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PROFESSOR:

Good afternoon. So last week, we started our discussion of atoms.

So these are, of course, the key players in a course of atomic physics. And we will reveal the structure of atoms going from the larger energies to the smaller energies.

That means we start with electronic energies mainly determined by Coulomb energy. And then we go to finer levels which are fine structure, hyperfine structure, Lamb shift, and all that.

So we have started last week to discuss the Schrodinger equation, discuss hydrogenic energy levels, and I pointed out some important results on typical length scales and the scaling of the wave function.

We will meet that later today. But before I continue with atomic structure, I want to start today to discuss the units. The atomic units we are using to describe the atom.

So the nat-- and for every problem in physics, you have what one may call natural units. And for us these are also called the atomic units. So what are atomic units?

Well, atomic units are the units for length, for energy, for velocity, for electric field. And all of these units, you should be able to construct them out of fundamental constants. The fundamental constants which appear in the Schrodinger equation for the electron within the atom are the charge of the electron, the mass of the electron, and \hbar .

Now, is there any other fundamental constant we should include here to construct our natural units? c , good question. What about c ? The speed of light. Should the

speed of light be part of our system of atomic units?

Let's not go there.

[LAUGHTER]

Because if you set it to one, you have made a choice. You have constrained your system. And you're almost obscuring the fact whether it should appear or not.

Well, the strong message I want to give you is at the level of electronic structure, at the level of the Schrodinger equation, it should not be there. Because we are talking at this point about solutions of the Schrodinger equation, the hydrogenic levels.

And there is no c , no speed of light in the Schrodinger equation. So c is not part of the fundamental constants we have to consider now. It will later come in the fine-structure constant, but this is a different story.

So we have three units, e , m , and c . And you can just play the game of combinatorics and see can you find a length which consists of those three units. And, well, it's $h^2 / m e^2$.

This is how you get the unit of length. And this length is called the Bohr radius. And indeed, this is sort of the RMS size of the electron in the 1s state.

You can play the game again and ask, can we construct an energy? Well, you find that if you take e to the four, if you take the mass and finally divide by h^2 , then you have a unit of energy.

And this unit of energy turns out to be one Hartree or 27.2 electron volts or two Rydbergs, twice the binding energy of the electron in the 1s state.

And we had some discussion last week that the factor of two reflects the virial theorem. This is actually that one Hartree is the Coulomb energy of the electron in the 1s state, which is the binding energy.

But then half of it is kinetic energy. And, therefore, the total energy of the 1s

electron is half the Coulomb energy. And it's that.

But no. OK, so, so far no c . The energy, the energy levels, the wave function. If there is no c , no speed of light in the Schrodinger equation, there is no c in the solution of the Schrodinger equation.

And if you set it 1, sure, it wouldn't-- I mean, if your relativity equation said c equals 1, you obscure the fact. But here, it's definitely not there.

But now we can also see, well, there are other important energies. One energy, and now I bring in the c just because I want to compare two energies which include the speed of light, the rest energy of the electron.

Or a very fundamental unit of length is \hbar/mc . Which is the Compton wavelengths. So that's λ_{Compton} , the Compton wavelengths of the electron.

And, well, if we try to figure out what is the ratio of the atomic unit of lengths. And the Compton radius, we have to multiply with a dimensionless unit which is hc over e^2 . Or if I take the reverse, e^2 over hc , $\hbar c$.

And similarly, here the dimensionless quantity to multiply is that. So what do we find now here is we find that what we get is a quantity which I want to call α , the fine-structure constant. And what I find here is the same constant, α^{-1} , times the Compton wavelengths.

Let me discuss the fine-structure constant in a second, but there's still two more atomic units we want to discuss. There is the velocity and there is the electric field.

I can simply get the velocity by saying, well, the velocity enters the kinetic energy in mv^2 . And if I said mv^2 , I want to skip all factors of unity. So that's not one half, it's just mv^2 . And if I said mv^2 equal to one Hartree, then I find that the atomic unit of velocity is e^2/\hbar . But this turns out to be αc . So again, what we find is α , the fine-structure constant.

α is, of course, dimensionless. It is $1/137$. So therefore, we see that if the velocity-- and this is actually the orbital velocity of the 1s electron. If this is α

times c that confirms that the electron non-relativistic.

We have solved the non-relativistic Schrodinger equation for it. And consistently, we find that the velocity of the electron is $1/137$ of the speed of light. It's actually physics trivia.

If somebody asks you how fast is the electron in the hydrogen atom, about 1% of the speed of light. Of course, if you had solved the non-relativistic Schrodinger equation.

