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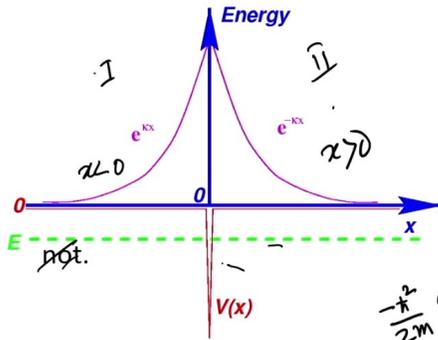
**Lec 8: Harmonic Oscillator, Hydrogen Atom**

So we have been discussing different type of potentials and the solution of Schrodinger equation in those kind of potentials. So let us finish some 1D, some more 1D problems. And let us start with a delta function potential. So delta function potential as we shall see that it has slightly different boundary conditions but nevertheless it is a tractable problem. Then we shall do linear harmonic oscillator and then we will go over to more than one dimension that is problems in three dimension and we will talk about Schrodinger equation solution of Schrodinger equation in three dimension and in particular we shall talk about hydrogen atom and the solution of the Schrodinger equation in hydrogen atom finding its stationary states and the bound state energies etc. And then we'll talk about angular momentum and the commutation relations. We'll keep this discussion short and rigorous derivations will not be given, but the main results and the implications and how to, you know, analyze the main results will be discussed. So let's talk about an attractive delta function potential and it's attractive. You see that it is in this minus a into V naught x. So that's the form of V of x. So there is a delta function which is like a sharp peak at x equal to 0. This 0 in the blue color shows that it's at x equal to 0 and this is the x axis shown by this arrow. And then we have energy, which is energy of the particle is negative. So and that's shown by this green dashed color. And now what it is saying is the following, that the solutions of this problem are written as this is a region one and this is region two. And we have this.

The solutions are written in region one, which is X less than zero. That's this region. And this is x greater than zero. And the solutions are as follows that at x less than zero, it's equal to a exponential. this kappa x and for x greater than 0 it's a exponential minus kappa x where kappa is given by this all these root over of minus 2m E by 8 cross square. Of course, E is the mod E here that is used. Psi is continuous but dPsi dx is not continuous. Pardon me, the part of it actually went to the next line. So, this psi is continuous, but so at x equal to 0, the psi is continuous, but the d psi dx, even if it is not continuous, it is discontinuous by a known amount and what we do here is the following.

We use minus h square by 2m d2 psi dx2 and minus a v0 delta x psi and psi of x is equal to E psi of x. And what we do is that we integrate this equation and that gives us this minus h square over 2m d dx of d psi dx. So, if you integrate this, it becomes d psi dx. This is at x equal to some plus epsilon minus x equal to this id x evaluated at x equal to minus epsilon and this is what is written there.

Now, we use this relation for the delta function. So, delta of x Psi of x integrated from minus infinity to plus infinity gives you an integrated over all x gives you Psi of 0. And so this is so Psi at 0 is continuous. So we can we can use this. And so this thing becomes equal to minus 2 m a V0 by h cross square and the right hand side which is E psi x dx integrated from minus infinity to plus infinity gives us 0 because you actually calculate this is equal to psi at epsilon minus psi at minus epsilon. It became a little messy, but I hope you understand that the right hand side does not give any contribution. So the only contribution to this d psi dx in just the left of the barrier and just the right of the barrier is given by 2ma V0 by h cross square psi at 0. And when you calculate this d psi dx from these expressions or from the solutions of psi of x, you get minus kappa and minus kappa. So, then minus 2 kappa is equal to minus 2 ma V naught by h cross square. So, kappa becomes equal to ma V naught by h cross square that gives the bound state energies and all these things to be minus ma naught square a square V naught square by 2 h cross square. And you can easily calculate this normalization by doing this, you know. So this is for so if you take this psi mod square x integrated over all x for if you take it of minus infinity to plus infinity, you have to really break it up into minus infinity to minus epsilon and use the first solution which is there.

