PROFESSOR: So our example is a well-known one. But it's important to understand it. And it's a good example. It's a familiar one. It's the hydrogen molecule ionized. And we spoke a little about it last time. So let's do that now. So H2 plus, hydrogen ion. So what is this system? Well, it is two protons sharing one electron. That's basically it.

It's the fact that if you have a hydrogen atom-- this is hydrogen-- you could bring another proton and form a bound state. That's an important thing in order to think about it-- you see, you can ask what is the bound state energy of your system? It's the energy you need to dissociate your system. But this system, if you have two protons-- proton, proton-- and one electron, it can be dissociated in many ways. It can be dissociated by just totally separating it and destroying it.

But it can be dissociated or liberated by just removing the proton. So this is already a bound state. So if you think of energies, you have the bound state the energy of hydrogen here, hydrogen itself, and the H2 ion-- H2 plus-- must be lower because you could imagine taking the proton out and somehow this system is a configuration in which this proton is captured here. So you should get lower energy than the hydrogen atom energy.

So that's the hydrogen ion. And that should be still more energy than if you bring another electron, which is the H2 molecule. You bring another electron. This should bind this and the other electron and lower its energy even more. So how does one solve for this hydrogen ion? Well, as we discussed, you first solve for the electronic wave function when the protons are separated at distance r.

So we said fix the lattice. So here it is. The lattice is fixed. It's a separation capital R. And now I'm supposed to find the electron wave function. Easy? No. It already is hard. We spent several lectures-- you've been studying this three times already, maybe, in quantum mechanics, the hydrogen atom, one proton, one electron. To protons, one electron is much harder. I don't think there's a simple analytical way to solve it. So already at this step we have trouble solving it. What is the electron, Hamiltonian in this case? The electron Hamiltonian is just one Laplacian here minus h squared over 2m for the electron variable, and then the potential that is the interactions of the electron with the two nuclei.

So if we call this distance r1 and this distance r2, that is the whole electron Hamiltonian. Now,

don't think of r1 and r2 as you have two variables, two positions. No, there is just one position. The dynamical variables for this electron, this p and r for this electron-- r is the position of the electron. It happens to be that r is equal to r1. And if you know-- so r1 is really the length of r, the position of the electron. And r2 is the length of capital R, if we wish, all the way here, minus r. r is the vector here, as well.

So there is r1 and r2, but it's not two electrons or two variables. It's just two distances that depend on the single position of the electron. And this is the momentum operator of the electron. OK, so you can't solve this. That's life. It can't be solved. But we can do something and we can do something variational. We can try to find some kind of approximation for the state of electrons and use that.

So there is an [INAUDIBLE] that you could try, a variational wave function, for even the electron. You see, in our argument in this lecture, we did the variation and approximation for the nuclear degrees of freedom or for that thing. But even for the electron wave function, I can't solve them. So I have to do a variational method. Now, these variational methods have become extremely sophisticated. People do this with a series of Eigenfunctions and find answers that converge with 15 digits accuracy. It's just unbelievable what people can do by now with this. It's a very nice and developed field.

But we'll do a baby version of it. So this baby version is going to stay. My wave function for the electron as a function of position and as a function of the separation is going to be simple. It's going to be a sum of ground state wave functions. It's going to be a number-- a, that's just a number-- times the ground state wave function based on the first proton plus the ground state wave function based on the second proton.

So these psis, or psi0 of r is the ground state wave function of hydrogen pi a 0 cubed e to the minus r over a0. This is called-- people have given it a name, even though it's-- you would say it's not that original to put some wave function like that. This is a simple approximation. And the technique is called LCAO technique. And this calls for Linear Combination of Atomic Orbitals. A big name for a rather simple thing.

It has some nice things about this wave function. This system is invariant. This molecule is invariant. And they're taking a reflection around this thing changing the first proton and the second proton. So that's the symmetry of your Hamiltonian. And it's the symmetry of [INAUDIBLE] with the Hamiltonian. So you can demand that your wave functions have that

symmetry. And this is nice here because if you change r1 and r2, the wave function is invariant.

So that's a very nice thing about this wave function. It shows-- you see, you can put in the variational method anything and it will still give you some answer. But if you put something that mimics the real wave functions and the real wave function of this system is going to have a symmetry under the exchange of the two protons. They're identical. So this lattice that you've created has a symmetry. So the electron configuration has to respect that symmetry.

So that's very nice. Now, this is electronic wave function. So I ask you, is this wave function better where the protons are far away or when the protons are very close to each other? Give you a minute to think about it. When is this approximation or this wave function better? If the distance between the protons is very little or the distance between the protons is very large? You're right in that when the two things collapse, this looks like a true wave function because this is a solution when there's a single nucleus and a single electron.

But this is the solution for hydrogen. And it gives you the ground state of hydrogen. But when the two protons collapse, it has become helium nucleus. It has two protons. So it doesn't have the right decay rate. It doesn't have the right Born radius. On the other hand, when they're far apart, it does have the right thing. So this is very good. It's excellent when the things are far away. But it's not great when they're close together. So here you go. You have to normalize this wave function. Even that takes some effort.

It turns out that the value of a for normalization-- the value of a is 1 over 2 1 plus a constant i. And that constant i is e to the minus capital R over a not times 1 plus r over a not plus 1/3 of r over a not squared. Wow, so very funny. It's not so easy to even calculate the normalization of this thing. But that's the normalization.

And then recall that what we have to do is just put the electronic Hamiltonian inside this wave function, this phi of r. And this is going to give us an energy which is approximately the electronic energy as a function of r. So you have to evaluate the Hamiltonian-- I'm sorry, that Hamiltonian there-- should have a square here.

