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3.091SC Introduction to Solid State Chemistry, Fall 2010  
Transcript – Session 5

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PROFESSOR: All right, a couple of announcements. Next week two minor celebrations, maybe receptions we would call them. Quiz 2 Tuesday based on homework 2, and periodic table quiz Thursday. I provide the numbers, you provide the letters. I guess that's how it works. And the contest ends Friday five PM.

Last day we looked at the Bohr Model and we developed equations for the radius of the electronic and the orbit of the one electron atom. The energy of the electron and the velocity of the electron. And we found that for all of these they were a function of  $n$ . Quantum number.  $n$  takes on discrete values. One, two, three, and so on. We say that these energies radii velocities are quantized. They take discrete values.

And then later in the lecture we started looking for evidence. And we found ourselves in an exercise of reconciliation with data taken by Angstrom about 50 years earlier and fit to an equation by J.J. Balmer. And we were part way through that and adjourned.

So I'd like to pick up the discussion at that point. I've done a different drawing of what's going on inside the gas discharge tube. Last day I had the ballistic electronic here, and this is boiling off the cathodes. The cathode is inside the gas discharge tube and this electron, if the voltage is high enough, will leave the cathode and shoot across this low pressure gas, which contains, among other things, atomic hydrogen.

And I'm trying to depict the atomic hydrogen atom here. Here's the proton, which is the nucleus-- that's the sum total of the contents of the nucleus-- and here's the lone electron that is orbiting the nucleus at some initial value.  $n_{\text{sub } i}$ . Could be ground state. Doesn't necessarily have to be. With some thermal energy this could be  $n$  greater than one.

Then we reason that if the electron, ballistic electron, and it's trajectory across the gas discharge tube over to the anode, which is charged positively. If it collided with this electron it could impart some of its energy, thereby promoting the electron from  $n_i$  up to  $n_f$ , the final level. And the electron would be up here.

And for this transition there would be an energy cost. That energy cost is  $\Delta E$ .  $\Delta E$  is the energy to go from  $n_i$  to  $n_f$ . And so the kinetic energy-- half  $mv^2$  squared of the incident electron-- is diminished by this amount. And the electronic continues on it's merry way at a slower speed. We assume it's mass doesn't change. The only way we can change its energy is to slow it down.

And there's a conservation of energy, so the sum of the energy of the scattered electron and the transition energy of the electron within hydrogen must equal the incident kinetic energy of the ballistic electron.

But there's more. This is a-- no pun intended-- a one shot deal. This is ballistics, and so the electron is not sustainably promoted. It falls back down. And when it falls back down we have the transition energy now given off. Here, to promote we had to call for energy. When the electron falls down it gives off that energy. And that energy is given off in the form of an emitted photon.

And it's that emitted photon and it's that emitted photon that ultimately gives rise to the lines. The lines in the spectrum are generated by the emitted photon here. Everything else is preamble to this event, and this event gives rise to the emitted photons. And I think that's about where we got last day with the reconciliation. So let's look carefully here.

We recognize that there needs to be conservation of energy again. In other words, the energy of the emitted photon, the energy of the photon, which we know from Planck is  $h$  times  $\nu$ . I'm trying to distinguish. This, I'm making  $\nu$ , the Greek symbol  $\nu$ . And I put a little descender on it. It looks like a  $v$ , but I put a little ascender here to distinguish it. This is lowercase  $\nu$ , as in  $mv$  squared. This is  $\nu$ .

So  $h\nu$ , or it could be  $hc$  over  $\lambda$ . Or it could be  $hc\nu$  bar. Three ways of writing the energy of the photon. And that must equal  $\Delta e$  of the transition.

So let's keep going. We know that the  $\Delta e$ , the transition is given by the Bohr Model.  $\Delta e$  transition will equal  $e_{\text{final}}$  minus  $e_{\text{initial}}$ , which will be minus  $kz$  squared-- I'm writing this generally, in this case with atomic hydrogen  $z$  as 1-- with minus  $k$  times  $1$  over  $n_{\text{final}}$  squared minus  $1$  over  $n_{\text{initial}}$  squared.

What we can do then is equate these and roll them around to isolate  $\nu$  bar.  $\nu$  bar, then, equals minus  $kz$  squared over the product of the Planck constant, the speed of light,  $1$  over  $n_{\text{f}}$  squared minus  $1$  over  $n_{\text{i}}$  squared.