# Attractive $\delta$ −function potential

$$\int_{-\infty}^{\infty} \delta(x)\,\psi(x)\,dx = \psi(0)$$

**Energy**

I

II

$e^{\kappa x}$     $e^{-\kappa x}$

$x < 0$     $x > 0$

$0$    $0$

$x$

$E$

pot.

$V(x)$

$V(x) = -aV_0\delta(x)$

The solutions are written as,

$$\psi(x) = \begin{cases} Ae^{\kappa x} & x < 0 \\ Ae^{-\kappa x} & x > 0 \end{cases} \qquad \kappa = \sqrt{\frac{-2mE}{\hbar^2}}.$$

while $\psi$ is continuous, $\frac{d\psi}{dx}$ is **not continuous**

$$\frac{d\psi}{dx}\Big|_{+\epsilon} - \frac{d\psi}{dx}\Big|_{-\epsilon} = -\frac{2maV_0}{\hbar^2}\psi(0)$$

$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - aV_0\,\delta(x)\psi(x) = E\psi(x)$

$-\frac{d\psi}{dx}\Big|_{x=-\epsilon}$

$-\frac{\hbar^2}{2m}\left[\frac{d\psi}{dx}\Big|_{x=+\epsilon}\right]$

The energy ei are obtained

$E\int_{-\infty}^{\infty}\psi(x)dx$

$= 0$

$\psi(\epsilon) - \psi(-\epsilon)$

$\psi(\epsilon) = 0$

$\int_{-\infty}^{\infty}|\psi|^2 dx = \int_{-\infty}^{-\epsilon}|A|^2 e^{2\kappa x} + \int_{-\epsilon}^{\infty}|A|^2 e^{-2\kappa x} = 1$

$-\kappa - \kappa = -\frac{2maV_0}{\hbar^2}$

$\kappa = \frac{maV_0}{\hbar^2}$

$\frac{-2mE}{\hbar^2} = \frac{m^2 a^2 V_0^2}{\hbar^4}$

$$\boxed{E = -\frac{ma^2 V_0^2}{2\hbar^2}}$$

So, it is a square e to the power 2 kappa x plus epsilon to infinity again a square into e to the power minus 2 kappa x, and that is equal to 1. From there, you can calculate a square and then put it back, and this problem can be solved. Now, you know the eigenfunctions and eigenvalues of this equation or of this problem, which is an attractive delta function. Similarly, a repulsive delta function can also be solved. We will probably see that in an assignment problem. So, let us look at the simple harmonic oscillator. You have encountered oscillators in different branches of physics, and you have looked at a classical oscillator. Most commonly, you have looked at a pendulum which is hung from a rigid support. So, there is a string of length L which ties a bob of mass M, and then for small oscillations, you have calculated the time period. The equation of motion for this case is a simple harmonic motion. You have also looked at a mass-spring system where the spring is attached to the left end with a rigid support, and then it's tied to the right end with a mass m. You have applied a force, which displaces it from its equilibrium position by, say, some amount given by x.

You have written down the equation of motion, which is nothing but m x double dot equal to minus k x, where k is called the force constant or the spring constant, which is a property of the spring. So, this is your F equal to minus k x, and k is nothing but minus m omega square. That gives you the solution x of t equal to x of 0 cos omega t plus V0 divided by omega sine omega t, where omega is given by the time period, which is in terms of the time period as 2 pi over T. The force can be written as the negative gradient

of a potential. It's a conservative force, so the potential corresponding to this is half m omega square x square, which is a simple parabola. You're very familiar with this, so I'm skipping all of that. The energy is, of course, a constant of motion, which is kinetic energy plus potential energy. As the displacement happens, once you pull this mass towards the right and then leave it, it will go back because of the restoring force. This is called a restoring force. The negative sign indicates that it will go in the original direction or rather the direction from which it's been displaced. It will press the spring towards the left and then again cross the equilibrium position and come to the right. If you neglect friction completely, the mass will keep executing simple harmonic motion. While it does, we can calculate the kinetic energy. The kinetic energy is maximum at displacement equal to zero, where you actually pull the spring or the mass.

