

PROFESSOR: We began our introduction to molecules last time and tried to get a picture of the scales that are involved. In these objects we spoke of a lattice of nuclei and clouds of electrons in which a molecule had some scale, A . Then we had electronic energies E , electronic. We had vibrational energies. This is from the nuclei.

And we had rotational energies. And they were one bigger than the other and bigger than the last. In fact, the electronic energies were bigger than the vibrational energies of the nuclei and bigger than the rotational energies of the whole molecule when it rotates as a solid body.

In fact, the ratio was like 1 to square root of little m over M , where little m represents electron mass, and capital M , the nuclear mass. And so this number could be 10 to the minus 2, and then you have m over M . So that's the proportions. So this is larger than the second one, like 1 is larger than that, and the ratio between these two is this.

So that's what we've discussed. And we said that, in some sense, there was an adiabatic approximation in the vibration of the nuclei. As the nuclei vibrate, they pull the electronic clouds with it in an adiabatic way. That is, if you solved for the electronic cloud as a function of position, that would be a family of eigenstates.

Say the ground state of the electronic cloud is a function of position, this would be a family of states. If the positions of the nuclei change in time, you could use those as instantaneous eigenstates. And there is a sense in which this is a good approximation, given that the timescale associated to the vibrations of the nuclei is much bigger than the timescale associated to any variation in the electronic configuration. This is just because of the scales of the energies.

So let's implement this idea in an approximation that is used to solve molecules. And we'll discuss it in all detail. I'll skip one step of the derivation. One calculation will be in the notes, but I don't want to go through the details in class. And we will appreciate the form of the nuclear Hamiltonian, how it behaves.

So this is going to be the Born-Oppenheimer approximation. And we will consider the situation where we have N , nuclei-- capital N , nuclei-- and little m , electrons. So it's a many-body wavefunction and a many-body situation.

In such cases, your notation is important. You have to define labels that help you distinguish this situation. So here are the labels we're going to use for the nuclei, P_α and R_α , where α denotes which nuclei you're talking about.

So it goes from 1 up to capital N , because there are capital N nuclei for each nucleus, the first, the second, the third. There is a momentum operator and a position operator, each one of which is three components, because molecules live in three dimensions. So this is one vector and another vector for each value of α . In fact, these are operators. We're doing quantum mechanics, so these are our canonical pairs for the nuclei, canonical pairs for the nuclei.

We need similar variables for the electrons, and we'll use little p and little r , both vectors, both operators. And this time this i runs from 1 to lower case n . And these are the canonical pairs for the electrons.

So when we write the Hamiltonian, it should be a Hamiltonian that depends on all those variables. And we can write the Hamiltonian, because we know the physics of this situation. We think of this is a lattice of nuclei, and there is the cloud of the electrons, and we have a coordinate system. Here is maybe capital R_1 and capital R_2 . They're all there.

And well, when we write Hamiltonian, we think of the electrons at some points and write things. So let's write the Hamiltonian. So this is going to be the total Hamiltonian. What should I include?

I should include kinetic terms for each of the nuclei. So I should put sum over α . I don't have to repeat here from 1 to capital N . You know already what α runs over. P_α vector squared over $2M_\alpha$. M_α is the mass of α nucleus. It could be a collection of protons and neutrons.

Then there's going to be-- and we get a little more schematic-- a potential that depends nucleus with nucleus. So the nucleus, among each other, have a Coulomb potential. So there's going to be a potential that represents here, and it will depend on the various R 's.

I could write-- this looks funny. You say, which R ? Well, it depends on all the capital R 's. So I could write depends on this set that, but it's a little too cumbersome. I'll just write V of R , like this.

And this is, if the nuclei lived alone, that would be it. This would be the kinetic energies and the potential between the nuclei. Then there's going to be what we can call a Hamiltonian that only

involves the electrons. In some sense, that gives dynamics to the electrons-- not only involves electrons, gives dynamics to the electrons.

And this Hamiltonian, H_e , is going to depend on-- well, this big Hamiltonian for all the molecules depends on the two canonical pairs for times N times little n . This Hamiltonian for the electron will depend on the p 's, will depend on the r 's, and it will also depend on the capital R 's. And you can think of it, and that's reasonable. Suppose you're an electron. Who affects you?

Well, you get affected by your electron friends, and you get affected by the nuclei and therefore, by the positions of the nuclei, as well. So this is the electron part of the Hamiltonian. And it would be given by a sum of kinetic energy, as usual.

So \sum_i , sum over i this time, little p_i squared over $2m$. Let's assume, of course, all the electrons are the same mass. And then we would have, just in this shorthand, a potential that represents the interaction of the electrons with the nuclei. And that potential would depend on the R 's, on the R 's.

And finally-- my picture maybe should be moved the little to the right-- there's a term, the electron potential that just depends on the R 's. So all these potentials are Coulomb potentials, Coulomb from nucleus-nucleus, nucleus-electron, electron-electron. So here it is. You've written the Hamiltonian.

And if you have three nuclei and five electrons, you could write all the equations. And it's a nice thing that you can write the Hamiltonian, and you could dream of putting it into a computer, and it will tell you what the molecule is, and that's roughly true. But even for a good computer nowadays, this is difficult. So you have to try to think how you can simplify this problem.

So one way to think about it is to think again of the physics of the situation. We'll have a separation of scales. It's lucky we have that separation of scales, very light electrons, very heavy nuclei. So let's think of a fixed nuclear skeleton, and consider electron states associated to that fixed nuclear skeleton.