Now for the Balmer series, that is to say the Balmer series of lines, that turns out to be a series where all of the transitions end up on  $n$  equals 2. We said  $n_{\text{f}}$  equals 2.  $z$  equals 1 because we're talking about atomic hydrogen. Then what we have is a set of translations that go  $1$  over  $2$  squared minus  $1$  over  $n_{\text{i}}$  squared.  $n_{\text{i}}$  must be greater than  $n_{\text{f}}$ , so  $n_{\text{i}}$  must come from the set 3, 4, 5, et cetera.

Furthermore, I'm going to put  $z$  equals 1. Let's evaluate  $k$ . We know that's  $2.18$  times  $10$  to the minus 18 joules, or 13.6 electron volts. And we know the Planck constant,  $6.6$  times  $10$  to the minus 36. And this is 3 times 18 of the 8th all in SI units. So this gives me  $1.1$  times  $10$  to the 7th in reciprocal meters. And if I put all this together I end up with exactly the equation that was published by Balmer.

Exactly Balmer's equation in 1885, rewritten to express it in SI units.  $1$  over  $2$  squared minus  $1$  over-- I'm just going to put  $n_{\text{i}}$  squared-- or  $n_{\text{i}}$  equals 3, 4, 5, 6. This is Balmer exactly. Balmer exactly.

So the assumption of this planetary model, with all of the restrictions that Bohr placed on it in order to get this set of equations, reconciled with laboratory data. Very, very significant.

So here we are. Those four lines all can be derived from the Bohr model. And here's another cartoon from your book and showing what I'm trying to depict here, namely it's the falling down, the return to the state from which the electron was promoted that generates the photon. And the set of those lines is what gives you this. There so there's the validation of the sixth piece.

So Bohr Model agrees with Angstrom's data, but it also suggests other experiments. Let's think about this for a second. OK, here's another cartoons from your thing.

You know, I told you that this thing is unstable. And in the Balmer series it goes from  $n$  equals 2 up. But there's a ground state,  $n$  equals 1. What was wrong with those electronics in Sweden in 1853 than Angstrom could never find any electron that would fall all the way down to the ground state? What's wrong with it?

Well, here's the answer. It has to do with instrumentation. So this is an example where science goes further thanks for the advent of new instrumentation that allows this to make measurements that previous people couldn't make, even though they were very competent experimentalists. Angstrom could have found  $n$  equals 1 series, but couldn't see them because he was using a photographic plate.

This shows you the range of sensitivity for photographic plates. Here's the electromagnetic spectrum. Out here you have low energy radio waves and up here you have x-rays and gamma rays and so on. And the visible spectrum is parked right here in the middle, and here it is unpacked for you. And it roughly runs from 400 to 700 nanometers. That's the invisible spectrum. So wavelength increasing from left to right, which means energy frequency in wave number increase from right to left. They're complimentary, right?

$\nu$ ,  $\bar{\nu}$  on the top,  $\lambda$  is on the bottom. Some spectra are plotted in  $\lambda$ , some are plotted in wave number, whatever.

And by the way, I want to show you the power of knowing a few things. I don't expect you to know a lot of facts, but I expect you to know a few things. Every educated person ought to know that the visible spectrum runs round numbers 400 to 700 nanometers.

But look, I can take 700 nanometers and use this formula and convert it to energy. And I'm going to get something like 3 times 10 to the minus 19 joules. Yuck. Instead, I go in electron volts. 1.8 eV. Over here, 400 nanometers is 3.1 eV. So round numbers, the visible spectrum spans 2 to 3 electron volts.

Our eyes are photo detectors that operate on the band width 2 to 3 electron volts. that's easy to remember. Those are good numbers.

So where does that leave us? It leaves us here. We go back and we see these numbers, 656, 486, 434, they're all in the visible spectrum. So I went and I did a little calculation. I said, well what would I have if we'd gotten the wave length for the transition from 2 down to 1? This is  $n$  equals 2 down to ground state.

If you plug in the numbers to the Bohr model, you'd find that that would give you 122 nanometers. 122 nanometers? Well, 122 nanometers is going to put you way over. It's too high energy, right? 122 nanometers is going to put you off to the left

there into the ultraviolet, where the photographic film was not sensitive. So he couldn't measure those lines.

So now I'm going to end by putting the master equation that captures all of this. And the master equation that captures all of this is here. It's that  $\nu$  bar goes as  $r$  times  $z$  squared,  $1$  over  $n_f$  squared minus  $1$  over  $n_i$  squared. So this is the most general form for all 1 electron atoms. That's why I've got  $z$  squared in there for all 1 electron atoms.

