Approximate Methods in Quantum Chemistry
Professor Sabyashachi Mishra
Department of Chemistry
Indian Institute of Technology Kharagpur
Lecture 07
Variational Principle

Hello students! Welcome to this lecture. In the last few lectures we discussed some exactly solvable models in quantum mechanics. We learned how we could analyze the solution of hydrogen atom problem and now in this lecture onwards we will start looking at more complex problems and how we cannot solve those complex problems exactly using quantum mechanical methods and how and where we need approximate methods to solve such complex problems. But before that we would do some basic discussion on such problems.

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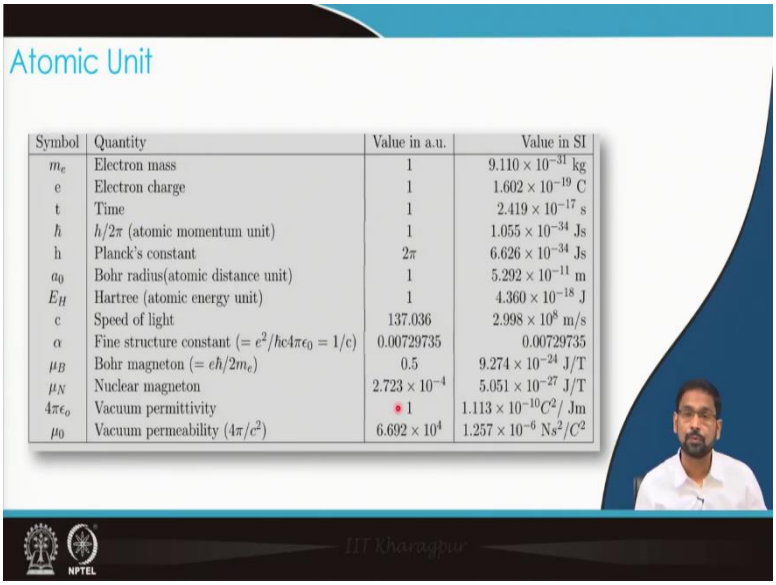

One important thing that comes to our help is the atomic unit system. You would see that when we write down the Hamiltonian of a multi-electronic atom or a molecule, we have many terms with same constants appearing repetitively. That apart, when we look at the energies of the molecular systems, we see that the magnitude of these energies is such that our regular SI units or CGS units are often not convenient to express these numbers. So, it was felt that perhaps we should have a different unit system and this unit system is called atomic unit.

In atomic unit, some of the commonly used constants are given the value of unity. Just like we have in our SI system, the unit mass, the unit length, and the unit time, we have

in the atomic unit, the unit of mass defined as the mass of an electron. All other masses, e.g., the mass of proton, the mass of a nucleus, etc. are expressed in the unit of electron mass. Its SI value is 9.1 x 10^{-31} kilogram, a small number if we use the SI unit. Life becomes difficult if we use SI unit for such masses. So, it is better if we use a different unit system that has a simpler value to write down and to communicate. So, mass of electron is 1 au. Similarly, the charge of electron is considered 1 unit charge in atomic unit whose SI value is given in the picture above. Of course, the electron is negatively charged and hence its charge is -1. When you have a positively charged particle, then you express it as + sign followed by the magnitude of the charge in the units of electron charge.

Like we have the unit of time in our SI system or CGS system, we have unit of time in atomic unit, which is expressed as the time taken by an electron to revolve 1s orbital of hydrogen atom which comes about to be 2.419 x 10^{-17} second. So, you see in SI unit this number is quite small. We can of course express it in terms of attosecond (10^{-18} second). The atomic unit of time is 24.19 attosecond.

The other commonly used quantity is $\hbar$ in quantum mechanical systems which is equal to 1 in atomic unit. Therefore, the Planck's constant in a.u. becomes 2π. The unit of length in atomic unit is expressed by the Bohr's radius which is 0.53 Angstrom. The energy is expressed in terms of Hartree, the atomic unit of energy (which is given, the symbol E_h). 1 E_h = 27.212 eV (which is actually twice the energy of hydrogen atom). If you remember, the energy of the hydrogen atom in its ground state was -13.6 eV which is essentially -0.5 a.u. of energy.

Similarly, other constants like speed of light, the fine structure constant, etc. are given in the slide above. The other quantity that we would be using in this course is the Bohr magneton, when we study the effect of external magnetic fields on the energy levels. The Bohr magnetons relation is given by as $e\hbar/2m_e$, e is the charge of electron = 1 au, $\hbar$ = 1 au and m_e = 1 au. Therefore, Bohr magneton in a.u. is 0.5. Like Bohr magneton, we can discuss the nuclear magneton, where I simply replace the mass of electron by the mass of proton. Since we know that the mass of proton is about 1800 times heavier than the mass of electron, you see the nuclear magneton is 3 orders of magnitude smaller than the Bohr magneton. Vacuum permittivity is another constant that appears in the Hamiltonian, when we express the interaction between electron and nucleus or

interaction between electron and electron as Coulombic interactions. In those expressions we often have $4\pi\epsilon_0$ which is made 1 in a.u.

