Approximate Methods in Quantum Chemistry
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Lecture 11
Applications of Linear Variational Method

Hello students! Welcome to this lecture. In the previous lecture, we started discussing linear variational method. In linear variational method, we express our trial function as a linear combination of several known functions. In this lecture, we would look at a few applications of the linear variational method.

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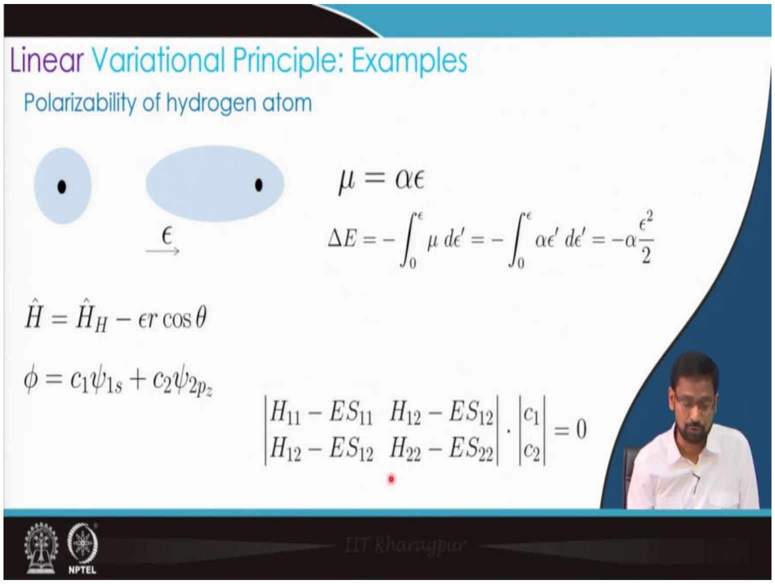

Linear Variational Principle: Examples

Polarizability of hydrogen atom

$$\mu = \alpha\epsilon$$

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

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

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

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

The first example concerns the polarizability of hydrogen atom. We formulated the problem in the last lecture. Just to refresh your memory, we are studying H-atom in the presence of an external electric field applied along z-direction. This causes a redistribution of the electron charge cloud around the nucleus developing a dipole moment that is proportional to the applied electric field with the proportionality constant representing the polarizability. The total Hamiltonian of this system comprises of the Hamiltonian of a H-atom and the potential energy of interaction of electron and the electric field. To solve this new Hamiltonian using variational approach, we considered a trial function as a linear combination of 1s and $2p_z$ eigenfunctions of H-atom. This leads to the 2x2 secular determinant shown above.

The next step of carrying out the variational calculation is the evaluation of the overlap and Hamiltonian matrix elements (S_{ij} and H_{ij}). Since ψ_{1s} and ψ_{2pz} are orthonormal functions (being the eigenfunctions of a Hermitian operator), $S_{11} = S_{22} = 1$ and $S_{12} = S_{21} = 0$.

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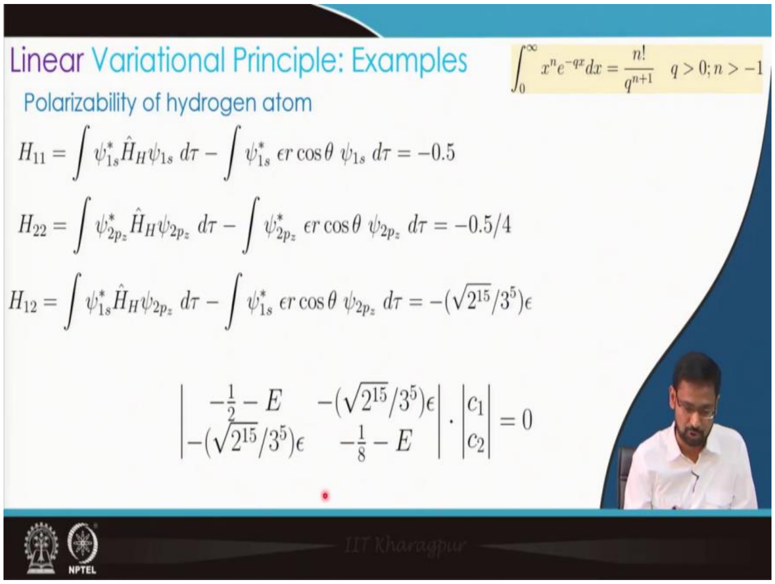

Linear Variational Principle: Examples

$$\int_0^\infty x^n e^{-qx} dx = \frac{n!}{q^{n+1}} \quad q > 0; n > -1$$

Polarizability of hydrogen atom

$$H_{11} = \int \psi_{1s}^* \hat{H}_H \psi_{1s}\, d\tau - \int \psi_{1s}^*\, \epsilon r \cos\theta\, \psi_{1s}\, d\tau = -0.5$$

$$H_{22} = \int \psi_{2p_z}^* \hat{H}_H \psi_{2p_z}\, d\tau - \int \psi_{2p_z}^*\, \epsilon r \cos\theta\, \psi_{2p_z}\, d\tau = -0.5/4$$

$$H_{12} = \int \psi_{1s}^* \hat{H}_H \psi_{2p_z}\, d\tau - \int \psi_{1s}^*\, \epsilon r \cos\theta\, \psi_{2p_z}\, d\tau = -(\sqrt{2^{15}}/3^5)\epsilon$$

$$\begin{vmatrix} -\frac{1}{2} - E & -(\sqrt{2^{15}}/3^5)\epsilon \\ -(\sqrt{2^{15}}/3^5)\epsilon & -\frac{1}{8} - E \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