And this is called the Rydberg equation. Named after another Swedish spectroscopist at the University of Lund. I think a Swede would probably pronounce this something Rydberg, but you don't have to say that. You can just say Rydberg and it'll be fine. And in honor of Rydberg, the constant here is given the symbol, capital  $R$ . The capital  $R$  as the Rydberg constant and it has a value of  $1.1 \times 10^7$  reciprocal meters in good SI units.

Well, there was more evidence for the support of Bohr's Model. More evidence for the support of Bohr's Model. By the way, as the detectors got better and better we could get more and more lines. You see these, as you get higher and higher series ending on higher and higher end numbers, you move off into the infrared.

Because this is not to scale. These  $n$  equal 4,  $n$  equal 5 are closer and closer to closer together in terms of energy. They're farther and farther apart in terms of spacing, but they're closer and closer together in terms of energy. Because they're farther from the nucleus.

You say, gee, shouldn't it cost more energy to go farther? Uh-uh. Because you're farther from the positive nucleus. Be careful. Don't let your intuition send you in the wrong direction. It's all about Coulombics.

Anyway, so the Lyman series ends at  $n$  equals 1. And these are different scientists. Paschen, Brackett, Pfund, Humphreys, and so on. So maybe, I don't know, if somebody hasn't claimed  $n$  equals 214, all the lines that end there, you know, maybe that could be your name on the series. As if anybody cares.

Looks like this quantum condition is validated. See this is really important because this was the big break away from classical theory. That the motion of a body, something with mass, could be quantized in its behavior shook this physics community. But this reconciliation of the data says that assumption is valid.

There's more that happens. So in 1913 in Berlin-- remember 1913 is when Bohr published the paper-- 1913 in Berlin there was James Franck and Gustav Hertz. James Franck and Gustav Hertz. And they were conducting experiments on gas discharge tubes. Only they filled a gas discharge tube, instead of with hydrogen, they filled it with mercury vapor. So gas discharge tube-- GDT-- gas discharge tube containing mercury vapor. The same thing. Put the electrodes, connect on a power supply, and started varying the potential.

So I'm going to show you what they found. This is the Planck voltage, and this is the current between electrodes, or if you like, across the tube. Between the electrodes, or through the tube. Or if you like, tube current. Meaning from one electrode to the other. The tube current.

Well, low voltage, low current. High voltage, high current. They get up to a certain value of voltage, all of sudden the tube starts glowing brightly and the current falls to 0. Then they continued to raise the voltage. More voltage, more current, up, up, up, up, up. And then they get to another critical value of voltage, even more intensity. And then the current falls to 0.

So you look at those data and say, well, what's that got to do with the Bohr Model? Because mercury is not a 1 electron atom. It's got a boat load of electrons. This is not a 1 electron atom.

So you say, I know what it is. It's ionization energy. Must be ionizing the mercury. So you go to the periodic table and you look up the ionization energy of mercury and you discover that that's 10.4 volts. 10.4 electron volts is the ionization energy. And this first null is at 4.9 volts. Well, 4.9 is a long way from 10.4. And this second null occurs at 6.7 volts. 6.7 volts.

So what's this telling us? What this is telling us is that when you get to a value of 4.9 volts, you've hit a certain value that allows you to promote electrons within mercury between one level and the next level. And those electrons are being promoted and then cascading down. And they're cascading down and they're emitting in the visible and it's blinding you.

Say, OK, so what does that mean? Well, it means that the Bohr Model, which is for a 1 electron atom, assumes that energy levels within it are quantized. These data indicate that on the basis the behavior of this gas discharge tube, there must be quantized energy levels inside of mercury, which means all atoms have quantized energy levels. You understand? Everything is quantized. That's really powerful.

It starts off with this nerdy little 1 electron atom, and now he's applying it across matter. And this is gas, this is more elaborate gas. Heaven forbid, it might exist in liquids and solids.

So that's the Franck, Hertz experiment. So his stock goes way, way up as a result of that. And they win a Nobel Prize. Here's James Franck. Here's Gustav Hertz. You know what the Hertz is. 200 kilohertz, so on. That's Hertz.

James Franck was at Gottingen when he won this, but he ultimately came to the United States when the political changes started occurring in the thirties in Germany. Franck decided to seek safer surroundings and ended up at the University of Chicago, where there is to this day the James Franck Institute of Physics. Very, very high-end physics institution.

So this is good. But all good things come to an end. So 1913 was a bittersweet year for Bohr. Because he got some good news, but he also got some bad news. So now I want to move over to limitations of the Bohr Model. Limitations of the Bohr Model.

