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**Contributor** So that's a summary of the important formulae we obtained yesterday. On Wednesday we had reduced hydrogen's problem to a one-dimensional Hamiltonian 1 Hl 1 for every particular value of the total angular momentum quantum number l. And we found that this thing at the top here was a ladder operator in the sense that it's out of a state of a certain amount of energy and a certain amount of angular momentum it constructed a state with the same energy and more angular momentum.

And using that and the idea that the sequence of states and more angular momentum with the same energy had to stop. We concluded that the energy was given by a certain constant 13.6ev divided by n squared where n is 1 more than the maximum angular momentum that you can afford that energy. Put another way the angular momentum quantum number is less than or equal to 1 minus this number N that controls the energy and is called the principle quantum number.

So what we want to do now is move forward to get the energy eigenfunctions. So to get the - these are of interest from the perspective of hydrogen, if you want to do any detailed calculations like how does hydrogen interact with the electromagnetic field? What happens when you scatter electrons off hydrogen? That kind of stuff. You'll need to know what these eigenfunctions, these wave functions are. But they're also the building blocks for atomic `[[the stones of 0:01:46]]` atomic structure generally.

So they're a complete set of states which you can expand any state, for example, a stationary state of an `[[Olshinat 0:01:54]]` you can expand in these states. And that's what people do when they do atomic physics calculations for the most part what they do. So these play a very big role in atomic physics. Okay so we want to find out what they are. Now from this, from the fact that l2 on e and l is equal to ll+1el, from the fact that this state here of well defined `[[energies 0:02:25]]` stationary state is an eigenfunction of the total angular momentum operator we know all about.

So the wave function question is this, right? The amplitude defined at x, the atom when it's in this state. The reduced particle strictly speaking when it's in this state. We know all about the dependence, the angular dependence of this. We know that this takes the form of some function which presumably depends on the energy and on the angular momentum times r, times ylm of theta and phi because we know that these the spherical harmonics are the unique eigenfunctions of this operator with this eigenvalue.

So this thing which we know is such an eigenfunction. Its angular dependence must be given by, strictly speaking, a sum potentially it's a sum of these for different values of m and the same value of l. But it's sensible to look for them one by one assuming a particular value of m and l. So the angular dependence you know out of that statement up there is this and all we're looking for right now is the radial dependence. And the radial dependence as I say you have to expect it to depend on the energy, I mean it has to depend on what's in here which is the energy and the angular momentum quantum number.

So that's what we're looking for and we're going to get it just as we got the wavefunctions for the harmonic oscillator stationary states by studying the equation that this operator, your ladder operator, kills the thing off in the appropriate circumstances. So what we do is we look at the equation which says that al well al for the maximum value of l so we're not allowed to make, the maximum value of this is n minus 1. So if we use an minus 1 on en minus 1 we get nothing, it's the end of the line.

So we look at this equation in the position representation and so we can forget about that a0 over root 2 because it's just a constant. So what we want is we're going to be looking at ipr over hbar minus and I'm putting l equal to minus 1 so that l plus 1 I suppose is going to be n over r plus z over na0. That operating on un n minus 1 must give you nothing. Now we know that pr is in the position representation. We figured it out. It was minus ihbar of d by dr +1 over r. So we put that fact into this equation. We have the i and the minus i make a one. The hbars cancel so we're looking at d by dr+1 over r minus this so we're going to have minus–n minus 1 over r + z over na0 un n minus 1 is 0.

Now this is [[Prelims 0:06:20]] Equation right? It's a first order linear differential equation. So it has an integrating factor e to the integral of with respect to r of this stuff, right? This from Prelims Maths. This of course on integrating just gives me an r on top. This gives me a log r and so we're looking at e to the minus some multiple log r. So that means that this is going to become r to the minus n minus 1 from the 3 to the minus n minus 1 log r times the exponential that we get from there e to the zr over n a0. So now we know pretty much what's going on because the original differential equation remember says that d by dr of the integrating factor times unn minus 1 equals 0.

In other words this thing is equal to the constant. In other words the wavefunction that we're seeking is a constant over the integrated factor. So we have that un n minus 1 is some constant which must be determined by the normalisation times r to the n minus 1 e to the minus zr of n a0. So that's wonderfully simple expression. So let's ask ourselves a few things. Let's have a look at the ground state of hydrogen. So this is the case n=1. How do we know that? Because l has to be less or equal to n minus 1, the possible candidates for l are 0, 1, 2 blah etc. So n has to start at 1 and then go up 2, 3 etc.

