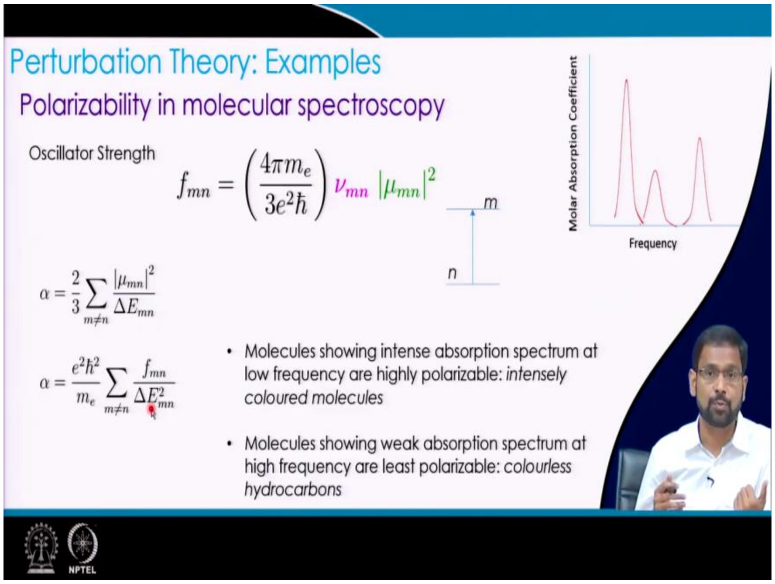

Perturbation Theory: Examples

Polarizability in molecular spectroscopy

Oscillator Strength

$$f_{mn} = \left(\frac{4\pi m_e}{3e^2\hbar}\right) \nu_{mn} \, |\mu_{mn}|^2$$

$$\alpha = \frac{2}{3}\sum_{m\neq n}\frac{|\mu_{mn}|^2}{\Delta E_{mn}}$$

$$\alpha = \frac{e^2\hbar^2}{m_e}\sum_{m\neq n}\frac{f_{mn}}{\Delta E_{mn}^2}$$

- Molecules showing intense absorption spectrum at low frequency are highly polarizable: *intensely coloured molecules*
- Molecules showing weak absorption spectrum at high frequency are least polarizable: *colourless hydrocarbons*

The response parameter polarizability has an important role in molecular spectroscopy. During a spectroscopic transition (absorption or emission spectrum), the system undergoes a transition from state *n* to state *m*. There are two important components associated with this transition: one is the transition energy and the second is the intensity of the peak. The intensity of a transition at transition frequency ν_{mn} is given by the quantity called oscillator strength f_{mn}

$$f_{mn} = \left(\frac{4\pi m_e}{3e^2\hbar}\right) \nu_{mn} \; |\mu_{mn}|^2$$

Using the above relation in the expression of polarizability, we can express polarizability in terms of oscillator strength as follows:

$$\alpha = \frac{2}{3}\sum_{m\neq n}\frac{|\mu_{mn}|^2}{\Delta E_{mn}}$$

$$\alpha = \frac{e^2\hbar^2}{m_e}\sum_{m\neq n}\frac{f_{mn}}{\Delta E_{mn}^2}$$

We have expressed oscillator strength in terms of two parameters: the oscillator strength, that is, the intensity of the peak, and absorption frequency. This shows that molecules showing intense absorption spectrum (large oscillator strength) at low frequency are highly polarizable, such as intensely coloured molecules. On the other hand, molecules showing weak absorption spectrum at high frequency are less polarizable, such as colourless hydrocarbons.

The take-home lesson of the above exercise was to show you that even though perturbation theory gives us an idea about the correction to the wave function and to the energy, we can express different molecular parameters in terms of the perturbation energy by using Hellman Feynman theorem and then can proceed to obtain different molecular properties.

Thank you for your attention.