So I know what you're going to say-- well, it only talks about 1 electron atoms, so that's a limitation. No, there's more to it than that. Even the 1 electron atom model doesn't capture everything. I'm going to summarize the limitations. I'm going to show you three, and they all fall under the general umbrella of fine structure. Fine structure. In other words, the Bohr Model is good, give us the big lines, but when you start looking more carefully it fails to capture some of the physics.

So first of all, let's go back to some earlier data. 1887. 1887, there were already data out there that were going to give heartburn to the Bohr Model. And those data were taken by Michelson and Morley. Michelson and Morley.

Everything I've taught you so far, with one exception, has been European science. Americans were not active in science because this was a young country. We were really good engineers because we were blockaded by the rest of the world. We had to live by our wits-- that's where you get the term "yankee ingenuity." Science was hifalutin stuff. We didn't have time for it.

But towards the latter half of the 19th century, we started moving into fundamental science. The first American to win the Nobel Prize was Michelson. Michelson was doing work at Case in Cleveland, which eventually became Case Western Reserve University. So he was at Case in Cleveland and he was studying optics. And he was a brilliant experimentalist. In fact, he made the first reliable measure of the speed of light. Back before 1900.

What they were doing is they were looking at Angstrom's lines and they noticed something peculiar. If you take a look at even this drawing, you notice the red line is a little bit fatter than the others. Now you might just say, well, that's just the artist taking liberties and somebody didn't catch it in proof reading. But in point of fact, what he found was that if you look at that line, which is really the line for the 3-2 transition-- the 3-2 transition in the Balmer series-- what you find is that if you look at the photographic plate more carefully, you find that this thing in fact is a pair of lines, but very, very closely spaced.

This is known as a doublet. Two lines very closely spaced, centered at 656 nanometers. And with his interferometer he gets super, super good data. And he could split the doublet.

Well, what's that mean for Bohr? Bohr has no way of explaining this. If you look at the Bohr Model, you've got  $n$  equals 2, you've got  $n$  equals 3, alright? So this is energy 2, energy 3, right? And so when the electron falls from 3 to 2, we get a photon of a certain value. It's going to be  $\nu_{3 \rightarrow 2}$ . That's the frequency or wave number, what have you.

Now, the fact that you've got a doublet here means that there must be two transitions, but darn close. There's either a 3 and a 3 primed, or there's a 2 and a 2 primed, but it's not simply 3 and 2. So that piece of information runs counter to the Bohr Model. Bohr Model is silent about it. It gets the big picture, but if you look more carefully it can't capture the doublet.

And Michelson ultimately gets the Nobel Prize. And I think I've got him here. There he is. The Nobel Prize. By the time he got the Nobel Prize he was at the University of Chicago, but he did the work that won the Nobel Prize for him at Case. So sometimes when you see even Millikan, Millikan did his work at University of Chicago, but eventually took a position at Caltech. So the Nobel Prize says, Robert Millikan, Caltech. But he didn't do that work at Caltech. He did it at Chicago.

Anyways, you can go to the Nobel website. You can read about these people. And what's really cool is when you win the Nobel Prize-- you notice I didn't say if-- I say, when you win the Nobel Prize, what you do is you get on an airplane, you go to Stockholm, and then you go and you have dinner in this beautiful hall. I've been

there and it's gorgeous, gilded and so on. Very nice kitchen, excellent wine list. And-- yes-- and you can go there and they serve meals. the menu is taken from previous Nobel Prize dinners. So you can sit and-- whatever it is, it could be the Nobel Prizes of 1927 and that's what's going to be on the menu today-- and after the dinner they have a presentation ceremony with the King of Sweden. You get your Nobel Prize, and then people listen to your lecture. And those Nobel lectures are really, really expository. So if you want to go and read the Nobel lecture that Michelson gave on the occasion of winning the Nobel Prize, you'll probably learn all of about this and more. It's really, really good, so go there and read.

Now back to the story. Second problem with the Bohr Model. 1896-- see, all this data had been accumulating-- 1896, there was a postdoc by the name of Zeeman. Piet Zeeman. He was a postdoc at Leiden. Leiden in Holland under Lorentz.

You'll learn about the Lorentz force when you study 802.

What he was doing-- again, gas discharge tube. So this was gas discharge tube, and what Zeeman was doing on his postdoc was in a magnetic field.

These people were doing all sorts of experiments. They were trying to block out the whole experimental space. So one guy, his specialty is high energy. One guy's specialty is low pressure. These people are taking a gas discharge tube and putting in the jaws of a powerful, permanent magnet and then measuring the spectrum. And what he found was that for certain lines, this was the rest-- b, I'm going to use as magnetic field-- in the absence of applied magnetic field you have a line.

