**PROFESSOR:**     OK, let's get started.

Last class, which also means last week, we discussed what happens when atom are exposed to external fields.

Well, you would say, isn't it enough if you understand atoms in isolation?

Well, not quite. Because whenever we want to talk to the atoms, whenever we want to manipulate them or find out in what states they are, we have to apply external fields. The way how we communicate with atoms is through electric, magnetic, and electromagnetic fields. And therefore, we have to understand what happens to the structure of atoms when we expose them to such fields.

We started out with structure in magnetic fields. And if I just show you this picture, this is what we discussed last week. However, I noticed that our discussion with the different coupling cases-- fine structure plus magnetic field, hyperfine structure, strong fields, weak fields. I noticed that when I was teaching, it's a lot of details and it looks a little bit messy. So what I want to do, therefore at the beginning of today, is I want to give you sort of a summary that you see the bigger picture. That you see beyond the details, that what I actually taught you about atoms in magnetic field is some paradigmatic example of quantum physics. What happens if you have two different terms in Hamiltonian and you have to interpolate between one and the other?

But before I do that, do you have any questions about magnetic fields, magnetic structure? Well, then let's try to summarize as follows.

What we have is we have a Hamiltonian. And it has one part, the hyperfine

interaction, which depends on I dot J. And then it has an external magnetic field part. And what couples to the magnetic field, which we assume is in the J-direction-- in the z-direction are the z-components of the magnetic moment. And the z-component of the magnetic moment are proportional to the mJ or mI quantum number, to the magnetic quantum number, of the atom and the nucleus.

So in a weak field, it is the hyperfine structure which dominates. So in a weak field, we first solve for the hyperfine structure. And then we use the eigenfunction of the hyperfine structure. And the eigenfunction of the hyperfine structure have the quantum number F where J and I have coupled to F.

And then we treat the magnetic Zeeman Hamiltonian perturbatively. And that led us to the formulation of the Lande g-factor, gF.

The other case is the strong field case where the magnetic field dominates. Then, we simply solve for the hyperfine structure in the magnetic field. It's one of those rules in quantum physics, or in physics, or maybe even in life, first things first. You should first take care of the big things. And this is now the magnetic field.

And since the magnetic field Hamiltonian is diagonalized when we have eigenfunctions where mJ and mI are good quantum numbers, this is sort of-- if you ignore the hyperfine coupling, this is the exact [INAUDIBLE] of the Zeeman term.

And then in perturbation theory, we look for the hyperfine coupling. And well, we do perturbation theory in eigenfunctions with mI and mJ. And that means if you have the I dot J term, it is only the component mI mJ which remains. So I've given you those two cases.

Now, what you should also learn here in this example is the language which we use. And sometimes, I would say, the language can be more confusing than the equations.

What we say here is we say that the angular momentum of the electron and of the nucleus are coupled to the magnetic field axis. They are quantized. The approximate eigenstates are those which have a specific quantum number in the z-

direction because the magnetic field points to the z-direction. So we're saying I and J are strongly coupled to the z-axis by the magnetic field. And then we treat the coupling of I and J with each other in perturbation theory.

Whereas in the previous case, we say I and J strongly couple. And when I and J strongly couple, F becomes a good quantum number. And that means I and J both precess around the axis of the total angular momentum f. And therefore, we say I and J couple to F. And then we solve for this coupling of F to the magnetic field in a second step. But I hope you see that there's two limiting cases.

We can exactly diagonalize one term, and then we perturbatively add on the result for the second term. Of course, in the age of computers I could have simply written down for you a Hamiltonian and said, well, it has to be numerically diagonalized. What I discussed instead were the two limiting cases.

Now, this discussion now allows me to discuss what happens when we go to even stronger fields. Well, when we go to even stronger fields, then we may have fields which are even stronger than the fine structure coupling, the coupling of the orbital angular momentum of the electron and the spin angular momentum to J.

And well, without even any deviation, which is obvious, you know what happens now is that each component which provides magnetic moment-- the spin, the orbital angular momentum, and the nucleus-- the dominant term for each of them is the coupling to the magnetic field. So in strong magnetic fields, these are the eigenstates. The eigenstates are labeled by mI, mL, mS. So we have taken care of the strong coupling term.

