Approximate Methods in Quantum Chemistry
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Lecture 20
Molecular Response to Electric Field

Hello students! Welcome to this lecture. In the last few lectures, we discussed the perturbation theory and its applications. In this lecture, we are going to take our discussion forward and look at the molecular response to an electric field. The electric field can have two sources of origin: it could be an external electric field applied to the molecule of our interest, or it can be an internal electric field experienced by the molecule of our interest due to the presence of another molecule. No matter whether it is an external or internal field, in both cases, the energy levels of the molecule of our interest get perturbed by the presence of this electric field which can be treated using perturbation theory.

Perturbation theory gives us a way to obtain the corrected wave function and energy. If we want to evaluate any other property of the molecule, we can obtain the expectation value of the related operator when the state is defined the wave function from perturbation theory. There is another way to obtain molecular properties (or molecular response parameters), which involves the application of the famous Hellmann-Feynman theorem. In this lecture, we will learn to use this theorem and obtain different molecular response parameters to the electric field.

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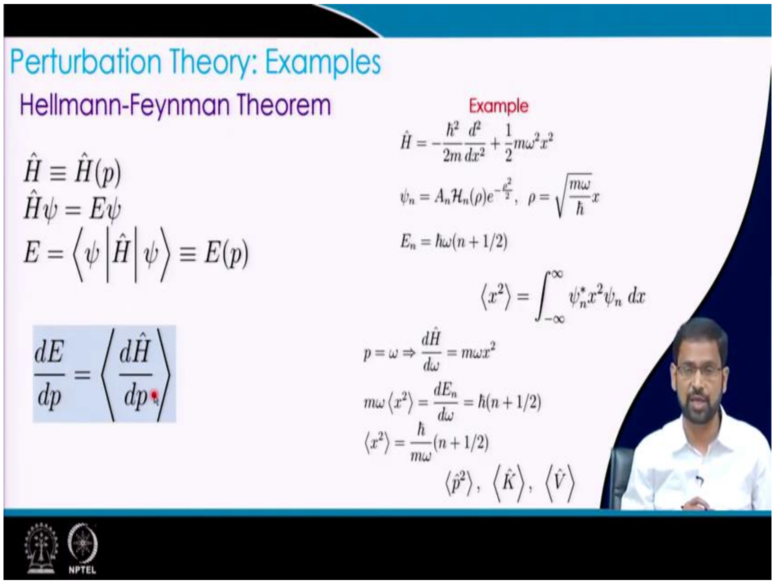

Perturbation Theory: Examples

Hellmann-Feynman Theorem

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

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

Example

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$
$$\psi_n = A_n \mathcal{H}_n(\rho) e^{-\frac{\rho^2}{2}}, \ \rho = \sqrt{\frac{m\omega}{\hbar}}x$$
$$E_n = \hbar\omega(n + 1/2)$$
$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_n^* x^2 \psi_n \, dx$$
$$p = \omega \Rightarrow \frac{d\hat{H}}{d\omega} = m\omega x^2$$
$$m\omega \langle x^2 \rangle = \frac{dE_n}{d\omega} = \hbar(n + 1/2)$$
$$\langle x^2 \rangle = \frac{\hbar}{m\omega}(n + 1/2)$$
$$\langle \hat{p}^2 \rangle, \ \langle \hat{K} \rangle, \ \langle \hat{V} \rangle$$

In the last lecture, we derived the Hellmann-Feynman theorem,

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

Let us consider a few examples that illustrate the power of this theorem. We have solved the 1-dimensional harmonic oscillator problem quantum mechanically and have obtained the eigenvalues and eigenfunctions as following

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

$$\psi_n = A_n \mathcal{H}_n(\rho) e^{-\frac{\rho^2}{2}}, \quad \rho = \sqrt{\frac{m\omega}{\hbar}}x$$

$$E_n = \hbar\omega(n + 1/2)$$

To obtain the expectation value of, let's say, x^2, we need to evaluate the following integral

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_n^* x^2 \psi_n \, dx$$

After laboriously evaluating the above integral by using the explicit form of the eigenfunction we will obtain (please try to do this exercise if you have not done it already in your previous QM course),

$$\langle x^2 \rangle = \frac{\hbar}{m\omega}(n + 1/2)$$

Now, alternatively, let us use the Hellmann-Feynman theorem (and do not consider the wave function at all!) to derive the same result. To use the Hellmann-Feynman theorem, we must decide which quantity to be considered as the parameter (*p*). Let us consider ω as the parameter.

