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**PROFESSOR:** I'm really sick today. And I hope I can make it through this lecture without disgracing myself. But this is a favorite topic of mine, too, so maybe it will be OK.

So we're going to talk about the helium atom, which is really an amazing thing because hydrogen-- it was possible to solve it exactly. All sorts of fantastic things happened. And it seemed like just a small step from hydrogen to helium. And nobody can take that step. It's entirely approximate. And you can do better and better on the approximations, but we'd like to have some physical sense of what's going on, and what are the important terms, and can we steal things from hydrogen?

The answer is, yeah, we can. And that was what last lecture was mostly about. The energies for hydrogen are minus  $z^2 hc$  times the Rydberg over  $n^2$ . And we have the ionization energy from the  $n$ th level. And so this actually is the way we make a link to this concept of electronegativity because the dominant thing in electronegativity is the ionization energy. And this is the ionization energy.

And when you put them together and solve for  $n$ , you get this arrangement  $hc z^2$  times the Rydberg over the ionization energy, square root. That's  $n$ , or the effective principle quantum number. And then we have all of these formulas that can be derived from hydrogenic wave functions, both for diagonal expectation values or off diagonal matrix elements. They're all closed form.

And this is wonderful because it then enables you to use the formulas that are obtained exactly for hydrogenic wave functions. And so if we know the dependence of an electronic property on  $n$  and  $l$ -- well,  $n$  is experimentally determined-- distance real ionization.  $l$  is determined from angular momentum. Then we can determine the expected scaling of everything on the quantum numbers.

And even if that's wrong, it tells you the qualitative effects when you get to more complicated systems in one electron atoms. And this is really what I meant by structure, where everything

is related to basically one observation.

There is one other thing that I didn't stress. And it's another concept from 5.112., and that's shielding. So suppose we have a sodium atom. Most of the electrons are in a compact core. The outer electron sees a charge of 1, even though the charge on the nucleus is larger than 1.

And if you ask, well, suppose we look at this in a region, and we have an electron inside of it, the charge that that electron sees is the amount of electrons inside the sphere defined by this radius. And so the  $z$ , we can call it the  $z$  effective, is a function of  $r$ . And you have a different function every  $o$ . And so it's a way of putting in more insight. And I've made a lot of mileage in my career on these sorts of scaling arguments.

OK, so helium-- the notes are beautiful. They're written by Troy. And they're very long. And they're very correct and incisive. And even if I weren't sick, I couldn't cover all those notes. So I'm going to make a rather express trip through the notes.

And the critical thing is we have two electrons. And so we can't simply solve the problem by using hydrogenic functions, although we would like to. And the crucial thing that is missing is if we could ignore the interactions between the two electrons, which are enormous, then we would be using hydrogenic functions, and everything would be fine.

So we can't. And we use what's called the independent electron approximation, where we're still using hydrogenic orbitals and energies, but we're using those to include the first order perturbation correction to the energies. So there's a term, the interelectron repulsion that leads to this extra correction energy. And that's most of the difference.

But then, we have identical particles. And when we have identical particles, the permutation of those two particles has to commute with the Hamiltonian because the Hamiltonian only knows that we're dealing with all the electrons. It doesn't put names on the individual electrons. And so there's a permutation symmetry that has to be imposed. And this is very subtle because the permutation symmetry has nothing to do with the energy, but it has to do with the energy states. And so we'll explore that.

Now, since we're going to be dealing with more than one electron, there's a lot of symbols that we're going to be carrying around. And so there's a useful thing called the atomic units, which sets most of the physical constants to 1. And that means all of the rubble that you have to carry around goes away. And it's not a big deal because if you use all of the things in your

calculation in atomic units, namely value 1 or something like 1, then at the end, you're going to get the energy in atomic units. And we know what that is in conventional units.

So it's a risky thing because you don't really know what you're doing. But at the end, you can probably convert your number, which is a pure number, into an actual energy.

OK, so let me start with the good news. Well, maybe I should leave this exposed. The good news is we have two particles for helium-- vector  $r$ , momentum, momentum  $p$  vector for particle 1, vector, momentum. OK, so these are the actors.

And when do we have to worry about commutation or non-commutation? Well, the answer is the coordinates associated with different particles, they contribute to the energy. But there is no problem of commutation. The momenta don't also commute. The coordinate for particle 1 and the momentum for particle 2, they commute.

