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**PROFESSOR:** OK, so let me just quickly remind you of what we've done what we did last time. So unfortunately, today is going to be a little bit of what I wanted to do this time and a little bit of what I would have wanted to have been done in recitation yesterday, because all recitations were cancelled. So today is going to include a few steps along the way that I skipped over last time.

OK, so to review from last time, we talked about central potentials. The energy operator had a radial derivative term, an angular momentum term, and a potential term. So this would be true regardless of whether we were central or not. But if we have a central potential, where this only depends on the magnitude of the radius vector, then we can use separation of variables, and write an energy eigenstate as a radial part-- which we will sneakily pull out a factor of  $1/r$  over the radius-- as we saw last time, that was particularly convenient. It took care of this  $r$  and made everything nice and simple.

So a radial part times a spherical harmonic. The reason we use a spherical harmonic is that neither of these two terms depend on the angular coordinates. The angular momentum, we know what its eigenfunctions are, so if we use a spherical harmonic, this angular momentum becomes just a constant.

And having separated in this form, and pulling out that sneaky factor of  $1/r$ , the energy eigenvalue equation reduces to a simple 1-D effective energy eigenvalue equation with a simple  $dr^2$ , and an effective potential, where the effective potential is the original central potential plus an angular momentum term, often referred to the angular momentum barrier-- which is proportional to-- as Matt says, as Professor Evans says, in 804, one is forced to say  $\hbar^2$  squared upon  $2m$  repeatedly. And he pointed out that it would be much more efficient if I would just

come up with a simple variable for saying it or sound. So I will attempt to henceforth call it pfft.

[LAUGHTER]

So the effective potential is pfft,  $l(l+1)$  upon  $r$  squared plus the central part of the potential-- props to Professor Evans. And this is true in general for central potential. The last thing we notice of this is that since the energy eigenvalue equation has been reduced to this form, which depends on  $l$ , but is independent of  $m$ --  $m$  appears nowhere here-- the energy can't possibly depend on  $m$ , although it can depend on  $l$ . It's just  $e$  of  $l$ . And thus, for every different value of  $m$ ,  $l$  will get the same energy-- fixed  $l$ , different  $m$ .

And there are how many values of  $m$  for a fixed  $l$ ?  $2l+1$ . So the degeneracy of  $E_l$  is  $2l+1$ . Right? That's general for any central potential. It only requires spherical symmetry.

So then we say the example of the Coulomb potential, where the potential is minus  $E$  squared upon  $r$ . And we solved-- or I quickly reviewed the solution of the energy eigenvalue equation. I'll write it that way-- where  $r$  of what I will call-- in place of  $E$ ,  $l$ , will simply write  $n$ .  $R_{nl}$  is equal to  $e$  to the minus  $r$  over  $2r$  naught  $n$  times  $r$  over  $r$  naught to the  $l+1$  times some simple function  $v_{nl}$  of  $r$  over  $r$  naught, with the energy  $E_{nl}$  being equal to  $E$  naught-- or I should say  $e$  Rydberg in our notation of last time-- upon  $n$  squared minus bound state.

So let's talk about this quickly. This term-- the fact that it goes exponentially-- falls exponentially at large distances-- came from the asymptotic analysis at  $r$  goes to infinity. And this is just saying it's a bound state. The probability density falls off exponentially as we get to large radius.

This term came from the asymptotic analysis near  $r$  goes to zero. And near  $r$  goes to zero, the only term that matters is in the effective-- this is one upon  $r$ . This is  $1$  over  $r$  squared, so this gets large more rapidly. This term is important, and that  $l(l+1)$  gave us  $r$  to the  $l+1$ .

We work in dimensionless variables,  $\rho$ . And here, I replace  $\rho$  with  $r/r_0$ , where  $r_0$  was the characteristic scale we computed last time.

And finally, this function  $V_{nl}$  satisfied-- it again satisfied the energy eigenvalue equation, but having pulled out these factors such that asymptotically, it's regular. So this function must be regular, smooth-- no divergences, no poles-- as  $r$  goes to infinity and to 0. OK.

And then we solved this by series expansion. And from termination of the series expansion, we got that the energy-- we got a relationship between the energy and  $l$  and  $n$ , and in particular the relationship-- this came from termination of the series, just like it did for the harmonic oscillator. And the termination series gave us that the energy was equal to minus a constant over  $n^2$ . With one additional condition, which is that  $n$  had to be greater than  $l$ .  $n$  had to be an integer greater than  $l$ . And  $l$ , of course, has to be greater than or equal to 0.

So let me just quickly tell you how this arises, because this is an important fact about hydrogen which I want you to understand. So the way that arises is we got the energy from a series expansion for this remaining function of  $r$  and  $l$  of  $r$ . And that series expansion started out by saying let  $v$  be of the form  $\sum_j a_j (r/r_0)^j$ , the dimensionless variable  $\rho$ , to the  $j$ , to the  $j$ -th power, so it's a power series.

And when we plug this whole form, together with this series expansion, into that differential equation, we get-- just like we did before for a harmonic oscillator-- we get a set of relations between the various coefficients in that series. And we solve that by saying  $a_{j+1}$ -- by deriving a recursion relation-- is equal to  $a_j$  times  $2, \sqrt{\epsilon} (j+1) - 1$  upon  $j+1, j+2$ .

OK, fine. We get this recursion relation. It looks absolutely awful, but it tells you that if you know  $a_0$ , say, is a constant which is not 0-- if it's zero, then they're all 0-- then this function is identically 0, because  $a_{j+1}$  is  $a_j$  times some constant. So this had better not vanish--  $a_0$ .

So the first term, the constant term doesn't vanish, which is good. It tells us  $V$  doesn't vanish, so we've already learned something. If  $V$  doesn't vanish identically at the origin, then we can determine  $a_1$  from  $a_0$  by multiplying by this.  $j$  is 0 in this, and  $l$  is whatever number we fix from  $y_{lm}$ .

And so on. We can deduce all the higher  $a$  sub  $l$ 's. It's a series expansion. This is the recursion relation for it.

However, note the following thing-- as  $j$  gets large, so we go to higher and higher orders in the series, then  $j$  is much larger than whatever fixed number  $l$  is, and much larger than whatever fixed number  $2$  is. So this asymptotes to  $a_j$  times roughly  $2^{\epsilon/j}$ . At very large  $j$ , this just goes to  $2^{\epsilon/j}$ .

Now, let's think about what that means. If I have that  $a_{j+1}$  is roughly equal to  $a_j$  times  $2^{\epsilon/(j+1)}$ , I guess, then this tells me that every time I increase  $j$ , I get a factor of  $j+1$  and another factor of  $2^{\epsilon/(j+1)}$ . This tells me that  $a_{sub j}$  is equal to  $a_{sub 0}$  times  $2^{\epsilon \sum_{k=1}^j 1/k}$ .

But those are the expansion coefficients of an exponential-- quantity to the  $n$  over  $n$  factorial. But that's bad, because if this series is the exponential series with argument  $2^{\epsilon/j}$ , then this series becomes  $E$  to the  $2^{\epsilon/j}$  over  $j!$ . But that's bad, because that would exactly swamp this term. That would defeat the asymptotic analysis we did at the beginning. If this term,  $V$ , is growing so large twice as rapidly as this is going to 0, then the net is diverging at infinity. That's bad.

So in order for this-- for the series expansion-- to describe a good function that really does vanish at infinity, we need that this doesn't happen. So it must be true that  $j$  doesn't get large enough that the exponential in  $V$  overwhelms the decaying exponential from the asymptotic analysis. Everyone cool with that?

So it has to terminate. But if it terminates-- let's look at the coefficient here. If it terminates, this says that  $2^{\epsilon/j}$  times  $j!$  plus-- and if it terminates, that says that there's some  $j$  maximum. Well, let me write it over here.