And this is not a doublet, triplet-- it's just a plain old line. Well behaved line. But when they take that gas discharge tube and put it into a magnetic field, they see a plurality of lines. And furthermore, the spacing-- I'm going to use  $c$  here-- the spacing in the lines is proportional to the intensity of the magnetic field. No magnetic field, single line. Modest magnetic field, modest amount of what is called line splitting. So a modest amount of applied magnetic field, modest splitting. Intense magnetic field, intense splitting.

Bohr Model is silent about that. Because you know, if you've got different lines, it means you must have different energy levels. It's as though the energy level diagrams opens up in a magnetic field. The Bohr Model can't account for that. And parenthetically, they got the Nobel Prize, too.

So there's Piet Zeeman. Got his PhD in 1896. He's got his Noble Prize, 1902. He's off to a good start, I'd say. And there's Lorentz. Two of them. We'll get to him in a second.

So third piece of bad news for the Bohr Model. And that comes, again, in 1913 in November. In November of 1913 there was a man by the name of Stark in Germany. And Stark was doing analogous experiments. He was studying gas discharge tube in electric fields.

Obviously, you've got an electric field across the electrodes to excite the electrons. But he's taking a whole gas discharge tube and putting it between flights and then applying an electric field. And what did he find? He found the same sort of thing. He got line splitting in an  $E$  field, and furthermore that extent of splitting, extent dependent upon the intensity.  $E$  intensity. So no field, no splitting. Modest field,

modest splitting. Intense field, intense splitting. Well, again, that's a headache for the Bohr Model.

So this is all three problems, and it's all under aegis of fine structure. So we know the Bohr Model has its limitations. OK, Stark. I know he's got his Nobel Prize. There he is.

So 1913 ends on a sour note. But people don't give up. 1916, Arnold Sommerfeld in Munich. He was a professor of physics and he proposed modifications. Modifications to Bohr Model. It's a patch, we would call it a patch. going? To put a patch on the Bohr Model.

And what's he going to do? What's the gist of his idea? Well, he retains the planetary structure. He liked that idea-- nice orbits, so on. But he took a page out of Kepler's book. The planets in the Kepler model, when they revolve around the sun their orbit is not circular. It's elliptical. So Sommerfeld said, why don't we give that a try? What if we said the electronic orbit can be elliptical or circular?

And he was quite specific. He said, suppose-- and this, again, is not to scale, but to emphasize this is going to be elliptical or circular, but very, very mild eccentricity. What I'm going to draw for you is extreme eccentricity to make a point. But suppose we had the circular orbit as I'm drawing it now, and then we had an elliptical orbit that is centered on that circle. So it's mild eccentricity. We might have another one-- let's do one more. This is good enough.

The gist here is that we have a circular orbit and an elliptical orbit, but the bandwidth here is very, very narrow. So this is very, very thin. And it's sort of like an egg shell. So if I asked you, what's the dimension of an egg?

You'd say, well, it's dimension of the surface of the egg.

Then I'd say, but the egg shell has some thickness, right? But that thickness is relatively small in comparison to the total dimension of the egg.

So an analogy. He said that the range of distance from the nucleus, whether it's circular or elliptical, is very, very narrow. So we can say the set of circular and elliptical orbits lie within a shell, as in egg shell. So this is a shell model. It's a shell model.

So now how do you designate the different orbits? You've got some that are circular, some that are elliptical. He needs to distinguish them and he needs to be able to label them. So he introduces new quantum numbers to allow us to name them. So let's go and take a look at the quantum numbers that Sommerfeld gave us.

So he starts off with  $n$ . He retains that from the Bohr Model and he calls that the principal quantum number. And its primary attribute is size. It captures the distance, the principal  $r$  from the nucleus. And it takes values 1, 2, 3, all the way up to infinity.

So  $n$  equals 1, small radius.  $n$  equals 10, large radius.

Oh, by the way, there's another numbering system. This is what we use, but the spectroscopists use letters. The spectroscopists use letters-- why? Because



remember the Balmer series? Everybody was hooked on the Balmer series and it ended up being  $n$  equals 2. And then later with better detectors we find there's an  $n$  equals 1. So the spectroscopists said, we're going to get fooled again. So we're going to use letters. And we're going to start with the letter k. It's in the middle of the alphabet. That way if we discover even lower energies, we've got some head room here, we can label those. But we never found any.