And now in addition, we are now treating in perturbation theory some fine structure coupling, but the quantum numbers are already distributed, mL, mS. There is a coupling become between mI mS and a coupling between mI and mL. So this is sort of the limiting cases.

But as a general illustration of quantum mechanics, I thought this was a nice example for a Hamiltonian where we have different scalar products, like B times S,

B dot L, S dot L, I dot J. And the question is, how do we take care of those different parts because they do not commute?

Of course, the theorist would just say, I simply diagonalize it and that's it. But if you want to develop intuition, then you have to discuss the limiting cases.

And in particular, the approach which allows an intuitive understanding is first things first. And we first treat the stronger terms and then the weaker terms. And we can quantitatively derive, analytically derive expressions, for instance, for the Lande g-factor in this vector model.

This vector model assumes, so to speak, that a state which has an eigenfunction of mJ rapidly precesses around the z-axis. And this vector model actually allows you to do easy calculation without Clebsch-Gordan coefficient. So the concept of the vector model is rapid precession for transverse components and projecting of vectors onto the axis around which you have rapid precession. But this is simply a tool to do calculations without the explicit use of Clebsch-Gordan coefficients.

OK, so this is what I wanted to tell you about atoms in magnetic field. Any questions? OK then, we can actually move onto atoms in electric field.

But before we do that, we should have some clicker questions about atomic structure and atoms comes in external magnetic fields. So get out the clickers.

So the first questions take us back to electronic structure. It's a question about, how do wave functions, how does density, and how does inverse size scale with principal quantum number?

So the first question is, how does 1/r, 1 over the size of the electronic wave function, how does it scale with n? 1/n, 1 over n squared, 1 over n cubed.

OK.

OK, yes. It's 1 over n squared. But I would have hope that 100% of you would know it because 1 over is the Coulomb energy. The Coulomb energy is 1/2 of the total binding energy because of the Virial theorem. So when you see 1/r, there should be

4

a flash in your head which says energy. And Rydberg energy is 1 over n squared. The energy levels of hydrogen are 1 over n squared. OK.

Yeah, next question. How does psi 0 of 0 square, how does the density of the electron at the origin scale with principal quantum number? 1/n, 1 over n squared, 1 over n cubed, or 1 over n to the sixth?

OK, yes, very good. So what I try to remind you here is that there are two different radii. There is one radius which scales with n squared. But if you calculate the density at the origin, if you would say, well, r scales with n squared. The volume scales with n to the sixth. And then you would say the density scales with n to the minus 6, you're wrong.

And we had a discussion that there are two different lengths case in the hydrogen atom and in hydrogenic wave function. One scales with n squared and the other ones scales with n. And therefore, the density at the origin is n to the minus 3.

Good. Next question, from hydrogen to helium. In helium, for the same electronic configuration, , are singlet or triplet states more tightly bound?

So we talked about a shift or splitting between singlet and triplet states. Which way does it go?

You want to try again? For the same electronic configuration-- the ground state has only one configuration. It has only one state in the ground state. But now we go to the excited state, to the excited states, and there are a number of excited states because they have the same configuration, but they can be classified by singlet and triplet states.

OK, we are converging. It is the triplet state. Some people are confused when they think about molecules. usually, in molecules the singlet state is more tightly bound than the triplet state.

But the magic word is for the same electronic configuration. You can have one orbital filled with two electrons only in a singlet state because of the Pauli exclusion

principle. It is only in the first excited state or in an excited state of a molecule or of the helium atom that you have two orbitals, 1s and 2s. And you can now put the electrons in with the same spin or with opposite spin.

So usually, it's only in an excited state that the question singlet versus triplet arises.

And then in the excited state manifold, the triplet state is lower because it has a symmetric spin wave function and anti-symmetric spatial wave function. OK, the next question.

OK, so we understand now there's a difference between triplet and singlet state in excited states for the same electronic configuration. And the question is, what is the origin of the energy which is splitting the singlet from the triplet state? Magnetic energy, spin-spin interactions, or electrostatic interactions?

Yes, the Coulomb interaction is electrostatic interactions. We discussed the singlet-triplet splitting and the structure of helium without any magnetic or spin-dependent interaction. All we had is the Coulomb interaction.