## Simple Harmonic Oscillator
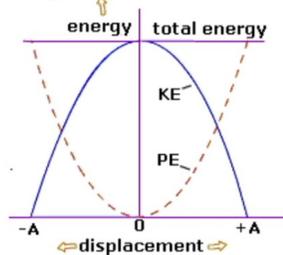### Classical Oscillator
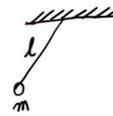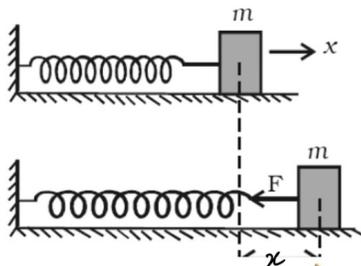
$$F = -kx = -m\omega^2 x$$

Solution: $x(t) = x(0) \cos \omega t + \frac{v(0)}{\omega} \sin \omega t$

$$\omega = \frac{2\pi}{T}$$

$$m\ddot{x} = -kx$$

$$F = -\nabla V \Rightarrow V = \frac{1}{2} m\omega^2 x^2$$

energy | total energy

KE

PE

−A    0    +A

⇐displacement⇒

As it goes to the extreme, the amplitude of the displacement—that's the maximum displacement—the kinetic energy will go to zero because the mass will stop momentarily. Then, it will again go towards the equilibrium position and overshoot the equilibrium position on the left, and this motion will keep going on. The potential energy will show a parabolic increase with this displacement. This capital A is the maximum displacement, and it's on both sides: plus A and minus A. The potential energy will undergo a sort of parabolic fashion. It will increase in a parabolic fashion and reach the maximum when the kinetic energy goes to zero. At each point, if you add both the graphs, you will get the

total energy, which is shown by this violet line. So, this blue line—if you take a point here and a point here, you get a point here. Even if you take a point here and a point here, you still get a point here, which is a constant energy. This system is known to have constant energy. So, coming to the solution, x of t or the displacement as a function of t will depend upon two factors. Because it is a second-order linear differential equation, there are two unknowns. We have sorted out these unknowns here. This is the amplitude of the cosine omega t term, which is equal to nothing but the displacement at t equal to 0.

And the second one is a sine omega t, which will involve the coefficient and a velocity at time t equal to 0, so it is V0 by omega, and the particle will execute this oscillation. Let us go to the quantum mechanical oscillator, and we now show this parabola that we talked about. And if you expand V of X about X equal to 0 by a Taylor expansion, then it becomes V at 0, you know, x equal to 0, plus del V del x evaluated at x equal to 0, and x minus x0 (where x0 is equal to 0 here, of course), plus half of del 2 V del x2. Evaluated again at x equal to 0, x minus x0 whole square, plus all the other terms. This term is a constant, okay? So, this term is a constant. You can actually remove it from the potential energy because a constant term will simply shift the energy up or down. It does not have any x dependence. But the terms that have x dependence are these two, okay? But this term is equal to 0, and the reason it is equal to 0 is that del V del x is nothing but the force. So, if there is no force acting on the system, then at equilibrium, this force will go to 0, and you do not need to consider the first term or rather the second term as well. So, the only non-zero and relevant term is this third term, which can be written as half k x squared. I said x not equal to 0 here, so that is why we have not put x0.

And this K, which, as I told, is called a force constant or spring constant, can be written in terms of the mass of the oscillator (that is, the particle executing the oscillation) and in terms of mass and the angular frequency, which is equal to m omega squared. So, half m omega squared x squared is the potential that the particle will feel in this kind of potential well. So, it's a harmonic potential well, and the particle cannot escape. That means the energies or the eigenstates will be like bound states, and we'll have to calculate the energy, the quantization of energy inside the well. Now, in the sense that these energies are called quantized oscillator energies, they will have something very subtle. It will be different in a subtle way from the energy levels that you have seen in the particle in a box. So, we'll have to calculate the energy and the wave function. And what are the properties of the wave function? The wave function should be continuous, and d psi dx should be continuous. Unlike the delta function case, here both psi and d psi dx must be