And you solve it for, let's say, a naked uranium nucleus where z , the charge of the nucleus, is 92, then you find that this fine-structure constant times z is on the order of unity.

You would find that the electron moves at the speed of light. And then you realize, gosh, I've solved the wrong equation. Because a non-relativistic Schrodinger equation when the solution is that something moves at the speed of light, I'd better start with a different equation.

But here, we find we are consistent. An electron in the hydrogen atom for low nuclear charges of a few hydrogen, helium, and so on is non-relativistic.

So let's just finish that. The electric field is the electric field felt by the electron which orbits the nucleus on the 1s shell. And this is 5.1×10^9 volts per centimeter.

So everything I've constructed here out of the three fundamental constants, e , m , and h are typical for the 1s electron for the ground state of hydrogen. We got the typical lengths, the Bohr radius, the typical energy, the Hartree, the typical velocity, which doesn't have a name, and the electric field experienced by this electron.

So let's now talk about α . So α is dimensionless. It is, you know, if a constant has dimension like \hbar , like c , actually the value of it reflects our system of metrology.

If you define the second in a different way, \hbar will change. c will change. So a lot of constants are not fundamental constants, being fundamental to the physics at hand. They are more kind of translating our metrological system into the equations we use to describe our system.

But if something has no dimension, it is not related to a unit like the kilogram or the second, it has really fundamental importance. So, therefore, α is the fundamental constant in atomic physics.

And if you have a fundamental constant, ultimately, there should be a theory of everything which should ultimately predict the value of α . Which, ultimately, we predicted by a complete theory.

So α , the fine-structure constant, is smaller than 1. It's $1/137$. And the fact that α is smaller like 1 is often phrased in these words. That since α is much smaller than 1 that this implies the electromagnetic interactions are weak.

OK, I want to explain that. I mean, I've heard this many, many times. But what does it mean interactions are weak? So let me give you sort of my, in 90 seconds, sort of my spiel on it. Why does α mean that the electromagnetic interactions are weak?

Well, we have to compare the electromagnetic interaction to something else. And the result will be for this situation I create, the electromagnetic interactions are weak.

Electromagnetic interactions of the Coulomb field gets, of course, stronger, and stronger, and stronger the closer you move two charges together. So what does it mean that the Coulomb interaction is weak? Weaker compared to strong interactions or other interactions.

Well, let me try to justify it as follows. We cannot go to epitary small distances. We can do it in classical physics, but not in quantum physics. So if you go to very small distances, if you localize particles very tightly, they have a lot of momentum uncertainty.

The momentum uncertainty means energy uncertainty. And the energy uncertainty may mean that we can create electrons and positron pairs.

So the moment we have an energy uncertainty, by our definition of bringing two particles close together, and this energy uncertainty is larger than the rest mass, we have to be very careful. We can no longer use a single particle description, or our concept of single particle physics breaks down if you have seen the particles prepared with an energy uncertainty, which would spontaneously create more particles.

So therefore, let me postulate that our picture how we think about those interactions, arranging two charges and writing down what the Coulomb energy is. That if energy uncertainties become on the order of the rest energy, then the concept of single particles breaks down.

Of course, that's not the end of physics. You need now a field theory for particles where particles are just excitations in your field. But here in atomic physics, you want to describe an electron bound to a nucleus. And we want to use those concepts.

So let's just sort of say, what does it mean with $\Delta E \approx mc^2$? Well, that means the momentum uncertainty is on the order of mc . And with this momentum uncertainty, I can localize particles to within \hbar/mc . And this just turns out to be the Compton radius of the electron.

So, therefore, I should be careful when I talk about the Coulomb energy between particles if I would go closer than the Compton radius. So, therefore, let me compare now the Coulomb interaction at the Compton radius to something else.

So these Coulomb energy is e^2/r at the Compton radius. And this turns out to be $e^2/mc\hbar$.

So unless I want to get into quantum field theory of particles, before I need a different description, the strongest Coulomb interaction I can create by putting two

particles at the Compton radius is that.

And I can now compare this Coulomb interaction, the Coulomb energy, to the rest energy, mc^2 . And, well, if I take what I had above, $e^2 mc / \hbar$, I divide by mc^2 .

I find that e^2 , that the result, the ratio, is $e^2 / \hbar c$. And this is just α .

So in other words, what I've shown to you, if you try to bring two charges as close as possible before spontaneous pair production sets in, then you find that the Coulomb energy is not the dominant energy in the system. The dominant energy is the rest energy, is the mass of the electron itself.

