Transcript for Video 5: The Hydrogen Atom

[1] Hello everyone, and welcome to our latest quantum mechanics video! Today we're going to apply the Schrödinger equation to systems in three dimensions, starting with some simple cases such as a particle trapped in a box. We'll then build up to spherical systems, which will allow us to understand the hydrogen atom, one of the most important quantum systems. We'll look at methods for solving the Schrödinger equation in this case, the radial and angular pieces that result, and how to use these to determine the quantum states of hydrogen.

[2] When we apply the Schrödinger equation to a particle in three dimensions, our particle can now move along all the axes of our co-ordinate system, not just the "x" axis. In this case, the old 1D Schrödinger equation must be generalised. The double derivative with respect to "x" that appears must be extended to include the contributions from the other dimensions as well, which are all represented by partial derivatives. This sum of double derivatives is called the Laplacian operator in mathematics. With this extension, the time-independent Schrödinger equation in three dimensions assumes the form shown on the slide, where the wavefunction and potential now depend on the "x", "y" and "z" co-ordinates. The 3D wavefunction is normalised in the same way as a 1D wavefunction, by ensuring the total probability it represents sums to "1". To do this we must integrate over three dimensions, which requires a multiple integral over the "x", "y" and "z" directions.

[3] To start with, let's think about the case of a particle enclosed in a 3D box, which is trapped by a potential which is zero inside a cube, and infinity outside these walls. A powerful solution method in cases like this is to search for something called a separable solution. This means that we assume the wavefunction, which in general can depend jointly on "x", "y" and "z" variables, depends on a product of separate functions of just one of the variables, which is a much simpler form. If I substitute this trial solution into the Schrödinger equation and re-arrange the result, I'll end up with the equation shown at the bottom of the slide, where I have used the fact that the potential is zero inside the box. Please feel free to pause the video and try this substitution if you would like to check it.

[4] Here's this equation again. We can solve this equation with a nice piece of logic. We notice that each term in the square brackets only depends on one of the variables "x", "y" or "z". The first term depends on "x", the second term depends on "y" and the third term depends on "z". But each of these variables "x", "y" and "z" is free to vary independently of the others so as I change each variable, those three terms might individually change their value. However, no matter how they change their value, the sum of these three terms must always equal the constant shown on the right-hand side. The only way I can ensure this always works is if each individual term inside the square bracket is separately equal to a constant. And if I put each of those individual terms equal to a constant, I can re-arrange each term to find a separate 1D Schrödinger equation. In other words, my product of functions "f", "g" and "h" will satisfy the 3D Schrödinger equation for the infinite potential well, if each of these component functions separately satisfies the 1D Schrödinger equation of an infinite potential well. And the total energy of the particle inside the 3D box will then be equal to a sum of the three separate energy eigenvalues of that 1D Schrödinger

equation. Please try writing these equations on paper yourself if you would like to see how this works.

[5] Since a 1D potential well is characterised by a single quantum number "n", which labels the energy eigenvalue and eigenfunction, then a particle in a 3D potential well will possess three quantum numbers, one for each axis. Each quantum number specifies one of the component eigenfunctions in the product, which are separately solutions to the 1D potential well. As we mentioned, the energy eigenvalues are the sum of the corresponding eigenvalues of the 1D potential well. Looking at this equation for the total energy, it's interesting to see that different eigenfunctions can have the same energy. For example, I could set "n_x equals 2", "n_y equals 1" and "n_z equals 1", and this eigenfunction would have the same energy as the different eigenfunction "n_x equals 1", "n_y equals 2" and "n_z equals 1", since the sum of the squares of these integers is the same in both cases. Different eigenfunctions which have the same energy eigenvalues are known as degenerate states. We'll be seeing more of these when we discuss the hydrogen atom!

[6] Let's now consider an important type of potential energy function known as a "central potential". This type of potential energy only varies with the radial distance "r" of the particle from the origin, not with the direction. An important example is an electron orbiting a hydrogen nucleus or proton at the origin, whose electrostatic potential only depends on the distance from the origin.

[7] When we have a 3D quantity depending only on radius, the best mathematical co-ordinates for analysing this problem will be the spherical polar co-ordinates, These consist of the radius "r" as well as the spherical co-ordinates "theta" and "phi" we met in the previous video. To write the Schrödinger equation in this co-ordinate system, we need to use the Laplacian operator as a function of "r", "theta" and "phi" co-ordinates. You can see it here on the slide! It's a complicated sum of derivatives, but this is not something you'll need to memorize.

[8] To find the eigenfunctions for a central potential, we'll use the same technique of a separable solution that we employed for the particle in a box. This time, we'll look for a separable solution which is a product of two terms, where the first term is a function depending just on "r", and the second term depends jointly on "theta" and "phi". In the next couple of slides I'll list some details for how to perform this solution – this is not a proof we'll need to derive ourselves, so I'll just give a summary to explain the argument. First I'll substitute this separable solution in the 3D Schrödinger equation for "r", "theta" and "phi" co-ordinates, and re-arrange the equation such that the terms depending on angles are on the left-hand side, and the terms depending on radius are on the right-hand side. I'll highlight here that I've replaced the symbol "m", which used to mean the mass of the particle, with the Greek letter "mu". That's because I want to use "m" to represent a quantum number. I'll now apply the same logic to this separable solution as I did when solving the 3D box potential – since the different co-ordinates can vary independently of each other, the only way this equality can always hold is if the two sides are separately equal to a constant, which I'll write as the Greek letter "lambda" for now.