So the ground state, the state with the least energy is n=1. So what's the wavefunction? So u1 and of course there should be a 0 here is going to be a constant e to the minus in hydrogen z is 1 so this is just going to be r over a0. So the ground state wavefunction is this mere exponential. A beautifully simple result. What else was I going to say about this? Yeah, one interesting, okay given that beautiful exponential one thing you notice is is this thing is never zero. The ground state wavefunction has non zero modulus all the way to r=infinity although the particle is classically forbidden to go beyond a certain radius.

And in fact so what this graph up here plots is the probability of finding the reduced particle at radius r measured in units of a0 over z there and a radius bigger than this. And the classically forbidden region stops at that number 2. And it turns out there's a 24% probability that you'll find the reduced particle in the region that's classically forbidden where the kinetic energy as it were would be negative right? So if you go beyond [[rs2 0:10:03]] the potential energy is more than the total energy of the particle. So there's less than nothing left for the kinetic energy and there's a very significant probability of finding the particle that far out.

So that's I think an entertaining result. It says that p forbidden is about 24%. Let's get the normalisation of this thing sorted out so we can work out a few expectation values working out the normalisation is fundamentally very straight forward. What we require of course, so we require that the integral d cubed xover all space of the complete wavefunction which consists of the un n minus 1 of radius ylm should = 1. This thing we write of course is dr r squared and then the integral sine theta d theta d phi d2 omega over the sphere, oops sorry I should have `[[mod squareded 0:11:17]]` this. Right, that's our requirement.

When we integrate over angles over the sphere we're integrating ylm mod squared over the sphere and that comes to 1. So we're left staring at an equation which says that dr times r squared times u, this thing squared. Now what did we say that was? That was c squared well we don't need to make it a modulus we can declare it to be real times r to the 2 n minus 1 e to the minus 2 z r over na0. So this should be 1. So the thing to notice here is that there‘s an additional factor r squared. You don't just take the radial wavefunctions, square it and integrate dr to get 1, you have an additional factor rsquared because fundamentally this is the normalisation condition we wish to impose. And the `[[y 0:12:23]]` lengths are normalised so integrating over a sphere we get 1.

So we've used here that the integral d to omega ylm mod squared is 1, they're properly normalised. Now this integral is nice and easy. So this can be written as c squared and what we need to do to bring an integral like this under control is to declare that this is rho. So we introduce a new variable rho which is 2zr over na0 and I want to make these, so what I have here is an r to the 2n and I want to make all of those r's into rho's which means I have to multiply by a load of factors na0 over 2z. I've got r to the 2n from these two and another one from there so its 2n plus 1 and then I can turn all these into rho's, `[[d-rho 0:13:38]]` rho to the 2n.where that's the definition. Ooh, I am missing the e to the minus rho.

Now this is a famous integral in mathematics so it's often called Gamma of 2n+1. I believe Euler's responsible for that absurdity. But what it should be thought of as is 2n factorial. So this integral is simply, this experiment up here factorial e is the proof. And you want to be able to recognise that because one often encounters that pattern and you want to just be able to say, "Aha that's 2n factorial so this tells me what C is. C is equal to 2 over na0 to the n+1/21 over the square root of 2n factorial., which enables me to write down the relevant wavefunction un n minus 1 of radius.

I need this factor here and I'm going to write it as follows. I'm going to say this is 2z over na0 to the 3 halves power. So I am borrowing from the 3 halves power, 1over the square root of 2n factorial. That's 2 have to be clear, so I need the bracket there to make sure it's the whole 2n that gets factorialised. And then for the rest these other factors, so the rest of the factors in here could be put together with those r's to make this rho to the n minus 1 e to the minus roh over 2. You see rho is defined as 2zr etc so the factors left over from here are just want we need to make that which was an r to the n minus 1 into rho's to the n minus 1.

So what does this, physically what is this? We are looking at the states with the highest angular momentum for a given energy. So these are the quantum mechanical analogues of circular orbits, not eccentric orbits but circular orbits. So what do we expect qualitatively? Well we expect classically if it was a circular orbit our probability would be a delta function at the radius of a circular orbit. And we know in quantum mechanics everything is a bit blurry because steep gradients of the wave functions are associated with large kinetic energies.

So we're expecting it to be sort of like this-ish. So how does that arise from this formula? When r is 0, rho is 0, this is going to be 0 and then it's going to shift itself off 0 slower and slower the bigger n is. So if n is 10 to the 30 or whatever it would be for a classical particle then this would rise ever so slowly from 0 and it would hug the origin for a long time. It would then rise and then when rho became on the order of 1 this exponential which previously had been harmless being e to the –something small would become a vicious cutting off thing and that's how we get cut off on this side here.