The only things that doesn't commute is  $r_1x$ ,  $p_1x$ -- those kinds of things. They're commutators  $ih$ , and that means there's some problems. So most of the variables are commuting variables, but some are not. And you have to deal with that.

OK. We know that if we have, as, for example, in a three-dimensional harmonic oscillator, if we have a Hamiltonian that doesn't commute-- if we can divide the system up into parts, then the Hamiltonian for each part commutes with the Hamiltonian for the other part, which is part of this. Then, you can write the Hamiltonian as a sum of individual system Hamiltonians that commute with each other, the energies as the sum, and the wave functions as the product.

And so we like that. And we'd like to be able to build a picture for helium that is like that. And so if we write the Hamiltonian for helium, we have  $p$  squared for particle 1 over to me with  $p$  squared-- I don't know. Let me see. Let me organize better. Minus  $z_b$  squared over  $4\pi\epsilon_0 r_1$ . And then we have another term like this for particle 2.

And we can call this Hamiltonian 1. I don't want to do that. Hamiltonian 1, and this Hamiltonian 2. And these are hydrogen atom Hamiltonians. And we know everything about them. So it's a fantastic way to build up a basis set consisting of energy, zero-order energies and zero-order wave functions, with which we can calculate anything. And so then we have this one other term, which plus  $e$  squared over  $4\pi\epsilon_0$  over  $1$  minus  $r$  minus  $r_2$  vectors.

That's the bad news. This says we have a Hamiltonian, where we can't use the eigenvalues and eigenfunctions of the hydrogenic things unless we do-- so we can say, well, these give the

first-order energies for whatever state we want. But we can calculate matrix elements of this term in the basis set associated with hydrogen.

And that's fine. That's a perfectly good way to calculate the first-order correction to the energy. But what about this? When we do perturbation theory and calculate the second-order corrections to the energy, what is that usually?

Maybe I didn't ask the question clearly enough. What do you have to do to get these second-order energies in an infinite dimension problem? I just gave it away. Somebody has to have the courage to say something here.

Remember, we have a sum of  $n$  not equal to  $n$  from 0 to infinity.

**AUDIENCE:** Yeah.

**PROFESSOR:** That's it. OK, I encouraged you. So the way we could use this basis set in a perturbation theory format is to calculate an infinite number of off-diagonal matrix elements of the hydrogenic wave functions. And that could yield results, but it's not the way it's done usually.

There's a variational calculation that you use to get the better wave functions. But we're not going to do that here. We're going to go as far as we can without actually addressing what's wrong if we stop here.

OK, so this guy is  $h^1$ , the source of all trouble. And how we deal with it is there are three steps. One is ignore it. The other is use our hydrogenic functions to calculate matrix elements of this and get an  $h^1$ , an  $e^1$ . And the third step would be to get the exact answer by doing an infinitely difficult calculation, OK? All right.

So this is going to be a notational voyage, which is horrible. Because we have many particles, and particles have coordinates and spins, we're going to have an explosion of stuff, even if we get rid of the extraneous units. But let's get rid of the extraneous units.

And so atomic units-- we can choose any internally consistent set of units we want. And in atomic units, we say that the mass of the electron is 1. The charge of the electron is 1. The  $\hbar$  is 1.  $4\pi\epsilon_0$  is 1. That's good. A lot of stuff just going away.

OK, and the energy in atomic units is not 1. The energy in atomic units is minus 2 times the energy of the hydrogenic 1s orbital. And that comes out to be 27.21 electron volts, in more

convenient units. So you calculate a number, and then you multiply it by this to get the real energy.

OK, and the unit of length is  $a_0$ , which is the radius of the  $n = 1$  hydrogenic Bohr orbital, or Bohr orbit. And that's 0.529 angstroms, with a lot more digits if you need them, OK? And the speed of light is 137 in atomic units.

So everything that you're going to need is either 1 or something that is related to-- OK, so you can do this, and I don't like it because it's so easy in a big calculation to get your units screwed up. But it's certainly great for lecturing and perhaps for writing computer programs.

OK, so let's start with a non-interacting electron approximation. And in the notes, it's represented by these letters. I don't know whether that this is Troy notation or widely-adopted in quantum chemical circles. But it's easier to write this than that. And that just means we're going to ignore this. We just forget about it.

Now, we know that's stupid because the electrons have charge of 1. And they repel each other. And the nucleus has charge of 2, in the case of helium. And so we know that this term is rather similar to  $h_0$ . And we can't expect to get very far completely ignoring it. But we can do it, and we can do a calculation, and we can find out how well it works.

