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PROFESSOR:

--afternoon. Our main subject for today is the fine structure of atoms, when spin couples and we bring spin into the picture. And if time permits, a Lamb shift.

But before I get started, I just want to finish up our topic of the last class, which was helium. And I said for many, many years, we only discussed single electron atoms, but I introduced the helium atom into the curriculum because there are two aspects which are really new and which we can learn from helium with a more simple example.

One was the fact of how the spin leads to interactions even if nothing couples directly to the spin. And we discussed it last class that because we have singlet and triplet states, they impose symmetry or anti-symmetry onto the spatial wave function. And that makes a big difference in the energy. And it is sort of this big Coulomb energy, which is connected to spin, which is actually responsible for magnetism in nature.

The second aspect, the second new feature, which is, of course, also related to spin is the presence of singlet and triplet states. And it gives me an opportunity-- and this was the last point we discussed on Wednesday-- to raise the question, what can cause a transition from triplet to singlet?

And at the end of Wednesday's lecture, we discussed the question, what kind of couplings would allow you want to drive a transition from triplet to singlet? And at least based on the clicker result, for most of you the surprising answer was none. Optical fields, not. Rotating fields, not.

Within the approximation we have so far-- namely, just a Hamiltonian with Coulomb interaction-- there is nothing in the system which connects the singlet to the triplet

world.

Well, there is a very weak transition, but the lifetime of the triplet counts it in helium, as I will tell you a little bit later, is 8,000 seconds. It's extremely long life. We have an extreme form of metastability here.

Just an anecdote. In the early days when people learned about the structure of atoms, they looked at spectra. And they never found any line which was connecting the singlet states with the triplet states. So it looked like if there were two different forms of helium, orthohelium and parahelium. So people even believed for a while there were two kinds of helium in nature because they seemed to be completely disconnected. But as we know now, of course, this simply reflects the high degree of metastability.

I want to emphasize before I give you the general framework and the symmetry, spatial symmetry and spin symmetry, and we discuss all that in exchange symmetry-- I want to emphasize what I said at the end of the lecture on Wednesday.

If you try to drive a transition between singlet and triplet, if you use a rotating magnetic field, you can't do that. Because a rotating magnetic field couples to the total spin. It just makes the total spin precess around the axis of the magnetic field. But what the magnetic field will never do is break up the relative angle between the two spins. And in a triplet state, the two spins are aligned. In the singlet states, they are anti-aligned.

And with a magnetic field, you address both spins simultaneously. They precess together, and you can never change the angle between the two. So a singlet-triplet transition really requires that you go deeper. You really have a handle on the spins relative to each other.

Let me make a second comment about the possibility of doing an optical transition. An optical transition, at least in the dipole approximation, has an electric field acting on the dipole moment of the electron. There is no spin involved.

And let me sort of accentuate it by saying, you should really have in your mind that, at least in dipole approximation, the laser, the light, optical beams, do not couple to spin. The only couple to the spatial part of the wave function.

And that has important consequences. In a lot of our research, we do Raman transitions. And with a Raman transition, we do spin flips. So how can a laser, or two laser beams through a Raman transition, flip the spin if the laser is not talking to the spin degree of freedom?

Well, if you have a Raman transition and you excite a state which has spin orbit coupling, you excite the atom. The spin does nothing during the excitation. But then in the intermediate state, spin and angular momentum may be coupled by spin orbit coupling. And the spin is starting to precess due to spin orbit coupling. And then the spin rotates, and then the second leg of the Raman transition transfers the atoms back to the ground state, but now the spin has rotated.

But it is never the laser which rotates the spin. What should be immediately clear from that is if you try to have a spin flip Raman transition in an atom which has no spin orbit coupling don't even look for that. It doesn't exist.

Anyway, we just encountered it here and I want to tell you that there is even more general consequences of that. But let's now go back to the helium atom and look at the spatial symmetry which comes, of course, because operators are symmetric with regard to the two electrons.

So what we have is we have the total spin is the sum of the spins of electron 1 and electron 2. And all spin operators-- the spin operator s and its components-- are symmetric against particle exchange. In other words, if you couple to the spin through a magnetic field, you couple to the two electrons symmetrically. And therefore, you have the selection rule that only symmetric and symmetric and anti-symmetric and anti-symmetric states couple.

Or, to express the same result in different words, both the spatial and the spin symmetry, each of them can be symmetric and anti-symmetric. Of course, the

product of them has to be anti-symmetric because we're talking about fermions. So both of these symmetries are good quantum numbers.

Or more formally, all observables commute with the particle exchange operator. So any arbitrary observable commutes. So the commutator of the particle exchange operator vanishes.

OK. But now, what is special to the approximation in which we have treated helium?

As long as wave functions and operators separate into spin-dependent and space-dependent parts. The wave function had a spatial part, and then we multiplied with a spin wave function. So the wave function factor-wise separated into a spin part and a spatial part.