And in the triplet state, which is the symmetric spin state, the spatial wave function has to be anti-symmetric. In the singlet state, the spatial wave function has to be symmetric. And the symmetric and the anti-symmetric spatial wave function have a different Coulomb energy.

So the spin through the anti-symmetry through the Pauli exclusion principle determines the symmetry of the electronic wave function. And it is then purely the Coulomb energy. That's why the singlet-triplet splitting is so big. Because it's not magnetic, it's Coulomb in origin.

OK, next question. Which interaction reflects-- oops, maybe you want to still read it. Which interaction reflects that the potential between nucleus and electron is not exactly a Coulomb potential 1/r? We've usually discussed Schrodinger equation, hydrogen, Bohr model for an exact 1/r potential. But then we discussed a lot of phenomena. And I want you to figure out now, which of those choices mean, in essence that you do not have a 1/r potential?

OK, we have three choices. So the volume isotrope effect, I think, is a no-brainer, is trivial. It means explicitly that the nucleus is not a point, has an extended volume, and that means inside the nucleus the electron is not experiencing a 1/r potential. So it's clear that C is always correct.

The Lamb shift is actually causing a deviation from a 1/r potential because-- well, both the vacuum polarization and the-- well, you can go ahead and say, the fact that we have QED, that we have other modes of the electromagnetic field mean that there's a deviation from the 1/r potential.

The interesting question is the Darwin term. And the people who clicked D included the Darwin term. That's a little bit trickier because I explained the Darwin term as Zitterbewegung, as this trembling motion of the electron which smears out the 1/r potential. So you would think coming from the non-relativistic Schrodinger equation, that there is an effect which is smearing out the 1/r potential.

On the other hand, the Zitterbewegung, the Darwin term, is just one term which is included in the Dirac equation. And the Dirac equation, which includes fine structure and relativistic energy corrections and the Darwin term is an exact relativistic formulation of the 1/r potential.

So in other words, I would say the correct answer is E. The people who included the Darwin term, I would say the Darwin term is not a deviation of the 1/r potential because it's simply a way to explain what is the result of the Dirac equation.

The Dirac equation uses exactly the 1/r potential without any corrections. So you can say that if you want to understand the relativistic solution to the 1/r problem, you include a term which in the non-relativistic equation slightly changes the Coulomb potential. Questions about that? OK.

Fine structure. The fine structure affects only states with L equals 0 through a coupling term L dot S. Is this statement, the way how it is written, true of false?

I would say it's false because the fine structure has three contributions-- the Darwin

term, the relativistic kinetic energy contribution, and this L dot S term. And it effects all states, also the S states, through the Darwin term and the relativistic energy contribution. So the fine structure is more than just an L dot S term.

Next question is for L equals 0, the orbiting electron creates a magnetic field. And spin orbit interaction can be simply regarded as the energy of the electron's spin in this magnetic field. Would you say that this sentence is true or false?

I thought it's true, but maybe people want to tell me what is false about the statement? Maybe the first sentence people did-- tell me, the orbiting electron creates a magnetic field. Yes.

**AUDIENCE:** I said false for this because I normally would picture that from the electron's frame of reference, the nucleus creating a magnetic field is the magnetic field [INAUDIBLE].

**PROFESSOR:** OK, the second part, that there is a magnetic field and it's been orbiting the action is the energy of the electron spin in this magnetic field is probably generally accepted. But the first question is, does the orbiting electron create the magnetic field?

Well, we have the two options. We can say the electron moves and in its own frame there is a v cross e term. And therefore, magnetic field. So we can say that the electron's motion creates a magnetic field in its own frame for the relativistic transformation. So in that sense, it is correct. but I would also side with you that there is an alternative view of saying in the electron's flame, the nucleus rotates around the electron. And it's the nucleus which creates the magnetic field. In the end, it's the relative motion between the two.

Well, isn't it a good thing that we are not giving scores on that? So yes, if you want, you everybody can feel that you have given the right answer.

Oh, yeah. In Dirac-- that should be easy, but it's just a warm-up question for the next one-- which states are degenerate in Dirac theory? And you have a few choices. That should be easy.