So first of all, it's clear in the notes. I'm just going to skip to the answer. So the energy for helium in the  $1s\ 1s$  orbital or  $1s\ 1s$  configuration-- when we're going to use this word configuration, what that means is the list of orbitals that are occupied. Now, we're listing principal quantum number and orbital angular momentum. There is more stuff which doesn't get listed, and that leads to very interesting stuff. But if we have a list of the orbitals are occupied. That's called the electronic configuration. And I'm an electronic spectroscopist, so you can be sure this is something I care a lot about.

So we can calculate this in the hydrogenic basis. And what you end up getting is-- where is it? I'm sorry. This is the experimental value. The calculated value is-- see, I'm trying to improve on my notes. And in my present state, I make a lot of mistakes. So that is 108.8 electron volts.

So this is the energy of the  $1s\ 1s$  state below the ionization limit. So that's what we predict. Except this is not the ionization limit. This is helium  $2+$  plus 2 electrons. Because we use the energy to ionize both hydrogen atoms, and so this is 108.8.

Now, you can measure this experimentally. You can do helium to helium plus an electron, and

then helium plus going to helium  $2+$  plus an electron. And the observed value is what I wrote before. Observed is equal to minus 79.0 electron volts.

Well, you might say, well, that's pretty good. It's the same order of magnitude. It's not even off by a factor of 2. But almost everybody in this room is a chemist. And this difference between the calculated value and the observed value is 30 electron volts. A chemical bond is typically 5 electron volts.

So this is totally ridiculous for chemistry. We can't use it. We don't even want to think about it because it's an order of magnitude away from what we need.

We improve on it by including  $e_1$  of  $n$ , which is related to  $h_1$ , which is that simple-looking thing over there. So the interelectron repulsions can be dealt with, not exactly, but by calculating diagonal matrix elements of the interelectron repulsion. And that's what the independent electron approximation is. So that's all there is.

But now we bring in something that we hadn't expected would be a problem. So we have this mystical, or mythical, or whatever operator--  $p_{12}$  operating on some function of  $r_1$  and  $r_2$ . And what it does is it permutes the electrons. We know that if something is operating on the names of the electrons, it has to commute with the Hamiltonian.

So that means that this operator has to have eigenvalues if these states are eigenfunctions of the Hamiltonian. And there are two possible eigenvalues because we know  $p_{12}^2$  on  $\psi$  is equal to plus  $\psi$ . So the only way you can do that is having the eigenvalue of the permutation operator be either plus 1 or minus 1.

And this is a fundamental symmetry. And I can't possibly tell you where it comes from or what I'm about to write on the board comes from. But so all half integer spins correspond to antisymmetry or belong to the eigenvalue minus 1. And they're called fermions. And integer spins are symmetric with permutations. And so integer or symmetric, and they're bosons.

So we have to write wave functions which are wave functions of the electrons, which are antisymmetric with respect to the permutation of every pair of electrons. So helium, we only have two electrons. It's not so bad. But when you think about something like carbon monoxide, which I always think about, or some other molecule where there's more than two electrons, there's a God awful number of permutations. And you have to build them all into the wave function.

And the normal feeling when you hear that is, oh, no, I can't possibly imagine how to do that. And if I could, there would be a ridiculous number of integrals that I would have to evaluate. And it's true. There are a ridiculous number of integrals. But there is a simple algebra that enables you how to deal with them. And it involves using what is called Slater determinantal wave functions.

And I'll talk about that. Slater was an MIT professor. He wrote a lot of books. But the thing-- integer. Oh, they're sort of a  $t$ . But the most important thing he did was to develop this way of dealing with an antisymmetric electronic wave functions.

So the next thing we have to do is discover how do we build symmetric wave functions for the simplest possible case where there's two electrons? And already, we discover some surprising consequences for this. And so I'm going to go through this, but I'm going to skip a lot of steps because it's so clearly written in the notes and because we don't really have time to deal with 15 pages of single-spaced notes. And I'm not sufficiently at my best to get through maybe 12. And you don't want that, anyway. OK, so let us see what happens here. And so let's get to work.

Suppose we have an electronic state  $1s$   $\alpha$  spin. We know  $\alpha$  is  $m_s$  equals plus  $1/2$ . And  $\beta$  is  $m_s$  equals minus  $1/2$ . So this is the spatial coordinate. This is the spin coordinate.

