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**ROBERT FIELD:** Let's get started. William Klemperer was my thesis advisor, and he died yesterday. It also happens that the subject of this lecture is really the core of what I got from him. He showed me how to evaluate matrix elements of many-electron operators, which is the key to being able to interpret-- not just tabulate-- electronic properties of atoms and molecules.

Our goal is to be able to reduce the complexity of electronic structure, which is really complicated. The electrons interact with each other really strongly, and there are a lot of them. And it's very hard to separate the complexity of the many-body interactions into things that we can put in our head and interpret. And the whole goal of this course is to give you the tools to interpret complicated phenomena. We have the vibrational problem as a way of understanding internuclear interactions-- nuclear motions. We have electronic structure and the hydrogen atom as a way of understanding what electronic structure is, and to reduce it to, basically, the things we learn about hydrogen.

When we go to molecular orbital theory, we take what we know about atoms, and build a minimally-complex interpretive picture, which is sort of a framework for understanding complicated molecular interactions.

So one of the most important things about understanding electronic structure is, how do we deal with many-electron wave functions? And one of the terrible problems is that the electrons are indistinguishable. And so we have to ensure that the wave functions are anti-symmetric with respect to permutation of every pair of electrons, not just two. In helium we just dealt with two, and that wasn't so bad. But when we deal with  $n$  electrons, what we are going to discover is that in order to anti-symmetrize the wave function, we have to write a determinantal wave function, a determinant of orbitals. And when you expand an  $n$  by  $n$  determinant, you get  $n$  factorial times. And when you calculate matrix elements, you have  $n$  factorial squared integrals.

So you're not going to be handling these one at a time, and looking at them lovingly. You're going to want to be able to take these things and extract what is the important thing about the

electronic structure that you're going to need to know.

And as a graduate student, I was collecting numbers. I was collecting numbers about spectroscopic perturbations, where non-degenerate perturbation theory breaks down, and interesting things happen. But this was something that nobody in the world was interested in because it was the breaking of the usual patterns. And I was convinced that I had collected some stuff that told an interesting story.

And I told Klemperer about this, and he said, well, have you thought about how to evaluate these integrals-- these numbers that you are extracting from the spectrum, by doing some tricks with the many-electron wave functions? And then he showed me, on a scrap of paper, how to do it. And I was launched. That was it. That has been the foundation of my career for the last 50 years. And I didn't think that Klemperer knew that. I didn't think anybody knew it, because I didn't think it was knowable. But he just gave it to me on a silver platter.

And so I'm going to try to give you at least the rudiments of what it is you're up against, and how you reduce them to things that you care about, that you can think about. And you can understand the hydrogen atom in rather complete detail. Or at least you can understand how one observable relates to another. And so the relationship between the effective quantum number and the ionization energy of a state then provides a hydrogen-atom-based structural model for everything you can observe.

Now spectroscopists have the unfortunate habit of saying we're interested in structure. Structure is static. Dynamics is magical, and special, and hard. But if you understand structure in a way which is not the exact eigenstates, not the exact wave functions, but something that the molecule was trying to do and sort of missed. And the dynamics is just what happens when this preparation isn't in eigenstate, which would be boring. And you get dynamics, which you can understand, as opposed to just saying, I'm going to tabulate the dynamics too. You don't know anything unless you have a reductionist picture of what's going on. And since the hardest part of dealing with molecules is the fact that they have a lot of electrons, this is really the core of being able to do important stuff.

Now it's a horrendously complicated problem, and notationally awkward, too. And let me just try to explain it. And I'm going to try to do this without too much reliance on my notes, because they're terrible.

We talked about helium. And helium has two electrons. And there's this  $1/r^{12}$  interaction

between electrons, which looks innocent enough. You can write it down. You know, it's just a few symbols. And we can call it the first order perturbation. But that's really a lie, because it's as big as almost everything else. And so, yeah, we can, in fact, do a series of approximations. One is, ignore it, the non-interacting electron approximation. And that's basically repackaging hydrogen, and it's not quite enough. And then we can say, OK, let's calculate the first order energy by calculating expectation values of  $h^2$ . So that's  $E_1$ . And that's almost enough to give us a sense of what is going on.

