Approximate Methods in Quantum Chemistry
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Lecture 08
Variational Principle - II

Hello students! Welcome to this lecture. In the previous lecture, we discussed about the variational principle and we would continue our discussion from there.

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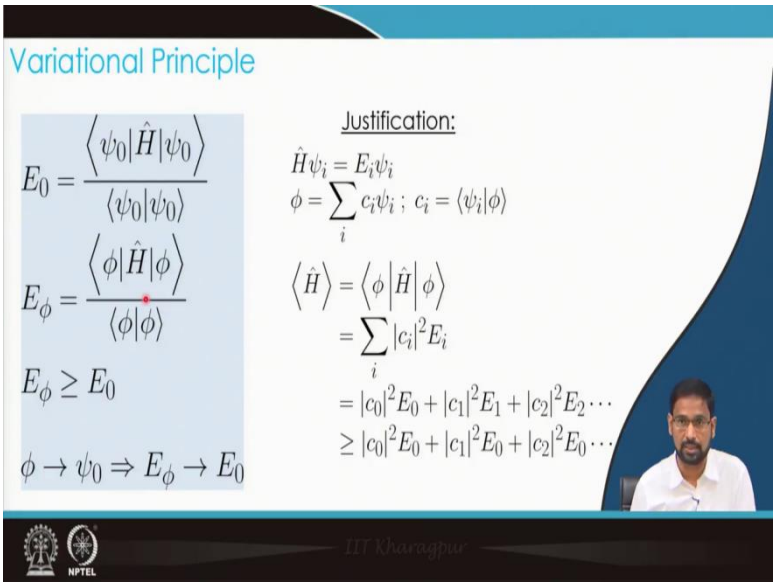

In the last class we discussed what variational principle offers. Just to remind you, the variational principle tells us that, if we have a system, whose Hamiltonian has some terms that make the Hamiltonian too difficult for exact solution of the Schrödinger equation, in that case we can start with a trial wave function ϕ, and the variational principle tells us how to get an approximate solution of the problem starting from this guess function.

Corresponding to the trial wave function, we evaluate the energy integral $E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$. If the trial function is a normalized, then the denominator becomes 1. What variational principle tells us is that no matter what is your trial wave function, the energy that you are going to obtain (E_ϕ) is always going to be greater than the ground state energy E_0.

But what is the ground state energy? If I had the exact solution of the ground state wave function, then I can, of course, obtain the ground state energy. But in those cases where the exact solution is not possible, we do not know exact values of ψ_0 and E_0.

But variational principle assures us that no matter what trial function we take, the energy that is going to come out of the evaluation of this integral is always going to be an upper bound of the ground state energy of the system. In other words, it also tells us that as the trial wave function would approach the real wave function, the trial energy would approach the true energy.

But we do not know the exact value of the ground state energy. How would we ensure that the trial energy is actually approaching the ground state energy? If you go on minimizing the E_ϕ and find the lowest possible value of the energy, that energy is going to be the best description of the ground state energy. Let us now discuss the justification of this principle.

Let us assume that the true eigenfunctions of a Hamiltonian are given as ψ_i. In those cases where I cannot solve the Schrödinger equation exactly, there is of course no way of knowing this solution. But in those cases where the true solution is available, we can start from a trial function and then see how the variational principle works for those systems. Suppose E_i's are the eigenvalues corresponding to the true eigenfunctions ψ_i's, which are the eigenfunctions of a Hermitian operator. The trial wave function (ϕ) can be expressed in terms of these ψ_i's, since the latter form a complete set of orthonormal functions. Using a complete set of orthonormal basis, I can express any arbitrary function (in this case, the trial function is $\phi = \sum_i c_i \psi_i$), where the coefficient c_i's suggest that what is the overlap or what is the similarity or resemblance of this trial function with an individual eigen function.