And, OK, so here is a simple product of two wave functions. And we know what they are. And so if we apply  $p_{12}$  to this, we get  $\psi_{1s\alpha} r_2 \sigma_2 \psi_{1s\beta} r_1 \sigma_1$ . We don't even know what this is relative to that.

So symbolically, these are two unrelated quantities. So weird, but they are eigenfunctions of the zero-order Hamiltonian. So we can take a linear combination of eigenfunctions that belong to the same eigenvalue, and it's still the same energy. So we do that.

And so what we can do is write a combination of this function and that function. And if we do that, so now we can have  $\psi_{1s2s}$ . And what we get is  $1/\sqrt{2}$  for normalization. And we have  $\psi_{1s\alpha} r_1 \sigma_1 - \psi_{1s\beta} r_1 r_2 \sigma_2$ .

And this, in fact, is anti-symmetric. If you apply the permutation operator to this, it is an antisymmetric function. So this does the job.

Now, since the Hamiltonian doesn't depend on spin, the energy of this state and the energy of

that state are the same. They are hydrogenic. And so using this wave function rather than the individual non-symmetrized functions doesn't change the energies.

So are we wasting our time?

**AUDIENCE:** I think you didn't [INAUDIBLE]. This should be the product of  $1s\alpha$   $1s\beta$ .

**PROFESSOR:** I'm sorry?

**AUDIENCE:** So the [INAUDIBLE] must be [FINGER SNAPPING]

**PROFESSOR:** Yes, yes, yes.

**AUDIENCE:** Minus the other one.

**PROFESSOR:** I just want to see what I wrote here. So yeah, what I wrote is wrong.  $1s\alpha$ , and we'll just put 1 in here.  $1s\beta$   $2$  minus  $1s\alpha$   $2$   $1s\beta$   $1$ . OK, this is what I should have written. And this is, in fact, antisymmetric. Thank you. I wrote what's in my notes, which is wrong. And I didn't realize I had done that because I knew the answer. All right.

OK, so we can use this kind of function. It's legal because it's an eigenfunction of the permutation operator with negative symmetry, which we're told that's what we have to use for electrons. I can't tell you where it comes from, although it came from Pauli. And the exclusion principle really is this, rather than what you have memorized. Its consequence is that you can only put one electron in an orbital. But this is the exclusion principle, and it is Pauli.

OK, so now we know what to do. And we can calculate the matrix elements.  $\psi$   $1s\alpha$  go in  $1s\beta$ . This is the antisymmetrized product of two electrons. Matrix element 1 for Hamiltonian  $1$  plus  $1$  over  $r_1$  minus  $r_2$   $\psi$   $1s\alpha$   $1s\beta$ .

Though this is a perfectly legitimate thing to calculate and we know how to do it, or McQuarrie knows how to do it. And you don't really need to worry about doing these integrals because this is at such a low-level approximation, it does nothing for you except teach you how to approach these problems. But we can still do these integrals. And it's useful.

And so what do you get? Well, you get minus 4y because these are hydrogenic with a nucleus of plus 2. And in the atomic units, the energy of a hydrogen atom charge of 1 is  $1/2$ , not 1. And these go as  $z$  squared, so we get  $4$  over  $2$  plus  $4$  over  $2$ . So we get this minus 4 or you get minus-- yes. And then we get something else. And that's this integral that we don't like, which



is integral of  $1s \alpha 1s \beta$  squared over  $r_1$  minus  $r_2$   $dr_1 dr_2$ .

So we can do this integral, or Mr. McQuarrie and many of his predecessors can do that integral, and you get a result. And this integral turns out to be  $5z$  over  $8$ . And converting that into units, and that's  $5/4$  au. And that's-- why is that? That doesn't seem right. Anyway, it's  $34$  electron volts or minus  $34$  electron-- plus. Plus  $34$  electron volts-- so the interelectronic repulsion for hydrogenic orbitals on the same nucleus is  $34$  electron volts. It's a big number.

And so we can correct our the calculated versus observed energy. And instead of having-- well, the experimental value is  $79$ . And now, the calculated value is minus  $74.8$  electron volts. So this is marginally relevant to chemistry because the error is about the typical bond energy. And so we can do stuff with this. We know that it's not accurate enough to do anything quantitative. But you can use it for qualitative arguments. And we can do much better than this using what's going to be called the variational principle, which is coming.