Using the expression for the Hamiltonian given above, we can show:

$$\frac{d\hat{H}}{d\omega} = m\omega x^2$$

Similarly, using the expression of the eigenvalue, we can show

$$\frac{dE_n}{d\omega} = \hbar(n + 1/2)$$

Now equating the above two expressions (due to the Hellmann-Feynman theorem), we obtain:

$$m\omega \left\langle x^2 \right\rangle = \frac{dE_n}{d\omega} = \hbar(n + 1/2)$$

Which can be rearranged to,

$$\left\langle x^2 \right\rangle = \frac{\hbar}{m\omega}(n + 1/2)$$

As you can see, we obtained the above expectation value with very little effort using the Hellmann-Feynman theorem. You can similarly use different parameters (by careful inspection of the Hamiltonian) to obtain the following expectation values:

$$\left\langle \hat{p}^2 \right\rangle, \ \left\langle \hat{K} \right\rangle, \ \left\langle \hat{V} \right\rangle$$

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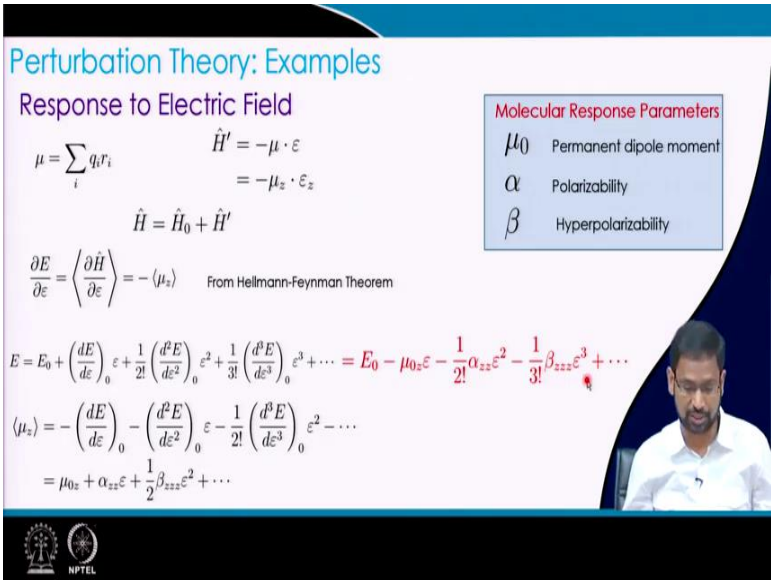

Perturbation Theory: Examples

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

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

$$\langle \mu_z \rangle = -\left(\frac{dE}{d\varepsilon}\right)_0 - \left(\frac{d^2E}{d\varepsilon^2}\right)_0 \varepsilon - \frac{1}{2!}\left(\frac{d^3E}{d\varepsilon^3}\right)_0 \varepsilon^2 - \cdots$$

$$= \mu_{0z} + \alpha_{zz}\varepsilon + \frac{1}{2}\beta_{zzz}\varepsilon^2 + \cdots$$

Now, let us come back to the discussion on molecular response to the electric field. Since the molecules are made up of charged particles (q_i) distributed over space (r_i), they generate an inherent electric dipole moment given by,

$$\mu = \sum_i q_i r_i$$

When this molecule is exposed to an electric field (ϵ), the molecular electric dipole moment interacts with the electric field, which is represented by the following perturbation Hamiltonian,

$$\begin{aligned}\hat{H}' &= -\mu \cdot \varepsilon \\ &= -\mu_z \cdot \varepsilon_z\end{aligned}$$

The second line of the above expression is valid when the electric field is applied along the *z*-direction. Together with the above perturbation Hamiltonian (*H'*), the total molecular Hamiltonian (*H*) becomes,

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

Now, using the Hellmann-Feynman theorem, we can write down the following expression by using the electric field as the parameter in the Hellmann-Feynman theorem,

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

Since the unperturbed Hamiltonian ($H_{0,}$ the molecular Hamiltonian in the absence of electric field) does not depend on the electric field, we can express the expectation value of the μ_z as the partial derivative of energy with respect to the applied electric field. This result is noteworthy. We have used different approximate methods that are designed to obtain the accurate energy of a complex system. Now a relation like the above allows us to evaluate other molecular properties that can be *derived* from the energy due to the Hellmann-Feynman theorem.