So here we're looking at rho to the n minus 1growth and here we're looking at e to the –rho over 2, well if this is the probability then we need to multiply, we need to square up right? This is an exponential decline. So precisely what it looks like is with luck given in the next diagram. So the top picture there shows just the first three. So the pure exponential is n=0 the ground state. Then the one that rises steeply at the origin and falls off after an early peak is n=2 and n=3is the next one. And what you can see is that the characteristic radius is moving outwards quickly.

So let's calculate some expectation values because that's now easy to do. Let's work out the expectation value of the radius right? So if we want to make a connection back to classical physics we should be thinking about expectation values because classical physics is the physics of expectation values. So this is easy to work out. It's going to be the integral dr r squared times r times un n minus 1 squared right? That's what it should be. And now that we've got this normalisation and everything sorted we can evaluate this. So we're going to have, yes well actually let's just go back, which is the best way to do this?

Alright let's turn all this into rho's, let's turn all these into rho's. Now so this we've already got more or less as a function of rho. So what we need to do is to deal with these other ones. So there are four powers of r there and I need to turn those into rho's which means I need an na0 over 2z raised to the 4th power. Then I need to write down this thing mod squared which is c squared which is 2z over na0 raised to the 2n+1 1 over 2n factorial - that's the rest of c squared. Then we need the integral d-rho rho cubed that's these three and then here we have rho n, I need to square that, so it's going to be n2n minus 2 e to the minus rho.

So what's this going to be? This is going to be 2n this'll be rho to the 2n+1 e to the minus rho. So this integral is going to be 2n+1 factorial. And on the bottom I've got 2n factorials so this on the top and that on the bottom gives me simply a 2n+1 everything else cancels in the factorial. And here something has gone wrong in that I've got far too many powers of n. What have I done wrong, what have I done wrong? Sorry I got confused as to which one I was doing, excuse me.

I was using this formula here which meant that the powers that I needed here, right I was using this formula for u. These require these powers. Now I'm using this formula so it's to the 3 halves power.

**Male** To the three?

**Contributor** To the three because I've squared it up, exactly. So we end up with three of these cancelled. So at the end of the day I'm going to have na0 over 2z just one of them and we're going to have what we said was this was 2n+1. In other words we're going to have if I put that 2 inside there we're going to have n n+1/2 of a0 over z. So the expectation value of the radius is going sort of like n2 and it's going like the scale radius we defined for hydrogen divided by z. Which tells you that if you increase the nuclear charge the size of the orbit's going to shrink like 1 over the nuclear charge.

So the interesting fact here is that the expectation value of r is sort of like going like n squared which is exactly what we expect because e remember goes like minus 1 over n squared. So therefore it's going like minus 1 over expectation value of r but we have a particle moving in a `[[coulomb 0:23:05]]` field so the potentially energy goes like 1 over r. And for the Virial Theorem we're expecting the potential energy to be minus twice the kinetic energy. So the total energy should be sort of a 1/2, minus 1/2, of the potential energy. So this is exactly what we're expecting. So that's a recovery of sort of classical-ish stuff.

Interesting fact here is because this grows like this it means the volume occupied by the atom is going like, which obviously goes like the expectation value of r cubed which goes like n to the six power is growing very rapidly with n. So states, so this grows very rapidly. This means that states in which you excite the electron to a large value of n cannot be seen. You will not be able to observe these, to measure these unless you're in an incredibly high vacuum. So e.g. if n's a 100 the volume is going to be 10 to the twelve times a regular atomic volume.

And in interstellar space you can see hydrogen atoms transitioning from n is 100 to n=99 and stuff like that by making measures at radio wave length, centimetre wavelengths. But you can't do that kind of thing in a laboratory because you can't get a high enough vacuum. So in a laboratory on Earth we're restricted to relatively small values of n, n less than 10 typically.

Right, what else can we say, what about, what about it's interesting to work out the expectation value of squared? It's essentially identical performance to what we've just done. I mean all we have is an extra r in that integral at the top there right? So what are we going to have if we come down here? We're going to have an na0 over 2z raised to the fifth power this time because we're going to have an extra power of r before the u starts. Then we will have 2z over na0 to the third power coming from the u. Then we will have our 2n factorial coming from the c and then we will have to do the integral d-rho. And we will have an extra power of rho so it will be rho to the fourth x that rho to the 2n minus 2. So we will end up with rho to the 2n+2 e to the –rho. In other words this is going to be 2n+2 factorial.

