

**PROFESSOR:** All right, so how do we solve this? This is a very interesting thing, and I think it points to all kinds of important things that people find useful in physics. So here it is, the way, maybe, we can think about it. Think variational method. What is the variational method?

You write a wave function and you try to see what is the expectation value of the Hamiltonian and that wave function. You calculate it, and now you know that the ground state energy is below that number. Because for the real ground state expectation value of the Hamiltonian is the ground state energy. For an arbitrary state it's more than that.

So the variational method says, OK, if you want to figure out what is a good wave function, compute the expectation value of your wave function in the Hamiltonian, and then you will see, you will get some energy. If you tinker with your wave function you can get to the right energy.

So this is what we're going to do we're going to try to take this  $\psi$  of  $r$ ,  $r$  and put the total Hamiltonian here. And now that  $\psi$  of  $r$ ,  $r$  is going to be this one from now on. This is  $\psi$  of  $r$ ,  $r$ . We'll put it here, and then I'll put another  $\psi$  of  $r$ ,  $r$ .

And I have to compute that. But think of it-- it's actually pretty nice, the situation. Computing this, you could say how can I compute that if I don't know the  $\eta$ s, the single  $\eta$  that is there? I know the Hamiltonian but I don't know the  $\eta$ , so I can't compute this. But think of this really, this is an integral, because there's an [INAUDIBLE] over all the capital  $R$ 's, an integral over the little  $r$ 's, and you can say, oh, I know the little  $r$ 's here. I know them very well. I found them. I found this  $\phi$   $r$ . I've determined it. Some way you did.

So if I know that, I know the little  $r$  dependence, and I can do all the little  $r$  integrals. If I can do all the little  $r$  integrals, means that this wave function is a product, this wave function is a product, this I can reduce to the following.  $\eta$  of  $r$ , because this one I don't know, and then  $\eta$  of  $r$ , and I claim that all the part that had to do with the  $\phi$  of  $r$ , we can take care, and then there's going to be some Hamiltonian here left. And this we're going to call  $h$  effective of the  $r$  degrees of freedom.

So a lot of physics in that step. Seems like we did nothing, but look, I'm supposed to minimize this by adjusting my trial wave functions. OK, but I don't have room to adjust the  $\phi$ , because I determined that it's a good one. So I put it in and I calculate this. Now I have to minimize this.

But if I have to minimize this for just  $\psi$  nuclear wave function, I have found the effective Hamiltonian for the nuclei, in which the electron has essentially disappeared from this interaction. It just doesn't play a role anymore.

This is the idea of effective Hamiltonians for slow degrees of freedom when you integrate fast degrees of freedom. The fast degrees of freedom are your electrons. We're getting rid of them, we're integrating them. We're going to try to do that. So this will be an effective Hamiltonian for the nuclear degrees of freedom.

So let me do one term in here. One term, you can play trying to do other terms, and the notes will deal with that. So let's consider the term  $H_e$ . This Hamiltonian is some terms plus  $H_e$ . It's over there. So let's calculate what  $H_e$  does.

So I now have to put effect of  $H_e$ . So I have to put here  $\eta$  of  $r$ -- so let me put the whole thing. It's integral over all the  $R$ 's--  $R_1, R_2, R_3$ -- integral over all the little  $r$ 's. That's an overlap.  $\eta$  star of all the  $R$ 's-- that's the [INAUDIBLE],  $\phi$  star  $R$  of little  $r$ ,  $H_e$ , then  $\eta$ s of capital  $R$ ,  $\phi$   $R$  of  $r$ . Everybody happy? That's my term. That's the contribution of  $H_e$  to the left hand side.

Good? Now  $H_e$  is an operator and looks at this thing and says, well, I don't think derivatives with respect to capital  $R$ , so I'm there. I take the derivatives with respect to little  $r$ , I have a multiplicative factor, another multiplicative factor. So I basically act just directly on this. But  $H_e$  already acting on that gives you the electronic energy. So this would be the electronic energy in the ground state. That depends on  $R$  times  $\phi$   $R$ . And lots of vectors.

OK.

So this integral now becomes integral  $dR$   $\eta$  star of  $R$ . Then I'll put the other integral, integral  $dr$ ,  $\phi$  of  $r$ , star of  $r$ . And then I have just this number times  $\eta$  of  $R$ .

All right, so what is this integral? Happily, this is just a number. It goes out of this, it's an orthonormal state. So this whole thing is  $dR$   $\eta$  star of  $R$ ,  $E_e$  of  $R$ ,  $\eta$  of  $R$ , which you could say is  $\eta$  of  $R$ , the number  $E_e$  of  $R$  times  $\eta$  of  $R$ , and therefore you've confirmed that the contribution to the effective Hamiltonian of all this electron cloud is just this number, the electronic energy like that. So in the effective Hamiltonian,  $h$  effective, there will be some terms and there will be  $E_e$  of  $R$ . That's one term.

