Approximate Methods in Quantum Chemistry
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Lecture 9
Variational Method: Applications 1

Hello students! Welcome to this lecture. In the last lecture we discussed about the variational principle, its justification, the strategy of doing a variational calculation and also, we discussed how we can use variational principle for excited states. In this lecture we will take some examples and see how you can use variational principle and obtain meaningful results from this method.

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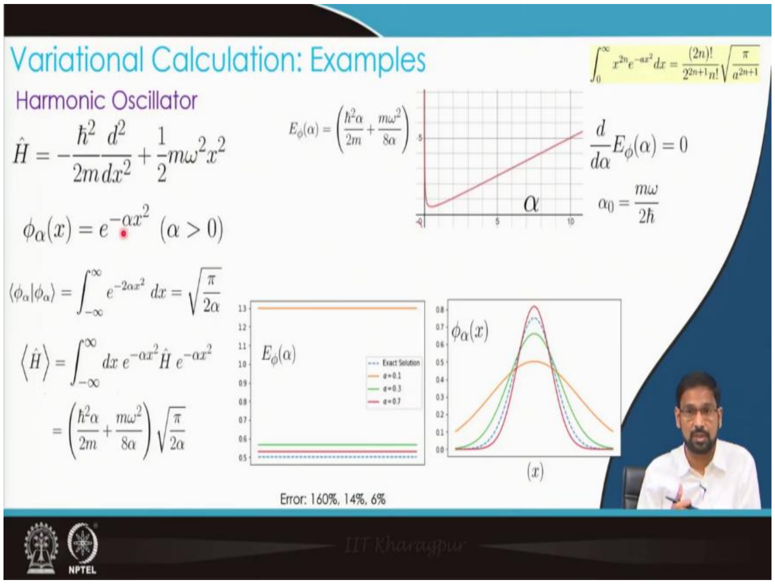

Variational Calculation: Examples

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{(2n)!}{2^{2n+1} n!}\sqrt{\frac{\pi}{a^{2n+1}}}$$

Harmonic Oscillator

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

$$\phi_\alpha(x) = e^{-\alpha x^2} \quad (\alpha > 0)$$

$$\langle\phi_\alpha|\phi_\alpha\rangle = \int_{-\infty}^{\infty} e^{-2\alpha x^2}\, dx = \sqrt{\frac{\pi}{2\alpha}}$$

$$\left\langle \hat{H} \right\rangle = \int_{-\infty}^{\infty} dx\, e^{-\alpha x^2} \hat{H}\, e^{-\alpha x^2}$$

$$= \left(\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\right)\sqrt{\frac{\pi}{2\alpha}}$$

$$E_\phi(\alpha) = \left(\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\right)$$

$$\frac{d}{d\alpha}E_\phi(\alpha) = 0$$

$$\alpha_0 = \frac{m\omega}{2\hbar}$$

Error: 160%, 14%, 6%

The first example that we are going to take is that of a harmonic oscillator. The Hamiltonian, of a 1D harmonic oscillator has got the kinetic energy operator and the potential energy operator given by a harmonic potential $(1/2\,kx^2 = 1/2\,m\omega^2x^2)$, where k is the spring constant of the harmonic oscillator, m is the mass of the oscillator and ω is its angular frequency. Although, we know the exact solution of this problem, here we will take a trial function and see if the variational principle can reproduce the exact result, as a benchmarking exercise.

Let's define a trial $\phi_\alpha(x) = e^{-\alpha x^2} \;\; (\alpha > 0)$ function

In fact, we know that the ground state wave function of harmonic oscillator is a Gaussian function.

Hence, we know the exact value of alpha. But we will try to see whether the variational principle gives us that value of alpha or not.

