Approximate Methods in Quantum Chemistry
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Lecture 10
Linear Variational Method

Hello students! Welcome to this lecture. In the last few lectures we have been looking at one approximate method in quantum chemistry, i.e., the variational method. So, far we have discussed the variational principle, how this principle is justified, what are the ways to implement this principle and do some variational calculations.

We studied a few examples. For harmonic oscillator problem, we took two different trial functions, and showed that if the trial wave function has the correct functional form, we can exactly reproduce the true solution. But when the functional form of the trial wave function obeys the boundary conditions, but is quite different from the real solution, in that case we saw that we can approach the ground state energy with some error. We also looked at one example for hydrogen atom by taking a trial function as a Gaussian function instead of an exponentially decaying function. From these examples we not only learnt how to do variational calculation, but we also understood a few things which can be summarized before we proceed to our next topic.

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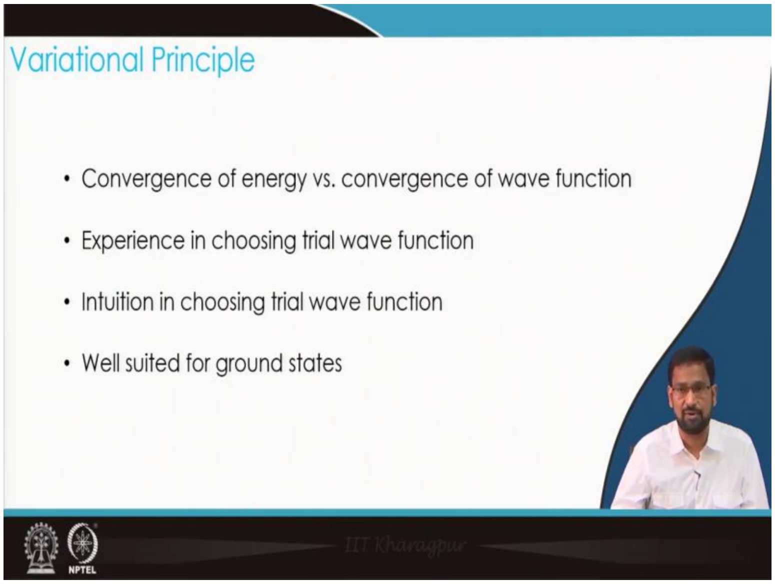

Variational Principle

- Convergence of energy vs. convergence of wave function
- Experience in choosing trial wave function
- Intuition in choosing trial wave function
- Well suited for ground states

Some key features that we learnt from our exercise is that in some cases the convergence of energy and convergence of wave functions do not go hand in hand. It is because the variational principle is designed to get the best estimate of energy, but when it comes to other properties of the system, the variational principle may not be always accurate. The other thing that we noticed is that, the functional form of the trial function is important. When it comes to choosing a trial wave function, our experience, our intuition to that particular chemical system play an important role. A method that heavily relies on experience and intuition is hard to apply in wide variety of problems. Other problem that we saw is that, even if we could extend variational principle for excited states, we realized that it is not always possible to have a trial function for an excited state which satisfies all the necessary conditions. In most cases we use variational principle to obtain the ground state energy.

In all the examples we studied, we took *one* trial function with *one* variational parameter. As long as we have a single function as trial function, we have some limitation. Because oftentimes a complicated system requires more flexibility to express its wave function, which is hard to get with one function and one parameter. To overcome this limitation and to some extent overcome some of the other limitations we discussed, we can use a different variant of variational calculation that goes by the name linear variational method.

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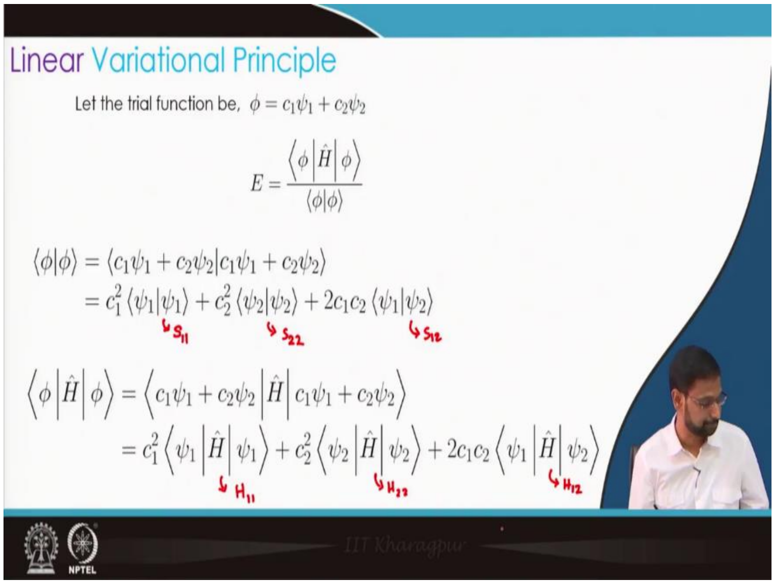