$1/r^2$ , commutate with any electron, that's not 0.  $1/r^2$ , commuted with any orbital angular momentum-- any momentum is not 0. So that means that  $l$  and  $n$  are not good quantum numbers.

What's a good quantum number? What's the definition of a good quantum number? Come on, this is an important question. Yes.

**AUDIENCE:** [INAUDIBLE] count, and then you put them into some formula, and then you can read off eigenvalues.

**ROBERT FIELD:** That's maybe 70% of what I want. You can put it into a formula. That means it's a rigorously good thing. It means it commutes with the Hamiltonian.

A rigorously good quantum number corresponds to a eigenvalue of an operator that commutes with the Hamiltonian. So hydrogen, we rely on  $n$  and  $l$  to get almost everything. But here we find that, in addition to this being that small, it destroys the foundation of our picture. And so how do we think that we can make any sense of many-electron atoms and molecules?

Well it turns out we can hide most of the complexity. And most of the complexity is just working out the rules for calculating these matrix elements. The matrix elements of operators that we care about, like transition moments, spin orbit, Zeeman effect, things that correspond to how we observe atomic and molecular structure.

And so the main obstacle to being able to evaluate these matrix elements is the permutation requirement. And it turns out that there is a really simple way of dealing with the requirements for electron permutation, and that is to write the wave function as a determinant of one-electron orbitals. Because a determinant has three really important properties. One, it changes its sign when you permute any two columns. Two, it changes its sign when you permute any two rows. And three, if you have two identical columns or rows, it's 0.

That's really fantastic. And that is the Pauli exclusion principle-- not what you learned in high school. What you learned is a small consequence of that.

So if we can build anti-symmetric wave functions, we have aufbau, we can only put one electron in an orbital. We have all sorts of stuff, but it's too complicated to tell a student in high school that you can't-- just the question of indistinguishable electrons is such a subtle thing that you can't say, well, they have to be anti-symmetric. But it's easy to say, you can't put more than one electron in a spin orbital. But we don't talk about spin orbitals. We say, we can't put more than two electrons in an orbital, because we're protecting you from unnecessary knowledge. OK, well, I'm not going to protect you.

[LAUGHTER]

OK, so we know that the Hamiltonian has to commute with-- these capital letters mean, many electrons' angular momenta. And this is the spin, this is the projection of the spin. We know this is true because the Hamiltonian doesn't operate on spin. It's a trivial result, but it's a very important result.

OK, so we have to worry about spin, and spin eigenstates, and other things like that. OK, so Slater determinants. J.C. Slater was an MIT professor in physics. He invented these things in 1929.

I have a reference. I don't know if I've ever read this paper, but it's probably beautiful.

So basically what Slater did is showed, yeah, you can do the necessary algebra to deal with any atom, and to be able to reduce an atom to a small number of integrals that you really care about. And there are two ways of doing this. One is the truth, and one is the fit model. Now the truth is really boring, because you lose all the insights, and the fit model gives you the things you have to think about and understand. And a fit model also tells you what are the important actors. And maybe they're in costume, maybe they're not, but we can deal with them. But the truth is really very complicated.

And as I said many times, when you go from hydrogen to helium, you can't solve the Schrodinger equation exactly. This was perhaps a little bit of a surprise, but I think it was only a surprise in newspapers. I think physicists knew immediately, when you go from a two-bodied problem to a three-bodied problem, there is no way you can have an exact solution.

And that's the truth. You can't solve helium or any more-than-one-electron problem exactly. But you can do it really well, and it just costs computer time. And if the computer is doing the work, you don't really care. Because once you've told the computer the rules, then it's off to the races. You can go have lives or you can go have a life, and come back, and the computer will tell you whether you made a mistake and you're getting a nonsense result, or that you have the correct result.