OK, so now, we're going to be dealing with a problem that has lots of symbols and equations. And it's best to start using notation called stick diagrams because it's completely transparent what they mean. And so it's a shortcut for writing the correct equations. So we have for the ground state of hydrogen-- I'm sorry.

We want to talk about excited states because  $1s$  with  $1s$  doesn't have enough complexity to attract our attention. And when we deal with excited states,  $1s$  and  $2s$ , we discover something important that's new. And it's the last thing we really need in order to understand electronic structure or how the electronic states that arise from a configuration are distinguished.

And so we have for the  $1s 2s$  configuration, there are four ways of writing this in stick diagrams. So we have  $1s 2s$ , and we can have spins up,  $\alpha \alpha$ . And we can have  $2s 1s$ . We can have spins up and down.  $2s 1s$ , and spins down and up. And  $2s 1s$  spins down.

So it's much easier to write these things because they have an equation to associate with them, and you can play with these symbols. So the first thing you notice is this symbol can be written as an antisymmetrized product. And so this symbol-- we just take the  $\alpha \alpha$ . And so let me just write it out.  $1$  over square root of  $2$  times  $1s r_1 2s r_2$  minus  $\psi 1s r_2 \psi 2s r_1$ . And then times a spin part,  $\alpha$ -- and we can just abbreviate the  $1$ -- and  $\alpha$ .

OK, so we have factored the wave function to a spatial part and a spin part. Now, I'll make an outrageous statement. Doesn't matter how many electrons. You'll always be able to factor it

into a spatial part and a spin part. Now, what is necessary is always this function has to be antisymmetric. And in this case, it's the spatial part that's antisymmetric and the spin part that's symmetric.

Now, when we try to do these two stick diagrams, we cannot write a correct equation for this guy. We have to do both of them. We have to combine the two. And that will give us a separated spin part and spatial part. And it's antisymmetric. You can't make in an asymmetric function of this just switching the coordinates. And what you find when you do this is going to be that we get functions which look like  $\alpha\beta + \text{or} - \beta\alpha$ . OK, so spin 1  $\alpha\beta + \text{or} - \beta\alpha$ .

And it turns out that there are three spin functions that we get, which are symmetric. And all three of these are associated with this antisymmetric spatial function. They have the same energy. And since they're three of them, we call them a triplet. And since we're talking about spins, this triplet corresponds to  $s = 1$ . You use  $s = 1$  and creation and annihilation operators or raising and lowering operators to show that these are, in fact, the three eigenstates of  $s_z$ . So we call it a triplet because they're three of them. And it also corresponds to  $s = 1$ .

And there's one,  $\alpha\beta - \beta\alpha$ , which is antisymmetric and is associated with a different spatial function, which is symmetric. And it has to have a different energy because the Hamiltonian operates on the spatial part and not on the spin part. So antisymmetry has forced you to have two different spatial wave functions, and that guarantees that these guys will have different energies. And since there's only one of them, we call it a singlet, and it corresponds to  $s = 0$ .

So now, we want to know, which is higher in energy, the singlet or the triplet? And how much higher? And so, again, we take the wave functions that are correct as far as permutation is concerned, but only approximate as far as using hydrogenic functions, and we evaluate the relevant terms in the Hamiltonian.

OK, so we can forget about the spin parts now. We know we're going to have two different spatial wave functions. And we're going to want to calculate-- yes?

**AUDIENCE:** For the top state, [INAUDIBLE] both spins [INAUDIBLE]?

**PROFESSOR:** That should be?

**AUDIENCE:** Would that also be  $s = 0$ ?

**PROFESSOR:** I can't hear. I understand the last word.

**AUDIENCE:** With the statement, both spins be also  $s = 0$ ?

**PROFESSOR:** No. Both spins up. The vector sum of  $1/2$  and  $1/2$  is  $1$ . And so the total spin is going to be  $1$ . And so we have  $3$ -- I mean, if we're applying  $s = 1$ -- suppose we start with--

**AUDIENCE:** I meant that the top spin [INAUDIBLE] both spins.

**PROFESSOR:** Sorry. I can't hear properly.

**AUDIENCE:** The topmost state with both spins on it?

**PROFESSOR:** Yes.

**AUDIENCE:** Would that have  $s = 0$  or  $s = 1$ ?

**PROFESSOR:** It has  $s = 1$ . OK. And now, I don't want to go into the angular momentum matrix element. That would be the last thing in this lecture. So yes, the projection quantum numbers are not uniquely associated with the total spin. But if you have  $\alpha$ , you can show that  $s = 1$ . And  $\alpha + \beta = 1$ . And  $\beta + \alpha = 1$ . But  $\alpha - \beta = 0$ . You can do that using creation and annihilation operators. It's clear, OK?