Now let us determine the Hamiltonian matrix elements. H_{11} is obtained as the energy expectation value for ψ_{1s}, i.e.,

$$H_{11} = \int \psi_{1s}^* \hat{H}_H \psi_{1s}\, d\tau - \int \psi_{1s}^*\, \epsilon r \cos\theta\, \psi_{1s}\, d\tau = -0.5$$

The first term is the ground state energy of H-atom (-0.5 au) and the second integral becomes 0 when the integration is carried out for theta variable. From symmetry arguments, the second term has $r\cos\theta$, which is anti-symmetric with respect to reflection along the XY plane, thus making the integral 0. Similarly, H_{22} can be obtained as

$$H_{22} = \int \psi_{2p_z}^* \hat{H}_H \psi_{2p_z}\, d\tau - \int \psi_{2p_z}^*\, \epsilon r \cos\theta\, \psi_{2p_z}\, d\tau = -0.5/4$$

Where the first term is the energy of $2p_z$ orbital of H-atom (-0.5/4 au or -1/8 au) and the second term vanishes (can be shown by explicit integration or similar symmetry arguments discussed earlier).

The matrix element H_{12} is obtained as,

$$H_{12} = \int \psi_{1s}^* \hat{H}_H \psi_{2p_z} \, d\tau - \int \psi_{1s}^* \, \epsilon r \cos\theta \; \psi_{2p_z} \, d\tau = -(\sqrt{2^{15}}/3^5)\epsilon$$

Where the first term is zero (after action of Hamiltonian on its eigenfunction $2p_z$, we will end up with an overlap of 1s and $2p_z$ eigenfunctions as they are orthogonal). Now, the second integral is over $d\tau = r^2 dr \sin\theta \, d\theta \, d\phi$. We can use the functional form of ψ_{1s} and ψ_{2pz} and carry out the integration over r, θ, and ϕ. After some algebra (use the formula given in the slide for integration over r) we obtain H_{12} as shown above. It can be shown $H_{12}=H_{21}$ (Hermitian operator).

If we plug in the matrix elements in the secular equation, we get

$$\begin{vmatrix} -\frac{1}{2} - E & -(\sqrt{2^{15}}/3^5)\epsilon \\ -(\sqrt{2^{15}}/3^5)\epsilon & -\frac{1}{8} - E \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

The solution of the above equation results in two values of energies and each energy corresponds to a set of c_1 and c_2, that can be used to express the variationally optimized wave functions.

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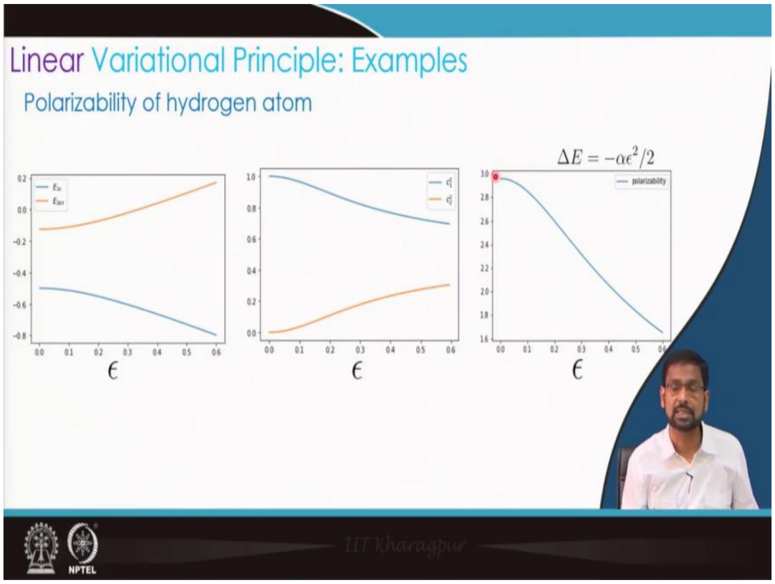

Linear Variational Principle: Examples

Polarizability of hydrogen atom

$\Delta E = -\alpha\epsilon^2/2$

Now, let us discuss the solution of the secular equations obtained from a simple numerical calculation. In the slide shown above, energy (in au) is plotted against increasing value of the electric field (ϵ). When the applied electric field is 0, the lower state is 1s (-0.5 au) and the upper state is 2pz (-0.125 au). As the external electric field is applied, the system gets polarized and as a result, the 1s energy decreases while the 2pz energy increases. The second figure shows the change in the coefficients corresponding to the lower energy solution. When electric field is 0, $|c_1|^2 = 1$ and $|c_1|^2 = 1$, i.e., the lowest state is 100% 1s state, as expected. As the electric field is increased, $|c_1|^2$ starts decreasing while $|c_2|^2$ stars increasing, suggesting an increased contribution of 2pz to the ground state wave function.

