

**PROFESSOR:** The molecules and Born-Oppenheimer approximation. OK, we all know that molecules are a lot harder to solve than atoms, and even atoms are not that easy once you have more than one electron because of the electrostatic repulsion, but molecules are significantly different in that one of the greatest simplicities that we had with atoms is that the atom is such that the potential created by the nucleus is spherically symmetric. When you have a molecule you have separate nuclei and therefore your spherical symmetry is gone, and whether you have one electron or more than one electron, there is no spherical symmetry. All our tools of angular momentum don't help us much. We have to start the problem anew.

So the difficulty with molecules is basically that the potential for the electrons, where they move is not spherically symmetric. There is another thing that helps us, however, is that there's a nice separation of mass scales. You have the mass, little  $m$ , of the electron and the nuclear mass, this could be the mass of one nucleus or a mass of a few nuclei or doesn't matter, but this is small, and typically it is  $10^{-4}$ . You know, an electron is about 2,000 times lighter than a single proton. If you already have a nice nucleus with a couple of them, you're several thousandths already there, so this is a nice number.

So we want to understand the scales of the physics of this, so let's assume we have a molecule, maybe it has few centers and then there's electronic cloud, and it has a size of the order of  $a$ . So we can estimate at first sight what are the energies involved here? What is the energy of the electron, for example? And you can say the momentum of the electron is of the order of  $\hbar$  times the size of the cloud. It's an estimate, and the energies, the electron energies, are basically determined by the size in which they are confined, which is  $a$ ,  $\hbar$ , and the mass of the electron. Those are the electronic energy, so  $\hbar^2$  over  $m$  squared, those are the right units, is  $p^2$  over  $m$ , the units, so it's natural like this.

So this is the electronic configuration and typical electronic energy, so what is the approximate picture of the physics of a molecule? Basically you have nuclei, and the nuclei repel each other, they want to be away. Now the electrons come in and then they fly around the nuclei, and the electrons attract the nuclei and attract the nuclei, so the electrons, reasonably placed, compensate the repulsion of the nuclei by creating some new attraction.

At the end you get some kind of equilibrium. It's not classical because you cannot create stable equilibrium between classical particles. This is one of the amazing things about

quantum mechanics. You know very well an atom would not exist without quantum mechanics, you would have stable classical orbits, circular orbits, but they radiate energy so they decay. If you have a molecule you have two repelling positive charged particles. In [? E&M ?] you saw the case when you put the negative charge in the middle and you create equilibrium, but that's absolutely unstable. You move that electric charge a micron and then off it goes, the whole thing is unstable.

But quantum mechanics solves those problems and our physical picture is that of repelling nuclei, an attracting cloud of electrons creating an equilibrium in which the nuclei are reasonably well-localized, they're quantum particles but they're reasonably well-localized, while the electrons are completely delocalized. That is our picture, they are moving in that way. So our picture will be-- we have that and we have slow vibrations of the nuclei that are mostly localized. And you can imagine calculating the electronic configuration for any particular separation of the nuclei and that's the cloud for this separation. As the nuclei vibrate, the electronic configuration probably adjusts adiabatically to this thing in the instantaneous eigenstates, and they work that way.

We're going to do that in trying to understand things. I also want to emphasize this kind of remarkable property of an electron to create the bound state. So we are not amazed on the fact that if we have a proton and we can have an electron here, we create a bound state, and that's a hydrogen atom. But suppose I bring in another proton from infinity. Well, I-- if I bring it, I'm going to start bringing it here, this kind of is neutral but eventually this proton is gonna polarize this thing. OK, I'm going to bring it and then if I come too close it repels it so it will be a force repelling it and we have to figure out what it does.

Suppose I try to bring it in. Do you think that an electron is capable of stabilizing two protons? Can they create a cloud in which an electron stabilizes the two protons? Is that possible or not possible? There's a lot of protons for one single electron. Is that possible or not? All right, you say yes, yes, any other opinions? Can that happen? Can the electric produce a bound state of two protons like that?

**AUDIENCE:** Isn't that just hydrogen?

**PROFESSOR:** Sorry?

**AUDIENCE:** Isn't that just hydrogen?

**PROFESSOR:** It is what?

**AUDIENCE:** Isn't that just hydrogen? Or [INAUDIBLE] hydrogen [INAUDIBLE]?

**PROFESSOR:** OK, yes, it can produce it, and this would be called, with an electron here, the hydrogen molecule ion, so  $H_2^+$ . It's a hydrogen molecule that had these two things and it lost one electron, and yes, this can be done and we'll analyze it.