Linear Variational Principle

Let the trial function be, $\phi = c_1\psi_1 + c_2\psi_2$

$$E = \frac{\left\langle \phi \middle| \hat{H} \middle| \phi \right\rangle}{\langle \phi | \phi \rangle}$$

$$\begin{aligned}\langle \phi | \phi \rangle &= \langle c_1\psi_1 + c_2\psi_2 | c_1\psi_1 + c_2\psi_2 \rangle \\ &= c_1^2 \underbrace{\langle \psi_1 | \psi_1 \rangle}_{S_{11}} + c_2^2 \underbrace{\langle \psi_2 | \psi_2 \rangle}_{S_{22}} + 2c_1c_2 \underbrace{\langle \psi_1 | \psi_2 \rangle}_{S_{12}}\end{aligned}$$

$$\begin{aligned}\left\langle \phi \middle| \hat{H} \middle| \phi \right\rangle &= \left\langle c_1\psi_1 + c_2\psi_2 \middle| \hat{H} \middle| c_1\psi_1 + c_2\psi_2 \right\rangle \\ &= c_1^2 \underbrace{\left\langle \psi_1 \middle| \hat{H} \middle| \psi_1 \right\rangle}_{H_{11}} + c_2^2 \underbrace{\left\langle \psi_2 \middle| \hat{H} \middle| \psi_2 \right\rangle}_{H_{22}} + 2c_1c_2 \underbrace{\left\langle \psi_1 \middle| \hat{H} \middle| \psi_2 \right\rangle}_{H_{12}}\end{aligned}$$

In linear variational principle, instead of using a trial function with a single function, it is defined as a linear combination of two or more functions. For the time being, let us restrict ourselves to defining a trial function as a linear combination of two functions, i.e.,

$$\phi = c_1\psi_1 + c_2\psi_2$$

Where ψ_1 and ψ_2 are some known functions with unknown coefficients c_1 and c_2.

$$E = \frac{\left\langle \phi \left| \hat{H} \right| \phi \right\rangle}{\langle \phi | \phi \rangle}$$

Using above expression, we can obtain the variational energy. This requires evaluation of two integrals, which can be given as

$$\begin{aligned}\langle \phi | \phi \rangle &= \langle c_1\psi_1 + c_2\psi_2 | c_1\psi_1 + c_2\psi_2 \rangle \\ &= c_1^2 \langle \psi_1 | \psi_1 \rangle + c_2^2 \langle \psi_2 | \psi_2 \rangle + 2c_1c_2 \langle \psi_1 | \psi_2 \rangle\end{aligned}$$

$$\begin{aligned}\left\langle \phi \left| \hat{H} \right| \phi \right\rangle &= \left\langle c_1\psi_1 + c_2\psi_2 \left| \hat{H} \right| c_1\psi_1 + c_2\psi_2 \right\rangle \\ &= c_1^2 \left\langle \psi_1 \left| \hat{H} \right| \psi_1 \right\rangle + c_2^2 \left\langle \psi_2 \left| \hat{H} \right| \psi_2 \right\rangle + 2c_1c_2 \left\langle \psi_1 \left| \hat{H} \right| \psi_2 \right\rangle\end{aligned}$$

Since ψ_1 and ψ_2 are known functions, these integrals can be easily evaluated. Let us define $S_{ij} = \langle \psi_i | \psi_j \rangle$ as the overlap integrals and $H_{ij} = \langle \psi_i | \widehat{H} | \psi_j \rangle$ as the energy integrals. This leads us to,

$$E(c_1, c_2) = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1c_2 H_{12}}{c_1^2 S_{11} + c_2^2 S_{22} + 2c_1c_2 S_{12}}$$