Also, the operators. If you have operator for total spin, if you have operator for dipole moment, the operators are either addressing the spatial degree of freedom or the spin degree of freedom. So as long as this is the case, we have an even extended conservation law for both spin exchange for an exchange of the particles in the spatial domain and in the spin domain.

So as long as wave functions and operators separate into spin and space-dependent parts, then the particle exchange operator can be regarded as the product of an exchange operator which only acts on the spatial wave function and on the spin part of the wave function. And both quantum numbers for spin exchange-- symmetric/anti-symmetric-- and for exchange of particles in the spatial part of the wave function, symmetric or anti-symmetric-- are conserved.

So often, we discuss symmetries and the reason why something is conserved because then we can think about how to evaluate it. Often, you can say, conservation laws are often written down just as a way to think about. How can we break them?

And in this case, we can break these symmetries which doesn't allow transitions between singlet and triplet. We have to break them to get intercombination lines. So in order to get a singlet to triplet transition, it's only possible when we violate the

assumptions we have just discussed.

And of course, an assumption was that the wave function factors into spin part and spatial part. But when spin and spatial wave functions are mixed-- for instance, by spin orbit coupling-- then the assumptions we have discussed are no longer valid. So what we need is, for instance, a mixing of spin and spatial wave functions by spin orbit coupling.

Well, as we will learn later today, spin orbit coupling is, actually, a relativistic effect. It naturally arises in the Dirac equation. And it scales with-- the nuclear charge is z to the 4. So therefore in helium, it is very, very weak.

Therefore, the triplet ground state is extremely long-lived. The lifetime in helium is 8,000 seconds. It's one of the most longest-lived metastable states you can imagine and which you find in atomic physics.

Now, since spin orbit coupling becomes rapidly stronger with nuclear charge, you would expect the metastable lifetime to be much shorter for the analogous state in the other rare gases. And indeed, the other rare gasses are on the order of 40 seconds.

You have other atoms where you have singlet and triplet lines. We need two electrons and the two spins can form singlet or triplet. So that naturally also happens in atoms which are in the second column of the periodic table. Magnesium, calcium, strontium have intercombination lines. And they are actually very relevant in current research because these are candidates for atomic clocks.

In those atoms-- magnesium, calcium, strontium-- physics is more complicated. The line width is typically kilohertz. But that's probably just what you want. If the line width is kilohertz, the lifetime is millisecond. You still have a matrix element that you can drive the transition and observe it.

For an atomic clock, you don't want a transition which is thousands of seconds or half the age of the universe because it's too weak to be observed, too weak to be driven. So intercombination lines of kilohertz, line widths of few hundred Hertz or

such, are almost ideal for optical atomic clocks. Any questions?

So maybe then I should just entertain you for a few minutes about, how do you measure an 8,000 second lifetime?

Well, there is a recent paper. Insert Picture. Desktop.

There's a recent paper a few years ago, *Physical Review Letters*, determination of the lifetime of metastable helium.

Traditionally, people have measured the lifetime of metastable helium in the following way.

No, they haven't observed helium for 8,000 seconds. Because if you have helium in the metastable state, maybe after a few seconds there is some collisions-- collision or deactivation. 8,000 seconds, you would just have many, many systematic effects.

What people did is they put some atoms into the metastable state, measured the number of excited atoms, and then-- maybe during 100 milliseconds, 1 out of 80,000 atoms should decay. And by determining what small fraction of the atoms has decayed, or how many photons you observe in 100 milliseconds divided by the total number of atoms, that's how you can measure the lifetime.

Of course, the problem is, yes, you can measure the number of photons. But if you want to divide by the number of atoms, you have to know very accurately how many atoms you have. And this Australian group used the very clever trick to eliminate this uncertainty. And this is as follows.

We have this extremely long-lived 8,000 seconds lifetime here. And this is the transition. But you can now excite the atom to the triplet P0 state, which is also sort of-- it's a triplet state.

Well, I assume because it is a P state, it has been orbit coupling. The lifetime is-- well, for an atom is very long. Typically, atoms decay in nanoseconds. But this lifetime is milliseconds.

So what they did is they just excited all the atoms with a strongly saturating laser to the triplet P0 transition. And then within a few milliseconds, all the atoms emitted. And so all they had to do is measure accurately the ratio of the VUV photons emitted by the triplet ground state and by the triplet P0 state. And then the number of atoms canceled out. All they had to do is measure the ratio of 2 VUV intensities. So based on that research now, we have higher accuracy on the lifetime of metastable helium.

The question is when I said we have to violate the above assumptions to get any decay between singlet and triplet. Metastable helium, pretty much everything you can think about it is forbidden.

So for a long time, people believed it was a two-photon transition. One-photon transition was forbidden, but a two-photon transition was allowed.

We know now that the decay path is one photon in one transition. Magnetic dipole transition. If you don't know what M1 is, we discuss it later in the course.