And the ratio of those two energies at this point is, of course, completely independent of what metrological system you use for energy lengths and such. It's really something which says something fundamental about the nature of interaction.

And what I just presented to you leads to the statement that the Coulomb interaction, the electromagnetic interaction, is weak. Because the fine-structure constant is much smaller than unity.

Of course, if you use a nucleus of uranium, naked uranium, and people have ion traps where they create uranium 92 plus and then they add an electron, you're really studying very interesting physics.

You're studying the physics of an electron for which the effective fine-structure constant is on the order of unity. And that's why people are very interested in it. And that's one area of current research.

Any questions?

OK, so that's our little excursion about units. Let's talk now about some general properties of one electron atoms with cores.

A lot of research in our field is done with alkali atoms. Alkali atoms are not the

hydrogen atom. But they have one outer electron. So they are hydrogen-like.

And now we want to sort of figure out what is the main difference because for one outer electron in rubidium and sodium. And the electron in hydrogen.

Well, if we have an electron. And this electron orbits around. In the alkali atom, there is an ionic core which has a charge of z plus. But then in this sort of compact core, there are also $z - 1$ electrons.

So the electron, the outer electron pretty much feels the electric field of a single charge, but there is a the of the core. So what I want to discuss with you is now what is the leading correction to the properties of this atom?

What is the leading correction to the hydrogen-like wave function due to the fact that we have an ionic core and not a proton.

So for hydrogen, we would have the Rydberg formula. that for principal quantum number n , the energy is-- oh, just one second. Yes.

OK, the hydrogenic energy would be z^2 times the Rydberg constant divided by n^2 .

I'm confused about the factor of z^2 , which I clearly have in my notes. I have to read up something about it. Let me take it out here.

You know, we have a charge of z . But what I'm talking about is one electron which is very far away from the nucleus. And this one electron fields, in effect, only a single charge. And so, ultimately, you would expect that the Rydberg spectrum, if you go to higher and higher end, would actually converge to the Rydberg spectrum of hydrogen which would not have the factor of z^2 .

I hope I'm not overlooking something, but I'm just correcting my notes on the fly. So this would simply be what an electron would do in the Coulomb field of a single charge. And the question is, what is the leading correction to this formula?

And I want to ask it as a clicker question. So that's the effect, that we have an ionic

core. Does it make a constant offset to the binding energy?

Or does it make the correction which, of course, is $1/n^2$. This would just scale the overall spectrum. It would actually lead to a modified rescaled Rydberg constant.

Or is the correction higher order in n ? Or finally, is it a correction which changes the effective principle quantum number n ?

Maybe you know the answer or maybe you want to try to guess the answer. So these are the four choices.

Of course δ has different units. I just used the same symbol for the correction term. But depending whether it appears it has units of energy or if it appears in the denominator with n , it is dimensionless.

AUDIENCE: Aren't these questions also C and D [INAUDIBLE]?

PROFESSOR: Yes, this is the first thing I wanted to tell you, that answers C and D are the same. Because if we assume δ is small and you do a Taylor expansion of the denominator, you just get this.

So c and d are actually equivalent. And so if I add up 20 people voted for c and d, which is equivalent.

So this is equivalent by Taylor expansion. And, indeed, this is also-- this time there's two correct answers.

So let me quickly derive it. The derivation is short. And it adds some insight. We want to do perturbation theory.

And in perturbation theory, we simply take the wave function of the simplified Hamiltonian and ask what is the energy correction due to the fact that we have a finite core size? Since the finite core is near $r=0$ at the origin, we only need the scaling of the wave function close to the origin. And this is r^l . And we have n to the power $3/2$, as we discussed last week.

So our Hamiltonian is now the Hamiltonian of the hydrogen atom plus a perturbation term. And the perturbation term is the derivation of the potential experienced by the outer electron, the deviation from a pure Coulomb potential.

So the energy correction, E_n , is the expectation value of the hydrogenic wave function with the perturbation Hamiltonian. And the only thing we have to know about the perturbation Hamiltonian is that this Hamiltonian is localized around the origin.

And then we immediately find because of the scaling of the wave function with n that this is $1/n^3$. And it's proportional.

And by factoring out the Rydberg constant, R , I can parameterize this matrix element with a quantity, δ_l , which is dimensionless.

So that means that the binding energy is the hydrogenic binding energy plus this correction. And then to leading order in δ_l , it's identical to this result.

And this parameter, δ_l , which is characterizing a whole Rydberg series for all n values for given l , this is called the quantum defect.