So if you go over to Building Thirteen and you do some x-ray refraction and you use the line that emanates from a copper target,  $n$  equals 1-- it's called the k alpha line of copper. To this day. So k, l, m, and so on. You can't get to infinity, obviously.

You know, I didn't think this thing through.

Now the l. l is, what's his name? Sommerfeld. And it's called the orbital quantum number. Why? Because he said that the electron is in an orbital instead of an orbit. Orbit is Bohr, orbital is Bohr-Sommerfeld. And it speaks to the shape. Somehow, I've got to distinguish between elliptical and circular. And it takes values 0, 1, up to  $n$  minus 1. So the  $n$  number controls the range of l.

And again, the spectroscopists, they're real number weenies, they're afraid, so they use s, lowercase. See this is uppercase, this is lowercase. s, p, d, f. For sharp, this is the sharpest line from the l equals 0-- then the principal because as you go to z they all seem to converge and look like hydrogen-- d is diffuse, f is fine, and then after that they ran out of ideas so g and h.

So you'll talk about the one s-orbital, meaning  $n$  equals 1, l equals 0. And there are some values here for shapes. I'm going to put that right above it. When l equals 0, l equals 0 means you have a circular orbit. And when l equals 1 it's elliptical. And when l equals 2 it's much more complex, and we'll just leave it at that. 1, 2, and 3. So there's l values.

And then m is the magnetic quantum number. And it talks about orientation. I'll show you what I mean by that in a second. The values are governed by l, which is governed by n. Starts at l, l minus 1, goes down through 0, goes to minus values and ends at minus l.

So for example, we could do something like this-- when  $n$  equals 1, then l must equal 0, so therefore m must equal 0. So this means for  $n$  equals 1, it's only a circular orbit and this thing is going to be immune to line splitting in a magnetic field.

When  $n$  equals 2, l can equal 0 or l can equal 1. When l equals 0, m equals 0. That's boring, that's circular. But here's another possibility. And that is, when l equals 1 then m can equal 1, 0, and minus 1.

Now I said it has something to do with orientation. Most of quantum mechanics doesn't translate into the Cartesian world, but this one does, mercifully, and I think it's a cute analogy. If I were to tell you that I've got three different quantum numbers and I've got an elliptical thing-- and one way to think, see, the number 0 looks like a circle and the number 1 has some asperity associated with it, so you can think of that as the ellipse-- so I know that I can, with no prior knowledge of where the true origin of the universe it is, I can arbitrarily define a set of rectangular coordinates, orthogonal coordinates, x, y, and z.

And that means I could put one orbital here, one orbital here, and one orbital here. So those are three orthogonal orientations, which I think is consistent with the fact that  $m$  takes on three values. OK, that's cute. So that's as far as Sommerfeld went.

I'm going to go and do something as a retronym. I want to get the fourth quantum number up here now, but we're going to pause the story. We're going to fast forward to 1925 so I can get the last quantum number up here. And that's called the spin quantum number. And it takes values plus or minus a half.

Where did that come from? Well, in 1922-- oh, you know everybody's getting Nobel Prizes and I didn't give Niels Bohr his proper recognition. He gets the Noble Prize, as well.

Oh, when Sommerfeld turned 80, they had a symposium in his honor and they published a book. And the book had papers and well-wishes, papers that were given at the symposium. And in the front they had Sommerfeld's picture and they also had this twin picture, this diptych. So on the right is Sommerfeld, and on the left is the same picture but they've morphed it.

Now remember, there's no Photoshop. Horrors, there's no Photoshop. Can you imagine? So how could they do this? They had to take the negative, which was a photographic plate, and when they were printing the negative using a light box they had to hold the negative on an angle to get the distortion. And in holding it on an angle to get the distortion, they turned this image into something that was a little more spread out.

And the caption that went with this, "To Arnold Sommerfeld, who taught us that the circle is the degenerate form of the ellipse." Now that's geek humor. I mean, they laughed. They thought that was so funny, hahaha. You know. They were having a great time. It was Germany, and nineteen twenties. And there he is.

OK, so now let's go to 1922. This is the Stern-Gerlach experiment. Very interesting experiment. This is really physical vapor deposition. Over here I've got a crucible and it's full of molten silver. So Stern and Gerlach were studying the magnetic behavior of liquid metals. So what they were doing is they had this-- over here you see it's red even though it's silver, because this is that about 1,000 centigrade. Silver melts at about 960. Everything, I don't care what it's color is at room temperature, at 1,000 degrees it's red. It's called red hot.