But you may find it interesting that until rather recently, it was not clear what the decay path is. Well, recently means probably a few decades ago. But for a long time, it wasn't even clear and the calculations were not accurate enough what was the mechanism by which the metastable count state of helium could decay.

When I prepared the class, I wanted to sort of give you a simple picture and say, hey, it is this mechanism which causes the transition from the triplet ground state to the singlet ground state, but I couldn't find a simple operator. It seems a little bit more complicated. The best I can tell you is that the decay path requires higher-order terms using the Dirac equation with coupling to the electromagnetic field. Any questions? Yes, Nancy.

AUDIENCE: In the measurement of the lifetime of that state, what is the limiting factor? What makes this measurement to be not more precise?

PROFESSOR: Here is the reference. I mean, this was a highly-accurate measurement for that it improved all previous measurements. What the current limit of accuracy is, I don't

remember.

But for instance, they had to put all atoms into the excited state or by strong saturation. Of course, saturation is never complete. Maybe there's a limitation to that.

Finally, you have to measure the ratio of photons emitted by that state and emitted by that state. Well, they're both in the vacuum UV, but you may have a systematic effect if your photo-detector has a slightly different detection efficiency for 58 nanometer and 62 nanometer.

Nothing is perfect, but I really have to refer you to the reference for details. OK. So that's pretty much what I wanted to tell you about electronic structure, the hydrogen atom and special features about the helium atom. So we can now proceed from electronic energies, which were on the order of Rydberg. Or remember atomic units, fine structure constant squared times rest mass of the electron.

So we've taken care of those energies and now we want to take care of smaller corrections. And what we discuss next is the fine structure and the Lamb shift. So this is now the title of our next chapter, Fine Structure and Lamb Shift.

The fine structure energies are alpha square times smaller than the Rydberg. So they're on the order of alpha to the 4 mc squared.

And well, if I write that as alpha square Rydberg, which is the same, but it may-- this explains to you why alpha is called the fine structure constant. People had learned about the hydrogen spectrum, Bohr's model and all that, and then they found finer corrections. And those finer corrections were on a scale alpha square times smaller.

And the constant which appears here, alpha, was called the fine structure constant because it described the structure of the fine structure corrections and the fine structure splittings.

Of course if you want, you can make the fine structure constant already appear for electronic energies. But this simply reflects that I have used the rest mass of the

electron as a reference energy, which unless you want to discuss fundamental units doesn't make any sense because c , the speed of light, it does not appear in the electronic structure as we discussed earlier. So therefore, the fine structure constant does enter the picture only when we now discuss fine structure corrections, fine structure splittings.

The Lamb shift, which we will then discuss, is even higher order. It's α^5 to the fifth. But just to tell you, the Lamb shift is on the order of a gigahertz. And you know that standard precision in all of your labs is now megahertz or better. So the Lamb shift, also it's α^5 , is a big effect on the scale of how we understand and prove the structure of atoms today.

OK, so let's talk about the fine structure. You will actually find a complete discussion of the fine structure in several textbooks on quantum mechanics-- [INAUDIBLE]. What I want to do here is to have a careful discussion of the physical origin and provide a clear understanding what is responsible for the fine structure.

So if you just want to get an accurate result, there's only one thing you have to do-- solve the Dirac equation. The solution of the Dirac equation for the hydrogen atom gives us the electronic structure, the same as comes out of the Bohr model, but now including the fine structure. So it's nice. It just comes out. You don't have to put in the spin of the electron by hand. It comes out automatically. But it also comes out as a result and you don't fully understand what is the origin of that. Because you've just treated everything fully relativistically. So what I want to show you here is I want to show you that we can distinguish three contributions. There are three physical effects which all come in at the level $\alpha^4 mc^2$.

One is relativistic corrections to the kinetic energy. The second one is spin orbit coupling. And then there is a third one, which goes by the name Darwin term. And we can get this physical insight and obtain those three terms separately when we use what is called the Pauli approximation to the Dirac equation.

If you do the so-called Pauli approximation to the Dirac equation, you simply expand the Dirac equation in powers of v/c . And then you get the Schrodinger equations

plus correction terms. And what you obtain then is a Hamiltonian, which is the rest energy, which is constant; the non-relativistic kinetic energy, the Coulomb energy. But then, we have three more terms. And these are the three contributions to the fine structure.

One is kinetic energy is p squared, but now there is a higher-order relativistic contribution, p to the 4. Then, there is a term, spin orbit coupling term. And then there is the third term, which will we identify as the Darwin term. Laplace operator e squared over r . So we have a kinetic energy correction. We have a spin orbit correction and we a Darwin term.

And what we want to do in the next 45 minutes or so is we want to look at each of those. Any questions?

The kinetic energy contribution is the simple expansion. You can get it from the Pauli approximation. You take the Dirac creation and deal with all the operators in the Dirac equation and do an expansion. But you can also just lean back and say, OK, what is the kinetic energy? And use the relativistic form of the kinetic energy, which is rest energy and pc squared. The square root of it.