The next step is to evaluate the inner product of the trial wave function with itself, which turns out to be $\sqrt{\pi/2\alpha}$. The next step of variational calculation is to obtain the expectation value corresponding to the Hamiltonian operator.

$$\begin{aligned}\left\langle \hat{H} \right\rangle &= \int_{-\infty}^{\infty} dx\ e^{-\alpha x^2} \hat{H}\ e^{-\alpha x^2} \\ &= \left(\frac{\hbar^2 \alpha}{2m} + \frac{m\omega^2}{8\alpha} \right) \sqrt{\frac{\pi}{2\alpha}}\end{aligned}$$

The Hamiltonian has got two terms: the kinetic energy operator which has a second derivative with respect to x and the potential energy operator. We can use the following relation to evaluate the integrals.

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{(2n)!}{2^{2n+1} n!} \sqrt{\frac{\pi}{a^{2n+1}}}$$

After evaluating this integral, we obtain the expression that contains some constants (m, omega, hbar, etc.) and one unknown alpha. Finally, we obtain,

$$E_{\phi}(\alpha) = \left(\frac{\hbar^2 \alpha}{2m} + \frac{m\omega^2}{8\alpha} \right)$$

The plot of the energy as a function of alpha is given in the slide above. For small value of alpha, the second term dominates, and as alpha increases the first term dominates. For a particular value of alpha, the energy will have a minimum, which we can obtain from the first derivative of energy with respect to alpha.

$$\frac{d}{d\alpha} E_{\phi}(\alpha) = 0 \qquad \alpha_0 = \frac{m\omega}{2\hbar}$$

At α_0, the energy attains its minimum value.

Let us do a numerical exercise. We plot the energy (in the units of $\hbar\omega$) and the wave function for a series of α values. If we express energy in the units of $\hbar\omega$, the true energy is of the harmonic oscillator ground state is 0.5. For $\alpha = 0.1$, the energy is a 160 percent over estimation of the true energy. For $\alpha = 0.3$, it comes much closer to the true energy (14% error), and for $\alpha = 0.5$, the true energy is reproduced. By further increasing α $(= 0.7)$, the energy again rises up. Now let us look at the wave function. For $\alpha = 0.1$, the wave function is quite different from the true wave function (α =0.5), although it improves when $\alpha = 0.3$ and 0.7, although they both have more or less similar resemblance to the ground state wave function.

In this example, we started with my trial function which just looks like the real solution. It is not surprising that we could get the exact solution using variational principle. But this proves the efficacy of the variational principle, when the trial function is a good guess. Next, we will take another example of a harmonic oscillator problem, but the trial wave function would not be a Gaussian function but would be something that would have overall similarities but not the exact functional form to that of the true solution.

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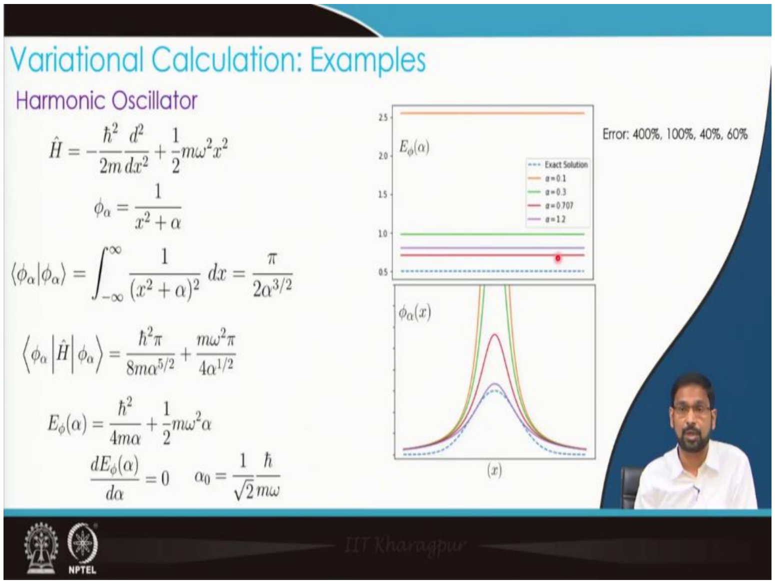