All right. So this is red hot silver and there's a vapor here and there's a slit and the silver atoms come out of the slit. And they go across over here to a substrate and then they pause it on the substrate. So making little band of silver on the substrate.

And furthermore, he sometimes put them through a magnetic field. So he's got a slit here that narrows the beam, and then he sends it through a magnetic field that is asymmetric. It's divergent.

Can you see here? Look at the end. The south pole as a tip and the north pole is this arc, this cup. So the field lines don't go just directly from tip to tip, they go from tip off to the side. So you can see the divergence of the magnetic field.

And so he looked at what kind of deposits he got as a function of the magnetic field. Here's what he observed. Very puzzling. The whole thing was about Maxwell's

equation. So he's got a silver beam. And when it went directly from the furnace to the substrate he just got the shadow of the slit. And they have the split crosswise with respect to the divergent magnetic field. So if you look at the substrate you just see a band. So this is a band of silver and you can imagine there was a slit out here and it just cast a shadow and that's the band of silver. This is PVD, physical vapor deposition of silver.

Now when  $b$  is not equal 0, what would you expect? You'd think the beam would bend, right? So what do you think happens? The beam bends up? The beam bends down? Or beam bends to the right or to the left? Think about it. I don't want to hear your answer. Think about it. What do they observe?

What they observe is, if this is where the original one is. Two. The beam splits in two. And it gets two deposits, one above, one below, of equal intensity. That's a problem. Beam splitting. But now it's a beam of matter.

Beam splitting. Boy, they had them scratching their heads on that one. No way to explain that.

So along come a couple of graduate students. 1925, couple of graduates. So this is 1992 in Frankfurt. 1925, two graduate students in Leiden, again. Gaudsmit and Uhlenbeck. They're just like my TA's. Grad students. And they looked at this thing, I don't know, maybe sitting around over a beer one night, and they said, you know, so far what we've been saying is the electron revolves around the nucleus. And sometimes it revolves in a circular orbit, and sometimes it revolves in an elliptical orbit, but here's the electron revolving. And they said, what if in addition to revolve, the electron rotated so that it's going like this? [GESTURES]

But there's two choices. It can be going like this, or can be going like this. [GESTURES] Now, it's a charged species and it's rotating, which means that it's going to have a magnetic moment depending on rotation. And now I'm going to send it through a divergent magnetic field. Doesn't it follow to reason that if I put it through a magnetic field and I've got some of them doing this and some of them doing that, they're going to go in different directions? Opposite directions?

And what do you think the numbers are? If I give you Avogadro's number of silvers, you think I'm going to get a dominant clockwise and a minority anti-clockwise? No. We're going to get equal numbers. Some are going to spin like this, some are going to spin like that. And you're going say, but electrons don't spin, they're not doing this. But if you model them as though they are doing this, you get those results.

Those results make sense. And so they introduced the spin quantum numbers.

And I think these are the ones that have been erased. Such is education.

OK. So you know it.  $S$  plus or minus a half.

By the way, Gaudsmit and Uhlenbeck were here during World War Two. They worked in Building Four. You go down the corridor, Building Four just off the Infinite Corridor, there's a plaque there for the Radiation Laboratory. That's where they worked, in the Rad Lab. That's where radar was first engineered. There was work in the UK, there was work in other places. But this is the Radiation Laboratory, started here and they were both here at the time. OK, well, I think that's a--

So this is a plate from the paper. No magnetic field with the magnetic field. And by the way, why did they choose silver? They chose silver because its atomic number is 47-- it has an odd number of electrons. You're going to learn later that you get two electrons in an orbital, and if you have two electrons, one will be spin up, one will be spin down. There's no magnetic moment. So they were clever about choosing an element that had an odd number of electrons so that there would, at the end, be an unpaired electron.

And there's Otto Stern with his Nobel Prize. And he came to the United States, as well. And you're going to see the ascendancy of American Science as people flee Europe up in the nineteen thirties. And America is the beneficiary, and then you see American science rise. But for now it's European science.

OK, so I'm going to talk a little bit about hydrogen and transportation. And we're going to talk about the Hindenburg because it was full of hydrogen. And to give you a sense of scale, this is what a 747 would look like and is what the Titanic would look like. It was almost as long as the Titanic.

It was built in Germany by the Zeppelin company. And the Titanic, the Hindenburg rather, was LZ129 serial number. That's Luftschiff Zeppelin. Airship Zeppelin. 135 feet in diameter. 804 feet long. How long is a football field? So that's a big boat. Seven million cubic feet of gas, giving you 112 tons of useful lift. You ever have to lift something very heavy, there's your sky crane.