And if you say the kinetic energy is the energy minus mc squared, and then you take the full relativistic expression for the total energy minus 1. And now you do a Taylor expansion of the square root. You find the non-relativistic kinetic energy.

And the first correction term with all the correct prefactors is this one. So this is the relativistic energy correction in the Pauli equation. That's all we have to say.

The second term is spin orbit interaction. And as such, it is, I would say, more interesting because it now really addresses the spin. So yes, the term comes from the Dirac equation and appears separately as an identifiable term if you do the Pauli approximation to the Dirac equation. So I could just stop there and say, here, that's what it is. But I think it's insightful if I re-derive this term for you by using a physical picture. What do we have to add to the Schrodinger equation to get it?

What we have to add to the Schrodinger equation is, of course, we have to put in

that the electron has a spin. The Dirac equation is formulated in spin. It's automatically formulated for spin 1/2 particles. But if you start with the Schrodinger equation, you can first write it down for a spin-less particle, and now you have to add the spin by hand.

So we have to add to the Schrodinger equation, or to the Bohr model, that we have an electron with an intrinsic spin. And the spin will couple to the rest of the world because it has a magnetic moment which is the g factor. We'll talk about g factors later in more detail. The Bohr magneton times the spin.

If you add it to the Schrodinger equation, we have to assume the experimental value or you can see the value of which-- the approximate value of the exact value from the Dirac equation, which is a g factor of 2.

So if you put in by hand that the electron has a spin, the spin is associated with the magnetic moment. Now we have a coupling because an electron which moves in the Coulomb field of the nucleus sees in its moving frame a magnetic field. And this magnetic field couples to the spin. So the moving electron "sees" a motional magnetic field.

Well, you know when you have an electric field and you look at the-- you have an electric field in one frame and you have a second frame, spatial relativity, which moves with a velocity v . Then, in the moving frame, you observe a motional magnetic field.

Well, our moving frame is now the electron. So that looks like coupling to the Coulomb field, but we can immediately write it in a form where we recognize angular momentum. So this is the Coulomb field. And it involves now v cross r . And v cross r is just minus L , the orbital angular momentum.

So this is now our motional magnetic field. And then the spin couples to it and we get spin orbit coupling.

By the way, an equivalent picture because you will read about it or hear about it is

you can get the magnetic field which couples to the spin by simply transforming the Coulomb field into the frame of the moving electron. But there is a more naive picture which is correct, too.

If you are in the frame of the electron, then the proton is orbiting around you. And the orbiting proton is a ring current, which creates a magnetic field. And this magnetic field is or it has to be the same as we just got by doing the relativistic transformation of the Coulomb field into the frame of the moving electron.

So therefore, let me just leave some room because I have to add something. If we want the spin orbit Hamiltonian, it's now the magnetic moment of the electron times this B field. And just collecting the terms, e squared, \hbar squared, m squared, c squared, 1 over r cubed. The magnetic moment is proportional to s , the spin. The motional B field is proportional to L . And now we have the famous spin orbit coupling term.

OK, that would be too simple. So we have to now consider one more thing. And this is-- I told you that we can transform the electric field into the moving frame of the electron, but those transformations from one Lorentz frame into the other are simple when you go from one frame to another and they move with a constant velocity relative to each other.

The electron is not moving with a constant velocity. It actually has a constant acceleration because it's on a circular orbit. So therefore, we have to use the relativistic transformation between coordinate frames. And it is in textbooks on spatial relativity.

What happens is if you have-- if you do relativistic transformations between different moving coordinate systems, then you find that if you have a velocity like this, velocity like this, and you do subsequent transformations, you are not just going into a Lorentz frame which has very solid and relativistic addition of the velocities. In addition, your final Lorentz frame is rotated against the first frame.

So adding a number of velocities which are not collinear-- and this is what we have

to do if the electron goes in a circle. We have to sort of follow the electron, follow different velocities and do relativistic transformations. Several relativistic Lorentz transformation executed in sequence are not a simple Lorentz transformation, they are Lorentz transformation plus rotation.

And that means that if we go-- and the result can be summarized as follows. There is a rotational angular velocity which can be written as follows.

You see immediately that this term is 0 when a, acceleration, and velocity are the same. So if you have a moving frame and you accelerate the moving frame, you don't get this term if everything is in one dimension. But if the acceleration is not in one dimension-- and that's the case when the electron goes on the circle, you get an additional contribution.

And if the acceleration is constant, you get-- and this is on the left-hand side-- a constant angular velocity. A precession velocity. And the letter T indicates that it's the Thomas precession.

Now, we have learned-- and that's nice to come back to the beginning of this course. We have discussed that if you have a magnetic field, we can go into a rotating frame and the magnetic field disappears.