Yeah, it's the S 1/2 and P 1/2. Dirac theory does not lift the degeneracy between states with the same J, 1/2 and 1/2. But between 1/2 and 3/2 states, there is, actually, the fine structure splitting, which we've just discussed.

OK, the next question is, what effects lift now the degeneracy between the 2 S 1/2 and the 2 P 1/2 term?

OK, we have three candidates-- the Lamb shift-- well, the Lamb shift is famous and the Lamb shift was discovered because it splits the degeneracy between the two. QED corrections have different effects on S 1/2 and P 1/2. The size of the proton does also shift it, because the size of the proton-- the volume effect is more important for S states than for P states. Maybe the question is, does the mass of the proton lift the degeneracy?

No, it doesn't. It would just mean if your nucleus has a finite mass, you simply have a two-body problem with a reduced mass, which is different from the bare mass of the electron. But nothing else is changed, no degeneracies. It's as if the electron has a different mass, which is the effective mass. So the correct answer here is D.

OK, four more questions. And this is about hyperfine structure.

So the question is, what-- well, hydrogen in the ground state has four states. Because the electron has a spin up and down and the proton has a spin up and down. And 2 times 2 is 4. So we're talking about multiplicity of 4. And I'm asking you now about the limits of high and low field. First at high fields, then at low fields. And the question is, what are the magnetic moments of those hyperfine states? And we neglect the nuclear magneton compared to the Bohr magneton. So what are t magnetic moments of those hyperfine states in units of the Bohr magneton?

Oh, yeah. What happens at high magnetic fields?

Remember, at high magnetic fields, this is actually the simpler case. Often, you think the low magnetic field is simpler because it connects more with the isolated atom. But you should take away the message that high magnetic fields are simple. Because in high magnetic field, each spin couplets to the magnetic field by itself

because the coupling to the strong magnetic field-- that's the definition of a strong magnetic field-- is stronger than the coupling of the two spins with each other.

So the problem I'm giving you is that you have an electron spin which can be up and down and it couples to the magnetic field. And then we have the nucleus spin, but the magnetic moment of the nucleus is so small that we neglect it. So what are the possibilities now?

Well, we have four states of hydrogen at high magnetic field. Two have the electron spin up, nucleus spin up/down. Two have the electron spin down. And then when the nucleus spin is up or down in those two states. So all the states at high magnetic fields have either the electron spin up or the electron spin down. So therefore, the correct answer is A. We have two states where the electron spin is up and two states where the electron spin is down.

It's just a complicated way of asking you, what are the possible energy levels of an electron in a magnetic field? And the answer is, well, plus-minus 1 Bohr magneton times the magnetic field. Questions about it?

OK. Now, we go to the more complicated case, to low magnetic fields. And again, same question. What are the magnetic moments of those hyperfine states?

So you have four states. The number of states, of course, doesn't change. That's the dimension of our Hilbert space. But now we are at low magnetic field, and what is the magnetic moment, which is nothing else than the derivative of the energy with respect to the magnetic field?

Yes, the correct answer is B. We have two manifolds, one is F equals 1, where one slope is 0 and one slope is plus-minus 1. And then we have an F equals 0 state. So it is 1, minus 1, and 0, 0. OK.

Let's now make it more interesting. Let's replace the proton by a positron, the anti-particle of the electron. So now we have a similar situation, but what happens now is, of course, the contribution to the magnetic moment form the nucleus, which is now the positron, is as important as the contribution of the electron. So you have

two spin 1/2's coupled now. One is positive, one is negative. And you should figure out again, what are the energies?

But before we talk about the energies, let's first talk about, how many hyperfine states do we have in the ground state-- 1, 2, 3, or 4?

Yes, we have four states because we have two particles-- positron, electron. Each of them has spin up, spin down. 2 times 2 is 4. And therefore, we have now four states. And the question is again, at high and low magnetic fields, what are the magnetic moments of those states?

So we have four states-- spin up, spin down-- of the electron and the positron. And the question is, what are the magnetic moments of those hyperfine states?

D is correct. We have 1/2, spin 1/2. If the two couple like up-up and down-down, we have the maximum spin. But since one particle is positive, one is negative, when the spins are aligned, the angular momenta are anti-aligned. And therefore, the magnetic moment is 0. So when they couple parallel, the magnetic moment is 0. When they couple anti-parallel, the two magnetic moments of one Bohr magneton each add up, and we have either 2 or minus 2 as the magnetic moment. Any questions?