[9] If I put the left-hand side of the equation equal to this constant, I find this equation for the angular piece of the solution. And we can recognise the left-hand side of this equation as exactly the operator for the total angular momentum squared that we met in the previous video! This is very convenient since we have already solved this equation, and we know that the eigenfunctions labelled by "Y" are the spherical harmonic functions. Also, the eigenvalues "lambda" are the possible values of total angular momentum, which are "ell" times "ell plus 1" times "h-bar squared", where "ell" is an integer. So, we have learned that the angular piece of the energy eigenfunctions for a central potential is just the angular momentum eigenfunctions we have already studied, and we can concentrate on the radial piece instead.

[10] Using this same value of "lambda" in the radial equation and re-arranging, we obtain the equation we can see at the top of this slide. Feel free to give these steps a try in your own working if you wish. We can simplify this equation with a useful change of variables, where we replace the radial function "capital R" with another function "u" which just scales it by the radial co-ordinate. This is useful because the first term in our radial equation now simplifies to a normal second derivative. We should remember that although this is the radial equation, it does also depend on the angular momentum state through the value of "l", which is specifying the total angular momentum of the system. We can now see that our radial equation has exactly the same form as a 1D Schrödinger equation, where the usual potential has been replaced by an effective potential including this angular momentum term. So through these steps we have understood that our complicated 3D Schrödinger equation in spherical polar co-ordinates is much simpler than it originally looked – it can be solved using a product of the angular momentum eigenfunctions we have already developed, and a radial function which is a solution of a 1D Schrödinger equation. In other words, the resulting eigenfunctions of this 3D Schrödinger equation are joint eigenfunctions of energy and angular momentum.

[11] Let's now look at some examples. We'll start with a particle trapped inside a sphere, which is a bit like the infinite cubical box but now with a spherical boundary. The potential is zero up to some radius "a", and infinity outside this radius. We can now write the equation for the radial term from the previous slide, setting the potential to be zero in the region "r less than a". The boundary condition is that the wavefunction must be zero at the edge of the sphere, since there is zero probability of finding the particle outside the sphere, and the wavefunction is continuous at this point. So we can set "u equals zero" at "r equals a". We will have different solutions for different values of "l" in the equation, and here is an example of the first energy eigenfunctions for "l equals zero" and "l equals one". You can check that these examples are solutions by substituting them in the radial equation, and the textbook gives more details of these solutions. These different "l" values correspond to different values of total angular momentum, and we also saw in the previous video that we can distinguish states which have different values of the "z" component of angular momentum by a quantum number "m". Therefore, we need three quantum numbers to characterise these joint eigenfunctions of energy and angular momentum – one for energy, which I've labelled "n", and two for angular momentum, which I've labelled "l" and "m". The full eigenfunction, as a function of the spherical polar co-ordinates, is the product of this radial piece and the spherical harmonic functions.

[12] Here we can see the first few radial eigenfunctions "u" as a function of radius "r" of the particle trapped inside a sphere, for these first two angular momentum states, "l equals 0" and "l equals 1". All the eigenfunctions hit zero at the edge of the sphere. If we want to determine the probability of finding the particle at different values of the radius, we need to compute the modulus squared of the radial eigenfunction, "capital R", at this point. However, we must also include an additional effect – as radius grows, there is more volume available for the particle, which creates more chance of finding it at larger radii. This effect produces an extra factor of "r squared" in the probability, which is the volume element in spherical polar co-ordinates. However, since our radial function "u" is already equal to "capital R" scaled by the radial co-ordinate, we can just say that the probability of finding the particle at different radii is the modulus squared of "u".

[13] Let's now apply these methods to the most important case: the hydrogen atom. In the hydrogen atom, an electron orbits the nucleus in a Coulomb potential, which scales as the inverse of the radial distance of the electron from the origin. I'll substitute in this Coulomb potential to the radial equation for a central potential, using the radial eigenfunction "u" as before, and I'll also introduce a new constant "a" which absorbs together the other constants. I then find that the radial equation in the Coulomb potential takes the form shown on the slide. Please feel free to pause the video and verify this equation if you wish to do so. We now need to find the radial eigenfunctions "u" which satisfy this equation.

[14] We can derive the form of the solution to the radial equation by considering two limits. First let's think about the limit where "r" tends to infinity, in which case one of the terms in the radial equation becomes negligible, and can be removed. The result is a simpler differential equation in this limit. We've already met this equation when solving the Schrödinger equation in one dimension, and we know its solution is a decaying exponential function of "r", where after substitution, the constant "a" is related to the energy. Now let's think about the opposite limit, where the radius "r" tends to zero. In this case the other term in the radial equation dominates. A trial function which is a power law in "r" satisfies this equation. This logic tells us that the complete solution to the radial equation must be a combination of a power law in "r" and a decaying exponential.