Well now, due to relativistic kinematics, we have an additional rotation. But using the same argument we used at the beginning of the course, this additional rotation corresponds to an additional magnetic field. So therefore, this precession is identical to the effect of an additional magnetic field.

So there is an additional magnetic field with the letter T, the Thomas magnetic field. Those magnetic fields are related to the precession frequency by the gyromagnetic ratio.

And if we use the value for the electron's gyromagnetic ratio-- and in addition, we use the fact that the acceleration term for this relativistic kinematics is nothing else than the Coulomb acceleration, then we find that the Thomas magnetic field is just minus 1/2 the motional magnetic field we derived earlier.

So therefore, if we go back and want to find an expression for the spin orbit coupling, we have to use the magnetic field, which is the sum of the two contributions we discussed, the motional contribution for-- as if the electron would move in a linear way, plus the Thomas precession due to the rotational motion due to relativistic kinematics. And this will just reduce the final result by a factor of 1/2.

Yes.

AUDIENCE: Two questions. Small one, what letter is the gyromagnetic ratio denoted by?

PROFESSOR: Sorry for the handwriting. We have usually used lowercase gamma. And the e means the electron. So gamma electron is the gyromagnetic ratio of the electron.

AUDIENCE: OK. And then my other question, or more substantively concern-- or confused, I guess. I wasn't sure where the h bar comes from in the expression for angular momentum. One line up. You go from $\mathbf{v} \times \mathbf{r}$ to $\hbar / m\mathbf{L}$. And I wasn't sure where the h bar came from.

PROFESSOR: Oh. It now depends. You're correct, angular momentum is $\mathbf{r} \times \mathbf{v}$. $\mathbf{r} \times \mathbf{v}$ gives angular momentum. And because it's $\mathbf{r} \times \mathbf{v}$ and not $\mathbf{v} \times \mathbf{r}$, the minus sign is absorbed into it.

Now, the angular momentum-- it depends now. It's just purely definitional. If you wanted, the angular momentum has eigenvalues of $L(L+1)$, which are dimensionless, then we have to account for h bar explicitly. So question is, do we want the angular momentum operator to have this kind of integer, or $L(L+1)$?

Yeah. This integer spectrum, or do we want to measure-- or, do we want to use operators which have units of h bar? That's where the h bar comes from. Other questions?

OK. So this is spin orbit coupling. Finally, the last contribution to the fine structure is the Darwin term.

The Darwin term is sort of peculiar, but there is sort of an intuitive picture in which I can derive it. Well, it starts by saying that an electron-- well, we know an electron is, as far as we know, a point object. But in order to derive the Darwin term, we assume that the electron is not arbitrarily accurately localized, but it is smeared out.

And you may remember when I discussed fundamental units and the fine structure constant α , and I told you that the fact that α is small leads to the fact that people say electromagnetic interactions are weak.

I discussed with you that if you want to do single-particle physics and do single-particle pictures and single-particle equations, you can never assume that a particle is localized better than its Compton wavelengths.

If you would localize the particle better than the Compton wavelengths, it would have a momentum uncertainty, which would lead to an energy uncertainty, which is larger than its rest mass. And you get into quantum field theory and pair production.

So at some point, you have to be aware that single-particle pictures break down when you assume a localization of particles better than the Compton wavelengths. So therefore-- and I'm waving my hands because it's a hand-waving argument. But we can derive the Darwin term by assuming that the electron is sort of smeared out over a dimension. And this dimension can only be the Compton wavelengths, which is \hbar/mc .

And there is a nice German word for it, how you can imagine that the electron is smeared out. It goes by the word [SPEAKING GERMAN].

I think the German word is much nicer than its translation, which is trembling motion. So at least in this picture you assume that the electron is sort of smeared out. It's not because the electron has a size. It just trembles. It just trembles and that leads to a smear-out over the Compton wavelengths.

But that implies now that if this trembling motion is sufficiently fast, we should not use in our Schrodinger equation the Coulomb potential. You should use the Coulomb potential which is spatially averaged over the Compton wavelengths.

So therefore, the phenomenological derivation of the Darwin term goes by replacing the Coulomb potential in the Schrodinger equation by the spatially-averaged Coulomb potential. So let me now derive what this means.

So if we assume there is a very small displacement s , now we can take the Coulomb potential and expand it into its Coulomb potential plus derivative times s plus the second-order Taylor expansion the x_i , the x_j component. And then we need the second-order derivative $x_i x_j$ of the Coulomb potential.

So the correction is now-- well, if you ever reach it in an isotropic way, the gradient term, a linear term doesn't contribute. It just averages to 0. So the leading correction comes from the curvature term. So therefore, we have to take the curvature or the Laplacian of the Coulomb potential. The scale of s_x squared, s_y squared, s_z squared is the Compton wavelength squared.

And well, maybe I'm taking the argument of the Compton wavelengths now too literally. But at least if I want to carry it through, s_x squared, s_y squared, s_z squared, each of them $1/3$ of s absolute value squared.