Then finally, the last question. Same situation, positronium, but now at low magnetic fields. What are the magnetic moments of the four hyperfine states of positronium at low magnetic field?

All right. Let's discuss it. What is the structure of the ground state at low magnetic field? What is the good quantum number at low magnetic field?

**AUDIENCE:**      F.

**PROFESSOR:**   F. It's hydrogen. It's like hydrogen. 1/2 and 1/2. If we have an S of 1/2 of the electron, the I of the positron is also 1/2. And 1/2 and 1/2 couple to F. And what are the values for F?

F equals 1 and F equals 0. OK, what is the magnetic moment of the F equals 1 state?

In order to get F equals 1 out of 1/2 and 1/2, you have to align the spin of the electron with the positron. So the F equals 1/2 state is the state where the two spins are aligned. What is the magnetic moment or this state?

**AUDIENCE:**     0.

**PROFESSOR:**     0. How many states are in the F equals 1 manifold? What's a multiplicity of F equals 1?

3. Plus, minus 1 and 0. So we have an F equals 1 state which has angular momentum but no magnetic moment, and it has a multiplicity of 3. So three states have 0, 0 magnetic moment. In other words, you would expect an F equals 1 state to have this kind of Zeeman structure. But because of the special situation in positronium, the Zeeman structure is like this. There is no linear effect. It's a quadratic effect. All three states start out with 0 slope because as long as the spins couple to F equals 1 and we don't have a magnetic field messing up with the coupling, the magnetic moment is 0. OK, now what happens in the fourth state, which is F equals 0?

In the fourth state, which is F equals 0, the two spins couple in an anti-parallel way. So now, what is the magnetic moment when the two spins couple in an anti-parallel way?

The spins subtract. But because of the different charge, plus and minus, the magnetic moments would add up. That's what we just discussed in the high field case. So you would think the F equals 0 state has a magnetic moment. But in an F equals 0 state, it cannot point anywhere because the angular momentum is 0. And therefore, in a most trivial way, this is hydrogen and this is positronium.

So positronium has four hyperfine states. And the slope of all four, for the reasons discussed, is all 0. So sorry, A is the correct answer, without any ambiguity this time.

OK. Any questions?

OK, then let's talk about atoms in electric field. We start out in-- we put the atoms in a uniform electric field. Again, we assume that it points in the z-direction and its magnitude is epsilon. And we want to ask, what is the electrostatic energy in this electric field?

And we are using the fact that electrostatic energy can be expanded in a multi-pole expansion. We have a monopole term, we have a dipole term, and we have a quadratic term.

So the charge, of course, is-- the atom, itself, is a neutral atom. So there is no monopole term.

The linear term in the electric field would correspond to a permanent dipole moment. And I will remind you in a moment that this is 0. And then the term which provides us with a stark effect, with the energy shift of atoms in electric field will be the third term here, which is characterized by the polarizability alpha. And it corresponds to an induced dipole moment. That there is an induced dipole moment, which is alpha times epsilon. And then the induced dipole moment interacts with the electric field. And that gives then, epsilon times epsilon-- epsilon squared. So this would be a classical multi-pole expansion.

And we will now derive results quantum mechanically. The perturbation operator for us is the dipole operator. And that could, in principle, include a permanent or an induced dipole moment. So it would take care of the second and third term, the dipole operator and its projection on the z-axis. So the dipole operator is the charge of the electron times the position.

And as long as the polarizability and the situation is isotropic. A minus sign. Minus E is the charge. If you apply an electric field in the z-direction, all the relevant dipole moments are in the z-direction. For anisotropic materials, you could have an electric field in the z-direction and the dipole moment points at an angle, but we do not have such a situation for our atoms.

OK, so the operator is then simply charge of the electron, the z-coordinate times the electric field. And this has o parity. And that leads us immediate to the result when we have an atom in an eigenstate n and we ask, what is the expectation value of H prime?

It is 0 because of parity. So the answer is, we have no permanent dipole moment until we have degenerate energy levels. If n is a non-degenerate level, this matrix element is 0 by the parity selection rule.