continuous because there is no infinite discontinuity at any point. So, this potential is smooth, which looks like half m omega squared x squared; it exists at any value of x and remains finite throughout. So, Vx becomes infinity as x becomes infinity. So, the particle cannot escape to infinity at any finite energy. And we can understand that, you know, if V becomes infinity, psi has to become 0 for the second term. I apologize for not writing the psi here. There should be a psi there. So, the second term demands that the wave function has to vanish at x equal to infinity.
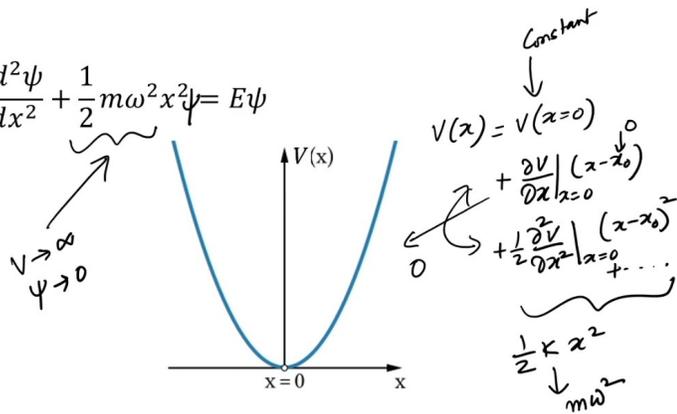
Quantum Mechanical Oscillator

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi$$

Wish to solve for $E, \psi$.

Properties of $\psi$ are:

$V(x)$

$V \to \infty$
$\psi \to 0$

x = 0        x

Constant
↓
$V(x) = V(x=0)$
$\quad + \frac{\partial V}{\partial x}\big|_{x=0}(x-x_0)$
$\quad + \frac{1}{2}\frac{\partial^2 V}{\partial x^2}\big|_{x=0}(x-x_0)^2$
$\quad + \cdots$

$\frac{1}{2}K x^2$
↓
$m\omega^2$

1. $\psi$ should be continuous

2. $\psi'$ should also be continuous

3. $V(x) \to \infty$ for $|x| \to \infty$, the particle can not escape to infinity at finite energy.

4. The solutions are bound states that should decay as $\psi(x) \to 0$ as $|x| \to \infty$.

5. The bound state energies are discrete.

So, the particle cannot escape to regions where x is very large or infinitely large. And the solutions are bound states that should decay as psi goes to 0 as mod of x on either side of x. Why we are writing mod of x is that this potential has an inversion symmetry. So, any point here has a corresponding point at minus x. That is why we are writing mod of x. And these bound state energies, as we shall see, will come out as discrete energies. Okay, there are some technicalities, but mostly I do not talk much about it, but I will only discuss the important results. Nevertheless, some mathematics will have to be there. So, what we do is make a variable transformation from x to y, where we write y equal to x root over of m omega by h cross, and E is equal to h cross by 2 and this epsilon. So, we introduce this epsilon to be the new energy scale, which is a dimensionless energy. And then, if you do that and write psi in terms of y instead of x, it takes the form minus h cross omega by 2, psi double dash (where you see here that d2 psi dy2 means we have

dy2). We have changed the variable from x to y, so whenever you need to take a derivative, what you should do is d psi dy is equal to d psi dx and dx dy. Okay, so dx dy can be calculated from the transformation that you have used for relating y and x.

And after that, this equation, Schrodinger equation takes this form, which you see here, and you can cancel h cross omega by 2 from everywhere because it is not equal to 0. So you get an equation which is psi double dash y plus y square psi of y equal to epsilon psi y. And if you further introduce this new variable f of y instead of psi of y, but by just scaling it with a Gaussian term, which is exponential minus y squared by 2. You get an equation which is minus f double dash, which means d2 f dy2 and minus 2 y f prime or f dash plus f is equal to epsilon f. And this becomes your new form of the Schrodinger equation that you need to solve. And we do not go into solutions, the rigorous solutions of that, but then it can be figured out that, you know, if epsilon does not have this quantization, then this f of y, this f of y that you see here, okay, so this f of y will grow rapidly as y going to infinity. So that, in fact, it grows as exponential y squared. And then when you multiply it by exponential minus y squared by 2, the whole thing goes as exponential y squared by 2. And this would certainly go to infinity as y goes to infinity.