So if I now use the Coulomb potential, I obtain the result where I have the Laplacian of $1/r$. And as you, of course, know is the $1/r$ function has a non-vanishing Laplacian only at the origin. So therefore, the correction is only valid for s electrons which have a non-vanishing probability to feel the origin of the Coulomb potential.

OK, I did a lot of hand-waving here. And yes, those factors of $1/2$ are the fact that the electron is smeared out over the Compton radius and maybe prefactors. But OK, this is the physical picture.

You can get an exact result by simply taking the Dirac equation, doing the non-relativistic approximation, and the term which appears in the Pauli equation is actually the same.

The only thing which is different is that the prefactor is not $1/6$. The exact prefactor is $1/8$. So the exact results actually validates that the physical picture we have used

is at least a reasonable approximation.

OK, so we have now-- let us summarize.

For the fine structure, we have three different terms. And they all have a different signature. We have the relativistic kinetic energy correction, we have the spin orbit coupling, and we have the Darwin term. We can now ask, which term contributes for an s electron?

Well, relative kinetic energy, of course. The Darwin term is only for s electrons. LS does not contribute because an s electron has L equal 0.

So if we go to p and d states, to states with finite angular momentum, then we get contribution of LS. We always get a relativistic kinetic energy contribution. But for finite angular momentum, we don't have the Darwin term.

And finally, we can also classify those different contribution by asking, what is the sign? Do those corrections lower or increase the total energy?

Well, the Darwin term reduces the binding energy because it sort of takes a cusp away from the Coulomb interaction. The kinetic energy has the opposite sign and spin orbit coupling is $L \cdot S$. And S can be parallel or anti-parallel to L. So therefore, the spin orbit interaction has plus or minus sign. Any questions about those three terms?

OK. The fact that we have spin and we have spin orbit interaction means that the spin orbit interaction, $L \cdot S$ is not diagonal in L or S. So what we have to do is we have to introduce now the total angular momentum J. And since $L^2 + S^2 = J^2$, we can write the product LS as $1/2 (J^2 - L^2 - S^2)$.

So therefore, the LS interaction is diagonal in the J basis. So if you couple L and S to J a given state of the operator J has a definite value for LS. OK.

Let's put in things together. So at the beginning of this class, we started out with a hydrogen atom where-- let me just focus on n equals 2, where we had n equals 2.

All n equals 2 states have the same energy, that's what comes out of the non-relativistic Schrodinger equation with a Coulomb potential. And that means we had a degeneracy for the $2p\ 1/2$, for the $2p\ 3/2$ and the $2s\ 1/2$ state.

If you now put in spin orbit interaction, well, nothing of course happens to the $s\ 1/2$ state because it has no orbital angular momentum.

And then in the $P\ 3/2$ state, L equals 1, 1 unit of orbital angular momentum, and the spin aligned. In the $p\ 1/2$ state, they are anti-aligned. So therefore, the two terms have opposite shifts. So the $p\ 3/2$ state is shifted up and the $p\ 1/2$ state is shifted down.

But then in the second step, we want to add in now the two other contributions to the fine structure, the kinetic and the Darwin term. And then, something happens which is really remarkable. We have split the three levels. We have lifted the degeneracy between the three levels. But if you now add the kinetic and the Darwin term, it turns out that the $s\ 1/2$ and the $p\ 1/2$ state become exactly degenerate again. So there is still a degeneracy in the spectrum.

If we would use a non-relativistic approach and derive the Darwin term, the spin orbit term, and the relativistic correction separately, there would be no reason. It would just look like a freak accident in nature that those two levels come out equal.

However, it's not a freak accident. It's the symmetry of the Dirac equation. So all those corrections have a deep connection in relativistic physics. And relativistic physics preserves the degeneracy in J . So let me write that down.

So the fine structure does not lift the degeneracy between $s\ 1/2$ and $p\ 1/2$. It turns out that when we use the Dirac equation, we can get an exact expression for the fine structure into the [INAUDIBLE]. And it's a principal quantum number.

And then the fine structure only depends on J and not on L and S separately. So that tells us that eventually the spin of the electron and the fine structure really have deep origins in the relativistic nature of the underlying physics. Any questions about

fine structure?

Let me get a white page and draw you sort of an energy-level diagram, put in a few numbers which then leads us to the discussion of the Lamb shift. So we have hydrogenic energy levels with n equals 1 and n equals 2. We have s states and we have p states.

We just discussed the fine structure which shifts down the energy of all those levels in the ground-- I mentioned that the fine structure is alpha to the $4mc^2$. And for the ground state, the prefactor is minus $1/8$. And this is the one-- the term designation is $s_{1/2}$.

Here, we get the $2s_{1/2}$ level and the shift is minus $5/128$ in the same unit alpha to the $4mc^2$.