If it terminates, that means there's some value  $j$  such that  $a_{j+1}$  is 0. But if  $a_{j+1}$  is zero, how can that possibly be? It must be that for that maximum value of  $j$ , the numerator vanishes-- specifically for that maximum value of  $j$ . Yeah?

Well, what's the condition for that numerator to vanish for a specific value of  $j$ ? If  $j = j_{\text{max}}$ , or  $j = j_{\text{max}}$ , the maximum value, such that  $a_{j_{\text{max}}+1}$  vanishes. So  $j_{\text{max}} + l + 1$  must be equal to 1. Or said differently,  $\epsilon_0$ -- which is the energy in units of  $e_0$ , must be equal to  $1 / (4 g_{\text{max}} + l + 1)^2$ . Cool?

So that means that our solutions, or states  $\psi$ , are now labeled by three integers. They're labeled by  $l$  and by  $m$  from spherical harmonics, but they're also labeled by the value  $j_{\text{max}}$ . And  $j_{\text{max}}$  can be any number from 0 to infinity, right? Strictly, it shouldn't be infinite, but any finite number, any countable, any integer-- because eventually the series terminates at  $j_{\text{max}}$ .

So it's labeled by these three numbers, and the energy of  $l m j_{\text{max}}$  is equal to  $e_0$  minus over 4. And this  $e_0 / 4$  we already saw was  $e_{\text{Rydberg}}$ , 13.6 eV, times what value? Well, here's the energy in units of  $e_0$ --  $j_{\text{max}} + l + 1$ , quantity squared. Where  $l$  is greater than or equal to 0,  $j_{\text{sub } m}$  is greater than or equal to 0, and  $l$  is 1.

But this is sort of cumbersome. We can just as well call this quantity  $n$ , where  $n$  is greater than  $l$  as an integer. It can't be equal to  $l$ , but it could be 1 greater than  $l$ , or any greater integer. Is that cool?

So instead of labeling it by  $j_{\text{max}}$ , the point at which the series terminates, we'll label it by  $n$ , and you can deduce what  $j_{\text{max}}$  is by subtracting  $l + 1$  from  $n$ . That tells you where the series terminates.

Notice that this tells you something nice. This power series for  $V$ , if  $n$  is equal to  $l + 1$ , has how many terms in it? So say it out loud, just think about it a second. If  $n$  is equal to  $l + 1$ , how many terms are there, that are non-vanishing in the power series? I won't call on you, but raise your hand when you have an answer.

What's the value of  $j_{\text{max}}$  if  $n$  is equal to  $l + 1$ ? So what term is the first one to

vanish in the series? OK, so how many terms are non-vanishing? Yeah, just the one-- just the first term.

So when  $l$  is as large as it can possibly be-- when  $l$  is equal to  $n$  minus 1,  $V$  is a constant function. It's just constant. When  $l$  is one less, when  $l$  is  $n$  minus 1, or  $n$  is  $l$  plus 2, then  $V$  has two terms in it-- a constant, and a linear. So the greater the difference between  $l$  and  $n$ , the more terms there are in the series. OK?

So anyway, this leads to this form of the energy. But as is usually the case, this sort of a brute force analysis doesn't give us a whole lot of insight into why we get the qualitative features we do. In particular, the qualitative feature that stands out most obviously to me-- I don't know about you guys-- is the fact that the degeneracy is now much, much larger.

In particular, we know from basic principles of a central potential-- as we just reviewed-- that anytime a potential is symmetrically invariant, is spherically symmetric-- any time the potential is spherically symmetric, rotationally invariant-- then there must be degeneracy of  $2l$  plus 1 for every energy eigenstate-- there must be. The  $l$  could be zero, but if there's any angular momentum, then that degeneracy must be  $2l$  plus 1. But this is much more degenerate.

And in fact, how degenerate is it? Well, for any given  $E_n$ , the degeneracy is equal to-- well, what are the possible values of  $l$ ? So we have some state for every different value of  $l$ .  $l$  could be equal to 0, and it can go up to  $n$  minus 1, right?

Because, again,  $n$  is some integer which could vanish,  $l$  plus 1. So as small as this can be is 0. So  $n$  can be  $l$  plus 1, or anything greater. I.e.:  $l$  can go up to  $n$  minus 1, but it can't be any greater.

Then for every value of  $l$ , there is a state  $n$ -- there's a value of  $n$  which could be minus  $l$  all the way up to  $l$  in integer steps. So how many states are there? Well there's one state for every value of  $n$ ,  $l$ , and  $m$ . So it's this sum. The sum on  $m$  for minus  $l$  to  $l$  is  $2l$  plus 1. So this is the sum  $n$  minus 1,  $l$  equals 0, of  $2l$  plus 1. And this is equal to, kind of beautifully,  $n$  squared-- just arithmetic series.

So we have this huge degeneracy, which is much larger than  $2l + 1$ . It's the sum over  $2l + 1$  from  $l$  to  $0$  to  $n - 1$ . Where is this degeneracy coming from?

Why?

So quantum mechanically, we know the following-- we've learned the following-- and I hope it's under your fingernails at this point-- that when you see a degeneracy, you should expect that degeneracy to follow from some symmetry. There's some symmetry of the system that is leading to a degeneracy by virtue of the fact that the generators of that symmetry-- for example, for rotation it's angular momentum-- commute with the energy. And when you have an operator that commutes with the energy operator, as we've seen, you can generally construct new states given a single energy eigenstate by acting suitably with that operator.

So we should expect there to be some new symmetry. But it's very hard to see what symmetry. I mean, this is hydrogen. This is central potential. It's just some stupid central potential. What's so special about the hydrogen system as opposed to, for example, the harmonic oscillator? Which hopefully you will see in recitation at some point.

The harmonic oscillator in three dimensions has degeneracy  $2l + 1$ . It's a central potential. It has to have degeneracy  $2l + 1$ -- but not  $n$  squared. Where did that come from? What's so special about the Kepler problem?

So there must be some symmetry, but it's not obvious what it is. But now let's use a note from classical mechanics. Noether's Theorem tells us when we have a symmetry, we have a conserved quantity. We also saw this in the quantum mechanical version for expectation values. We have a conserved quantity.

And in quantum mechanics, having a conserved quantity means that the energy commutes with some quantity. Because that controls the time evolution of the expectation value. So there must be some quantity, which I've written by a question mark, that commutes with the energy operator, specifically in the case of the harmonic oscillator. So what is that quantity?

So actually, this quantity in classical mechanics was studied, because the same thing is true in the Kepler case. In the Kepler case, the orbits close, and they have simple ellipses, and they have all sorts of nice properties that beg for an explanation in terms of symmetry. And it was pointed out by a number of people-- Laplace, Runge, Lenz, various people-- and this is often called the Runge-Lenz vector, but I think you can blame it on any number of people-- that there's a vector that in classical mechanics, for the Kepler problem-- or for the Coulomb problem, is conserved. And that quantity is  $\mathbf{p} \times \mathbf{l}$ -- momentum cross angular momentum-- minus  $m e^2$ -- and let me write  $m$  sub electrons-- it's the mass rather than the quantum number little  $m$ --  $e^2$ ,  $\mathbf{r}$  vector.

So it turns out this quantity is classically conserved, and if you make a quantum operator out of it, then  $\hat{H}A$  is equal to  $0A$ . Add  $\hbar$ . This was enormously non-obvious. If it's obvious to you, you're a freak. It's really, really not obvious. You can go through and do the calculation. And when I say really not obvious, I mean-- well, I'll show you what I mean in just a second.

So you can go through and do the calculation classically. Is this quantity conserved in the Kepler problem using Newton's law? And the answer is yes. It's amazing.

Quantum mechanically, you can do the same thing. But I'm going to warn you for anyone who has the chutzpah to try-- because I encourage you to, but it takes a little bit of brawn-- think about this operator for second. Does this classical quantity have an obvious interpretation as a quantum operator? No, because  $\mathbf{l}$  is  $\mathbf{r} \times \mathbf{p}$ .