The nuclear skeleton is not fixed. In principle, the nuclei are not classical particles with fixed positions. They're going to vibrate. But we're trying to understand this problem, and to some approximation, we can roughly think of them localized. So let's exploit that and use the

vibrations.

So for large M , this [INAUDIBLE] to large M , consider a fixed nuclear skeleton. So that means fixed R , all the R 's, and fix. And now calculate the electron states as a function of our α .

So you simplify the problem. Ignore all this dynamics of the nuclei, all this nuclear-nuclear interaction. Focus on the electrons as if the nuclear are completely fixed, and try to figure out the dynamics.

So there are going to be many electronic states. This is electrons in some fixed potential. Any particle in quantum mechanics in a fixed potential. There are many energy eigenstates. So these electrons are going to have many energy eigenstates.

So let's try to decide on a name for this wavefunction. So I will call them ϕ for electrons. If there are wavefunctions that are wavefunctions of the electrons, naturally, they just depend on the electron positions, nothing else.

A wavefunction for a particle depends on the position. Now, this r hides a little of-- thing. This really means that ϕ of r_1, r_2, r_3, r_4 , because they're little n electrons, so it's not just one variable. So I can say this is r_1, r_2 , all of them, r little n . That's a wavefunction.

Now, we said there are many of those states. So there will be the ground state, the next one, the next one, the next one. So we should put an i in this. Maybe an i in this is the wrong letter, given that they have i there-- k in this.

But there is more dependence here. There is implicit dependence on the positions of the lattice, because these wave functions depend on what lattice square did you place the nuclei. At this moment, you're placing them arbitrarily.

So this means that this wavefunction really depends, of course, of how did you build the lattice? Did you build the lattice this way, or did you build it this way? It makes a difference. So it depends on the capital R 's, as well, which is the position of the lattice.

So here is our wavefunction. I will simplify the writing by writing ϕ of capital R , little r , and k here, see. So what equation do we demand from this? Well we have the electron Hamiltonian. So that's what we should solve.

We should solve H electron, on $\phi_{R, k}$ of r . We'll have some energies, and those energies will be electronic energies. That's for electronic energy. It will depend on k -- those are the various energies, as well-- and what else?

Certainly the energies don't depend on r . That's your eigenstate. But they can depend and will depend on capital R . Capital R is the parameters that define your lattice. Clearly they should depend on that. And then you have $\phi_{k, R, r}$.

So this is the equation you should solve in order to find electronic states associated with a skeleton. And now suppose you wanted to find a complete solution of the Schrodinger equation. You say, ah, approximations. Why should they do approximations? I can solve things exactly, which is almost never possible, but we can imagine that.

So what would be a possible way to write an n -set would be the following. You could write a ψ for the whole thing now that depends on the R 's. And the R 's wavefunction for the whole degrees of freedom of the molecule could be written as a sum over k of $\phi_{K, R}$ of r times solutions, η_k , that depend on capital R .

That is, I'm saying we can try to write the solution in which the full wavefunction for the molecule is the sum of states of this form, a solution here and a solution there. This is correct, but then how do you determine the η 's? The only way to determine the η 's is to plug into the full Schrodinger equation-- this is the full Hamiltonian. So you would have to plug this into the full Schrodinger equation and see what you get.

So what are you going to get? Presumably, you did solve this first part. So the ϕ 's are known. So if the ϕ 's are known, you're going to find differential equations for the η 's. So this problem has become now a problem of finding solutions for the η 's. And there are many η 's, and they are all coupled by the Schrodinger equation.

So by the time you plug this into H , the total H , capital ψ_{Rr} equals $\sum E_k \psi_{Rr}$, sum energy eigenstate-- I don't have to put the thing-- ψ_{Rr} , to find the energy eigenstates of the molecules. This equation is going to imply a set of differential equations, a couple differential equations for the η 's. And that's not so easy to do. That's pretty hard in general. So this is very difficult.

On the other hand, there is a way to think of this in a simpler context. We can try-- and now we are approximating-- so try to believe that you can get an approximate solution, approximate.

And I will justify this solution using just one term in this equation, and ψ ϕ R of r .

And this may be the ground state of the electronic system. That's why I don't put an index here. I could put a 0 there, but let's think of this as the ground state. And then, well, this would be accompanied, if there is some solution, by $\sum \eta$ of R . And I can try to say that your wavefunction is this, one term in this equation, the one in which I pick the ground state and leave it there.

Now, this is definitely not going to be an exact solution ever of the Schrodinger equation. So you really are-- if you just take one of these terms-- out of luck in terms of solving this exactly, because this differential equation, this Hamiltonian, has terms mixing the two degrees of freedom. It doesn't separate.

You cannot show that the Schrodinger equation has a solution which is one thing that solves an equation and one thing that solves another equation that are products like that. It will not happen. That's why in this equation when you plug in, the various η s get coupled.

But this is the spirit of the adiabatic approximation, in which we sort of have an electronic cloud and a nuclear state, and when the nuclear state changes slowly, the electronic cloud adjusts, and you don't have to jump to a state with another electronic cloud. The electronic cloud adjusts. So this is in the spirit of the adiabatic approximation, to try to find the solution of this kind, in which an electronic cloud is not forced to jump, because the coupling between those states, saying that if you start with one η of one ϕ , you need all the rest, as the Schrodinger equation tells you. It is a statement that the electronic cloud just cannot stay by itself where it is.

So here we go. This is what we're going to try. And you can say, well, all right. So you're giving up the Schrodinger equation, because exact Schrodinger equation is not solved by this. How are you going to try to understand now the η ? Because we found these guys, so how about the η s? How are we going to find them? That is our question.