We have the exact degeneracy between the $s_{1/2}$ and the $2p_{1/2}$ state. Whereas, the $p_{3/2}$ state is only shifted by minus $1/128$.

To put in some numbers in electron volt, the fine structure in the ground state is on the order of 10^{-4} electron volt. The splitting here, which is the fine structure splitting of the $p_{1/2}$ and the $p_{3/2}$ state is 4×10^{-5} electron volt. So that means at the level of 10^{-4} electron volt, we understand atomic structure.

Well, but we want to go further. And the next thing we want to discuss is that-- what is the exact degeneracy between $s_{1/2}$ and $p_{1/2}$ is actually lifted when we introduce photons. When we allow the electrons to couple to the electromagnetic field, that's QED, Quantum Electrodynamics. And that introduces the Lamb shift, which in the n equals 2 state is 10^{-6} electron volt, which is approximately 1 gigahertz. And that's what we want to derive next.

Since I have this nice, level diagram I want to also indicate to you what we do next week. And this is when we bring in the proton. So far we have said there is a point charge, but the proton is a particle which has finite size. But also, it has finite angular momentum. And then we have to bring in fine structure. And we will learn

that the $s_{1/2}$ ground state splits into two hyperfine components.

And the hyperfine structure will be at a similar energy scale as the Lamb shift. And actually, this fine structure splitting is the famous 14-- it's about 1 gigahertz. It's the famous 1,420 megahertz line, which everybody who does astrophysics knows about it. It's also, in other units, the famous hydrogen measure, which has an emission line at 21 centimeter.

Anyway, this is sort of our roadmap. We have taken care of everything down to 10^{-5} electron volts. And now we want to proceed today and in the next lecture to 10^{-6} .

First, the Lamb shift, where we are still holding on that the nucleus is a point charge, has no structure. Then, we have done everything we can do. What happens in the Coulomb field of a point charge?

We have the spin of the electron. We have QED. We have done everything. And then what remains is to put in the structure of the proton, which will lead us to hyperfine structure. Any question?

OK, then let's get started with the Lamb shift. Just to make sure that you're not getting confused, there is also a lamp shift. This is actually an old-fashioned word for an AC Stark effect.

People in the '50s and '60s found that spectral lines in a mercury discharge shifted when you took another mercury lamp and illuminated the mercury with a strong light of another lamp. So a lamp shift is simply a shift due to the electromagnetic radiation emitted by a lamp. But that's what we are talking about.

We want to talk about the Lamb shift, which is named after Willis Lamb, who received the Nobel Prize for the discovery that the $2s_{1/2}$ and the $2p_{1/2}$ level in hydrogen are not degenerate. And he wouldn't have gotten the Nobel Prize if it would have been simply of one little feature in the spectrum of hydrogen. But the discovery of this lifting of the degeneracy actually opened up the field for the development of quantum electrodynamics. So this was the experimental discovery

which led to quantum electrodynamics. And this is why it's a very famous effect done by a now very famous man, Willis Lamb.

The full description of the Lamb shift would require QED. And later in this course, we are developing the tools to do that. I don't want to do it here. I want to give you a simplified physical picture which actually nicely relates the Lamb shift to the Darwin term which we have just discussed.

But sort of just in full disclosure, what you have to do is, if you fully quantize the electromagnetic field, you have a vector potential which describes the vacuum mode. And you have a vector potential, which is the operator of the fully-quantized field. And if you now carry out second-order perturbation theory in this operator A of the quantized electromagnetic field. In other words, you allow the atom or the electron in the atom to couple to all the empty modes of the vacuum, then you obtain the Lamb shift in its full beauty. This is discussed nicely in "Atom Photon Interaction" by Claude Cohen-Tannoudji, et al.

So this is the nature. The nature of the Lamb shift is the coupling to the vacuum modes. But I want to capture that now in a semi-classical picture.

So the picture I am presenting here is due to Welton and Viki Weisskopf. And yes, it has to address the nature of the Lamb shift. And this is the coupling of the electron to the vacuum, but the vacuum is not empty. The vacuum is filled with a zero point energy of the electromagnetic field.

What we need is that we have electromagnetic modes and they have a zero point energy. And each mode has a zero point energy of $\hbar \omega$.

And maybe before I do any equations, which will take five minutes and about one page, I should just give you the physical picture. I think it's much clearer to understand that.

So the moment each mode has an energy, then each mode has a fluctuating electric field. Now what we have to do is we have to multiply the contribution-- the

energy of each mode by the density of modes. We have to sum over all modes.

But then in the end what we get is an expression for the fluctuating electric field. And remember, in the Darwin term, we assumed that the electron is trembling by itself and is smeared out over the Compton wavelengths.

But now in addition to its own trembling motion, the electron is now shaken by the electric field of the vacuum. And this leads to an additional smear out. And this is the Lamb shift. So that's what we want to put together. So we want to calculate an additional contribution to a trembling motion of the electron. But this time, it is driven by the electric field which persists even in the vacuum. So that's the Lamb shift.