And that is not a desirable case for any wave function because the wave function should be finite and it should be finite and continuous everywhere because of the reason that your psi of, I am just writing it as x, we no longer have x as a variable, position variable, but in general, this thing will always be true. And this tells you that for the square integrability of the wave function, this is called square integrability because when you integrate the square of that, it should give you some finite number. And clearly, if the wave function goes to infinity as y goes to very large values, then the square integrability is going to be harmed.

Solution of Schroedinger equation:

$$\psi''(y) = \frac{d^2\psi}{dy^2}$$

Use: $y = x\sqrt{\frac{m\omega}{\hbar}}$, and $E = \frac{\hbar\omega}{2}\epsilon$

$$\frac{d\psi}{dy} = \frac{d\psi}{dx}\frac{dx}{dy}$$

$$-\frac{\hbar\omega}{2}\psi''(y) + \frac{\hbar\omega}{2}y^2\psi(y) = \frac{\hbar\omega}{2}\epsilon\psi(y)$$

$$-\psi''(y) + y^2\psi(y) = \epsilon\psi(y)$$

Now introduce, $\psi(y) = e^{-\frac{y^2}{2}}f(y)$

$$-f'' + 2yf' + f = \epsilon f$$

$$y^2 \cdot e^{-y^2/2} \sim e^{y^2/2} \to \infty$$

$$\text{on } y \to \infty$$

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1$$

And that's not a sort of desirable situation. And if that's not a desirable situation, we fall back on to the other option that we have, that epsilon has some quantized values. And this quantization goes as 2n plus 1, which is like an odd integer. That's for any n, including 0 here. And that's the subtle difference that I was referring to compared to the case of the particle in a box, which did not have n equal to 0 to be an allowed solution. And if this is true, that is when epsilon n becomes equal to 2n plus 1, that is an odd integer, f of y becomes a polynomial in y, which is called as a Hermite polynomial of degree n, okay? And it's a nice polynomial. And in fact, there's some physics that I want to discuss here.

I've written, of course, in terms of n, z and z. So this H n z is what you see here. So for n equal to zero, as I said, n equal to zero is allowed. And so n equal to one is equal to two z, which means two y if you write it in terms of y. And for n equal to 2, it's minus 2 plus 4 z square or minus 2 plus 4 y square and so on. So there are a few Hermite polynomials, values of the polynomials that are listed here. One important thing to note is that whenever n is even, the polynomial has even powers of z. That is, if you invert z to minus z or y to minus y, they remain invariant. That is, the Hermite polynomials do not change their sign. But for the odd ones, that is n equal to 1, 3, 5, etc., it involves odd powers of z, which means that they would invert their sign or they will change their sign if z goes to minus z. So under this inversion operation, they change their sign. And that precisely is meant by the inversion symmetry. And this inversion symmetry ensures that the entire linear vector space actually fragments into odd solutions or odd ends and even solutions

or even ends. And this is a special property when you have this right-left symmetry, which is called as a parity or as the inversion symmetry. There are many other important relations about these recurrence, I mean, these Hermite polynomials. In fact, the Hermite polynomials, they can be, you know, if you know n, n, n minus 1, then you can generate the n plus 1 and so on by this relation. They have generating functions, etc., that comes in mathematical physics.

Two situations arise:

(i) When $\epsilon \neq 2n + 1$, $f(y)$ grows rapidly for $|y| \to \infty$, undermines the gaussian term $e^{-\frac{y^2}{2}}$, eventually giving rise to an unacceptable divergent solution.