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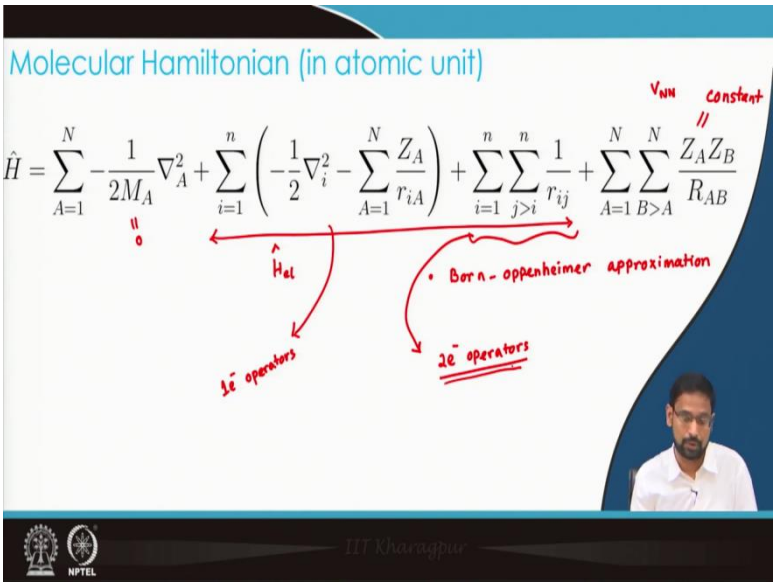

Now let us use this atomic unit to write down the Hamiltonian of a molecule in general. A molecule is composed of many atoms and each atom would have one or many electrons. Hence, the molecule would have several electrons. A molecule is therefore a multi-nuclear, multi-electronic system. For such a system I want to write down the Hamiltonian. I already know that Hamiltonian would have two different contributions, one would be from kinetic energy, the other would be from potential energy.

Each particle in my system would contribute to the kinetic energy because each particle with a mass would have a kinetic energy. If I have *N* number of nuclei and *n* number of electrons, then I have those many number of kinetic energy terms coming out from nuclei and electrons respectively.

So, the first term in the Hamiltonian expression shows $-1/2M_A$ the Laplacian corresponding to the nucleus, is the kinetic energy of nucleus *A*, where the index *A*, goes from 1 to *N*. Each nucleus contributes to 1 kinetic energy operator. Here you see the mass of the nucleus is kept within the summation because in a molecule I would have different atoms and these atoms will have different atomic mass.

The next term that you see in the Hamiltonian has two terms kept in brackets. The first term corresponds to the kinetic energy of the electron. I have *n* electrons in my system.

I have *n* kinetic energy terms arising from these electrons. The Laplacian here corresponds to each electron, which is $\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$. The Laplacian is the operative part of this kinetic energy operator and the expression of the kinetic energy has $-\hbar^2/2m_e$ multiplied to it which is -1/2 in au. The second term within the brackets has a negative sign and this is a potential energy term between a nucleus *A* and an electron *i*. If I have *N* nuclei, each nucleus in my molecule can interact with each of the *n* electrons present in my system. So, if I have small *n* electrons, *N* nuclei, I have *n* x *N* number of electron-nuclear interaction terms. The r_{iA} is the distance between electron *i* and nucleus *A* with Z_A nuclear charge. This electron kinetic energy term plus the electron-nucleus interaction term are called one electron operators because each term here corresponds to one electron.

The next term in the Hamiltonian is the electron repulsion term. If I have *n* electrons, each electron interacts with every other electron (*n*-1). I would have *n*(*n*-1)/2 number of electron-electron interactions. Finally, the last term is the nuclear-nuclear repulsion, between atom *A* and atom *B* that are separated by a distance R_{AB}.

While solving this problem quantum mechanically, we invoke an important approximation, the so called Born-Oppenheimer approximation. The idea behind the Born-Oppenheimer approximation is that the mass of electron is very small compared to the mass of the nucleus. So, when the electrons are moving around, the nuclei are essentially more or less static. Since they correspond to such different dynamics, we can decouple the electronic degrees of freedom from the nuclear degrees of freedom. Essentially what we say is that when you are solving the electronic degrees of freedom, we can assume that the nuclear degrees of freedom are all frozen. As if the nuclei are frozen and in those frozen nuclear conditions, we are trying to solve the electronic part of the problem. Under this approximation, the kinetic energy of the nuclei becomes 0 and if the nuclei are not moving, the distance between them is fixed. So, the inter nuclear repulsion becomes a constant. Here, I have the first term becoming 0 and the last term becomes a constant within the Born-Oppenheimer approximation. We know that if I have a constant term in my Hamiltonians I need not worry about it. I can simply solve the remaining part of the operator and I can simply add this constant to the eigenvalues that I get.