OK, so it's $\frac{1}{2} h \bar{\omega}$ per mode. We have to use the density of modes. And the density is, of course, per unit volume and frequency interval. So we have a density. μ is the frequency and you probably remember that the density of modes scales with frequency squared. So that means the density of the zero point energy is $\frac{1}{2} h \mu$ per mode times the mode density. And this means it scales now with μ cubed, the frequency cubed.

And since we want to introduce now the electric field, the [INAUDIBLE] electric field. If you go from electric field to energy, the energy density of the electric field is proportional to e Squared. So therefore, what we derive from this picture that the vacuum is filled with an oscillating electric field.

And this oscillating electric field is characterized by a value, by a spectral density E squared, which is proportional to μ cubed. And if I collect the constants h and speed of light, it's this. So the question is, what does this electric field do to the electron?

Well, let's not discuss the electron in a hydrogenic orbit. Let's, rather, discuss in a simplified picture, what is the effect of such a field on a free electron?

And we will later discuss that for very high-frequencies, an electron can be regarded as free. So therefore, if s is the coordinate of the electron, and you drive it with an oscillating electric field at frequency μ , then the driven amplitude of the electron is

the electric field.

I just want to make sure we keep track of the powers of μ . Because we take the second-derivative acceleration, we get two powers of μ . So we have an extra μ squared term.

Of course, the phase is random, so we're not interested in the amplitude. We are interested in sort of an average amplitude square or an RMS amplitude, which is-- the amplitude was proportional to the electric field. The amplitude squared is proportional to the square of the electric field. And our prefactor involves now μ to the 4.

Just in the equation at the top, we had an expression for the spectral density of the electric field E squared which goes μ cubed. So that means now that the spectral density of the motion of the electron s μ squared goes as 1 over μ . And yup, e squared \hbar pi squared m squared e cubed.

And now, yes, I wanted to do it in the same lecture as the Darwin term because we know that there was a change to the Coulomb potential in the Darwin term which came because the electron was smeared out over an area s squared. Remember, this was the Compton [INAUDIBLE] squared.

And it involved the Laplacian of the potential Taylor expansion second order, second derivative in three dimension is the Laplacian. And for the Coulomb potential, this is non-vanishing, of course, only at the origin.

So therefore, we have now executed what I discussed before. We calculated the sort of displacement of the free electron driven by the vacuum fluctuations of the electric field. And these smear out of the electron leads to a change of the-- of the average Coulomb potential. We average the Coulomb potential over the first motion of the electron.

And that means now that we get a change of the binding energy of the electron, which is nothing else in perturbation theory than the matrix element of the perturbation operator. But this perturbation operator was a delta function. And we

have the prefactor, which is the spectral density of the displacement $s \mu$ squared. So let's wrap up.

So we know because of the delta function, it only affects s electrons. And remember I discussed at great lengths that for an electron with principal quantum number n , the probability to be at the center was n cubed. So here again, we have the n cubed factor, which we discussed for the hydrogenic wave function.

And the only thing which is non non-trivial we have to do is we have to integrate over all modes μ . So therefore, what we had so far was the shift caused by one frequency of the electromagnetic spectrum. But now we have to integrate over all frequencies.

So what we have to do is-- our spectrum s squared goes as 1 over μ . And if you integrate 1 over μ over all frequencies, you get a logarithm. You get logarithmic divergences.

So therefore, our result is-- and I'm using now atomic units, α cubed z to the 4 the n cubed factor. Everything is in units of atomic units. The atomic unit of energy is 1 Hartree or 2 Rydberg. But the factor which is now non-trivial is from the logarithm, we integrate. And we have divergences at both ends. So we need a cutoff at a minimum and at a maximum frequency.

For the maximum frequency-- well, there is a natural cutoff. We have to cutoff at the rest energy of the electron, otherwise we are no longer doing single-particle theory.

And the cutoff, the lower cutoff, is the following. We have used a picture here for free electron, but we can regard the orbiting electron only as a free electron on time scales which are much faster than one orbital period. So therefore, we have to use as a lower cutoff the frequency of the orbiting electron, which is z squared n cubed in atomic units.

So with that, then I should stop because time is over. We have a little bit hand-wavily, but it appears in a logarithm anyway. We have gotten for the ratio of the

upper and the lower cutoff an expression which is n^3 over z^2 times α^2 .

And if we apply it to s state where it's most important because there is the degeneracy between $p_{1/2}$ and $p_{3/2}$ to be lifted, we get a result that the energy splitting is now-- and with the assumptions we have made, the logarithm is $8/a^2$, α^2 . And from that, we would have derived a Lamb shift of 1,600 megahertz.

Well, the exact value is 1,058 megahertz. I'm missing five minutes to discuss the result in terms of vacuum polarization, but that's something we do on Monday. Any quick question?

OK, great. See you on Monday.