So what we know is this permutation operator, operating on any two-electron function, has to make-- OK, I'm skipping steps, and my notes are really kind of stupid sometimes.  $P^2 = 1$ , which has to be equal to minus. And now if you apply the permutation operator twice, you get back to the same thing. So there's only two possible eigenvalues. You can have minus 1 or plus 1. And the minus 1 corresponds to fermions, things that have half-integer spin, like electrons. And the plus 1 corresponds to things that have integer spin, like photons, and vibrons, and other things.

And actually, it's harder to construct a symmetric function than an anti-symmetric function. But the thing is, you've got lots of electrons, and you have very few quanta of vibrations in a single mode, and you have very few photons interacting with a molecule at once. And so the boson symmetry is less important in most applications. And so we just have to kill this one.

OK, so suppose we want to talk about something like this, the 1s, 2s configuration. A configuration is a list of the occupied orbitals-- not the occupied spin orbitals, which is a spin associated with an orbital. The world of spin orbitals is where I live, but we do that for a reason. And so this two-electron thing can be expressed as a space part-- there are various conventions that-- times the spin part. And  $\alpha_1, \beta_2$ , and then we have minus or plus  $\beta_1, \alpha_2$ .

I'm looking at my notes because some people always keep the electron in the first position, and some people keep always the orbital in the first position. And it doesn't matter, because you can permute rows or columns. But I just want to write what is in my notes.

OK, so this thing, this two-electron function, has two anti-symmetrized possibilities. And one is a singlet, and one is a triplet. So  $s = 0$ ,  $s = 1$ . We recognize this  $\alpha\beta - \beta\alpha$  as the singlet spin state, and  $\alpha\beta + \beta\alpha$  as the triplet spin state. So we have  $\alpha\beta + \beta\alpha$ , and  $\alpha\alpha$  and  $\beta\beta$ , and we have  $\alpha\beta - \beta\alpha$ . So we call  $s = 0$  a singlet, and this a triplet, because of the

number of states. And this wave function has the necessary spin symmetry and the necessary permutation symmetry.

OK, so if, instead of two electrons, we have 1, 2 dot dot dot N, then Mr. Slater says we do this-- whoops. OK, N, 1, and then K1, and KN N. So that's a determinant-- an N by N determinant. And the rows correspond to the electrons, and the columns corresponding to the orbitals.

Now this, because of the properties of the determinant, is anti-symmetric with respect to permutation of any two electrons or any two orbitals. But we don't really care about the permutation of the orbitals, because it's really the same thing is permuting the electrons. And so this N factorial is a consequence of normalization, because when you expand an N by N determinant, you get N factorial, additive products of N functions. It looks horrible.

And because we're normalizing, we need this 1 over the square root of N factorial in order to have this thing come out to be 1 when you calculate the normalization integral.

Now this notation is horrible because you've got too many symbols. And so depending on what you're trying to convey, you reduce the symbols, and you can reduce it simply by, instead of writing psi every time, just writing the state. Or you can-- since you don't need psi, you don't need the state letter, you can just have the state number. But the best way to do this is simply to say-- this is just the main diagonal of the determinant. It conveys everything you need. Again, if you permute any two of these guys, any adjacent pair, the sign changes. And it contains everything you need, and it doesn't require you to look at stuff you're not going to use. And your goal is going to be to take these things, and calculate matrix of them. And so you'll be dealing with the orbitals one or two at a time. And this is very convenient. And soon, you start to take this for granted. And it's a very simple thing, but it isn't, because you're doing a huge number of tricks.

OK, I'm going to skip over what's in my notes. Demonstrating that for a two by two, that what I asserted is correct, you can do that very easily.

OK, so we can count, and we have an atom, and we know how many electrons it has. And so we immediately know what our job is going to be. We're going to be having to write some Slater determinant of those number of electrons. And the goal is to be able to do the algebra in a way that maybe you can't describe to your friends because it's too complicated. I'm faced with the problem of trying to explain how to do this algebra.

But it is something that you can learn, and you can ask a computer to do it, and there are all sorts of intuitive shortcuts where you can look at a problem, and you could say, I understand.

OK, so you're used to orbitals. And that's perfectly reasonable, because for hydrogen, we have orbitals, and there's only one orbital, and it could have either spin. We don't mess with that.