Right so now we're taking 2n+2 factorial and not 2n+1 factorial dividing by 2n factorial. So this is and we're going to get an extra power here. So this is going to be n squared coming from here because this fifth power will be reduced to the second power when we multiply this one. So we're left with n squared a0 over 2z squared and then we will have 2n+2 2n+1. It's interesting to express that as a multiple of the expectation value of r which we've already derived as being nn+1/2 a0 over z. So a0 over z is essentially expectation value of r. So this is going to be, these twos I can take out. There are two twos in here. I take them out and use them to clean that up.

So this is going to be n squared n+1 n+1/2 of a0 over z squared which itself is the expectation value of r squared over n squared n+1/2 squared. So we can cancel many things and we find that that's n+1 over n+1/2 of the expectation value of r squared. So what does that mean? That means that the uncertainty, well so once the rms variation in r, now you'd think this thing would go to zero right because what we're doing is looking at the quantum mechanical analogue of a circular orbit. In a circular orbit the particle does not move in and out. So we would expect that this rms variation in r went to zero was then went to large values and we would have thought we would have recover classical physics.

We'll see that that's not the case because what is this rms variation? Well it's rsquared expectation value minus r expectation squared. Take the square root of that, okay? So here is the expectation value – let me write it in again, r squaredexpectation. So all I want to do is from this I want to take 4 squared and then take the square root. So this is equal to the square root of n+1 over n+1/2 minus 1 expectation value of r. So you can easy see that this is going to come to something like the square root of a half over n+1/2 of the expectation value of r.

So what's happening is that the rms variation in the radius is becoming small with respect to the radius, relative to the expectation value of the radius. But jolly slowly right? That's on the order of expectation value of r divided by root n. So it's becoming small relative to the radius itself but only slowly but it's absolutely large right? Because this thing is growing like n squared, this is looking like n to the 3 halves power. And I think you can just about see that in those pictures up there that as you, well I've only shown the first 3 but you can't see the peak becoming narrow. It doesn't become narrow. So that's a remarkable result.

Okay so those are the wavefunctions for the essentially circular orbits. What about the non-circular orbits? As we see they're not very circular but that's the best we can do. So how do we expect to get these wavefunctions for non-circular orbits? Well in the case of the simple harmonic oscillator we found the ground state wavefunction by solving a on ground state wavefunction equals zero. And that's essentially what we've just done. And then we found the excited state wavefunctions by taking that wavefunction we first found and multiplying it by a dagger an appropriate number of times.

And every times we multiplied a dagger we got a more complicated wavefunction right? So the ground state wavefunction harmonic oscillator was a Gaussian. The ground state wavefunction here was a well this is a slightly more complicated problem, it is a more complicated problem because we have all these different values of the angular momentum. So here our starting point is l is r to the n minus 1 times an exponential as in the same sense as our starting point is in the case of a harmonic oscillator was just a Gaussian. But that's the strategy.

And what we would hope is that al dagger does the business right? Al increased our angular momentum at fixed energy and drove us up against the equation that we solved to find the circular orbit wavefunction. And al dagger we would hope would move us from the circular wavefunction back down to more eccentric orbits. But this has to be done in a slightly subtle manner. Okay. So let's look at a formula that we have here somewhere.

Let's look at this formula here al, al dagger is equal to the difference of h's. So let me write that down with l reduced by 1: al minus 1, al minus 1 dagger, this is just a relabeling operation right, is equal to, can I remember which way up it is? No, a0 squared of a mu, a0 squared mu over hbar squared of hl minus hl minus 1. Now let me commute this entire equation, both sides of it, with respect to al minus 1 dagger. You'll see why we're doing this when we've done it.

So we're going to say that this is al minus 1, al minus 1 dagger, al minus 1 dagger. So that's the left side of the equation commuted with al minus 1 dagger. And that's going to be `[[bhoring 0:33:15]]` constant times hl, al minus 1 dagger which is what I want minus hl minus 1, al minus 1 dagger. Why am I doing this? I am doing this because I want to calculate this which we haven't so far calculated. We could calculate it by going back to first principles and stuff but working out these commutators is quite wearisome. So it's best this is a reasonably slick route.

But what I want to do is calculate the commutator of this with h sub l and what I know at the moment is only the commutator of this with hl minus 1. Okay, so I am going to rearrange this equation now because this is my target as hl, al minus 1 dagger that's what I want to find the value of because it'll turn out to be the key, is equal to hbar squared over a0 squared mu, open a big bracket, then let's write this out turning this into its product. So I'm going to expand this inner commutator because as a general rule I hate to expand general commutators but you'll see in a moment that it's an expedient thing to do.

So this is going...