And now we evaluate this. We have to go even more into gross and get what is the potential energy contributed by the electronic cloud. So here is the function that you get. So our plot here I'll call-- this calls for a variable x, which is going to be the separation divided by a not. This is the separation between the protons divided by a not.

So here is going to be the electronic energy as a function of x. And here is x. And all right. So as x goes to 0, means the nuclei are going on top of each other. That's the place where the wave function is not all that great. And that's not so good. It turns out that here you get minus 3 Rydbergs. Remember, the Rydberg was e squared over 2 a not. And it's about 13.6 ev. It's just the ground state energy of the hydrogen. You do get that the energy due to the electronic configuration is negative and it goes to this value.

And then it starts to grow quadratically and goes up. And I want to know, in your opinion, what's going to be the next asymptote? So what is it going to asymptote as x goes to infinity? Let let's make the analogy. The right answer is it actually stops here. And you'll remember this problem that you've solved many times, probably. If you have a-- suppose a square well. You have a wave function that is like that.

Now, if you have two square well-- and it has a ground state energy. If you have two square wells like that and you ask, what is the ground state energy? The ground state energy is roughly equal to the ground state energy for a single square well because what happens is that the wave function goes like that and then like-- well, actually, like that. So yes, the wave function spends equal time. But it's the same energy as if there would be a single square well.

So here it is. The protons are very far away in the symmetric state, the ground state. The electron is half the times here, half the times there. But the energy is the same energy as if it would be in either one. So this is an intuition that you may have from 804 or 805. So here it is. That's what it does. That's good. In fact, if you ride the ee of x over Rydbergs, it behaves here like minus 3 plus x squared plus dot, dot, dot. So it starts growing and then asymptotes with an exponential there.

OK, but what did we say was the Born-Oppenheimer approximation was the idea that then you have dynamics of the nuclei based on-- so Born-Oppenheimer tells you that the Hamiltonian for the nuclear degrees of freedom is given by h. This h effective is capital P over 2m squared plus the nuclear nuclear potential, plus this electronic energy.

So this electronic energy we already calculated. The nuclear nuclear potential, in this case, is the proton proton potential, v m n is e squared over r. It is repulsive. You see, this-- if you wanted to minimize the electronic energy, you still don't get anything. You get a system that collapses to zero. That's certainly not the molecule. But this n n is this, so we can write it as e squared over 2a0 and then put a 2 over r over a 0 to get all these numbers nicely. So the nvv

is a Rydberg times 2 over x.

So in terms of x there, vnn is a 2 over x-- oops-- a 2 over x potential like that. So now you have the possibility of getting a stable grounding, so the potential for the nucleons. So the total potential for the nucleons is the sum of these two potentials. And how does it look? Well, some of the two potential-- so ee of x plus vnn of x. Let's divide by Rydberg as a function of x, goes-- here is minus 1.

And it goes more or less like-- OK. Let me try to get this right. 1, 2, 3, 4, 5. OK. It goes up here, down, crosses the minus 1 line, and moves to a minimum here. And then it goes like that. Pretty much it's something like that. It's a rather little quadratic minimum. It's rather flat. And these are the numbers you care for. This is the minimum. Maybe it doesn't look like that in my graph too well. But it's a very flat minimum.

And r over a0 at the minimum is, in fact, 2.49. And e over Rydberg at the minimum is minus 1.297. Those are results. Now, you have a potential. You could calculate the quadratic term around the potential. And then you get an approximate oscillation Hamiltonian that those would be the nuclear vibrations. You could calculate the frequency of the nuclear vibrations and the energy of the nuclear vibration. It's a very simple but nice model. You can calculate everything pretty much about this molecule and compare with experiments.

So how does it do the comparison with experiment? It does OK. It doesn't do very well. So let me tell you what's happening. So again, we do get this system. Happily, the minimum was below minus 1. The minus 1 was the situation in which you have a hydrogen atom and a free proton. So there is a bound state energy but the bounds state energy is not conceptually right to think of it as this big energy. It's just this little part here in which this is the extra binding that you can have when you bring a proton near to the hydrogen atom.

So this extra part-- so the bound state energy-- I'll write a couple of words here and we'll stop. The bound state energy is E. This E that we determined here at the minimum is minus 1 Rydberg minus 0.1297 Rydbergs which is minus 1 Rydberg minus 1.76 ev. So this is what you would call the bound state energy of this system because it's the least energy you need to start to dissociate it-- not to dissociate it completely, but to start to dissociate it. 1.76.

True value is 2.8 ev, so not great, but sort of order of magnitude. Another thing that you can ask is, what is the separation between the nuclei in this ion? How far away are they? And this

gives a prediction that it's about 2.49 a0. So separation is r equal 2.49 a0, which is 2.49 times 0.529 angstroms. It's about 1.32 angstroms. And through value's 2.8. Experimental value, the value of r, our experiment is not that far. It's 106 angstroms.

So it's 20% there, 25% there. But it gives you a way to think about this system. You get all the physics. You understand the physics. The Born-Oppenheimer physics is that the electron energy in the fixed lattice is a potential term for the nuclei. Added to the nucleus nucleus repulsion gives you the total potential term for the nuclear degrees of freedom. You can find the stable situation. And if you want to do quantum mechanics and vibrations of the nuclei, well, do the harmonic oscillator associated with this thing.

The nice thing is you can complicate these wave functions a little and get better and better answers. And it's fun. It's things that can be done numerically. And you have a remarkably powerful tool to understand these things. So with this, we'll close our whole chapter in adiabatic physics. And next time, we will begin with scattering.