OK, now we want to do perturbation theory. So our perturbation operator is this. And since we have the clickers, I just want to ask you two quick questions.

I will do the perturbation theory and I will explain everything, but maybe you want to predict the result, which I want to derive in the next 10 minutes. And the question is, what will we actually get for the expectation value of H prime? Will we get the expectation value of the dipole operator times the electric field or will we get the expectation value of the dipole operator times the electric field over 2? And the next question would be the same, but what do we get for the total Hamiltonian? So these are the questions.

I want to discuss with you in the next 10 minutes, simply using perturbation theory, expectation values. Expectation values of the total energy each, not plus H prime. But also, expectation values of the electrostatic energy, which is H prime. And the question is-- I mean, you can say for dimensionless units, what we get is a dipole moment times an electric field. And this is one of the situation where factors of 1/2 are not just bookkeeping. Factors of 1/2 really reflect interesting physics. And I want to sort of highlight it by asking you, what would you expect what we get for those expectation values when we solve for atomic energy levels in electric fields?

So we're discussing first question 1. OK, let's go to question 2.

OK. Anyway, now I know I'm not boring you with the derivation I want to give you in the next 10 minutes. I want to give you the answer right away by drawing up another problem where maybe the answer is more intuitive. And this is we have a

mass on a spring with spring constant k. And now the equivalent to the electric field which we switch on is-- we switch on gravity. And due to gravity, the object zags by an amount delta z. So the question is, what is-- and delta z is like the dipole moment. What is the gravitational energy gained by the object because it has fallen down? It is zagging down due to gravity.

Well, I think you would agree that the answer is, it is mg times delta z. This is the work done by gravity with a minus sign. So the expectation value of the perturbation operator is minus mg times delta z. Or in electrostatic units, it's simply the dipole moment times the electric field.

But what happens is the-- so this is gravitational energy. How much is the total energy affected when we switch on the gravitational field?

1/2 of it, because the negative energy which is gained in the gravitational field, 1/2 of it is used to stretch the spring. 1/2 of it goes into the internal energy of the system.

So therefore, the electrostatic energy H prime-- H prime is the operator of the electrostatic energy. The answer here is A. But the total energy is B because part of the energy is needed to stretch the spring. And as I want to show you, stretching the spring is-- we admix to the ground state some excited state. This costs energy, like stretching the spring costs energy. And this is responsible for the fact of which is exactly 1/2.

Well, I could stop here. I think I've explained it all, but let's follow the usual-- the standard approach. And let's do second-order perturbation theory and calculate the energy, calculate the dipole moment, and see that everything is as we expect now.

So we want to do second-order perturbation theory. We know already the first-order term is 0. This was a discussion about parity. And in second-order perturbation theory, the state n has an energy, which is the unperturbed energy. And then in second-order, we have the matrix element to all other states. We square it. We divide by the energy denominator. We sum over all states m, but I make a prime

here. Of course, we are not summing over the state-- we exclude n from the summation.

And the prefactor here is electron charge squared times electric field squared. OK, pretty much that's the resulting second-order perturbation theory. So this is the energy and we want to relate the energy to the dipole moment. So the next step is now we calculate d. and we calculate d from the first-order wave function because we already get an effect in first order and everything here is about leading order.

So the expectation value of the dipole operator-- so we take the expectation value of the dipole operator and we use the 0-th order, the unperturbed state, plus the first-order correction. And we know already that the diagonal terms do not contribute. This is a parity selection rule. So we get contributions from the course term, which is n0 the dipole operator with n1.

So let's just suppress vectorial notation. We know everything is along the z-axis. So we have the 0-th order wave function. Our operator is z. And now we have to write down the first-order correction to the wave function. And the first-order correction is the sum over all other states.

We make an admixture of the state m, and this admixture uses a matrix element. And here, we have the energy denominator. So what we obtain is-- we have the electron charge here from the dipole moment. We have the electron charge due to the perturbation operator. So it's electron squared.

We have the electric field. And then, this is due to the admixture of the wave function with the dipole operator. And now because we take the matrix element of the dipole operator, we get another occurrence of the dipole operator. So therefore, we do first-order perturbation theory, but we take the first-order result and ask, what is the expectation value for the dipole moment?