So people realized early on in the early days of quantum mechanics before they understood it that the spectrum of many atoms followed a formula which was not $1/n^2$ is hydrogen. It was $1/(n - \delta_l)^2$. They didn't understand it. But this is, of course, now the derivation.

There are many other derivations which you may enjoy reading about it in our atomic physics wiki. There's a derivation using the semi-classical approach and using the very nice physical picture that an electron, when it comes close to the core, experiences scattering phase shift.

And this scattering phase shift is directly related to the quantum defect. Or you can make a model Hamiltonian which is exactly solvable where the perturbation Hamiltonian is not completely localized at the core.

But it's proportional to $1/r$ squared. And then you can exactly solve it because you have already a term which is $1/r$ squared in your Schrodinger equation. Which is the centrifugal term.

So therefore, the perturbation is only redefining the centrifugal term. It's redefining what l is. And eventually, you can solve it directly.

Questions?

OK. Then let me spend five to 10 minutes on spectroscopic notation. So the next five or 10 minutes, how we describe the configuration of an atom, well, I don't particularly like to teach it.

Because it's more nomenclature about old-fashioned symbols. On the other hand, if you're working with atoms, you have to learn the language how to describe atoms.

And I also know that an appreciable fraction of oral exams there will be one person in the community and say, what is your favorite atom? And what is the configuration of your atom? So it's something if you're an atomic physicist you're supposed to know.

So the spectroscopic notation, the term designation focuses on the fact that if you have an isolated atom, we have angular momentum conservation. And so we have at least two quantum numbers.

Which are sometimes also two good quantum numbers. We have some approximate quantum numbers where we have additional terms which break certain symmetries.

But an isolated atom lives in isotropic space. The total angular momentum of this atom is conserved. It's absolutely conserved. It's absolutely good quantum number. And the good quantum numbers is the total angular momentum, j , and its protection energy.

So in the language of atomic physics, we call j a level. It's different from states. So one level has now $2j + 1$ sub-levels or states.

So usually when we talk about a level, we assume the level has degeneracies because there is the M_j quantum number.

So j , you're talking about electronic structure. So j can have, when we have an isolated atom, can have contributions from several electrons.

It can have contributions and these electrons can contribute through spin, s , and orbital angular momentum, l .

In many situations, especially with alkali atoms, the inner core is completely filled shell. There is no s , no l from the inner electrons which contribute. And all the contribution with the angular momentum comes from the outer electron.

Especially for the lighter atoms. The non-relativistic atoms. The different electrons undergo l s coupling.

In other words, if you have multiple electrons, their orbital angular momentum couple up to the total orbital angular momentum, l . And all the spins couple up to the total spin, s .

So therefore, before we introduce spin orbit coupling, l is a good quantum number. s is a good quantum number. And then they couple to a good quantum number, j . Of course, once l and s couple to j , orbital and spin angular momentum precess around the total angular momentum.

Anyway, I just want to say when I talk about j , what are possible ingredients? So let's assume we have an atom which has total angular momentum, j . And which is the sum of orbital angular momentum and spin angular momentum.

And then in this case, we use a term designation. A level is designated by a term which is written as l , the value of orbital angular momentum.

The spin multiplicity, $2s + 1$ is an upper left index. And a lower right index is j . And of course if l is 0, we use the letter s , p , d . This is sort of the historic letter designation for l equals 0, 1 and 2.

So in other words, if you have an atom where the total angular momentum is composed of orbital angular momentum and spin, you can always write this symbol. And this symbol is the term designation which characterizes the state, the ground state or an excited state of your atom.

If you have the hydrogenic atom, often you precede the term by the principal quantum number, n .

So let me give you an example. If you have the sodium atom, the outer electron has n equals 3. It has 0 orbital angular momentum.

It has spin $1/2$. And $2s$ plus 1 is 2. And the total angular momentum is $1/2$.

If you go to the first excited state, you're still in n equals 3. But you have promoted the electron from an s state to p state. So, therefore, the orbital angular momentum is now 1 designated by p .

The spin is still spin $1/2$. But now orbital angular momentum of 1 and spin $1/2$ can form a total angular momentum which can either be $1/2$ or $3/2$.

So if you're asked what is the state you prepare your atom in, you would give it a symbol 3 doublet p $1/2$. And I've explained to you what it means.

There is one addition. And sometimes you want to not just mention what is the principle quantum number of the outer electrons. Sometimes you want to specify the whole configuration.

So this would mean you want to sort of build up the electron shell and say that I have two electrons in $1s$, two electrons in $2s$, one electron in $2p$, and so on. So you use, I think this would now be beryllium atom?