So, if we can, in principle, express this trial wave function as a linear combination of this eigenfunctions of the Hamiltonian, then we can obtain the expectation value of the Hamiltonian operator by evaluating the energy integral. You would see that when I evaluate this energy integral by using the linear combination of ψ as ϕ, in both bra and ket I will end up in getting an expression like this.

$$\begin{aligned}\left\langle \hat{H} \right\rangle &= \left\langle \phi \left| \hat{H} \right| \phi \right\rangle \\ &= \sum_i |c_i|^2 E_i\end{aligned}$$

We have seen this expression when we were discussing the postulate 4 of quantum mechanics. Here. $|c_i|^2$ represents the probability of observing energy E_i, So, if the system

is one of the eigenfunctions of the operator, then I will get only that corresponding eigenvalue with coefficient of that eigenvalue as 1. All other eigenvalues will have 0 probability to be found, because the system exists in one of these eigenfunctions. But if the system does not exist in one of these eigenfunctions that means we are talking about a trial function ϕ over here, then I would get a distribution of energy.

Now let us expand this term by taking first few terms.

$$= |c_0|^2 E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 \cdots$$
$$\geq |c_0|^2 E_0 + |c_1|^2 E_0 + |c_2|^2 E_0 \cdots$$

Note that in the second line all energies E_1, E_2, … are replaced by E_0. Since $E_i > E_0$, the equal sign of the first expression is replaced by the greater than/equal sign. This relation tells that the expectation value coming from that trial wave function ϕ is always going to be greater than the ground state energy. It would become equal to the ground state energy, only under one condition when $\phi = \psi$. Only in that case, the $E_\phi = E_0$.

Now the next question is that, how do we implement this idea for a system?

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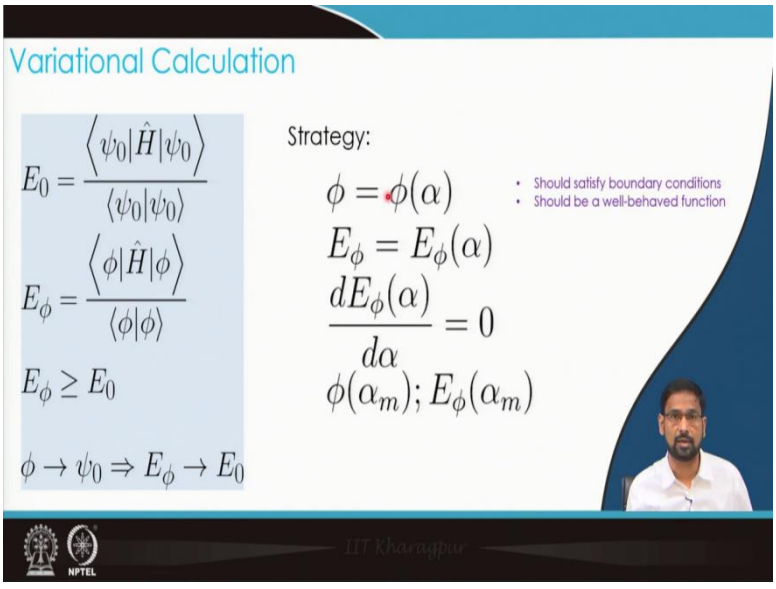

We use the following strategy for a variational calculation. Since, variational principle tells that $E_\phi \geq E_0$, we can minimize E_ϕ and obtain E_0. If we define the trial function (ϕ) as a function of a parameter α, i.e., $\phi(\alpha)$, then the energy expectation value $E_\phi = E_\phi(\alpha)$. We can now minimize E_ϕ by evaluating $dE_\phi(\alpha)/d\alpha = 0$. This will give the

best α_m, the value of alpha which minimizes the energy. We can readily evaluate $\phi(\alpha_m)$, the best description of my wave function that gives the lowest energy $E_\phi(\alpha_m)$.

By following this strategy, I get the best possible description of the wave function, best possible description of the energy, *given the choice I made with respect to the trial function*. So, this procedure works well if my trial function is good. If my trial function is, by design, a poor trial function, no matter what I would do, I would not be anywhere close to the real solution. Now you may take a different trial function and evaluate the variational energy. Upon comparison of the variational energy of the two trial functions, we can see which trial function gives lower energy.

While choosing a trial function, we must ensure that it satisfies the boundary conditions of the problem and it is a well-behaved function.

So far, what we have discussed the variational principle for the ground state energy. Can we use variational principle for the excited states? The answer is yes but with some caveats.