But now we have  $\mathbf{p} \times \mathbf{r}$ . There's an ordering ambiguity. So you have to decide which order do you put that  $\mathbf{p}$  and that  $\mathbf{r}$ , and the other  $\mathbf{p}$ --  $\mathbf{p} \times \mathbf{r}$ ,  $\mathbf{r} \times \mathbf{p}$ ,  $\mathbf{p} \cdot \mathbf{r}$ -- right? You can write out which components you mean here.

For example, you mean for the  $z$  component of  $\mathbf{a}$ , you're going to get  $p_x l_y$ , and  $l_y p_x$ . But within that, how do you order the  $\mathbf{p}$ 's and the  $\mathbf{r}$ 's, because  $l_y$  contains  $p_x$ , and in particular, it contains  $x$ . So there's an ordering ambiguity.

So just be a little bit careful about this as a quantum mechanical operator if you do



play with this. But if you do it, and you're thoughtful about it, it's pretty easy to see that it can be computed and checked that, in fact, the commutator vanishes. So at this point, it's tempting to say, aha! There's an extra conserved quantity. We declare victory.

The problem is, this didn't give us the symmetry. This just told us there's a conserved quantity. What's the symmetry behind this? What's the symmetry that insures that this is a conserved quantity? It's obviously not rotations. It's something else.

And so there are many answers to this question. One answer involves an explicit expression for in phase space, the change of variables  $dx$ -- and this is a variation that depends on  $f$  of  $x$  and  $p$ . So there's a little vector parameter, and the change of the physical coordinates depends on both the coordinates and the momenta.

This is a slightly strange thing, because it's like a change of variables where the position gets mapped into some non-linear function of the positions and momenta. That's a little bit weird, but you can do this.

But I don't find it a terribly satisfying answer. And here's the answer I find most satisfying-- it's not terribly useful for our present purposes, but you're going to run into this again in 805, when you do what's called the operator method for the Coulomb potential, and it turns out to be an enormously useful machine. We're not going to use it in 804, but I want to advertise it for you. I want to give you a description, though, that isn't the description you're going to get in 805.

The description is the following-- 1935, guy named Fock, crazy guy, amazing, amazing physicist-- played a huge role in the development of quantum field theory. I'm not exactly sure why he was thinking about this problem, but he was, and this was a very sort of Soviet thing to do at the time, I guess, to be hard core and mathematical.

So off he was going, computing things, and he observed the following fact-- how he observed this, again, crazy long story. He observed the following fact-- if you take a

Kepler problem and you work in momentum space-- so you write everything in terms of the momentum-- it turns out that the Kepler problem, or he referred to as the Kepler problem, but I'll refer to it as the Coulomb problem in 3D, three spatial dimensions-- this is really crazy-- is exactly equivalent.

There's a change of variables-- it's kind of complicated, but it's just a projection, it turns out. It's exactly equivalent to the problem of a free particle in four dimensions, constrained to the surface of a sphere-- to a three sphere in four dimensions.

So you take a three sphere in four dimensions. You take a marble. You kick it, but make sure that it's stuck to the sphere. It will move in perfect circles, right? Obviously-- it's moving on a sphere, it's just going to move in great circles. OK, that's nice and simple.

What's the symmetry group of that system? Well, the sphere is invariant under any rotation in four dimensions.

**STUDENT:** [INAUDIBLE].

**PROFESSOR:** Ah,  $SO_4$ -- there's a symmetry  $SO_4$ -- special orthogonal transformation. Special means it doesn't change length. Orthogonal means that it's a rotation. So it's orthogonal rotations in four dimensions, and so now, this should sound familiar, because the angular momentum group in 3D is  $SO_3$ . It's rotations that don't change the length in three dimensions. OK?

How many elements does it have? How many conserved quantities go along with this? Well, how many conserved quantities go along with rotations in three dimensions? What's conserved by virtue of rotational invariance in three dimensions? Angular momentum-- how many components of angular momentum are there?

Three, right, there are three. So it turns out that if you calculate in  $SO_4$  how many conserved quantities are there, there are six. And when you do this mapping back down from the free particle in 4D to the Coulomb problem in 3D, three of them are the  $l$ 's, and the other three of them are this  $A$  vector-- comes out spot on.

So what it's telling you is that the spectrum of hydrogen-- or at least the I shouldn't say of hydrogen, the spectrum of the Coulomb system-- has an enhanced symmetry. It's the symmetry group of rotations in four dimensions. Why?

I don't know, it's just kind awesome. But I think that's about the best that can be said. It's just true.

So for certain very special potentials, we find that this sort of thing happens. It happens in other systems, too. You discover that there are accidental symmetries in your system. They shouldn't be referred to as accidental symmetries. They are enormously nontrivial functions of the rest of the system, and we're going to break the symmetry in a minute, and you'll see why we shouldn't refer to it as accidental.

But in any case, the answer to the question, why do we have this giant degeneracy in the Coulomb problem-- why is it  $n^2$  rather than  $2l + 1$ -- is that there is an enhanced symmetry group. There's more symmetry than you would have thought. And there's a conserved quantity associated with it. And that conserved quantity corresponds quantum mechanically to an operator that commutes with the energy operator. OK? Yeah.

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** Indeed, indeed.

**AUDIENCE:** So how do you get three conserved components [INAUDIBLE].

**PROFESSOR:** Excellent. What do I mean in classical mechanics for a quantity to be conserved? I mean that the time rate of change of that quantity, under the classical dynamics, under classical evolution, is preserved.

So what's the quantum mechanical version of that? So the mechanical version of that is, well, can we say that  $d/dt$  of some operator-- or of some observable  $a$  is 0. Does this makes sense?

No, because it turns out, in the language we've been using-- in the Schrodinger

evolution description that we've been using-- this doesn't really make sense, because this thing is an operator. That's not a quantity. Quantity is something you measure.

So what do you measure? Do you measure the operator? In a state, you measure its expectation values. You might measure its eigenvalues, but the more general thing is expectation values.

So this is something that depends on time, because the wave function depends on time--  $\psi$  of  $t$ . OK, so the best to say something is conserved, is to say  $d/dt$  of  $A$  is 0. But we've seen what the condition is for the expectation value to not change in time.

In general, for any operator  $A$ , the time rate of change of its expectation value is given by the commutator of  $E$  with  $A$ . I can do the symbols-- good.

OK, so in particular, if this commutator vanishes, if the commutator vanishes-- equals 0-- , this is equal to--

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** Sorry? Well, the wave function can be time variant, and I'm going to assume for the moment that the energy operator and the  $A$  operator are not, themselves, explicitly time dependent. Yes, that's an important assumption. So let me just assume for simplicity that neither the energy nor the operator  $A$  that I'm looking at are explicitly time dependent. Like, it shouldn't be, like,  $x$  plus  $tp$ . That would be annoying. So let me assume that that's not the case.

You do have to deal with that sometimes. For example, if you are dealing with a system that changes in time, where there's a background magnetic field, or something like that, that changes in time. But module that sort of detail. And also, there's an  $i\hbar$ , so where do the  $i\hbar$  bars go? Do the units make sense here?  $A$ ,  $A$ , good.  $E$  and  $d/dt$ -- whoops. So where do the  $i\hbar$  bars go? Well, it can go on either side. You have to tell me if they go up or down.

What is the Schrodinger equation? Yeah, exactly,  $i\hbar$ , OK so we need an  $i\hbar$ .

[LAUGHTER]

OK, this spring has got to us all. So now, in the case that  $e$  with  $A$  as 0, imagine we have an operator  $a$  that commutes equal to 0. Then  $d/dt$  of the expectation value of  $A$  in any state is equal to 0. And that's what I'll call conserved. So classically, to be a conserved quantity means that it's time independent. Quantum mechanically, to be a conserved quantity means that it commutes with the energy.