$1s$. So $1s$ is hydrogen, $1s^2$ is helium. Then we go to lithium.

AUDIENCE: [INAUDIBLE] is boron.

PROFESSOR: It's boron, no? OK, so this would be boron. So what we use is here we use the

products. We use products of symbols n, l, m .

So to come back to the example of sodium, so sodium is filled up. As in the first shells. So it's $2p^6$. And then we have one electron, the outer electron in $3s$.

However, let me point out that this way to specify the configuration strongly depends on a hydrogenic model. It assumes that the electrons are non-interacting. And is, therefore, an approximation.

In contrast, the term designation with a total angular momentum is always exact. Well, at least the total angular momentum is an exact quantum number. Whereas the configuration is based on the independent electron approximation in hydrogenic orbits.

And usually when you have a real atom and you calculate with high precision what the electronic wave function is, you find actually that total many-body wave function is a superposition of many such configurations.

But as long as one configuration is dominant, this configuration designation makes sense. Any questions?

OK, so we come back to the hydrogen atom when we discuss smaller features of the energy levels. Fine structure, hyperfine structure, and so on.

But in our discussion of electronic energies, that's all I want to say about one electron atoms. So let's now proceed and discuss the helium atom.

So we want to understand now what are the new effects when we have not only one electron, but two electrons. And don't worry.

We are not proceeding to three, four, five electrons. I think to go from one to two, we actually capture the most important state. Namely, the interaction between the two electrons and what the results of that is.

For the helium atom, there are some excellent treatments in standard textbooks of quantum mechanics. One is the famous quantum mechanic text by Cohen-

Tannoudji et al. But also the text of Gasiorowicz.

The reason why I have added the helium atom to the curriculum is because it is a simple system where we can discuss singlet and triplet states. And singlet and triplet configuration is important for population of inoptical lattices for quantum magnetism and such.

Actually, you can say if you have two electrons and they align in a triplet state or a singlet state, one you can say is ferromagnetic. The other one is paired and antiferromagnetic.

It's the simplest example where we can discuss magnetism. So that's my motivation why I want you to know something about the helium atom.

So, therefore, let's now discuss energy levels of helium. And let's just start with the most basic model.

The helium atom has two charges. So if you regard it as a hydrogen problem and we put two electrons into the 1s state, we would expect that based on the hydrogenic model that the binding energy of that is, per electron, is the Rydberg energy as in hydrogen.

But now we have to scale it with z squared, the nuclear charge. And this gives us a factor of 4. So we would expect that per electron, the binding energy in the more simple hydrogenic model is 54 electron volt.

So that would mean that the binding energy of the ground state is minus 108 electron volt.

However, the experimental result is that it's only 79 electron volt. So we find that there is a big discrepancy of 29 electron volt. Which is really huge.

So what is responsible for this big discrepancy? Well, what we have neglected, of course, is the interaction between the two electrons.

So we can fix that in the simplest way by keeping the wave function from the

hydrogenic model. But now calculating the electronic energies, the electron-electron energy, by using the electron-electron interaction as a perturbation operator.

So we still use as the wave function for the ground state, electron 1 in the 1s state.

So 1-0-0 is a designation for n, l, m for the hydrogenic quantum numbers. And we assume that the ground state is simply the product of two electrons in the 1s state.

So if I calculate for this perturbation operator the expectation value with this ground state, we find that there is an energy correction which is 34 electron volt.

So this removes most of the discrepancy. You can improve on it by a variation wave function if you use hydrogenic eigenfunctions as your trial wave function.

But you are now calculating those hydrogenic wave functions not for nuclear charge 2, but in nuclear charge z , which you keep as a variation of parameter.

You find that you find even better wave functions. And you can remove $2/3$ of these remaining discrepancy of five electron volts. This variational wave function is left to you as a homework assignment.

So where z is z equals 2 is replaced by a variation of parameter. Anyway, that's all I want to tell you about the ground state of helium.

It's pretty much finding a wave function which correctly captures the Coulomb energies. The interaction between the two electrons.

But what is much more interesting, and this is what I want to focus on for the rest of this lecture, is what happens in the excited state. Before I do that, let me just tell you what we just discussed.

So we have to this hydrogenic estimate and eventually the Coulomb energy raises the energy level to what we have just discussed. But, you know, as the ground state has no degeneracy.

And so we all talk about quantitative shifts. However, when we go to the excited

state, we will find the degeneracies. And degeneracies are much more interesting because something which was degenerate can split. You have two different terms.

So suddenly there is richer physics. So, therefore, we want to discuss now the excited state. So starting again with the hydrogenic model.