This leaves me with the terms which are called as the electronic Hamiltonian. So, this is my molecular Hamiltonian which has the kinetic energy of the electron as well as the nuclear-nuclear repulsion and if I exclude these two terms what I am left is the so-called electronic Hamiltonian. Of course, when you solve the electronic Hamiltonian, you also add afterwards this constant V_{NN}. Compared to a molecular Hamiltonian, the Hamiltonian of a multi-electron atom has some minor differences, e.g., N=1 (as there is one nucleus) but $n > 1$, as it depends on the atom that I am considering. If I am considering helium atom or lithium atom, I will have $n = 2$ or 3, whereas N=1.

Whether molecule or a many electron atom, the Hamiltonian contains the two-electron operators which create trouble in getting the exact solution of the Hamiltonian operator. As long as I have a system which depends only on 1 electron operators, I can solve such problems exactly. But the moment I have inter-electron interactions, that means 2 electron operators, coming into the picture, I fail to solve the problem exactly through quantum mechanics. Now in those cases we would use some approximate methods and that is what we are going to discuss next.

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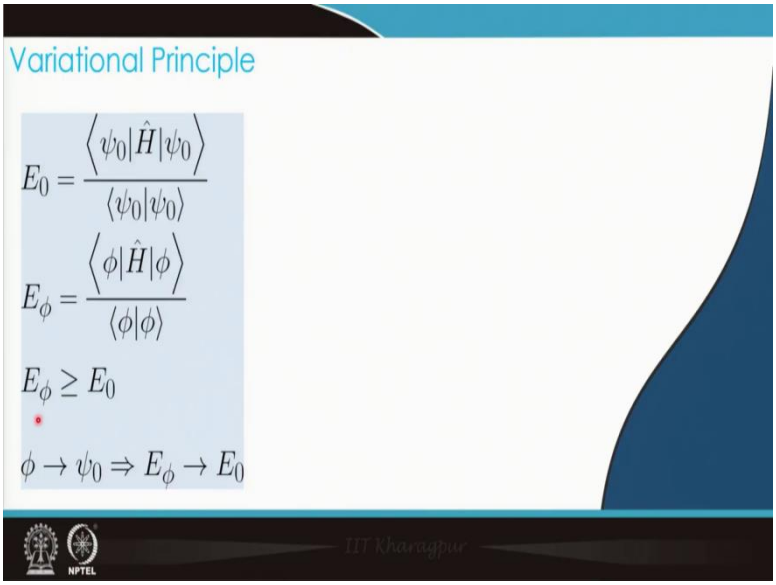

The first approximate method that we are going to discuss is the variational principle. What does variational principle tell and how we can use then this principle to solve quantum mechanical problems, is what we are going to discuss next. Variational principle is quite simple in its statement.

For a complex system, we can write down the Hamiltonian and we would like to solve the corresponding Schrödinger equation, with the ground state eigenfunction as ψ_0, which is the solution of the Hamiltonian with corresponding eigenvalue E_0. Since ψ_0 is an eigenfunction, I would get the expectation value of Hamiltonian as a single value of energy E_0 without any uncertainty. But this is the case when I know the exact solution of the Hamiltonian, but as we have realized whenever I have more than 1 electrons I do not know the exact solution.

When I do not know the exact solution (the wave function ψ_0, which contains all the information), variational principle tells me that I can take another trial function (ϕ) and use it in place of the exact solution. When you do not know the exact solution, we are making a guess. Now this guess function is ϕ.

With this guess function, I can evaluate the energy integral $E_\phi = \langle\phi|\hat{H}|\phi\rangle/\langle\phi|\phi\rangle$, either analytically or numerically using a computer. If the trial function is a normalized function, the denominator is 1. What variational principle guarantees me is that no matter what guess function I choose, E_ϕ is always going to be greater than the real value of the energy E_0. At best it can become equal to E_0, but it can never become less than E_0.

That means variational principle gives me an upper bound to the ground state true energy. If a trial wave function gives the energy close to the true energy then that trial function is a good approximate solution of the system. Now I have a way to find out whether my trial wave function is a good guess or not. How do I do that? This is where variational principle comes to help. Because variational principle tells me that try your best to minimize the energy because you can never get E_ϕ lower than E_0, at best it will become equal to E_0.

In this lecture we discussed about the concept of variational principle. How it is justified and what are its consequences, are the topic of our next discussion. Thank you for your attention.