Now, going back to the question-- the question was, look for angular momentum. There are only two numbers you can know at any moment in time. You can't know three. You can know the total angular momentum, little  $l$ . And you can know the angular momentum in a particular direction, which we conventionally call  $z$ -- little  $n$ , right?

But you can't know some other angular momentum, like angular momentum in  $x$  direction simultaneously. So what does it mean to say that there are three conserved quantities? I can't know three conserved quantities at the same time. They're not even well defined at some moment in time.

The answer is there are three operators--  $l_x$ , and  $l_y$ , and  $l_z$ -- which I will simply write as  $l$  vector-- all of which commute with  $E$ . So while it's true that systems don't have definite values of  $l_x$ ,  $l_y$  and  $l_z$  simultaneously, nonetheless  $l_x$ ,  $l_y$  and  $l_z$  all commute with the energy operator. And as a consequence, their time expectation values are all 0 in a central potential. So the time derivatives of their expectation are all 0s in a central potential. They're all constant in a central potential. Yeah.

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** You mean  $1/r$ ?

**STUDENT:** Yeah,  $1/r$ .

**PROFESSOR:** So the question is, if you don't have  $1/r$ , do you get extra-special things that happen for other potentials that aren't  $1/r$ , but something else?

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** It's not quite a unique case. So the question is-- this is a very good question. So the question is this-- this is a great question-- look, there's something peculiar about  $1/r$  classically. The orbit's closed. You get ellipses.

You don't get progressing ellipses. That's what you get if you have an  $n$  harmonic. If you have an extra  $1/r$  to the sixth term, or something, a small correction to  $1/r$ , which we do in the real solar system. It's a many body system instead of a two-body system, so  $r$  orbit doesn't close. It's close, but-- so that's special.

And here we see that there's an enhanced symmetry. Are these things related to each other? So the answer is almost, in the following sense-- for the harmonic oscillator, we also have it close, but there isn't a Runge-Lenz vector. However, the orbits close, so there's something special about that one, too.

Is there a conserved quantity there? And it turns out the answer to that is yes. There's an enhanced symmetry there as well. But it's not like this.

It doesn't lead to this gigantic degeneracy. There is just extra structure that's nice about the harmonic oscillator. But for the harmonic oscillator, of course, it also closes. It's not this orbits this.

So there's a nice structure there, but it's not quite so simple. OK, yeah, one last question.

**AUDIENCE:** [INAUDIBLE] Kepler's problem. I was wondering if it's at all correct thinking [INAUDIBLE] symmetry or degeneracy [INAUDIBLE] equal time instead of equal area?

**PROFESSOR:** Yeah, it's not unrelated. I don't know how to make that connection sharp, but the thing I can say sharp-- so the question is, look, is that conserved quantity somehow related to the fact that there's equal time in equal-- equal areas swept out in equal time at all points in the orbit? Which is a true thing about a Kepler problem.

That's a good observation. I don't know how to make that connection, but it is true in the following sense-- that both of those facts are guaranteed by the fact that you have closed orbits with a particular ratio. And that is, indeed, can be blamed on the conservation of the Runge-Lenz vector. I don't know how to make that connection direct and explicit, but indeed it is. So that's fun question. I'll have to think about that. That's a good one.

One of the totally awesome things about teaching 804 is that every single time, someone asks a question I've never even thought of before-- forget never answered. Never even thought of. I never thought of that. It's a great question.

OK, so everyone cool with the degeneracy? We have this gigantic degeneracy. So knowing what the degeneracy is, or where it's coming from, at least more or less-- is progress. But if you really understand why something is conserved, then you can break that conservation. You can break that degeneracy.

So here's my question, is it possible-- can we, or indeed must we, can we break or lift this degeneracy? So first, let me tell you what those words mean. So we have this gigantic degeneracy of the  $n^2$  of the Coulomb potential. Can we break that degeneracy or lift it?

What I mean by lift the degeneracy, what I mean by lift the degeneracy is the following-- suppose I have a system that's degenerate, so it's got two energy eigenstates with the same energy eigenvalue. So this is energy. Then if I can kick the system in some way, or modify it, or bend it such that the energy levels are no longer to degenerate, one state has been lifted above the other. And so we use the word to lift a degeneracy.

Now you can see that they're two different states by measuring the energies. It's also said to split a degeneracy, or to break a degeneracy. So those are just words.

OK, so can we break or lift this degeneracy? So sure. How do we break a degeneracy? How do we lift a degeneracy? We need to break the symmetry.

So if we don't have the symmetry, we won't get the degeneracy. We've seen this

before. So first off, let's think about what are the two symmetries that we want?

Well, we got this degeneracy of  $2l + 1$  from spherical symmetry. And we got this extra degeneracy of  $n^2$  from conservation of the Runge-Lenz vector. And conservation of the Runge-Lenz vector came from the fact that we had exactly the Coulomb system. So anything that isn't exactly the Coulomb system, but is still rotationally invariant, should still have the  $2l + 1$  degeneracy, but not the  $n^2$  degeneracy-- like the harmonic oscillator, for example.

So let's change the system. Let's find a small correction to the system that leaves it mostly the Coulomb problem, but with some small correction. So what comes to mind? So one good way to think about a physical, natural way to break this degeneracy, to break the symmetry, is to think a real system that's described by the Coulomb potential.

So the system that we usually talk about is hydrogen. Hydrogen is the proton. It's got a plus charge, and it's got electron. And it's attractive with a minus  $E^2$  upon  $r$ .

So in hydrogen, is this the energy operator for hydrogen? Is this a good description of the energy operator for hydrogen?

It's a good start, but it's not exactly right, for a bunch of reasons. And in fact, in your first problem set, when you computed the time it takes for hydrogen, classically, to decay from the classical Bohr radius, one of the things you discovered is that the electron starts out being non-relativistic, but very rapidly becomes relativistic. And rapidly is  $10^{-15}$  seconds.

This is a non-relativistic,  $p^2$  upon  $2m$  kinetic energy. That's probably not a perfect approximation. So the first example is going to be relativistic corrections.

Now, will relativistic corrections break rotational symmetry? They can't, because relativity doesn't say, this is the  $z$  direction. In fact, it does quite the opposite.

Relativity, among other things, says, don't get too hung up on what's the  $z$  direction.



But relativistic corrections will not break the symmetry. So if we include relativistic corrections to the kinetic energy, this will change  $E$ , change the energy operator. But it will preserve the rotational symmetry.  $E$  with  $L$  is equal to 0.

So we won't break this rotational symmetry, so we'll preserve the  $2l + 1$ . So let's check to see that this is true. So to check to see that this is true, let's actually estimate out the correction to the energy due to the first nontrivial relativistic effect in the atom. The first nontrivial, relativistic effect can be calculated [INAUDIBLE] kinetic energy in special relativity, of a particle of mass  $m$ .

So that's easy. It's the total energy is the square root of  $m^2 c^4 + p^2 c^2$  minus  $mc^2$ . That's the rest energy. That's the total energy, so this is the kinetic energy.

But this is equal to-- well, if we pull out a factor of  $m^2 c^4$ , this is  $m^2 c^4$  times the square root of  $1 + p^2 / m^2 c^2$  minus 1. And now if we Taylor expand this-- because if the momentum is small compared to  $mc$ -- or  $mc$ , I should say-- the momentum is small compared to  $mc$  which is, morally speaking, at low velocity is, the velocity is small compared to  $c$ , then this is 1 plus a small number, and we can Taylor expand this to get 1 plus  $1/2$  a small number. And the 1s will cancel, giving us only  $1/2$ .

So this is going to be equal to  $1/2$  of that small number,  $p^2 / m^2 c^2$ , times  $mc^2$  upstairs, giving us the first term, which is  $p^2 / 2m$ . That's the familiar classical kinetic energy. Rock on.