And now you can get greedy and say, can you get an electron to stabilize three protons? Yes or no?

**AUDIENCE:** [INAUDIBLE]

**PROFESSOR:** No, cannot get it, it's just too much work for an electron. It cannot do it. There are theorems like that, Elliott Lieb, a mathematical physicist, has proven all kinds of these things, and we might discuss some of that in the homework, it's kind of nice stuff. So we will be looking at the physics of those things with a little detail.

So now of let's go back to our molecule here and estimate the vibrational nuclear energy. So we have this picture, the electrons are there, the nuclei are kind of semi-classical, they are roughly localized and they're varying, and how would we estimate the nuclear vibration frequency? So estimate nuclear vibration. So we think of a harmonic oscillator,  $b^2$  over  $2$  mass of the nucleons, plus a restoring force,  $H$  subnuclear oscillation. So this is an estimate so it's not very rigorous, but I think it will be clear enough.

Now this restoring force has to do with the cloud of the electrons that adjusts and does things. As you separate the nuclei you have to restore the restoring energies due to the electrons and the Coulomb forces, but it does not depend on the mass,  $M$ , the restoring force. So this  $k$  depends on the electrons and Coulomb forces but definitely not on the mass of this quantity. So  $k$  has units of  $E$  over  $L$  squared, and for energy we have this energy of the electron and length, the length, the scale of the molecule, so  $k$  is proportional to  $h^2$  over  $ma^4$  to the fourth. It just cannot depend on the mass of the nuclei, that's definitely not the origin of the restoring force, so if the only mass you can use is the mass of the electron it can only be that.

But then the frequency,  $\omega$ , is square root of  $k$  over  $M$ , that is the mass of the nuclei, so the nuclear frequency is this, and it's therefore equal to  $h^2$  over  $ma^4$  one over  $M$ , that was  $k$ , and this is square root of little  $m$  over capital  $M$  times square root of  $h^2$  over  $m^2 a^4$  to the fourth, I borrowed a little  $m$  up and a little  $m$  down.

So from here we get that  $\hbar \omega_{\text{nuclear}}$  is square root of  $m$  over  $M$ ,  $\hbar$  squared over  $m a$  squared. If you take the square root here you get  $\hbar$  over  $m a$  squared, but there was another  $\hbar$  I put in. And now we get a sensible equation in which we see that the nuclear energies for oscillation are much smaller, significantly smaller, so  $E_{\text{nuclear}}$  oscillations go like square root of  $m$  over  $M$  is  $10^{-4}$ , we say square root is  $10^{-2}$ , times  $E_{\text{electronic}}$ .

So it's considerably less which is this, so if you think-- I want to make another observation here on timescales, so  $\omega_n$ , we have it here,  $\omega_n$ , or we have it here as well, is equal to this times this quantity, so let me say it this way. The  $\omega_{\text{electronic}}$  for vibrations is the electronic energy divided by  $\hbar$ , I need  $\hbar$  over  $m a$  squared, but here we see that that's precisely that square root, so the  $\omega_{\text{nuclear}}$  is equal to  $m$  over  $M$   $\omega_{\text{electronic}}$ .

Now that is nice because it says that the frequency associated to the nuclear thing is much smaller than the timescales associated with electronic changes. So this is a good reason for our idiomatic thinking that as the nuclei slowly oscillate, the electronic cloud remains in that particular eigenstate and thus and jump. It's our use of the adiabatic approximation.

A last comment is that the rotational energy of the molecule goes like the angular momentum squared over twice the moment of inertia,  $L^2$  is  $\hbar^2$  times some numbers, as usual,  $L$  times  $L + 1$ , and here you get the mass of the molecule times the size squared of the molecule. These energies are like  $m$  over  $M$  times, this is roughly  $\hbar^2$  over  $m a^2$ , and therefore the rotational energies are even smaller than the electronic energies. The rotational energies go like  $m$  over  $M$  times the electronic energies.

So you have the electronic energies, the nuclear energies of oscillation, which go like square root, and then finally the smallest of them are the rotation, in which the molecule rotates like a solid object. We'll continue this next time and calculate a few more things and molecules.