In hydrogen, the 2s and 2p state are degenerate so we have two configurations contributing to the same energy. 1s 2s and 1s 2p.

The binding energy in the hydrogenic model is a quarter of a Rydberg. Rydberg over n^2 and ns^2 . We have to scale it by z^2 . And we find 13.6 electron volt.

But now what happens is that we have to introduce the Coulomb energy between the electrons. And if you do that, it shifts up the levels in different ways. So this is 1s, 2s. This is 1s, 2p.

So why is this different? Well, you can say the following.

You have two electrons. And you have the helium nucleus. And you first put in the 1s electron. And now the second electron when it is in a p state, in a 2p state, it's further out.

And it pretty much experiences out there the charge of the helium nucleus shielded by the 1s electron. And, therefore, it sees in effect a smaller nuclear charge.

Whereas, the two s electron penetrates deeper. Gets closer to the nucleus and will still realize that the nucleus has a charge of 2. And not a shielded charge.

So, therefore, you would expect that the shielding effect due to the innermost electron is more important, has a bigger effect for the 2p electron than for the 2s electron.

So let me just write that down. So the 2p electron it sees a shielded nucleus.

In other words, what it experiences more as an inner core, the Coulomb potential of

helium plus. And not so much of helium 2 plus.

This is due to the 1s electron. And, therefore, the 2p electron has a smaller binding energy.

It's actually comparable to the binding energy of the 2p state in hydrogen. Which is on the order of 4 electron volt. And this effect is smaller for the 2s state.

So let's go back to the energy diagram. So we have now the situation which I just described. We have two degenerate configurations for in the hydrogen model.

And when we add in Coulomb energy between the electrons, there is quite a big splitting of several electron volts. But now, each label undergoes further splitting. And this is what I want to discuss.

So we are still sorting out just the preliminaries. What I really want to discuss with you is the singlet and triplet thing. But now we are there where we can do it.

So if you have a configuration with 1s, 2s, there are two possibilities for the total angular momentum. Two electrons in an s state, there is no orbital angular momentum.

But there are two spins, $1/2$. And they can add up to 1 or can add up to 0. So, therefore, we will have two different terms.

One is singlet s_0 . And one is triplet s_1 . And this splitting is 0.8 electron volt. And this is what we want to discuss in the following.

For completeness, but the physics is similar, let me mention that the 1s, 2p state also gives rise to two terms. We have now the total orbital angular momentum, p . Orbital angular momentum of 1.

The spin angular momentum is 0 or 1. So we have singlet and triplet. And the total angular momentum is 1 in this case. Or in this case, 2, 1, or 0.

And the splitting in this situation is also on the order of a fraction of an electron volt.

So what we want to understand now is why do we observe a splitting between those two levels which seems to depend on the spin? How can the spin cause a splitting?

Because the spin so far has not appeared in our Hamiltonian. We rarely have a Hamiltonian which has only the Coulomb energy. And the spin is not part of it.

So we don't have a magnetic field to which the magnetic momentum of the spin would couple. And also we have not yet introduced spin orbit coupling. But if this is on your mind, take it off your mind.

Spin orbit coupling is a much, much smaller effect. Energies on the order of 1 electron volt, you just cannot get from spin orbit coupling. Spin orbit coupling is smaller than electronic energies, as I will explain to you on Friday, is smaller by the fine structure constant.

So the typical scale for spin orbit coupling is maybe 10 or 100 million electron volt. It's much smaller.

So, therefore, we want to understand now why do we have a spin dependent energy. Also we haven't coupled at this point the spin to any field.

OK, so we are focusing now on the splitting. So we have the 1s, 2s configuration. We get two terms, as I just discussed.

One is singlet and one is triplet. And still using the hydrogenic model of non-interacting electrons, we want to write down the wave function.

So the wave function of the twin electrons is we have one electron in the 1s state. We have one electron in the 2s state. But now since we have fermionic atoms, we have to correctly symmetrize it.

So whether we want the symmetric or antisymmetric combination, we exchange the two electrons. So now we have r_2 and r_2 in reverse order.

Of course, the total wave function for two fermions has to be antisymmetric. But the total wave function is the product of the spatial wave function which I just wrote

down times the spin wave function.

The spin wave function can be antisymmetric and symmetric. And the antisymmetric spin wave function has to combine with the symmetric spatial wave function, and vice versa, to make sure that the total wave function is antisymmetric. And the correct description for fermions.

The designation here, symmetric and antisymmetric for the total wave function reflects the spatial part. The total wave function, of course, including the spin wave function is always antisymmetric.