So you have to take it on faith until you prove what I've just said. And it takes about two minutes.

OK, so we can evaluate the integrals. And something very beautiful occurs. And it's done very, very clearly in the notes. And it would take me more time than we have left to do it, and I didn't plan on doing it anyway.

So we get the energies for the singlet and triplet states, which are  $E_{1s} + E_{2s}$ . Now, remember, these are for a  $1s$  orbital on helium, so it's going to be four times the energy of the  $1s$  orbital on hydrogen. But we know what they are. Plus what we call  $J_{1s2s}$  plus or minus  $K_{1s2s}$ .

So this is clear. And the integral associated with this is taking the square of the wave function. And basically, we're evaluating the interaction between an electron  $1$  in the  $1s$  orbital and

electron 2 in the 2s orbital. So that's a perfectly doable thing. It's a classical quantity. We have two charged distributions, and we're calculating the energy interaction between two electrons in these two charged distributions.

So this is called the Coulomb integral. And that is an entirely classical quantity. And this is called the exchange integral. And the reason we call it an exchange integral is, basically, we're switching the electrons between the two orbitals. And this is something which is entirely quantum mechanical. It comes about because of the permutation symmetry that's required for fermions.

And so this is the surprise. And it also depends on whether you have a symmetric, or an antisymmetric, or a singlet, or a triplet. And so you end up getting an energy level diagram for the state of a configuration, which looks like this.

So we start out with  $E_0$  1s2s. And then we allow the charged distributions to interact. And the electrons are going to repel each other. It's a positive energy. And so this is  $E_0$  plus  $J$ . And then, we include the exchange interaction. And so this is the difference  $2K$ . And this is  $E_0$  plus  $J$  plus  $K$ . And this is  $E_0$  plus  $J$  minus  $K$ .

And this is the triplet state. And this is a singlet. And for helium, we call the singlet state singlet s because total angular momentum is 0. And spin, it has 0. And the triplet we call a triplet s.

Now, if we did 1s 2p, we would get singlet and triplet p states. But the important thing is, how big is  $K$ ? And remember,  $K$  is an approximation. It's a real quantity, but for hydrogenic orbitals, it's going to be incorrect. And so  $2K$  is 2.4 electron volts. And that's a perfectly doable calculation because you're dealing with simple functions. And you can do this integral. And you can actually do it in closed form. But it's 2.4 electron volts. And experiment, it's 0.8.

And this tells you something really important. The repulsion between two electrons, when you have the correct wave function, is less than it would be if you're using the wrong wave functions. And basically, whenever you do anything using the wrong wave functions, your energy levels are too large or the energy differences are too large.

And in this case, the electrons. And when you solve the exact Schrodinger equation, the electrons know about how to absorb it to avoid each other. It's called correlation energy. And this is what makes all the calculations hard because there is no closed form analytic expression for the correlation energy. And the way you optimize the correlation energy is

throwing a huge basis set at the problem. And this is why it takes a long. And you never know that you've converged until you fill in another million functions.

OK, but so there are several lessons. And that is we have something that's completely classical, and we understand what it is. And then, we have this extra thing that is a consequence of the permutation symmetry.

And so this extra thing we calculated too big. But it says that if we have states that belong to the same electronic configuration-- in other words, if we specify the orbitals that are occupied, there's going to be more than one electronic state. And so configurations split into many different electronic states. And we know the machinery that enables us to calculate their relative energies. And some of it is simple Coulomb's law. And some of it is something that's caused by the required permutation symmetry.

So I'm over time. But I can't believe that I got to this point because I delivered everything that was really important. When we have more than two electrons, everything I've said is true, it's just more complicated. And we have to evaluate matrix elements between determinantal wave functions, which looks like, if you have  $n$  electrons, there's  $n$  factorial terms in a determinate. And we have  $n$  factor  $n$  squared matrix elements.

And you don't want to do that. But there turns out to be a simple algebra that makes it all pop out, almost with the same level of effort as this. And so we'll talk about many electron atoms, and then we'll go on to molecules after the many electron atoms lecture. OK.