What's next correction? The next correction is the next term for this Taylor series, which is going to involve this quantity squared, so it's going to be  $p^4 / m^4 c^4$  times  $mc^2$  to the 4th. The coefficient is a minus  $1/8$ , so we get minus  $p^4 / 8m^3 c^2$ .

And that's down by a factor of  $m^2 c^2$  from this guy,  $p^2 / m^2 c^2$  upstairs-- which is what you'd get--  $p^2 / m^2 c^2$ , OK? So the correction to the kinetic energy for a given momentum  $p$  is to correct it down by

$p$  to the 4th term. Everyone cool with that? Yeah.

**AUDIENCE:** Why do you make the assumption [INAUDIBLE].

**PROFESSOR:** Because you, like Schrodinger, did problem Set One. And problem Set One said, if you have an electron at the Bohr radius classically, its velocity is about  $1/400$  of the speed of light. 200? It's small. It's a couple of orders of magnitude smaller than the speed of light. So that number, that ratio there, is 1 upon 200, or 400-- I don't remember-- squared. That's a very small number, so it's a reasonable approximation.

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** Because what is the typical-- that's an excellent question. So why am I talking about it as if the electron is sitting at that radius? And the answer is, well, look-- what is the average momentum? What is the average value of  $p$  squared in, let's say, the ground state of the hydrogen atom? What's the average value of  $p$ ? What must be the average value of  $p$  in the ground state of the hydrogen atom?

Zero on two grounds-- first off,  $p$  is a vector, and the ground state of hydrogen is rotationally invariant. It doesn't break anything. Secondly, it's not going anywhere. It's a bound state, so it's just sitting there. It's got an average momentum of 0. If it carried momentum, it would be cruising.

So it's got average momentum 0. OK, fine, but what's the average momentum squared? What's the average of  $p$  squared? We can actually do out that calculation. You're going to have to do that calculation on the problem set.

And it's a small number. And it's, in fact, almost exactly what you'd guess classically from the Bohr radius. So you have to know the  $\hbar$  to compute the Bohr radius in the first place.

So the answer is, to the best of anyone's ability to define what's the momentum, or the typical scale of momentum, that typical scale of momentum for the electron in the ground state of hydrogen is extraordinarily small compared to the speed of light

by a factor of 100, 200, or 400. Does that answer your question?

**AUDIENCE:** Yes.

**PROFESSOR:** It's a very good question. OK, so here's the kinetic energy. And by the way, another way to say that this approximation must be good is that we've already computed-- ignoring the relativistic correction-- we computed the ground state of energy, and it was 13.6 eV, which is pretty good, since the binding energy of hydrogen is about 13.6 eV. So apparently, that was a good approximation.

And you might be disgusted by answer analysis like that, but that's what physics is. You write down some stupid, cockamamie model that you know is wrong, but if it does a good job of fitting the data, you declare triumph, and you call Stockholm.

[LAUGHTER]

So it depends on the problem you've just solved approximately. So here's the first correction. And now, what this tells us is therefore, the energy of hydrogen-- or at least a better model of hydrogen-- I'll call it hydrogen tilde-- is equal to  $E_{\text{Coulomb}} - \frac{p^4}{8m^3c^2}$ .

OK so this, however, we know is small compared to the kinetic energy, because 13.6 is pretty close to 13.6. Notice I didn't include the rest of the significant digits. So this must be in the insignificant digits.

So this must be small. So here's what I want to ask-- we know that the energy of the Coulomb problem,  $n^2 m$ , is equal to  $e_0^2 / n^2$ , independent of  $l$  and  $m$ . What's the energy in this toy model of hydrogen that includes the first relativistic correction--  $n^2 m$ .

Well, to answer that question we have to resolve the energy eigenvalue equation, right? We have to refine the energy eigenstates, and we have to solve that. And this is going to be a much worse problem, because it's going to involve a  $p$  to the 4th term, which is going to involve four derivatives. That sounds horrible.

Can anyone think of a better way to just approximate, estimate the magnitude and

the value of the leading correction from this quantity? Yeah.

**AUDIENCE:** Some variation on take an eigenvalue, plug it in, see what the error is, correct for that error-- something like that.

**PROFESSOR:** There's an iterative method for doing that. It's a very good guess, but there's an even easier way to estimate it. That's something we will call perturbation theory when we do this in 805. And doing that systematically is exactly the right answer. However I want you to do just the leading part of that. Yeah.

**AUDIENCE:** Dimensional analysis.

**PROFESSOR:** Oh, dimensional analysis would be awesome. That's fantastic, brilliant. So how would you compute  $p$ ? OK, so we didn't calculate  $p$ . You can do a dimensional analysis and get a  $p$ , because you have an  $e$ , you have an  $l$ , you can probably do it.

But here's the problem with that, though-- this is the correct first answer to any question of this kind-- correct first answer is plug in dimensional analysis, and get an estimate for the order of magnitude. But we want more than the order of magnitude here. We're interested in splitting the degeneracy due to this interaction.

So what that means is we want to see that different values use of  $l$  lead to different energy. What we care about is the  $l$  dependence that comes out of this correction. And we're not going to be able to get the  $l$  dependence from dimensional analysis, because  $l$  is an integer. It is dimensionless. Yeah, so that will give you the correct magnitude, and that is the first thing you do. What's the second thing you do?

**AUDIENCE:** Stick in the expectation value of  $p$  to the 4th.

**PROFESSOR:** Excellent. Let's just stick in the expectation value  $p$  to the 4th. That's not exactly the right thing to do, but if this is small, that's probably pretty reasonable.

And what you'll find when you do it systematically using perturbation theory, as was pointed out earlier, we can take the entire system, the entire energy eigenvalue equation-- we can think of this  $1$  over  $m$  cubed  $c$  squared as a small number, and

we can do perturbation theory on that small number. We can Taylor expand everything in that small number.

And when you Taylor expand the exact equation, what you discover is the leading term in that Taylor expansion is the expectation value  $p$  to the 4th over  $8m$  cubed  $c$  squared. OK, so this is a fantastic guess.

OK, so let's compute it. So  $E$  hydrogen is going to be equal to  $E_{nlm}$ , which I'm just to write as minus  $E_0$  over  $m$  squared. OK, so what is the correct answer here? So it's this quantity minus-- so this is making it more tightly bound. Notice the sign, because  $p$  to the 4th is strictly positive if  $p$  is real.

So minus  $E_0$  over  $m$  squared, and if you go out and you do this expectation value, which I really should have put on the problem set-- oh, I still can. It hasn't been posted yet, so it'll be posted this afternoon. But I won't. It's not that bad, actually.

[LAUGHTER]

Matt, what do you think?

**AUDIENCE:** No!

[LAUGHS]

**PROFESSOR:** We'll discuss this afterwards, OK? Which may or may not appear on your problem set. So if you go ahead and you do this calculation, what you find is the correction is  $E_n$  squared, so  $E_0$  squared over  $n$  to the 4th-- this time it really is  $n$  to the 4th-- and now you have to worry about dimensional analysis. This is two energies. We want one energy, divided by-- wait for it--  $mc$  squared, because it's a relativistic correction. That shouldn't be too surprising. Times the quantity  $4n$  over-- and here where life gets awesome--  $1 + 1/2 - 3$ .

[LAUGHTER]

**PROFESSOR:** You laugh, but I feel delighted by this for so many reasons. One is, that's beautiful.

What a crazy combination of symbols.

But the second and more important one is, look it has an  $l$  in it, and the  $l$  is downstairs, right? That's good. It has more leverage that way. But so we've got this  $l$  appearing, so the energy depends on  $l$ .

Good, we've broken the degeneracy. Different values of  $l$  give different energies. So let's do that graphically. So in particular, what this tells us is that now while the Coulomb energy commuted with the Runge-Lenz vector, it must be true that the energy of this model of hydrogen, which includes the first relativistic correction, does not commute with the Runge-Lenz vector.