But now we're going to talk about spin orbitals. And that's just the combination of the name of the orbital with whether the spin is up or down. And the reason for this is it's easier to do the algebra. And the reason the algebra is-- it's initially harder to do the algebra, because there are certain selection rules, and stuff like that. But once you know how to do it you do the algebra. And then all of a sudden, everything pops out in a very useful form.

So the stick diagrams are very important. But now I'm specifying the stick diagrams as spin orbitals rather than orbitals. Now another point, there are rules for how-- the number of spin orbitals is different between the left-hand side and the right-hand side of a matrix element. There are rules that are easily described-- and so for every kind of orbital, an orbital that is a scalar, that doesn't depend on quantum numbers, that has a selection rule  $\Delta S = 0$ ; and for something like a one-electron operator that has a selection rule  $\Delta S = 1$  and  $0$ ; and then we have our friend  $1/r_{ij}$ , that has a selection rule  $\Delta S = 2, 1, \text{ and } 0$ . And the algebra for each is something you work out, and then you know how to do it. And I'm going to try to give you just a little bit of a taste of this.

So we already looked at something like this. But we use a slightly different notation. So I'm going to go back. And we have  $1s\alpha, 1s\beta, 2s\alpha, 2s\beta$ . And so for the ground state of helium  $1s^2$ , and we would do this.

And the stick diagrams are great, because it's easier to see on a picture, who are the actors, and have I included all of them, or have I left something out? And so now we're interested in the stick diagram for the  $1s2s$  configuration. And there are several kinds of  $1s/2s$  configurations, depending on what the alpha and beta are. So we have  $1s\alpha, 2s\alpha$ . And we have  $1s\alpha, 2s\beta, 1s\beta, 2s\alpha, 2s\beta$ . So there's four guys, and we can put our arrows on these things, and we know everything we need to know about these guys. It tells us what to do.

Well, when we do this, the diagonal matrix elements of the  $1/r_{ij}$  Hamiltonian can be expressed. And we use this notation,  $J - K$ . So for every two-electron thing,

we're going to get this kind of-- now these are simple integrals, and some of them are 0. Because this doesn't operate on spins. And so if you had a  $1s\alpha$ ,  $2s\beta$ ,  $1/r_{ij}$ ,  $1s\beta$ ,  $2s\alpha$ , then the  $1s\alpha$  with the  $1s\beta$  is 0. The  $1s\alpha$  with the  $2s\alpha$  is not 0, et cetera. There are all sorts of stuff.

But this tilde notation says, well, this is what we start with, and we have to convert it into things that really matter. So the operation of removing the tilde requires a little bit of work, a little bit of thought. And that's why my notes are crap, because I can't explain it well enough to really teach this.

So when we do the  $1s$  squared, the  $J$   $1s$  squared tilde, is equal to the  $J$   $1s$  squared, because the spins take care of themselves. But  $K$  tilde  $1s$  squared is equal to 0. Because when we do  $1s$  squared, we have an  $\alpha$  with an  $\alpha$  for the  $J$  term, and an  $\alpha$  with the  $\beta$  for the  $K$  term. And  $\alpha$  with  $\beta$  is 0, because the operator cannot change the  $\alpha$  into  $\beta$ .

So this tilde notation is a convenient thing, because you can use any Slater determinant, and you can express it in terms of  $J$ 's and  $K$ 's. And the sign comes from switching the order of the orbitals. That's how the determinants work. And so you're going to see a whole bunch of stuff. But removing the tildes is the tricky business.

OK, now when you get a problem where you have a configuration where a single Slater is not sufficient-- in other words, in order to make an eigenstate of  $s^2$  or  $s_z$ , you sometimes need two or more Slaters, and you have to use a particular linear combination of them to get the right value of  $s$  and  $s_z$ .

And then what happens is you're looking at matrix elements of the  $1/r_{ij}$  operator, between Slaters. Now this is a headache. And I could talk until I'm blue in the face, and I cannot make it clear how to do this. Because it's just awful. But some things in life are worth suffering for.