(ii) When $\epsilon_n = 2n + 1$ (odd integer), $f(y) = H_n(y)$ : Hermite polynomial of degree $n$.

$$H_n(z)$$

| $n_z$ | Hermite($n_z, z$) |
|-------|-------------------|
| 0 | $1$ |
| 1 | $2z$ |
| 2 | $-2 + 4z^2$ |
| 3 | $-12z + 8z^3$ |
| 4 | $12 - 48z^2 + 16z^4$ |
| 5 | $120z - 160z^3 + 32z^5$ |
| 6 | $-120 + 720z^2 - 480z^4 + 64z^6$ |

Recurrence relation:

$$H_{n+1}(y) = 2yH_n(y) - 2nH_{n-1}(y)$$

So we'll skip these special functions or the study of the special functions from this course because it's condensed in terms of its contents. There are many things that need to be done, but you can read from Afgan or Kreyszig books. Any of these books will give you a nice introduction to all these special functions, including the Hermite polynomial that we are discussing here. So what we have nicely obtained is that this epsilon becomes equal to 2n plus 1. If you look at this, the transformation is E equal to h cross omega by 2 epsilon, so E becomes equal to h cross omega by 2 and then 2n plus 1, which tells you that this is equal to n plus half h cross omega, and that is the result you must have seen. This is how the energy levels of the harmonic oscillator are quantized, where n can take any value n equal to 1, 2, 3, and so on, including 0. This n equal to 0 is called the zero-point energy. So, the half h cross omega is a zero-point energy, which is not equal to 0— meaning it is greater than 0. And so, even the lowest energy state of the oscillator will have some finite energy, which is equal to half h cross omega. So, what are the different eigenstates of this oscillator?

The different eigenstates are: the ground state, for example, is written as a constant multiplied by a Gaussian. This factor is known as a Gaussian exponential minus some alpha x squared. And the first excited state is— which is psi 1 of x. We have gone back from the y variable to the x variable and this is the final form of the eigenstates that we are representing. So, it is a1 x where a1 is some constant x exponential minus m omega by 2 h cross x square and so on. So, you have, so this is basically the first Hermite polynomial, which is H1x. Of course, you see there is a factor of 2 here. There is a 2z, which should be 2x here. So, that 2 factor has been absorbed in this A1. And if you want how to get these A0s, A1s and A2s and so on, So, in general, they would be written as A n H n and then there is alpha x and then there is an exponential minus alpha square x square where alpha is given by root over m omega by h cross. And how did we find out these values of a 0 and a 1? That's easy because your psi 0 mod squared dx is minus infinity to plus infinity should be equal to 1. So, that tells you that A0 squared—in principle, I should write it as |A0|^2 because it can be complex—but here, of course, we have real values. And we have exponential terms. Now, there are two alpha squared x squared terms because there is a factor of 2 here and also here.

So, let me write, forgetting this factor of 2, you can adjust this alpha. Let me then call it beta so that you don't confuse it with the same alpha. So, beta is something that can be written in terms of alpha, and this is nothing but a Gaussian integral with a standard value, which is equal to the square root of pi by beta. Then put it here— and make that equal to 1, and you can get A0, which is how it is obtained as m omega by pi h cross whole to the power one-fourth. Similarly, you can normalize the first excited eigenstate, which is psi 1x, and by the similar prescription, and you can get this A1. So, in general, this psi n of x is has a polynomial which is Hn of alpha x and a Gaussian. So there is a polynomial which has a name, now we know that it is called as a Hermite polynomial, which has a property that for n equal to even, it is an even polynomial in x, and for n equal to odd, it is an odd polynomial in x, which means that as x changes sign, x to minus x, whether the even will not change sign and the odd will pick up a negative sign. All right, so that's the solution for the harmonic oscillator. I'll show you a depiction of these eigenstates—the different eigenstates there. And so, what we said earlier—let me remove this so you can see it clearly. Now, since you know how to do that integral, let me write it here.