And indeed, if you check this-- which is effortful, but not intellectually difficult-- indeed, it doesn't vanish. And the failure of this conservation equation, the failure this commutational relation to vanish, tell us that it's possible for the system to not be degenerate. And lo and behold, it is not degenerate. OK? Yeah.

**AUDIENCE:** So I just wanted to clarify something that-- did you say before that the actual first term when you encounter relativity just includes substituting the non-relativistic  $p$  to the 4th?

**PROFESSOR:** Yes. Sorry, I should have said that. There are other things are important for relativity that we'll come to in a little bit. But if you just look at the kinetic energy, this is the first non-trivial correction. Yeah.

**AUDIENCE:** So we still have the  $2l + 1$  degeneracy.

**PROFESSOR:** We still have the  $2l + 1$  degeneracy, exactly. Because does this correction violate rotational invariance? No, that's  $p$  squared. That's a scalar under rotation. It's just the number, not a vector.

But  $E$  still commutes with  $l$ . And you see that because this is independent of little  $m$ . This is the mass of the electron. So this is independent of the quantum number little  $m$ . It only depends on the quantum number little  $l$ . So indeed, it is still degenerate.

So let's go through this and see the degeneracy explicitly. And let me do that by

drawing you the following diagram. So what happens if we have  $E_1$ , which is the ground state?

It has some energy which is negative, which is minus  $E_0$ . And when we include this first correction, what does it do? Well, it decreases it by some amount. Everyone cool with that?

It doesn't change the number. It doesn't split any degeneracy, because there was only one ground state in the first place, because  $l$  had to be 0 when  $n$  is 1.  $l$  has to be one less than  $n$  or smaller. And if  $n$  is 1,  $l$  has to be 0. It can't be any smaller than 0, so it's 0. There's just a one state, with degeneracy  $2l + 1$ , which is 1.

OK so that's fine. It just changes the ground state by some amount. Let's consider the second excited level.

So in the second excited level, we have the states-- and let me name this slightly differently, so this has energy minus  $E_0$ . The ground state had  $l$  equals 0, and  $m$  equals 0. It had to.

For the second excited state,  $n$  equals 2, how many states are there? 2 squared is 4, so there are four states, two, three, four. And what are their values of  $l$  and  $m$ ? Well, if  $n$  is 2,  $l$  can be either 0 or 1. If it's 0, then  $m$  has to be 0. If it's 1,  $m$  could be 1, or it could be 0, or it could be minus 1. So this, again, is  $l_m$ ,  $l_m$ ,  $l_m$ .

So those are the four states with energy  $E_2$  in the hydrogen atom. And now when we ask, what are the energies of these three states, when we include this so-called fine structure, what is this going to do? Well, the ground state is going to get pushed down by some amount.

I should draw this differently to make it more vivid. This gets pushed down by some amount, with some value of  $l$ .  $l$  here is 0. But for these three states, which all have the same value of little  $l$ , 1, the denominator is larger.

So the amount by which it gets pushed down is less. So these three states get pushed down less, but the same amount as each other. That cool?

So these three states-- degeneracy is 3, and this state degeneracy is 1. Now, notice that  $1 + 3$  is equal to  $4$  is equal to  $n$  squared. So these states split into multiplets-- groups of states-- which have to have the same energy by rotational invariance. If they have  $l$  equals  $1$ , there must be three states with the same energy-- there must be. And states with  $l$  equals  $0$ , there's just the one state. And if we did the same thing for  $E_3$ , let's just think about what would happen.

So I'm just going to write the  $l$ . I'm not going to include the  $m$ . We have the  $l$  equals  $0$  times  $1$ . We have the  $l$  equals  $1$  state, times  $3$ . And we have  $l$  equals  $2$  state. And how many states are there in the  $l$  equals  $2$  state? Times  $5$ , good.

And again, this gets pushed down to some value. This gets pushed down to some value. This gets pushed down to some value, where this is one, three, and five. And again, these add up to  $9$ , which is  $3$  squared-- the degeneracy.

So by turning on the relativistic corrections, we break this degeneracy. We lift this degeneracy. You break the symmetry, you lift the degeneracy.

Now, unfortunately, this isn't one we can control by turning a dial in the lab. No experiment that I can do in the lab will change the value of the speed of light. Well, actually there are experiments that will change the value of the speed of light. If you work in medium, the effective speed of light is different. So that's going to change relativistic effects.

So that's interesting. That tells you that you can actually vary this continuously if you can vary continuously the index of refraction of the ambient system. I invite you to think about how you might do that experimentally, because it's a fun question.

OK, however, what I'd really like is something where Professor Evan in his lab can actually turn a dial, and change the spectrum in a way that explicitly breaks the symmetry. Meanwhile, I also want an example that breaks the rotational invariance. I want to break the  $2l + 1$  states up into  $2l + 1$  states with different energies. I want to make them depend on the angular momentum in some direction. What must I do in order to lift that degeneracy?



**AUDIENCE:** Add a magnetic field.

**PROFESSOR:** Fantastic. If you add a magnetic field, why is that going to break the degeneracy?

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** Give me an answer that depends, not on your knowledge of chemistry, but give me an answer that depends on symmetries. Why does turning on a magnetic field have the potential to split the degeneracy of the  $2l + 1$  states?

**AUDIENCE:** You don't have rotational symmetry.

**PROFESSOR:** Thank you, exactly. You have no rotational symmetry, exactly. So that's pretty good. So let's break the  $2l + 1$  by breaking rotational symmetry.

There are many ways we could break rotational symmetry. We could turn on an electric field. We could turn on a magnetic field. We could put a shovel in the room.

But anything that breaks rotational symmetry will do it, but a very convenient way is to do it with a magnetic field. Magnetic field is particularly beautiful. So this effect is now called the Zeeman effect. I believe it was Faraday-- one of the classic electromagnetists of the 19th century attempted to look at the spectral lines coming off glowing gas, and see if they changed by turning on an electric or a magnetic field. It turns out to be a tricky experiment to do, because you need to have a very well-controlled magnetic field, otherwise what you get is just a bunch of schmutz.

So to get a clean spectrum, you have to have a very uniform magnetic field, which is not trivial. It has to be time independent. So Zeeman, at the very end of the 19th century-- in fact, this experiment was done, I believe, in '96. So I think the paper came out in '97 but the experiment was done in '96.

Zeeman did this experiment. He said look, if I turn on a magnetic field next to a hot, glowing gas and look the spectrum that comes off, anything happen to it? Why would you think that anything might happen?

And the answer to this one is really quite nice. Look, if we compute the energy, the energy is going to be equal to the Coulomb energy plus a correction, which is the following-- if you think of the atom as an electron that carries some angular momentum in the presence of a proton, if you think of the electron as a thing carrying some angular momentum, and a thing with a charge-- it has a charge and angular momentum. It's going to have magnetic moment,  $\mu$ .

And the magnetic moment is going to be equal to the current of the charge times the area swept out divided by  $c$ , because we work with sensible units. And this is equal to minus-- for the case of the atom-- minus  $\mu$ , the magnetic moment of the system dotted into the magnetic field that you turn on in the background. So this is a background magnetic field.

I am turning on an electromagnet, which induces a magnetic field in some known direction, with some known magnitude. So my dial is the magnitude of that  $B$  field. I could make it large, or I could make it small. And it's in a known direction.

And the point is, our electron because it's orbiting, because it carries some angular momentum and it carries some in charge, has some magnetic moment. So it behaves like a little bar magnet. And that bar magnet wants to anti-align with the background magnetic field that I've turned on. So there's an energy penalty to not being aligned. This is the usual dipole-dipole potential from electrostatics.

OK and  $\mu$  here is equal to minus  $E$  over  $2mc$ -- angular momentum. So this can be computed from a simple model of the atom. Whatever, it's easy to compute.

So this is slightly annoying, because if  $E$  is in some arbitrary direction, let's just simplify our life and say that's equal to  $E$  Coulomb minus  $\mu B$ . And I want to turn on a magnetic field of known amplitude in a known direction. Let's call it the  $z$  direction. So this is  $\mu_z$ .