And so anyway, in the  $1s$ ,  $2s$  situation, when you do everything right, you get-- this is just a general notation for a two-electron wave function--  $1/r_{12}$ ,  $\psi^2$ . So these guys are eigenfunctions of  $s^2$  and  $s_z$ . And when you do that, you get  $1/2$  times  $2J$ ,  $1s$ ,  $2s$ , minus or plus  $2K$ ,  $1s$ ,  $2s$ .

Remember, when you have mismatched  $\alpha$  and  $\beta$ , the  $K$ 's are 0. But when you have  $K$ , the  $1/r_{ij}$  matrix element between two Slaters, you can fix that. And so this is why it's so hard to explain, because-- yes, I'm not even going to apologize anymore.

OK, so this is what you do. And the notes are pretty clear about how to do them, and what the problems are. But lecturing on it would be a little bit hard.

OK, so now what are we going to do with it? Well, we'd like qualitative stuff and interpretive stuff. Qualitative is Hund's rules. Now if you looked at 100 textbooks, I think 95% of them will have Hund's rules wrong. You're never going to make that mistake.

And interpretive-- well, we want to know the trends of things, and we want to be able to do something like what you did in freshman chemistry on shielding. Now you probably memorized some rules about what shields what. But I'm going to give you a little bit more insight into that. So we're going to talk about this for the rest of the lecture.

OK, so you specify a configuration. And this configuration might be two electrons, two spin orbitals, two orbitals times  $e$ , or three, or 10. And often, when you specify the occupied orbitals, you neglect the field ones, which is nice, because you have fewer things to worry about. Because field orbitals have spin 0. And you don't have to do anything. They're automatically asymmetricized, and they basically act as a charged distribution in the core that is sampled by the electrons outside. And so you need some sort of a set of rules for how does that work. And that's shielding.

So first, we specify a configuration. And you also learned-- in high school, probably-- how to determine the L, S, J terms that result from this configuration by some magical crossing-out of boxes. And if you didn't, I'm glad. Because it would have just clouded your mind, and caused earlier insanity than MIT causes.

So anyway, so we have orbital angular momentum. And we can add the orbital angular momenta of the electrons following certain rules. And we have spin angular momentum. And J is equal to the vector sum of L and S. And we say we have an LS term-- like triplet P. And it can have J is equal to L plus S, L plus S minus 1, down to L minus S absolute value. These are the possible J's.

And so Hund's rules is all about, of all of the states that belong to a particular configuration, which one is the lowest? One-- which one, not the second lowest. Which one is the lowest? And why do we care? Because in statistical mechanics everything is dominated by the lowest energy state. And so if you can figure out what is the lowest energy state, you've basically got as much as most people are going to want.

So you want to know what are L, S, and J for the lowest energy state of a configuration. Configurations are typically far apart in energy. So if you know what the lowest energy configuration is, and the lowest energy state of it, as far as your friends-- the statistical machinations, you can tell them how to write their partition functions. And the rest is details. And mostly, you don't want details. If your friends tell you they want details, well, you tell them, this is what you have to do, but it's no simple three Hund's rules.

OK, so Hund's rules-- you look at all of the L, S, J states that are possible for a particular configuration. And you can use the crossing out of ML/MS boxes if you want. And I could tell you why you would do that. But I don't want to cause insanity at this stage, either. But I'm an expert at that. And you can also use lowering operators to generate all the states, once you know stuff.

OK, so once you know all the states, Hund says, which one of these has the largest S? which one? And that's easy to know. And for example, if you had 2p squared, you're going to get singlet D, triplet P, and singlet S. And well, here's the triplet. That has the largest S. So the triplet P is the lowest energy state.

Now if there were multiple triplets, as there would be, say, for 2p3d, then you'd have to decide which of those triplets is the lowest. And all you care about, all you're allowed to say is which one is the lowest. And it's the one with the maximum L.

And then the last step is, what is the lowest J for that LS state? And that's kind of cute. Because you have the P shell, there's-- for a P shell, you can have six P orbitals to fill the shells. 1 alpha, 1 beta, 0 alpha, 0 beta, et cetera. So the degeneracy of a P orbital is 6.