Let us now express the energy as a Taylor series expansion (around E_0) in terms of the electric field (ϵ),

$$E = E_0 + \left(\frac{dE}{d\varepsilon}\right)_0 \varepsilon + \frac{1}{2!}\left(\frac{d^2E}{d\varepsilon^2}\right)_0 \varepsilon^2 + \frac{1}{3!}\left(\frac{d^3E}{d\varepsilon^3}\right)_0 \varepsilon^3 + \cdots$$

We can take the first derivative of the above expression with respect to ϵ and equate it with $-\mu_z$ to get,

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

where we defined certain quantities μ_0, α, β as the first, second, and third derivatives of the energy with respect to ϵ. The quantities μ_0, α, β are also known as the permanent dipole moment, polarizability, and hyperpolarizability, respectively. Since the electric field is applied along the z-direction, the permanent dipole is expressed as its *z*-component, the polarizability is a tensor expressed as its *zz*-component, and the hyperpolarizability is expressed as its *zzz*-component. The other components are expected to be small when the electric field is applied along the z-direction.

Using these definitions in the expression for the Taylor series expansion of energy, we can write the energy (E) as,

$$= E_0 - \mu_{0z}\varepsilon - \frac{1}{2!}\alpha_{zz}\varepsilon^2 - \frac{1}{3!}\beta_{zzz}\varepsilon^3 + \cdots$$

We have now successfully expressed the total energy in terms of the unperturbed energy (energy before the electric field is applied) and some molecular response parameters. We will now use this information together with our knowledge in perturbation theory to carry our discussion forward.

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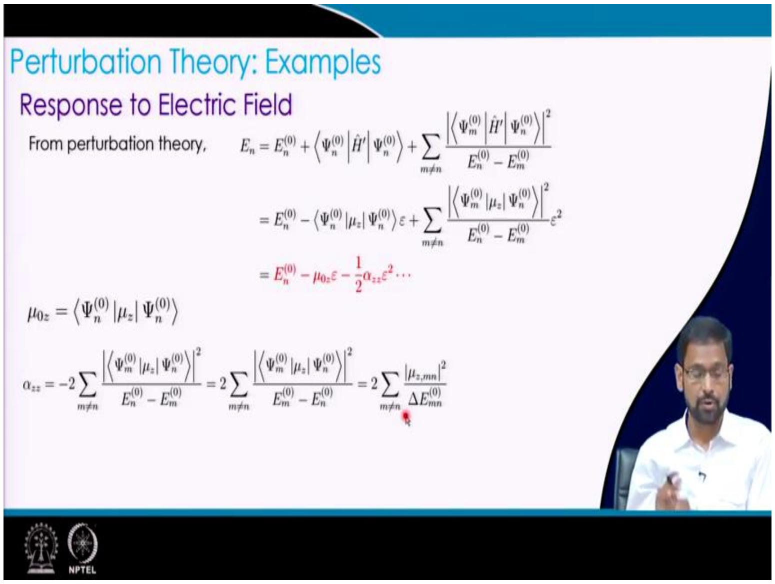

Perturbation Theory: Examples

Response to Electric Field

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

$= E_n^{(0)} - \left\langle \Psi_n^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle \varepsilon + \sum_{m\neq n} \frac{\left| \left\langle \Psi_m^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} \varepsilon^2$

$= E_n^{(0)} - \mu_{0z}\varepsilon - \frac{1}{2}\alpha_{zz}\varepsilon^2 \cdots$

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

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

From perturbation theory expression, we know the energy as

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

$$= E_n^{(0)} - \left\langle \Psi_n^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle \varepsilon + \sum_{m\neq n} \frac{\left| \left\langle \Psi_m^{(0)} \left| \mu_z \right| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} \varepsilon^2$$

where the perturbation Hamiltonian is given by $-\mu_z \epsilon$. Comparing the above expression with

$$= E_0 - \mu_{0z}\varepsilon - \frac{1}{2!}\alpha_{zz}\varepsilon^2 - \frac{1}{3!}\beta_{zzz}\varepsilon^3 + \cdots$$

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

and

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

If the applied electric field is isotropic, we can express the above relation for the polarizability to express mean polarizability as

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

We will use the above relations and learn about their consequences in our next lecture.

Thank you for your attention.