But this  $\mu_z$ , that's just  $\mu_z$  is  $l_z$  times minus  $E$  over  $2mc$ . So this is going to be plus  $E$  over  $2mc$ ,  $B_z$ -- I'm going to put this all together,  $B_z l_z$ . Everyone cool with that?

So where this is coming from, again, is just the angular momentum is telling you the velocity. The velocity is telling you the current. And then the area is the radius. So that's what's giving you the radius and the angular momentum.

So this is our energy. What does this tell you about the energy eigenvalues? They depend on  $m$ , right? And do we have to solve the energy eigenvalue equation again? No, because our energy eigenfunctions of  $E_c$  are proportional to  $Y_{lm}$ , so they're already eigenfunctions of  $L_z$ . So when I take this beast, and I act on the wave functions I erased, but on the  $1$  upon little  $r$ , capital  $R$ , sub  $nl$ ,  $Y$  sub  $lm$ -- when I act on the  $Y_{lm}$ 's, this is just going to give me  $\hbar m$ , right?

So this is just a constant when acting on the Coulomb energy eigenfunction. So this is a much easier problem. That way, we don't even have to make any approximations. We can just say exactly energy Zeeman is equal to minus  $E_0$  upon  $n$  squared,  $nlm$  plus  $E \hbar$  upon  $2mc$ ,  $B_z$ -- the background magnetic field, and this is the  $m$  of electron mass-- times little  $m$ . And I'm going to write little  $m$  sub  $l$ , just to distinguish little  $m$  sub  $l$  from  $m$  sub  $E$ .

So when we turn on the prediction here, when we turn on the magnetic field a la Zeeman, our energy levels will get split according to the different values of  $m$ . Now if instead of working with the pure Coulomb system, if we were in fact a little clever, and we'd already noticed that there's a fine structure-- because they already knew that there was a fine structure at this point-- they could see the different spectra in lines coming off of hot gas. So it's just an experimental fact you can't turn off the fine structure. This is going to be equal to  $e n l m$  of our correction to the hydrogen atom, with the fine structure corrected.

So the  $l$  equals  $1$  states and the  $l$  equals  $0$  states are split. Let's focus, for example, on  $E_2$ . So these guys have a different energy. The  $l$  equals  $1$  guys have a different energy than the  $l$  equals  $0$  guys. What does this predict is going to happen if I look at my spectral line?

So what this predicts is the following-- it says that if you have some spectrum that

looks like this-- so this is as a function of wavelength and i'm looking literally at what comes off a prism. I'm looking at spectrum lines. And I'll have a line here. And these are going to be the  $l$  equals 0 states. This is  $n$  equals 2. And then there's the  $l$  equals 1 states. This is with zero magnetic field--  $B_z$  equals 0.

If we turn on a magnetic field,  $B_z$  not equal to zero, what should we see? Well, what happens to this state? Nothing-- it's the same thing, because the  $m$  is strictly 0, so it's the same value.

And this guy, what happens to it? The  $m$  equals 0 state is the same. But then it breaks up-- as everyone said, it breaks up into three lines that are equally spaced. It breaks up into three lines, because one of them has  $m$  which is plus 1, one of them has  $m$  which is 0, and one is  $m$  is minus 1. So energies will increase or decrease.

Let's say this is frequency. So we get this splitting. And another way to draw this is as a function of  $B$ , let's draw the energy levels. So there's the 1. There's the 0. And this stays constant. And these guys-- one is constant, one increases, and one decreases.

When you start getting into strong magnetic fields, weird things happen, like these guys cross, and all sorts of subtle things can happen. But let's ignore the strong magnetic field case, and just focus on this.

So we see that these guys split. So this is what the Schrodinger theory, or the full story would predict-- it came a little bit after this, but this experiment was done in '96, so there's actually kind of an entertaining story about people trying to explain this effect classically. Well, look you could have some angular momentum in the  $z$  direction, some angular momentum in the  $x$  direction, some angular momentum in the  $y$  direction.

The part that has angular momentum in the  $x$  direction doesn't do anything, or in the  $z$  direction. The part with the  $x$  and part with the  $y$  can have different polars. There's a whole classical song and dance.

It's crazy. It doesn't make any sense. But that's because they were trying to

classical mechanics to do quantum mechanics, which doesn't work. So I'm not even going to bother explaining what they were thinking.

But anyway, so people came up with a sort of classical crutch to say, well that's not totally insane. So this is what Zeeman got, for example, by looking at hydrogen. But he did more than just look at hydrogen. I can't remember exactly-- I think he did it with sodium. Matt, do you remember? I think he did sodium and iron.

But anyway, here's the funny thing that he got with sodium and iron. So this is a different experiment. It's exactly the same set up, but he was looking at spectral lines in sodium. And spectral lines in sodium did a very similar thing.

There were some where  $l$  went to  $l$ . And there were others where  $l$  went to-- why did we have three here? Just as quick reminder, why do we have three states here?

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** Because we have three states for  $l$  equals 1. This one state went to one, two, three, four states, with none of them in the middle. And in fact, it's worse than that, because they didn't go to equally spaced states in general. In general, they did something slightly funny. And the beautiful plot in his paper looks like this.

There are four states, and as you take the magnetic field to 0, these four states all coalesce exactly to this one state. So this one line is representing four different states. And this already included the fine structure, so we know that this is all a single value of  $l$ . But that apparently has four states.

That's should worry you. What does that tell you about  $l$ ? What does  $l$  have to be in order to have four states in your tower?

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** Half integer-- in particular, what value?  $3/2$ , crap. We already know that these wave functions are described by the  $Y_{lm}$ 's, right? We solved that problem. We explicitly solved it. Here's the exact answer. It's the  $Y_{lm}$ 's.

But we've observed experimentally that  $l$  has to be  $3/2$ . But if  $l$  is  $3/2$ ,  $g_{lm}$  is equal to 0, because it's equal to minus itself. This is bad. This is 0. So this effect is called the Zeeman effect, and this effect is called the anomalous Zeeman effect.

[LAUGHTER]

Which is strange for two reasons. The first reason it's strange is they showed up in the same paper. And the second thing is, OK, you call it the Zeeman effect, because there's some guy named Zeeman. Is there some guy named Anomalous Zeeman? It's a very strange name.

Anyway so this was called the anomalous Zeeman effect, despite appearing in the same paper, because it's weird. It was deeply disconcerting to people. We now just call it the Zeeman effect, but we have the bad habit-- for entertainment value-- of referring to it still as the anomalous Zeeman effect. I'm not the only one responsible for that bad habit.

I'm going to point out that at the end of this paper-- it's a totally awesome paper, by the way-- it's very readable and short-- he says-- I was looking at it last night-- it says, quote possibly the observed phenomenon will be regarded as nothing of any consequence.

OK, so a few years later, Pauli says the following-- so Pauli says this, actually, and this is also totally lovely in *Science* from 1946 Pauli was in the US during the war. After the war, he was at the Institute for Advanced Study. At the Institute for Advanced Studies, while he was there, he got the Nobel Prize. And he gave-- for the exclusion principle, which we are about to get to-- and he gave a little spiel, and it's written up in this edition of *Science*.

And he says, quote, a colleague who met me strolling rather aimlessly in the beautiful streets of Copenhagen said to me in a friendly manner, "You look very unhappy." Whereupon, I responded fiercely, "How can one look happy when he is thinking about the anomalous Zeeman effect?"

[LAUGHTER]

So this troubled people. Yeah.

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** Yeah he found all sorts of crazy states. So this isn't the only example. It's just the only one I'm going to draw. But indeed, you can find five half states you can find states with six.

**AUDIENCE:** Why [INAUDIBLE]?

**PROFESSOR:** Oh, I didn't draw all the states. The spectrum is complicated and messy, because it's sodium. And so there's all sorts of crap. So I'm just not drawing it. I'm just focusing on a specific set of spectral lines. Maybe the best way to draw that is-- OK.