Now, to obtain the polarizability, we can see how the energy of the lowest state is changing, and we can evaluate ΔE (the change in energy with respect to the energy at 0 field) and use $\Delta E = -\alpha\epsilon^2/2$, to obtain the value of α (the third figure in the slide above). Since the equation we used is valid for weak field, we can estimate α from very small values of ϵ, which turns out to be 2.91, a good approximation to the experimental value.

Now, of course, there is a lot of room for improvement. However, with a very little additional calculation, we can get a somewhat good estimation of the polarizability of hydrogen atom. Mind you, so far in this exercise, we have evaluated only one additional integral that was H_{12}, all other integrals were simply what we already knew from hydrogen atom solutions.

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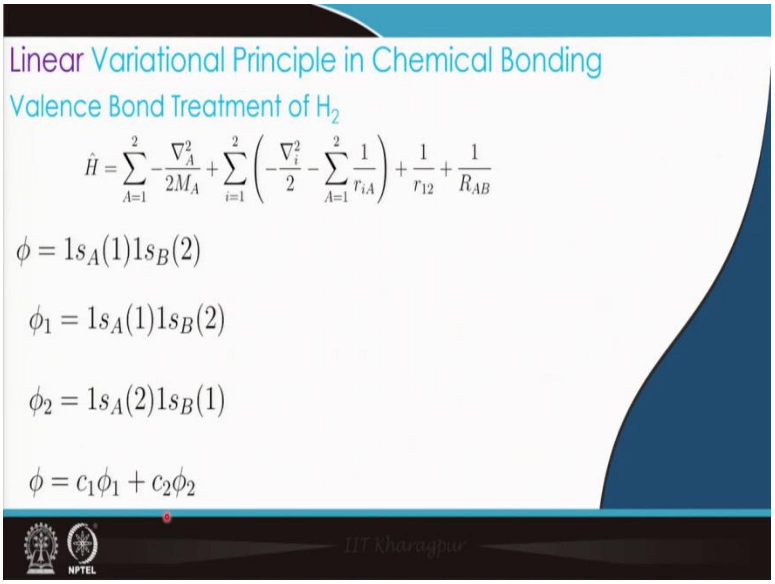

Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

$$\hat{H} = \sum_{A=1}^{2} -\frac{\nabla_A^2}{2M_A} + \sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \sum_{A=1}^{2}\frac{1}{r_{iA}}\right) + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$

$$\phi = 1s_A(1)1s_B(2)$$

$$\phi_1 = 1s_A(1)1s_B(2)$$

$$\phi_2 = 1s_A(2)1s_B(1)$$

$$\phi = c_1\phi_1 + c_2\phi_2$$

Now, we would use the linear variational principle to one of the most important topics in chemistry, that is, chemical bonding. In chemistry we are often interested in the formation or the breaking of a bond during a chemical reaction that can be an organic, inorganic, extended solid state, or biochemical reaction. A chemical bond formation or breaking always involves sharing of electrons or transfer of electrons, that are pure quantum mechanical phenomena. In our present discussion, we will restrict ourselves to the bonding in simple system, although the formalism can be easily extended to larger and more complex system with the help of a computer.

Let us first discuss the application of linear variational principle in the valence bond treatment of hydrogen molecule, the simplest of the systems where a chemical bond is present. The first step of our approach is to write down the Hamiltonian of the molecule (written in au),

$$\hat{H} = \sum_{A=1}^{2} -\frac{\nabla_A^2}{2M_A} + \sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \sum_{A=1}^{2}\frac{1}{r_{iA}}\right) + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$

The first term is the kinetic energy of the two nuclei (hydrogen atom A and B). The second term is the kinetic energy of electrons and the third term is the electron-nuclear interaction. The last two terms are inter-electronic and inter-nuclear repulsion terms. With the given Hamiltonian of the problem, we would try to design our trial function. Since the hydrogen molecule is composed of 2 hydrogen atoms, we can take use 1s function of each hydrogen atom and construct the trial function as,

$$\phi_1 = 1s_A(1)1s_B(2)$$

But this wave function has a problem. When a bond is formed, the electrons are indistinguishable, while the above wave function distinguishes the electrons according to their nuclei. To invoke indistinguishability of electrons into my trial function, we can introduce,

$$\phi_2 = 1s_A(2)1s_B(1)$$

and express the trial function as a linear combination

$$\phi = c_1\phi_1 + c_2\phi_2$$

The above wave function preserves the indistinguishability of electrons.

We have now defined the Hamiltonian and trial wave function. We will carry out the remaining part of the variational calculations in the next lecture.

Thank you for your attention.