Variational Calculation: Examples

Harmonic Oscillator

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

$$\phi_\alpha = \frac{1}{x^2 + \alpha}$$

$$\langle\phi_\alpha|\phi_\alpha\rangle = \int_{-\infty}^{\infty} \frac{1}{(x^2+\alpha)^2}\,dx = \frac{\pi}{2\alpha^{3/2}}$$

$$\left\langle \phi_\alpha \middle| \hat{H} \middle| \phi_\alpha \right\rangle = \frac{\hbar^2\pi}{8m\alpha^{5/2}} + \frac{m\omega^2\pi}{4\alpha^{1/2}}$$

$$E_\phi(\alpha) = \frac{\hbar^2}{4m\alpha} + \frac{1}{2}m\omega^2\alpha$$

$$\frac{dE_\phi(\alpha)}{d\alpha} = 0 \qquad \alpha_0 = \frac{1}{\sqrt{2}}\frac{\hbar}{m\omega}$$

Error: 400%, 100%, 40%, 60%

Consider the trial function $\phi_\alpha = 1/(x^2 + \alpha)$. For x = 0, this function has a finite value and for x > 0 or x < 0, this function decays and vanishes for large values of x (both positive and negative), thus satisfying the boundary conditions.

Next, we evaluate the overlap and energy integrals and get the variational energy as a function of the variational parameter (α).

$$\langle \phi_\alpha | \phi_\alpha \rangle = \int_{-\infty}^{\infty} \frac{1}{(x^2+\alpha)^2}\, dx = \frac{\pi}{2\alpha^{3/2}}$$

$$\left\langle \phi_\alpha \middle| \hat{H} \middle| \phi_\alpha \right\rangle = \frac{\hbar^2 \pi}{8m\alpha^{5/2}} + \frac{m\omega^2 \pi}{4\alpha^{1/2}}$$

$$E_\phi(\alpha) = \frac{\hbar^2}{4m\alpha} + \frac{1}{2} m\omega^2 \alpha$$

$$\frac{dE_\phi(\alpha)}{d\alpha} = 0 \qquad \alpha_0 = \frac{1}{\sqrt{2}} \frac{\hbar}{m\omega}$$

By minimizing the variational energy with respect to the variational parameter, we can get the optimal value of $\alpha (= \alpha_0)$ that would minimize the energy and using this α_0, we can write down the variationally optimized wave function $\left(\phi(\alpha_0)\right)$.

Now, let us do a numerical exercise by plotting the energy and wave function for different values of α. When α = 0.1 and 0.3 the calculated energies overestimate the true energy (0.5 $\hbar\omega$) by 400% and 100%, respectively. When $\alpha = \alpha_0 = 1/\sqrt{2}$, the variationally optimized energy is now closer to the true energy, although still 40% overestimation is seen. If we further increase α, (=1.2), the energy goes further away the ground state energy.

Now let us look at the corresponding wave functions. When $\alpha =$ 0.1 or 0.3, the wave function is has a poor resemblance with the true wave function, although for α = 0.707, the variational wave function resembles the true wave function. This gets better when $\alpha =$ 1.2, although from energy point of view, $\alpha =$ 1.2 performs poorly compared to $\alpha =$ 0.707. This is a typical feature of variational calculation. You have to remember that variational principle blindly minimizes the energy. It does not have any other condition as to what happens to the wave function. The wave function contains all the information, including energy. Energy is one manifestation that we can get out of the true wave function. Since variational principle emphasizes on the energy, it often gives a poor estimation of other properties. But so far as energy is concerned, the variational principle works well.

Since many of our problems in chemistry, such as chemical reactions, chemical reactivity, etc. can be expressed through molecular energy, the variational principle has a lot of applications in chemistry.