So this was really troubling. So let's put this on pause for the moment, and we'll come back to it in just a second.

So meanwhile, there's something else that's sort of annoying about this system. We've got the Coulomb potential, and the Coulomb potential has the following beautiful property-- the degeneracy of any energy state is equal to  $n^2$ . Meanwhile, various people were fond of observing the fact that the number of states, which I will-- in an abuse of language-- call the degeneracy of the level  $n$  in the periodic table, is equal to-- well, the first one there's two. And then there's eight, and then there's 18. So two, 8, 8, 18, that's almost  $2n^2$ . Two four 8, 9, 18. Cool, maybe there's a relationship, right?

And meanwhile, it's very tempting to think there's a relationship, because imagine you have four electrons. If you have four electrons, what do you do? Well, you put an electron here, and then you could put an electron here, or you could put another electron here. You could also put another electron here and here. Or you could put them in any combination-- two here, two here, two here, one, one-- you could do all sorts of stuff, right?

But if, for the moment, you imagine that electrons have this funny property. Imagine

for a moment that electrons have the property that they can't be in the same state at once. Then if you have four electrons-- I don't know why. I'm desperate. I'm thinking about the anomalous Zeeman effect, among other things. I have nothing better to do.

So just for fun, let's imagine if I put an electron here, I can't put another one. So if I have a two electron atom, the second one goes with one of these. A three-electron atom, a four-electron atom, and these guys are all related to each other, because they live in the same energy level, but they have different  $l$  values, so they'll have slightly different properties. That suggests that the one  $l$  equals 0 state should be different from the 3  $l$  equals 1 states, chemically.

But wait-- there aren't groupings of one and three. They're groupings of two and six. Ah, two-- well, so Pauli staring at this in 1925 said the following-- he said, look, I'm going to conjecture two things. The first is that no two electrons can live in the same state-- inhabit the same quantum state.

That doesn't give us the periodic table, though. It gives us half the periodic table. There are twice as many states in hydrogen as you think.

And you might think that I'm being facetious, that he said something a little more sophisticated. But he really didn't. What he said is, I posit of the existence of an additional quantum number which the electron can have, which takes one of two values. Which translated, says, there are twice as many states as you think. So that's exactly what he said.

So this is called the Pauli exclusion principle. And now this does a totally spectacular thing-- and you've probably all seen this in high school chemistry, or even college chemistry. Now, first electron goes here, second electron goes here, because there are twice as many states as you think, but then I can't put another state in there, because that's as many as you can have. One can go here, and you can put up to six in here. And that's it.

So the  $E^2$  states, the  $n$  squared, which is 4 times 2 states, are somehow related to



each other naturally. And this gives you the structure of the periodic table. In fact, an awful lot of chemistry follows directly from this.

So this is the Pauli exclusion principle. However, it's a little bit disappointing, because while this is whatever-- some ridiculous rule, but we're doing quantum mechanics and they're all ridiculous rules. On the other hand, this one is just stupid. Right? This is just, like, look, it wouldn't it be nice?

So in '25, a couple guys-- really interesting characters-- named Goudsmit and Uhlenbeck-- so Uhlenbeck-- wow, we're really low on time. OK, so I'll just tell you this, and then I'll get to the last of it later.

So Goudsmit and Uhlenbeck-- who were young, kind of naive-- said, look we've got two effects here. One effect is the anomalous Zeeman effect, and there's this weird fact that states have the wrong total angular momentum. And we have this second thing, that there are twice as many states for an electron as you think in the Coulomb potential. How can these two things fit together naturally?

Well here's a guess-- suppose that the angular momentum that we calculated when we did the estimate of the braking due to the Zeeman effect, suppose that angular momentum was not the right angular momentum. Maybe there's more angular momentum in the system. There's angular momentum in the system from the electron orbiting around, but maybe like a little, tiny Earth, the electron itself can have some intrinsic angular momentum.

It turns out Pauli had had this idea before. In fact, Kramers had suggested this to him, who was a very young guy at the time. And Pauli said, you're a blithering idiot, because if you calculate how small an electron has to be in order to fit all the other things we know, and you figure out how fast it would have to rotate to explain the anomalous Zeeman effect, the surface would have to be moving faster the speed of light. That's ridiculous. Leave my office.

So then Uhlenbeck and Goudsmit-- these two guys-- write a paper, and say aha! Well, we can explain this, but let's just not assume that the stupid thing is rotating.

Let's just say an electron has some intrinsic angular momentum. I don't know, why not?

Electrons have intrinsic angular momentum, and if you assume that electrons have an intrinsic angular momentum-- which I'll call  $S$  for the moment-- so then the total angular momentum,  $j$ , is equal to  $l$ , its orbital angular momentum, plus some intrinsic angular momentum, which-- I don't remember what symbol they used, but we'll call it for the moment  $S$ -- where this has the property that  $S$  squared, for an electron, sorry, the principle quantum number, which I will call little  $s$  is equal to  $1/2$ , so  $m_s$  is equal to plus or minus  $1/2$ .

So this is like the  $l = 1/2$  state, but it's not  $l$ . It's something intrinsic. It has nothing to do with anything rotating. It's just a fact about electrons.

Suppose electrons have a little bit of spin. Then what you discover is if you have the  $l = 1$  state, and the electron has spin  $1/2$ , what's the total angular momentum?  $3/2$ , right? So what do you get? You get quadruplets, like that. So this turns out to explain-- if you include a small relativistic effect-- this turns out to explain the anomalous Zeeman effect bang on.

Meanwhile, there was an experiment done in 1922, which is the Stern-Gerlach experiment, in which Stern and Gerlach discovered that nickel, when sent through a magnetic field gradient, bent into one of two different spots-- never three, never zero, always two. How can that be?

Electron spin-- that wasn't realized until 1929, that the connection was there. So these guys came up with this ridiculous postulate. This was Uhlenbeck and Goudsmit. And let me just quickly-- U-H-L-E-N-B-E-C-K-- so Uhlenbeck-- amazing, amazing scientist, also the father of the mathematician Uhlenbeck, and she was a total badass, and has inspired an awful lot of physics-- Karen Uhlenbeck, who's at UT. So this is a pretty interesting and prolific guy.

But he was also prolific in the following way-- he ran a program at the Rad Lab at MIT during World War II. And Goudsmit worked with him. And when they were

finishing up, when the war was ending, Goudsmit became the scientific adviser to something called Project Alsos.

Project Alsos was a project where the military went to the conquered territories in Germany to catch the German atomic scientists, and bring them to a place called Farm Hall in England, where they listened and eavesdropped on them-- Heisenberg, all the good guys. Well, bad guys-- it depends on-- all the great physicist in the German territory at the time were deeply complicated people.

And they listened to them. Something called the Farm Hall Transcripts are the transcripts of those recordings. They were written up in a book called "The Epsilon Project," which is totally breathtakingly awesome.

And Goudsmit wrote a book called "Alsos" about this process of hunting down the German scientists. So Goudsmit, G-O-U-D-S-M-I-T, I think, he wrote a book called "Alsos", which I heartily recommend to you, because it's like a combination adventure story and beautiful bit of physics history.

So these guys both were at MIT during the World War. So there's a nice connection here. So these guys-- fascinating characters, and they came up with this idea of some intrinsic angular momentum.

Pauli then calls it spin. He gives it the name. And he develops a mathematical theory of spin. And the mathematical theory of spin will lead to quantum field theory, relativistic quantum mechanics, and will eventually lead to quantum computation, which is going to be the topic of the last week of our course.

So what we've done so far is we've explained the discreteness of atomic spectra, and we've explained the structure of the periodic table. What we haven't done, is we haven't explained why atoms form molecules or solids. And we also haven't explained what spin is at all.

Those are the topics in the next three weeks. See you next time.