And that means the dipole operator, or the perturbation operator appears twice. And our result is as expected. Quadratic in the matrix element and it has this energy denominator. So the definition is that a dipole moment is alpha times the electric

field. So therefore, all that equals alpha.

And if you compare now the result for the dipole moment with the second-order perturbation theory for the electric field, for the energy, we find-- here's a factor of 2, but there is no factor of 2 up there. We find that the energy or the energy shift delta En, it has exactly the same matrix element as the polarizability. It is-- yes. It is this, 1/2 alpha epsilon squared.

Since the perturbation operator, I'm just writing it down here, was dipole moment times electron, that means that the energy shift is-- and this is what we expected now, is 1/2 times the expectation value of the dipole moment times the electric field.

So now we have obtained with a quantum mechanical calculation the result. I told you that the energy shift of the energy levels is 1/2 the dipole moment times the electric field. Let me just redo the calculation in a way I like. And this is I want to determine now the total energy, but sort the terms in a little bit different way.

So I want to know, what is the energy in our result? And what we do is we are calculating the energy using our wave functions. We take the total Hamiltonian and take the wave function.

So this leads us to three terms. One is the unperturbed energy. The unperturbed energy, the energy contribution of the first-order correction.

This is the part due to H0. And the part due to H prime is simply the dipole moment times the electric field. So the first part is, of course, simply the energy E0 times the norm of the wave function n0.

For the second term, we use the first-order perturbation theory for n1. This is our sum over m. Em minus E0. m H prime 0. Because n1 is on either side, this is the amplitude of the state n1. We have to square it. And since we calculate what is the expectation value of H0, we multiply with the energy Em.

OK, so we are done. We calculate the total energy. We get three terms. One is the unperturbed energy, one is the dipole energy in the electric field, and one is the

extra term, which I want to discuss. Actually, this term is the internal energy, which would correspond to the stretching of the spring in Hooke's law.

Now, in order to show it to you explicitly, I want to use E0 equal 0 for the energy. Because then this term is 0. I can neglect this. And one of the squares, 1 over Em squared, cancels with the Em.

It confused me for a while. If I don't set E0 to 0, the result looks different. But what happens is, if you do perturbation theory, there are certain issues with the normalization of the wave function. And the wave function n0 has to be-- the contribution if you look at the wave function in perturbation theory of a state, the 0-th order wave function has an amplitude of 1. And this amplitude of 1 only changes in second order.

So since I'm doing a second-order calculation here, I have to include those non-standard terms. But I can also bypass it by setting E0 to 0, then the second-order term in the norm doesn't matter. So in other words, if you set E0 to 0, you make your life easier. If you do not set E0 to 0, you have to include some more terms in your calculation.

But the result is-- just one second. But yeah, the result which I wanted to emphasize is this one here. It is a positive energy. You can immediately inspect that t positive energy is the dipole moment times the electric field over 2. This is exactly analogous to the energy of the spring in the gravitational problem. So in other words, this is the energy, internal energy, because we admix excited states to the ground state. This crosses energy and it exactly accounts for the occurrence of the factors of 1/2.

Anyway, this is just the standard theory of the DC stark effect of the atomic polarizability, but I put a little bit of emphasis on those factors of 1/2 and tried to explain in greater detail the contributions to the AC stark effect-- to the DC stark effect which come from the electrostatic energy and which come from the internal energy. Questions? Yes.

**AUDIENCE:**     Sure. I have a study question. What is allowing you to use non-degenerate

perturbation theory? What's the operator that [INAUDIBLE]?

**PROFESSOR:** Well, I'm looking-- what allows me to do non-degenerate perturbation theory.

Well, I assume we don't have degeneracies. If you would go to very high Rydberg states-- and actually, we do that not today, but on Monday-- we are looking at a situation where the splitting between states of different L become so small that the electric field mixes them.

Then, we have to do degenerate perturbation theory. And that means we get now a linear term, linear stark effect, not a quadratic stark effect.

Here, I would say we are doing perturbation theory of the ground state. It's an S state. It's not degenerate. Maybe your question is also addressing, but we have multiple ground states. We have hyperfine structure.