So why are they using hydrogen? Well, when the Nazis came to power in Germany, Congress passed the Helium Control Act. The dominant supplier of helium to the world was the United States. Helium comes from helium wells in the earth. And so as of 1933 the United States refused to sell Helium to Germany, so the engineers were forced to use hydrogen. Next best thing.

Here are some posters. "Only 2 1/2 half days to Europe." And here one, a German one. "And now over the North Atlantic." That's Manhattan. That's the lower tip of Manhattan. There's the Chrysler Building, look at that. Now look at that picture, isn't that magnificent?

10 transatlantic flights, 1936. 1002 passengers. Cruising speed, 78 miles an hour. Took two and a half days. By the way, 100 feet in diameter-- when people traveled, they traveled in style. They had a ballroom there and a grand piano. People didn't sit like this. [CROUCHES] With a plastic knife and fork. That's progress, right? Two and a half dancing, tux, tails, champagne. Now, like this. [CROUCHES]

May sixth, 1937. Arrival of first flight to the U.S. while docking in Lakehurst, New Jersey. Why were they docking in Lakehurst, New Jersey? If you go to the top of the Empire State Building, look and you will see at the corners moorings. Moorings sticking out. The plan was to dock airships at the Empire State Building. So you'd come in from Europe, you'd dock at Fifth Avenue, get on the elevator, and there you were.

When they tried to dock the air currents were so violent that they couldn't safely dock the ship. So then they moved across to the fair grounds at Lakehurst, New Jersey, where obviously this mooring is much closer to the ground than the top of

the Empire State Building. The wild currents, they're bad, but they're manageably bad. At the top of the Empire State Building, impossible. There's another image.

So what happened? It did not explode. It did not explode. It couldn't explode. Seven million cubic feet of hydrogen to explode requires seven million cubic feet of oxygen instantaneously. And air is 20% oxygen. So it was a very violent fire, roman candle from the point of egress of the hydrogen. Most of the people on board walked off the Hindenburg. Most of the people walked off the Hindenburg uninjured.

They think it was electrical discharge in the vicinity of a hydrogen leak. Recent research has indicated the skin was made of resin finished with a lacquer dope. And then to make it shiny they put aluminum powder. And why they put iron oxide on the inside I don't know, but this is what NASA uses for solid rocket motor grains. So when this thing catches fire, this is a thermite reaction and could be very violent. And this spelled the end of rigid error ships in commercial air transportation.

Now this a U.S. Navy airship filled with helium. And there was a small gasoline fire, look what happened. Again, it was the skin. That's a blow up of that one. So I looked at that and I thought, geez, that looks Lichtenstein, doesn't it? You know this one? This one. Look at that. Look at that. So you know, I can be an artist, too, right?

OK, I'm going to tell you one more story. Another Niels Bohr story. So in 1896 there was a guy, and astronomer at Harvard called Pickering. Pickering at Harvard, 1896, and he was studying the lines in star light. And he attributed to some of the spectra that he was getting, he said he was seeing atomic hydrogen in star light. And then there was a fellow in London called Fowler. And Fowler, in 1912, reproduced the experiments in the laboratory. He put gas in a tube and got the same thing in the lab. So this guy's at Harvard and the other guy is at London.

Well, Bohr looks at this stuff and he says, you guys are wrong. You guys are wrong-- your lines are off by a factor of 4x. You've got the right series, but you got the wrong element. What you guys are looking at is helium plus. You're not looking at hydrogen, and you know, from-- it goes to  $z^2$ . So the lines are going to be shifted by factor of four because this  $z$  is equal to 2. So Fowler was a pompous ass and he didn't like being called on his bad science. So he does a calculation and he looks more carefully and he says, Bohr, you're wrong. In fact, our lines are off by 4.0016. Now don't laugh. The reason is the spectroscopy was so precise that they could go to five significant figures.

So Bohr says, hmm. And he goes back and he says, you know, we've been doing all these calculations with a one electron atom just neglecting the center. So he redoes the calculations for the entire Bohr model, including considerations of the mass of the nucleus and the mass of the electron in the form of the reduced mass. The reduced mass is-- you're learning this in-- the reciprocal of the sum of the reciprocals. And when he does that, he gets that the value of the line shift should be 4.00163.

So he says, you guys are wrong. It should be 4.0016. You got 4.0016, you idiots. You're looking at helium plus. That was Bohr. Did not want to get into an argument with Bohr.

All right. Have a nice weekend.

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