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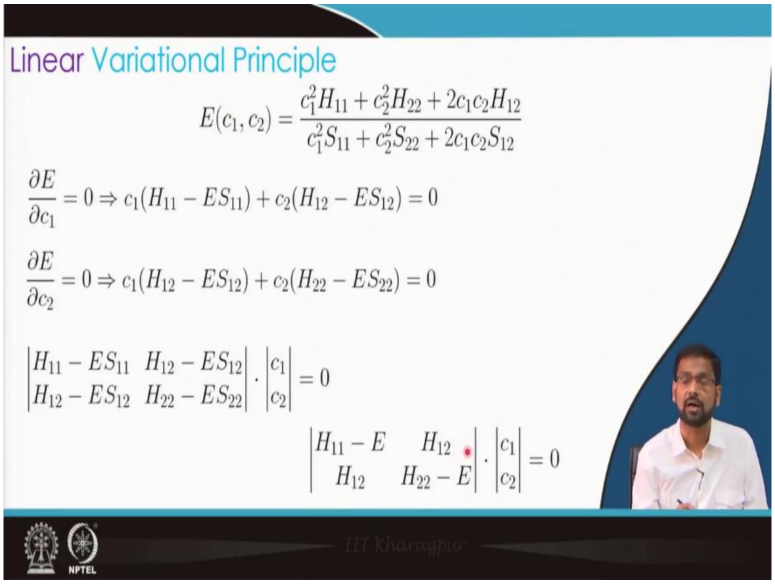

Linear Variational Principle

$$E(c_1, c_2) = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1c_2H_{12}}{c_1^2 S_{11} + c_2^2 S_{22} + 2c_1c_2S_{12}}$$

$$\frac{\partial E}{\partial c_1} = 0 \Rightarrow c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

$$\frac{\partial E}{\partial c_2} = 0 \Rightarrow c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

Here, the energy depends on the known functions H_{ij} & S_{ij} and the unknown coefficients c_i, which are the variational parameters in linear variation method. We have to find the values of c_1 and c_2 that minimizes the energy, i.e.,

$$\frac{\partial E}{\partial c_1} = 0 \Rightarrow c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

$$\frac{\partial E}{\partial c_2} = 0 \Rightarrow c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$$

We have now two linearly dependent equations, with two independent variables c_1 and c_2, which can be written as,

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

The first determinant contains the Hamiltonian matrix elements H_{ij} and the overlap matrix elements S_{ij} and the second determinant has the coefficients. Discarding the trivial solution ($c_1 = c_2 = 0$), the non-trivial solution can be obtained by evaluating first determinant and finding the root of the corresponding quadratic equation. Now these two roots are the energies of my system. After obtaining the energy, we can plug these values of E in the secular equation and obtain the values of c_1 and c_2.

It is possible to show that using the linear variational principle, if we have a 2 x 2 determinant and we get two energy solutions: the lowest energy solution is the upper bound of the ground state while the upper energy solution is the upper bound of the first excited state of the system. In many cases, the ψ_1 and ψ_2 are taken from the eigenfunctions of some Hermitian operator. Hence, they are orthonormal. This leads to $S_{ii} = 1$ and $S_{ij} = 0$. This gives rise to a simpler form of the secular equations:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

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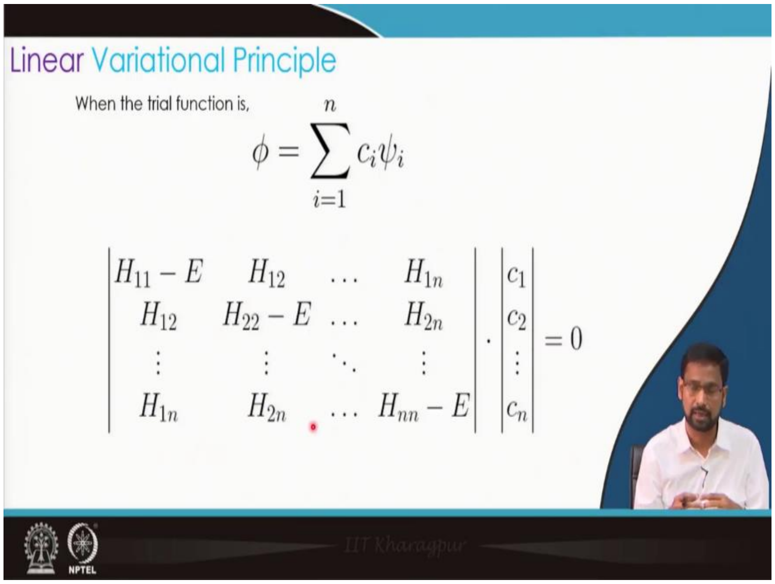

Linear Variational Principle

When the trial function is,

$$\phi = \sum_{i=1}^{n} c_i \psi_i$$

$$\begin{vmatrix} H_{11} - E & H_{12} & \dots & H_{1n} \\ H_{12} & H_{22} - E & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{1n} & H_{2n} & \dots & H_{nn} - E \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{vmatrix} = 0$$

If the trial function is expressed as a linear combination of *n* functions, the resulting secular equation can be expressed as a *n* x *n* determinant as shown above. The non-trivial solution of this problem can be obtained if I express it in terms of a matrix, such that I will have a *n* x *n* matrix that can be diagonalized to give *n* eigenvalues and *n* eigenvectors.