OK, so what is the whole answer for the effective Hamiltonian? No way to guess it, I think, unless you're-- well, you have incredible intuition. It's going to be a little complicated. If you think about it, why? Suppose this term is going to create no trouble whatsoever. It's just going to copy itself. This thing doesn't act on the electronic wave function, so the electronic wave function's going to cancel, is just going to contribute by itself. So this term we've done.

This term is easy. It just gives itself. But this term is tough, because this term takes derivatives with respect to capital R, and your wave function depends on capital R. So it's going to be interesting.

So what is the answer? I want to give you the answer rather than do that calculation. And it's almost like sometimes physics seems to have just a limited bag of tricks, and things come out in some way or another in a simple way. So what is the effective Hamiltonian?

You could say, OK, it's going to be the sum of kinetic terms,  $2m \alpha$  over  $\alpha$ , and you have  $p \alpha$  squared. Well, it's not going to be just  $p \alpha$  squared. There's going to be a little more. And then there's going to be a potential, a great potential of R, and that great potential of R is going to include the nuclear nuclear R potential. We said that this nuclear nuclear term would just copy along. The He we calculated, and that gives us the  $E_e$  of R. And you say, well, maybe that's it, but no, it's not that, that's it. So let's see what it gives you.

OK, so here it comes. You remember electromagnetism, you could change this thing here? Well, it gets changed, and it will become  $p$  minus  $a$ . Like if there would be a connection. Like if there would be an electromagnetic field. There's no electromagnetic field here, nothing whatsoever. But there is one thing, and what is it? As we'll write here, it turns out to be a Berry connection. Because you have the adiabatic thing and you have your states that depend on R, the Berry connection shows up.

So it shows up like this here. And here it shows up in a couple of funny terms. A term of the form  $\alpha \hbar^2$  over  $2m \alpha$ ,  $\int v_r \text{gradient sub } r \alpha \text{ of } \phi_r \text{ squared}$ , minus  $\sum \text{over } \alpha \text{ } a \alpha^2$  over  $2m \alpha$ . So that's the whole thing, but I haven't defined the  $a$ .

What is the  $a$ ? Well, it's sort of a Berry connection. So you know what a Berry connection is. It's a  $v$  with a R in configuration space of a wave function with the star wave function,

integrated. That was kind of a Berry connection. So it turns out to be very similar here. The  $\alpha$  vector of  $R$  is  $i\hbar$ , the integral over the little space-- the electron space. That's where you integrate things-- of the electric wave function star times the gradient with respect to  $R$   $\alpha$  of the electron wave function of  $R$ .

That is the Berry connection. If you remember, it's an overlap of wave function, wave function and the gradient with respect to the configuration space. So that's a good Hamiltonian for a molecule in the adiabatic approximation. If this looks complicated, it's already much simpler than what the real problem is, because of the adiabatic approximation. If you have these wave functions, these electronic wave functions you can calculate these  $a$ 's. And this plays the role of the effective Hamiltonian for the nuclei in this approximation.

So the variational principle essentially told us what is the right way to describe the interactions of the nuclei, given that the electrons have already been fixed into a class of wave functions. Now in general, this is the complete solution, but in general it's hard to do it, still complicated. So many times, people simplify.

Well, it might happen, for example, if you have a simple enough molecule that your wave functions  $\phi(r)$  are real. Now you remember that the Berry phase vanishes when the wave functions are real. These things have to be imaginary. With another  $i$  they have to be real. Connections are always real operators in the sense of  $r$ . So if the electronic wave functions are real, forget it, there's no Berry connection.

So many times the Berry connections are not there. Even if there are no Berry connections, this term might be there. This is the gradient of this wave function with respect to the  $R$ . And this term can be important, even if there is no Berry connection.

So in some cases, the lowest order approximation of this-- I think that's what this classically called the [INAUDIBLE] Oppenheimer-- ignores the Berry phase and ignores this extra term. So in that approximation, the lowest order approximation, the effective Hamiltonian, is just the sum over  $\alpha$  minus  $\hbar^2$  over  $2m$   $\alpha$ , Laplacian  $R$   $\alpha$  plus the nuclear nuclear potential, plus the electronic contribution to the potential.

So you keep-- basically, forget about Berry. That's higher approximation, higher order approximation, higher order approximation. Keep just the  $p$ , keep the nuclear nuclear, keep the electronic. And people have done a lot with this.

So that's how our treatment of molecules. A pretty interesting thing. And perhaps the most important lesson of all of this is your way in which you can see how light degrees of freedom impose dynamics in slow degrees of freedom.

And that's something you do in physics, in quantum field theory, all the time. You have the slow-moving degrees of freedom and the fast-moving degrees of freedom. And you integrate the fast-moving degrees of freedom, and you find an effective Hamiltonian for the big things. You may have quarks and all kinds of complicated things. But at the end of the day, they form protons and neutrons, and you can integrate the interactions of the quarks to sort of find the dynamics of the particle that you observe.

So that step in that top blackboard is pretty important.