Different Eigenstates of an oscillator

Ground state: $\psi_0(x) = A_0 \exp\left(-\dfrac{m\omega}{2\hbar}x^2\right)$

First Excited state: $\psi_1(x) = A_1 \, x \exp\left(-\dfrac{m\omega}{2\hbar}x^2\right)$
$\quad\quad\quad\quad\quad\quad\quad\quad H_1(x)$

Normalization yields: $A_0 = \left(\dfrac{m\omega}{\pi\hbar}\right)^{1/4}$, $A_1 = \left(4\dfrac{m^3\omega^3}{\pi\hbar^3}\right)^{1/4}$

$$E = \left(n + \dfrac{1}{2}\right)\hbar\omega$$

$$n = 0,1,2 \dots.$$

Zero point energy!!

General form of the bound state eigenfunctions
$$\psi_n(x) = A_n H_n(\alpha x)\exp(-\alpha^2 x^2)$$
$\quad\quad\quad\quad\quad\quad\quad$ Polynomial

with $\alpha = \sqrt{\dfrac{m\omega}{\hbar}}$

$e^{-\alpha x^2}$

$\int_{-\infty}^{\infty}|\psi_0|^2\,dx = 1$

$\Rightarrow A_0^2 \int_{-\infty}^{\infty} e^{-\beta x^2}\,dx = 1.$

$\int_{-\infty}^{\infty} e^{-\beta x^2}\,dx = \sqrt{\dfrac{\pi}{\beta}}.$

So, exponential minus beta x squared dx from minus infinity to plus infinity is equal to root over pi by beta. So, E is equal to, I can put an n here because n means that there are different energy levels that are allowed for the oscillator to take, and they are in integer multiples of h cross omega by 2. So, the lowest one is h cross omega by 2, then it is 3h h cross omega by 2, 5h cross omega by 2, and so on and so forth. So, these are ground state, first excited state, second excited state, and so on, okay, whose eigenfunctions are given by these polynomial convoluted with, you know, the the Gaussian, which means that for the ground state, this polynomial has a value 1. So it's purely the Gaussian, which, so a Gaussian looks like this. And, you know, the first excited state, which is already written there, which is a1 x into exponential minus m omega by 2 h cross x squared. So the second one will have a value that is, you know, will have a value like this, and so on. We'll see that. I probably didn't draw it properly, but so this is the lowest one and then this will also be like this and so on. So, They are shown as this. As you see, the lowest one is simply a Gaussian with an energy which is half h cross omega. The first one has a node here. This is what I was trying to show with an energy which is minus, I mean, which is three half h cross omega, not minus. It's three half h cross omega. And the second one has, of course, two nodes inside the well, which is five half H cross omega. Then there are three nodes, four nodes and so on, so forth. So these are different these quantum numbers.

So n is called as a quantum number because that precisely sort of distinguishes different states including the ground state and then of course the first excited state and second excited state. And there is a picture that shows that this is how the wave function looks like. So the wave function as opposed to the particle in a box which abruptly ends at the boundaries because it cannot go anywhere out. Here, of course, the potential is finite and the wave function actually has some extent in the classically forbidden region, which are these regions that you see here and here and here and here and so on. And so they are nice gaussians.

Pictorially
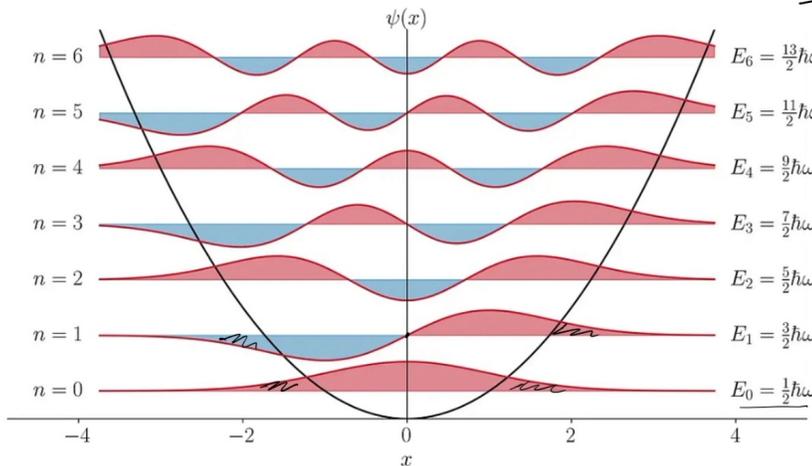


$$2D \text{ harmonic oscillator}$$

$$V(x,y) = \frac{1}{2}m\omega^2(x^2+y^2)$$

$$\psi_{n_x,n_y} = H_{n_x}(\alpha x) \cdot H_{n_y}(\alpha y) \cdot e^{-\alpha^2(x^2+y^2)}$$