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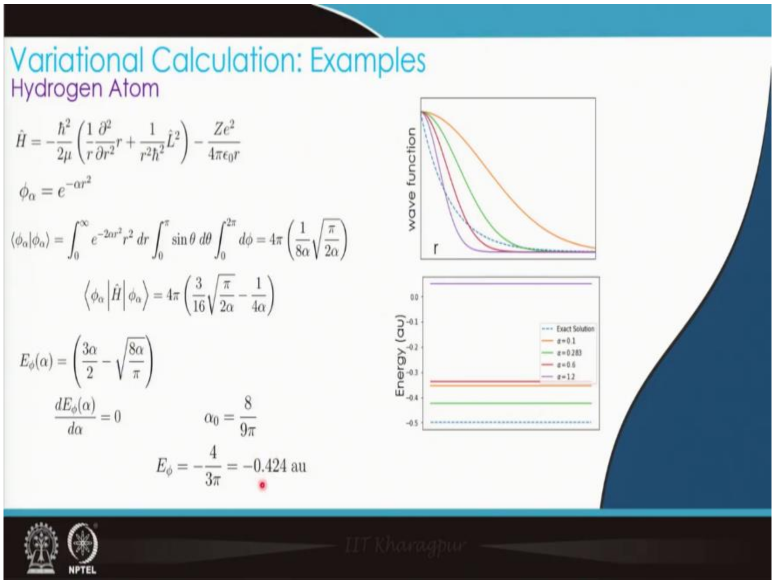

Variational Calculation: Examples

Hydrogen Atom

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\hbar^2}\hat{L}^2\right) - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\phi_\alpha = e^{-\alpha r^2}$$

$$\langle\phi_\alpha|\phi_\alpha\rangle = \int_0^\infty e^{-2\alpha r^2} r^2\, dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = 4\pi\left(\frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}}\right)$$

$$\left\langle\phi_\alpha\middle|\hat{H}\middle|\phi_\alpha\right\rangle = 4\pi\left(\frac{3}{16}\sqrt{\frac{\pi}{2\alpha}} - \frac{1}{4\alpha}\right)$$

$$E_\phi(\alpha) = \left(\frac{3\alpha}{2} - \sqrt{\frac{8\alpha}{\pi}}\right)$$

$$\frac{dE_\phi(\alpha)}{d\alpha} = 0 \qquad \alpha_0 = \frac{8}{9\pi}$$

$$E_\phi = -\frac{4}{3\pi} = -0.424 \text{ au}$$

Now let us take yet another example, this time, a hydrogen atom. The Hamiltonian can be seen in the slide above. We know the exact solution of this problem, where the radial part of the ground state wave function is an exponential function. In this example, we take a trial function as a Gaussian function. We can obtain the internal product of the trial function and also obtain the energy expectation value by following the standard procedure. The resulting variational energy is obtained as,

$$E_\phi(\alpha) = \left(\frac{3\alpha}{2} - \sqrt{\frac{8\alpha}{\pi}}\right)$$

$$\frac{dE_\phi(\alpha)}{d\alpha} = 0$$

Which can be minimized with respect to the variational parameter α. The optimal value of $\alpha (= \alpha_0)$ is $8/9\pi$ and the variationally minimized energy is -0.424 au, as compared to the true energy of -0.5 au for the ground state of H-atom.

If we carry out a numerical exercise similar to the previous examples, we can see that the agreement with energy gets better as α approaches α_0, and deviation increases when α goes away from its optimal value. When we compare the wave functions, the trial wave functions are not able to reproduce the shape of the true wave function, which is expected since we have taken a wrong functional form of the function. This indicates that other properties estimated from this function may not be accurate, although despite taking a wrong functional form of the trial wave function, the variationally optimized energy is rather close to the true energy.

From these examples we learn that even when the functional form of the trial function is not accurate, variational principle can give us a very good estimation about the ground state energy, although the same is not true for other properties.

Thank you for your attention.