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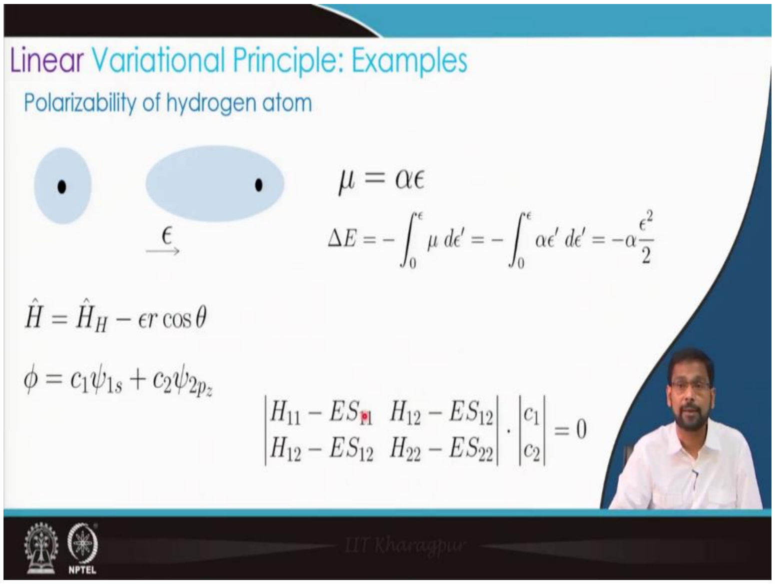

Linear Variational Principle: Examples

Polarizability of hydrogen atom

$$\mu = \alpha\epsilon$$

$$\Delta E = -\int_0^{\epsilon} \mu \, d\epsilon' = -\int_0^{\epsilon} \alpha\epsilon' \, d\epsilon' = -\alpha\frac{\epsilon^2}{2}$$

$$\hat{H} = \hat{H}_H - \epsilon r \cos\theta$$

$$\phi = c_1\psi_{1s} + c_2\psi_{2p_z}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

We will now apply linear variational principle to a system. Let’s find out the polarizability of hydrogen atom. We know that an atom is composed of a centrally located nucleus surrounded by electrons. For H-atom, one electron goes around the central nucleus. When I apply electric field to this hydrogen, the positively charged nucleus and the negatively charged electrons respond differently to the applied electric field. The positively charged nucleus gets pulled along the direction of the electric field, whereas the electron gets pulled along the opposite direction of the applied electric field. This results in a polarization of the atom. This polarization develops a dipole moment in the system. The dipole moment (μ) of the system depends on the applied electric field (ϵ). For weak electric field, $\mu = \alpha\epsilon$, where, α is the polarizability of the atom. The value of α indicates how easily can we polarize the atom (or molecule). If we can induce a strong dipole moment by applying a weak electric field that would mean that the system has got good polarizability.

Now let us try to find out how much energy do we need to induce a dipole moment μ in a system. The energy required to create a dipole moment μ by an applied electric field ϵ is given by

$$\Delta E = -\int_0^{\epsilon} \mu \, d\epsilon' = -\int_0^{\epsilon} \alpha\epsilon' \, d\epsilon' = -\alpha\frac{\epsilon^2}{2}$$

where, $\mu = \alpha\epsilon$ relation is used. The above equation provides a relation between energy and polarizability. Since variational principle allows us to estimate energy of a complex system, we are now in a position to use variational principle and the above relation to estimate polarizability of H-atom.

The total Hamiltonian of the system is the Hamiltonian of the hydrogen atom before application of electric field and the additional potential energy that is arising because of application of the electric field:

$$\hat{H} = \hat{H}_H - \epsilon r \cos\theta$$

Where, we are considering the electric field along the *z* direction ($r\cos\theta$ in spherical polar coordinate system). We have solved the above problem in the absence of electric field. For the solution of the new problem, we need to define trial wave function. Our trial function can be a linear combination of some eigenfunctions of the H-atom. When the polarization is along z-axis (as is the case here), we can include some p_z functions in our trial function.

$$\phi = c_1\psi_{1s} + c_2\psi_{2p_z}$$

Here, c_1 and c_2 are the unknown coefficients that would determine the final composition of the variationally optimized wave function of the system. With the linear combination of two functions, we can now solve the 2 x 2 problem.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

In the next lecture, we will discuss the evaluation of the above matrix elements. Thank you for your attention.