OK, so we have two wave functions. One has a symmetric spatial wave function. The other one, an antisymmetric.

The symmetric spatial wave function has an antisymmetric spin wave function. And that means we have $s = 0$.

That's up, down, minus down, up is antisymmetric. Where as the antisymmetric spatial wave function goes together with the symmetric spin wave function $s = 1$.

So this is the situation which gives rise to that triplet $s=1$ term. And this here is the singlet $s=0$ term.

OK. As long as we have non-interacting electron, the two wave functions are degenerate. But now we want to bring in the Coulomb energy between the two electrons which we had already discussed before.

And if you calculate the energy using this as a perturbation operator, well, remember the wave function had two parts.

It was $100, r_1, 200, r_2$. And the part where our 1 and our 2 were flipped. And now if we have the wave function, the perturbation operator, we get a total of 4 terms.

2 times 2. We have to sort of x it out. And we will then have the sort of diagonal parts. And we have the parts which are off diagonal. And for the off diagonal parts, it

matters whether we had the plus or minus sign.

You know, if you have plus, plus and minus, minus, you give a positive contribution. But if you connect the wave function before and after the operator, plus with minus, we get minus signs.

So in other words, we have one contribution where it doesn't matter whether we have the symmetric or antisymmetric spatial wave function.

But then we have another term where it matters whether we have the symmetric and antisymmetric wave function. That's where the plus or minus sign from the symmetrized wave function appears.

So we have two contributions now to the energy correction. One is independent of the spin wave function whether we have the symmetric or antisymmetric configuration. The other one is not.

The first term is called the Coulomb energy. The second term is called the exchange energy.

So what we find is-- we have to trace back the sign, but you find that the triplet state symmetric in spin. And antisymmetric in the spatial wave function.

Has the lower energy, is more strongly bound because the antisymmetric spatial wave function reduces the repulsive interaction between the two electrons.

So in other words, we do not have any spin term in the Hamiltonian. It's just that whether the spin wave function is symmetric or antisymmetric, it requires the spatial wave function to be the opposite.

And now when we calculate the Coulomb energy for the spatial or antisymmetric spatial wave function, we find a big difference. And the big difference is the exchange energy.

So it is a spin dependent term for the total energy. But what is behind this energy is simply the Coulomb energy. So the spin through the symmetry of the wave function

leads to a difference in the Coulomb energy.

And actually what I'm telling you is the explanation why we have magnetism at room temperature. It was Heisenberg's idea when he realized for the first time what can cause ferromagnetism.

It was pretty much the model of the helium atom expanded to many, many electrons in a lattice. So the result is that the Curie temperature of thousands of degrees, we have magnetism below 1,000 degrees.

This energy scale is an electronic energy, is in Coulomb energy scale and not an energy scale where spin interactions comes into play. If it were not for the exchange energy, we would not have magnetic materials above 1 calorie.

So this is what you see here in the helium atom. How speed leads to an energy splitting which is an electronic Coulombic energy splitting.

OK, let's make it maybe even more obvious. The above equation can be rewritten. So this energy splitting can be written as a constant, alpha, plus a constant beta, times the product of s_1 and s_2 .

Well, what happens is-- let me just give you as a sidebar, the product of s_1 and s_2 can be written as $s_1^2 - s_2^2$, plus s^2 .

s_1^2 is one half times $3/2$, it's $3/4$. s_2^2 is $3/4$. And s^2 is either 0 or 2 depending whether you're in the singlet or triplet state.

In other words, I just want to with the sidebar, which you have seen many, many times, just remind you that the product of s_1 and s_2 has only two values. One for the singlet state, one for the triplet state.

So, therefore, if I have a singlet level and a triplet level, I can always parametrize it like this. And I can make it more obvious by showing what this formula on the right hand side has two values.

One for s equals 0. And one for s equals 1. And this can be rewritten as alpha. You

find a more explicit calculation in the [? video, ?] but it's also just one more line of algebra. You can write it in the following way.

So, therefore, the alpha and beta parameter are just a way of, you know, you have two energy levels. And with two constants, you can always describe two energy levels. Here, I've done it with alpha and beta.

But before, I did it with the Coulomb energy. And the exchange energy which we obtained in this equation when we perturbatively calculated the integral.

So by writing it as $s_1 \cdot s_2$, I even suggest that the two spins interact like a dipole-dipole interaction. But they don't. It comes from the Coulomb interaction, but it is equivalent to a gigantic dipole-dipole interaction.

So, therefore, the conclusion of this is that what I have derived for you for the helium atom, it looks like a ferromagnetic spin-spin interaction.