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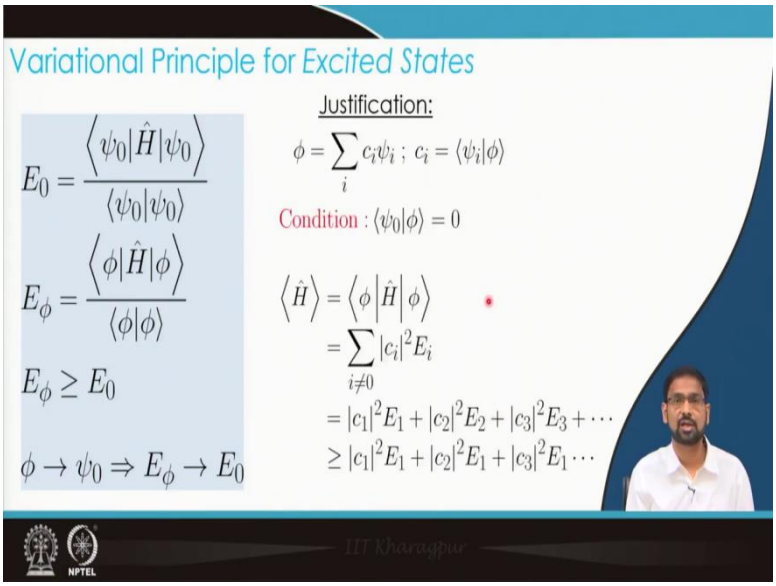

The statement of the variational principle remains the same when we want to apply variational principle for the excited states. We again express the trial function as a linear combination of the true eigenfunctions of the Hamiltonian (ψ_i), which form a complete set of orthonormal basis.

For the excited states, we impose one more condition, i.e., the trial wave function, in addition to satisfying the other condition that we discussed earlier, *must be orthogonal to the ground state wave function.*

$$\langle \psi_0 | \phi \rangle = 0$$

When this condition is met, c_0, the coefficient of ψ_0, in the expansion of ϕ becomes 0, i.e., the contribution of the ground state eigenfunction to the overall trial function becomes 0.

Now, when we evaluate the expectation value of the energy, we will get,

$$\begin{aligned}\left\langle \hat{H} \right\rangle &= \left\langle \phi \left| \hat{H} \right| \phi \right\rangle \\ &= \sum_{i \neq 0} |c_i|^2 E_i \\ &= |c_1|^2 E_1 + |c_2|^2 E_2 + |c_3|^2 E_3 + \cdots \\ &\geq |c_1|^2 E_1 + |c_2|^2 E_1 + |c_3|^2 E_1 \cdots\end{aligned}$$

Here, $c_0 = 0$. When we expand this sum, the first term is $|c_1|^2 E_1$. Following the steps like the previous case of the ground state, we would see that the inequality in the last line will turn out to be equal only under one condition and that condition is when is $|c_1|^2 = 1$ and all other coefficients become 0. The resulting energy is the energy of the first excited state.

Just like the variational principle for the ground state wave function, we can also use it for the first excited state function, but with one additional condition, i.e., the trial wave function must be orthogonal to the ground state wave function. Now if I am interested in getting the second excited state what should I do? Again, the same procedure can be shown to work, but under the condition that trial wave function must be orthogonal to the ground *and* the first excited states. Only under that condition I can use variational principle for the second excited state. This can be extended to higher excited states.

But it is not always easy or it is not even always possible to define a trial wave function which is simultaneously orthogonal to so many different functions. In some cases, at least the first excited state can be obtained using variational principle.

If you remember the eigenfunctions of the harmonic oscillators, you would know that the ground state eigenfunction is an even function while the first excited state

eigenfunction is an odd function. In such a situation, if I am interested in getting the first excited state energy using variational principle, then my trial wave function, which has to be now orthogonal to the ground state wave function, can simply be an odd function. But imagine if I do the same for the second excited state of harmonic oscillator problem, this simple principle will not work because the second excited state is an even function and then it does not necessarily satisfy the condition that it is simultaneously orthogonal to ground state (even function) and first excited state (odd function). Therefore, the application of variational principle for the ground state is somewhat challenging.

In this lecture we discussed about the variational principle, its justification, procedure to do a variational calculation, and finally if we can apply it to the excited states. We will look at some examples and study variational principles in greater detail in our next class. That you for your attention.