If you have p to N, where N is less than 3, you have a less-than-half-filled shell. And then lowest is J equal L minus S, absolute value. And if N is greater than 3, you have the lowest being-- the highest possible value of J is equal to L plus S-- so for L, N greater than 3.

And now when you have a half-filled shell, the lowest state is usually an S state with maximum spin. But it doesn't matter. When you have less-than or more-than-half-filled shell, you have generally a state with orbital angular momentum not equal to 0. And you have spin orbit splitting of that. And so you do want to care what is the lowest J. But when N is equal to 3, the lowest state is usually an S state. It doesn't have a spin orbit splitting, and it just has one value of J, which is whatever the spin is.

So Hund's rules tell you how to identify, without knowing beans, what is the lowest energy state, and it's never wrong. Well, maybe sometimes wrong, but that's because of one of my things where you have a perturbation between states belonging to two configurations. But people get really excited when they discover a violation of Hund's rules. And it's just trivial. So there is this.

What time is it? I have a few minutes to talk about shielding, and I will.

OK, so we have a nucleus. And it has a charge of  $z$ . Bare nucleus-- there's no electrons, so the atomic number is the charge. And then we have a filled shell around it. It's spherically symmetric. And so if we penetrate inside of it, what we see-- suppose we penetrate inside, to this point, what we see is only the plus  $z$ , minus the number of electrons inside this sphere. Now if you took Electricity and Magnetism, you can prove this. If you didn't, you can accept it. And so outside the nucleus, the charge is plus one, because you have a neutral atom. And then when you penetrate inside this region of dense charge, and all of the spins are generally paired, this is spherical. So what you end up seeing is  $z$  effective, as opposed to  $z$  true. And let's say here here's  $r_0$ -- or this is  $r_0$ .

And so beyond  $r_0$ , the charge that you see is plus 1. Add 0, you see a charge of  $z$ . And so what ends up happening is you get  $z$  effective, which is dependent on distance from the nucleus. And it goes from the integer value that you know, from the atomic number, down to 1, because you've taken one electron away from a neutral atom, and taken it outside.

And now we have this wonderful thing called the centrifugal barrier. So if we have a state that has a non-zero of  $l$ -- well, if we have a state with a zero value of  $l$ , it can penetrate all the way into the core, to the nucleus. And so that means that the shielding is less for  $s$  orbitals.

And now if we have a non-zero  $l$ , it can't get in so far. And the larger the  $l$  is, the less it can see this extra charge. So high  $l$ 's are very well shielded. Low  $l$ 's are not so well shielded. And the shielding goes  $s$  least shielded,  $p$ , less, so on.

Now there's some other interesting things. Which, you know, I hate to say this, but comparing 5.111 or 5.112 to 3.091, there is this business of what happens when you start to-- you start with potassium, and so you put an electron in the  $4s$ , not in the  $3d$  orbital. Right? Why is that? Well, the  $4s$  sees the larger charge is less shielded. So it goes in. Then when you go from potassium to calcium, you put another electron in this. And that's true. So for calcium, you have a  $4s$  squared. And  $4s$   $3d$  is a higher-lying state.

Now you take an electron-- I'm cooking my own goose. If you take one of these electrons away-- this is not the way I wanted it to come out-- you find yourself in a 3d state. Because 3D penetrates a little bit under 4s. I can't explain it in a way that's going to make sense. I really wanted to, because I care so much about these simple arguments. But I will just be wasting your time.

So the order in which you feel orbitals comes out, naturally, different from the order in which you remove electrons from orbitals. And the shielding arguments are capable of explaining that.

OK, so this is the end of atoms. And I've asked you to observe some complicated algebra which you're never going to do, or at least never going to do much of. Everything you need to know about atoms, you can tell a computer, and it can do it.

Now molecules are much more complicated. And that's we're going to start on next time. We're going to start with molecular orbital theory.

And I'm not going to be presenting the normal textbook approach. I'm going to present an interpretive approach, where you understand why things happen, as opposed to memorize just symmetries, and filling orders, and so on.

OK, I'll see you on Wednesday.