And, well, it looks like it, it is actually an effective ferromagnetic spin-spin interaction. However, the coupling is purely electrostatic here and not magnetic.

Questions? OK, yes?

AUDIENCE: So since we're still using the hydrogenic wave function as a basis, how closely does this get to the actual measured values?

PROFESSOR: The question is, how close do we get with hydrogenic wave functions to the actual measured energy? I don't know.

I don't know the exact numbers for the excited state. I assume that it's similar to the ground state. You saw that for the ground state, we had a big discrepancy. Most of that was closed by using hydrogenic wave functions. And just calculating the perturbative terms.

So you pretty much get qualitatively or semi-quantitatively, you get the picture out of it. And unless you're really interested in the absolute values, you can stop there.

But one way to go further and reduce the discrepancy by 75% is to use this variational wave function where you use hydrogenic wave function, but you use z , the nuclear charge, as a variation of parameter.

And I mean, this is, I mean, it's amazing. I mean, you have a two electron atom and you use a hydrogenic wave function with one free parameter. And you get binding energies which are on the order of 70 electron volt accurate to within better than 3%, 4%, 5%.

But by adding other terms or using a little bit more fancy wave functions, I'm sure you can get further and further.

OK, so the last thing I wanted to discuss is the new feature of two electrons is that we have singlet and triplet levels.

So we have a letter of states which are singlet states. And then, and this is what we just discussed, let me just make dashed lines. Because of this ferromagnetic spin-spin interaction, we have triplets states which have lower energy.

So these are n equals 2 triplet states. n equals 2 triplet states. j equals 1. j equals 0, 1, 2.

So of course, there are transitions between those levels. And from a p state, you can have transitions down to an s state. The question I have is what about possible transitions between triplet and singlet?

So what I want to ask you know with a clicker question is what kind? So those transitions here are transitions between singlet and triplet.

And the technical term for transitions between singlet and triplet are intercombination lines.

So the question I have for you is what fields or couplings drive singlet triplet transitions?

So I want you to think about the model we have discussed so far. All we have is

Coulomb energy. Coulomb energy between the nucleus and the electrons. And between the electrons. That's it.

We do not put any other terms into the Hamiltonian. And now we have obtained those wave functions. We have obtained those energies splittings. And now we want to ask are there transitions possible?

So one possibility is that we can drive the transition with optical fields. Let's say our dipole operator. Which many of you have encountered in life.

We have already discussed rotating magnetic fields in the first part of the course. Is it possible to use both magnetic fields and optical fields?

Or the last answer is none of the above. It's not possible with any of those fields to create any kind of transition between singlet and triplet.

OK, all right. We have to spend the first 10 minutes on the class on Friday to discuss that. But the answer is none. There is no way how you can get a transition between singlet and triplet using the approximations for the description of the helium atom we have done so far.

Since I don't want to end with such a cliffhanger, let me just say, we have actually a selection rule which says, we are not changing the total spin.

And you would say, hey, come on. Can't I just take a magnetic field and flip one of the spin, go from a triplet to a singlet state? Well, the answer is no.

And let me just give it to you qualitatively and deformatize it on Friday. First, as far as transverse magnetic fields, rotating magnetic fields, are concerned. transverse B fields.

Remember, transverse B fields create some \vec{f} of the spin. But both spins precess equally. So you can never even classically, you cannot change the angle between the two spins.

When the two spins are interparallel, they stay interparallel. When they stay parallel

when they are parallel, they stay parallel. Or to say the transverse B field means we have a coupling, s_x , s_y .

And s_x and s_y can be written as ladder operators, s_+ and s_- . And as you know, s_+ and s_- only change the magnetic quantum number. But they do not change the value of the total s .

In other words, if you have a spin which is $s = 1$ triplet state, you can change the angle, how the spin equals 1 points. But it still will be spin 1 where both electrons are aligned parallel.

There is no magnetic field which can selectively talk to one spin and rotate spin 1 with respect to spin 2.

And coming to the other questions about optical fields with a dipole operator, the answer is also a resounding no. Because the dipole operator of the electromagnetic field, the dipole operator acts only on the spatial wave function.

Not on the spin part. So a laser beam through the dipole operator can never ever flip the spin. It only acts on the spatial wave function.

So anyway, I wanted to just give you the answer why you cannot go from singlet to triplet state with sort of our standard operators, with the electric dipole operator or with the rotating field.

And I hope it was worthwhile to explain in detail why each of them cannot do it. But on Friday, I explained to you that there is a general symmetry behind it that even more fancy combinations will not be able to do that.