However, the electronics-- the stark effect, the electric field does not couple to the spin at all. So therefore, all the magnetic energies-- the hyperfine energies are completely unaffected. And also, if we apply an electric field, all the hyperfine states experience the same shift and there is no coupling between them. So also, we have multiple ground states. We have hyperfine structure. It's a non-degenerate problem because there is no coupling between the different hyperfine states.

In other words, the theory or the discussion of the DC stark shift is you have an S state, you couple with an electric field, and there is no degeneracy in the S state. Other questions?

Well, then we've talked about alpha. The only parameter which comes out of this treatment is alpha. And now we want to discuss, how big is alpha? Or first, what are the units of alpha?

Well, the units of alpha were-- you can go back to the second-order perturbation result. But the units of alpha were the charge, time [INAUDIBLE]. This was the dipole operator. It was squared. And in perturbation theory, we divided by energy because we had an energy denominator.

Well, we can write that as q squared over l times l cubed. But q squared over l is the Coulomb energy. And therefore, when I'm interested in the units, the units cancel. So therefore, we find that the unit of the polarizability, at least in [INAUDIBLE] unit or atomic units, which I've chosen here, is simply the volume. The question is, what volume?

Well, if you would calculate the polarizability for hydrogen, and simply make the assumption that the only important matrix element goes from the S to the P state, then we have a matrix element which is on the order of [INAUDIBLE]. And the energy splitting between the first ground state and first excited state is three quarter of the Rydberg constant.

So for hydrogen in the 1s state, if you only use the coupling to the 2p state, we find that alpha is the Bohr radius cubed. And the prefactor is 2.96. If you do the summation over all states, the prefactor would be 4.5 because there are higher states, especially continuum states, which contribute to the sum.

We have only five minutes left, but that allows me to show you that this is not a coincidence that we obtain-- here, what we obtain is the Bohr radius cubed, which is pretty much the volume of the hydrogen atom. But we can now do an approximation. It's not really relevant, but it has an historic name-- [INAUDIBLE] approximation. It's just nice to show how things work out.

We have a second-order matrix element, so we couple the state n with the operator z to a state m. But if we assume that all energy denominators can be taken out of the summation by assuming that we have some kind of average excited energy, then the sum of-- maybe I should have said it the sum m z n, which we sum over m and it just cancels out.

So what we have is, if you take the energy, an average energy denominator out of the summation, what we find is that what matters is the matrix element z squared.

And we can even assume that in the energy denominator, the excited state energy is negligible. The hydrogen atom has a binding energy of 1 Rydberg and the first

excited state has a quarter Rydberg. So at the 25% level, we can set that to 0. So I'm waving all my hands, but I'm getting a simple expression for the polarizability in the ground state. And this goes as follows-- the ground state energy is-- we have discussed Coulomb energy, Virial's theorem, and all that. We need just 1/r in the ground state. And for the z squared matrix element, we can simply say for an S state that it is x squared y squared z squared. It is 1/2 of r squared in the ground state.

So therefore, continuously waving our hands and making approximations, we find that the polarizability is r squared expectation value divided by an r to the minus expectation value. So this is some r cubed expectation value which is an atomic value.

So you see the nature of the perturbation expression suggests that cannot be anything else than the atomic volume. I sort of like that because when people discuss, for instance in my group, does lithium or rubidium have a bigger polarizability?

Well, the bigger atom has a bigger volume and the more fluffier atoms have the larger polarizability. And that's pretty much based on that result.

Now, let me finally do a comparison. There is another system for which you have done calculations of the dipole moment. And this is in classical E and M for conducting sphere. For conducting [INAUDIBLE] electric field, you can exactly solve the boundary conditions, the boundary value problem, get the electric field, and find the dipole moment.

And the exact result is that the dipole moment is the electric field times the cube of the sphere. So in other words, the dipole moment, or the polarizability of this sphere, is-- and neglecting factors, which are only factors of unity. The dipole moment-- sorry, the polarizability of a conducting sphere is the volume of the sphere.

The dipole moment of a hydrogen atom, or using [INAUDIBLE] approximation for all

simple atoms is the volume of the atom. So I find it sort of interesting that when it comes to dipole moments and to polarizability, that atoms pretty much behave like metallic-conducting spheres of the same volume.

Any questions? OK, then let's stop here and we meet again on Monday.