[15] The textbook gives a lot more details about deriving the hydrogen atom eigenfunctions, which I won't reproduce here since we won't need to know the full derivation. I'll just summarise some key aspects. It turns out that the energy eigenvalues only depend on a single quantum number, "n". And a given energy value has a number degenerate radial eigenfunctions, which depend on the value of "l", the total angular momentum quantum number. In fact, "l" can take on values which range from "l equals 0" to "l equals n minus 1", so there are "n" different possibilities. I've included some example radial eigenfunctions in this table, and you can find more in the textbook. As we predicted, these solutions are a combination of a polynomial and a decaying exponential in "r". There is no solution for "n equals 1" and "l equals 1" because the value of "l" is limited to a maximum of "n minus 1", which only includes "l equals 0" in this case.

[16] The radial extent of these hydrogen atom eigenfunctions is characterised by the parameter "a" we introduced earlier. This parameter is known as the Bohr radius and is equal to around 5 times 10 to the minus 11 metres. The Bohr radius characterises the size

of an atom. Here's a plot of the first few radial eigenfunctions of the hydrogen atom, expressing these as a radial probability density for the electron by plotting the modulus squared of "u". These radial probabilities start from zero at the origin, have an exponential tail at high "r", and contain some polynomial oscillations in between. These graphs tell us the probability of finding an electron as a function of the distance from the nucleus, for each of these quantum states.

[17] As we mentioned, the energy levels of the hydrogen atom only depend on a single quantum number "n". These energies are described by the famous Bohr formula where the energy is proportional to "1 divided by n squared". The ground state, or lowest energy state of the hydrogen atom, has an energy of 13.6 electron-volts. As electrons transition between these energy levels, they can release or absorb light at specific frequencies.

[18] Let's summarise the steps we used to solve the quantum mechanics of the hydrogen atom. We started with the Schrödinger equation in three dimensions. For the case of a central potential, where the potential energy only depends on the distance from the origin, we looked for a separable solution where we split the wavefunction into a radial piece and an angular piece. We saw that the angular piece was just the same as the spherical harmonic functions, which are the eigenfunctions of angular momentum. Hence, these eigenfunctions have angular momentum values which are characterised by values of the quantum numbers "l" and "m", just as in our discussion of angular momentum. For a Coulomb potential as found in the hydrogen atom, the energy eigenvalues do not depend on "l", but only on a single quantum number "n", as described by the Bohr formula. A given energy value can be obtained by many different possible angular momentum states. So overall, the hydrogen atom is described by 3 quantum numbers: for the energy, the total angular momentum and the "z" component of angular momentum.

[19] Here's an image where we have visualised some 3D energy eigenfunctions of the hydrogen atom by taking a 2D cut through them. The intensity of the image corresponds to the amplitude of the wavefunction, and you can think of the image as showing where the electron is most likely to be distributed in each case when viewed from above. We can see some interesting patterns!

[20] How many distinct or degenerate eigenfunctions are associated with each energy eigenvalue? For a given energy level labelled by "n", we can have "n" different values of the quantum number "l", which ranges from "l equals 0" to "n minus 1". For each "l", we can have "2 l plus 1" values of the quantum number "m", which ranges from "minus l" to "plus l". When we combine all of these possible states together, we find that there are "n squared" different possible states of angular momentum associated with each energy eigenvalue. So for example if the electron is in the fourth energy level with "n equals 4", it can have 16 possible angular momentum configurations consistent with this same energy. That is, there are 16 distinct but degenerate eigenfunctions with this energy.

[21] Let's summarise the key quantum mechanics of the hydrogen atom on one slide. We've seen that the hydrogen atom has discrete energy levels, given by the Bohr formula. For each energy state, there are "n" different possible states of total angular momentum. And for each state of total angular momentum, there are "2 l plus 1" different states of the

"z" component of angular momentum. Specifying each of these quantum numbers allows us to specify the radial piece of the eigenfunction, which depends on "n" and "l", and the angular piece of the eigenfunction, which are the spherical harmonic functions depending on "l" and "m". We can combine these pieces together to form the total energy eigenfunctions.

[22] Here's a brief reminder of the points we've covered in this video. We started by introducing the 3D Schrödinger equation, and the techniques to solve it which involve separable solutions. Considering the case of a particle in a box, we showed that there are different eigenfunctions with the same energy, which are known as degenerate states. Then we considered central potentials, which only depend on the radius of a particle from the origin. In this case the energy eigenfunctions can be expressed as the product of a radial function and an angular function. The angular piece of the solution is always the spherical harmonic functions, which are eigenfunctions of angular momentum, and the radial equation can be reduced to a 1D Schrödinger equation. The hydrogen atom is the most important example of this situation, and we studied its energy and angular momentum quantum numbers and corresponding eigenfunctions. That's all for this video, and see you soon!