$$E_{n_x,n_y} = \left(n_x + \frac{1}{2} + n_y + \frac{1}{2}\right)\hbar\omega$$

$$= (n_x + n_y + 1)\hbar\omega$$

Say $n_x + n_y = 5$

| | |
|---|---|
| 0 | 5 |
| 1 | 4 |
| 2 | 3 |
| 3 | 2 |
| 4 | 1 |
| 5 | 0 |

They do not end abruptly at the edge of the oscillator, but smoothly dies off to zero as exponential minus some constant into alpha squared. Okay, the next problem that we want to do is that the solution of the Schrodinger equation in 3D and precisely what we will do is the hydrogen atom. Let me just go one slide back and just introduce a 2D harmonic oscillator. What do you think this would be? Would it have any special feature as opposed to what we have seen here? So we'll have, say, a particle is executing simple harmonic oscillation in x-axis along x-axis, and it is also executing simple harmonic motion in along y axis. So, you know, it is kind of making an oscillation in the xy plane with having, you know, displacements along both x and y direction. So, we will simply write the Vxy is equal to half m omega square.

x squared plus y squared, and the entire thing that we have done in just 1D oscillator will replicate that for the 2D, and what we have is that we'll have this psi nx, ny, now no longer just a single quantum number, but there are two quantum numbers, and this will be like hnx, alpha x, and some hny, alpha y, And then, of course, this exponential minus beta, well, let me write it as just keeping the notations there. So, it is alpha square x square. So, minus alpha square x square plus y square. So you see that what we have done is that we have simply replicated the problem and have appropriately added or rather here multiplied the wave functions. And the energies will not be something any different. We'll have these indices that need to be considered and this will give you a nx plus half plus ny plus half. h cross Omega. So, there will be a zero point energy corresponding to each one of this. This will give us a nx plus ny plus 1 into h cross Omega and that tells you that there is something new that comes up. There will be suppose nx plus ny is equal to say 5 say and So, we are just talking about this 5 half h cross omega that you see or now it will not be 5 half but it will be like 6 h cross omega because it is a 5 plus 1. Now, how can you make 5? You can make 5 by 0, 5. You can make 1, 4. You can make 2, 3. You can make 3, 2. You can make it 4, 1. You can make it 5, 0. All these choices of nx and ny will give you the same result as 5. So, which means that all these states are degenerating energy, they have the same energy, but they would not correspond to the same eigenfunction. So, the notion of degeneracy is very important in larger than one dimension where

The energy of the particle, the energy of the electron, or the energy of whatever you are considering will remain the same for different values of their quantum numbers. However, their eigenfunctions are not identical. In fact, they would be orthogonal to each other. Each of these choices, like nx equal to 0 and ny equal to 5, will be orthogonal to nx equal to 1 and ny equal to 4, and so on and so forth. So, this degeneracy is an important thing, and this is going to be discussed even for the hydrogen atom. There is another thing that one can think about: suppose this oscillator is charged, so not only does it have mass, but it also has a charge, some charge, positive or negative, whatever. And suppose you place it in an electric field while it executes simple harmonic oscillation. So, when you put it in an electric field, there is an additional potential that comes, which is equal to, say, qEx. We are not committing to what the sign of q is, but any charge would do, and E is the electric field. So, let me change this symbol because E is also energy. So, E here represents the electric field. And so, this electric field would introduce another potential energy, which is equal to P. It's like a P·E, where P is the dipole moment. So,

the oscillator will develop a dipole moment, and because of the dipole moment, it will have a potential. So, the total potential energy—let's call this a dipole potential.

So V is equal to half m omega square x square plus q E x. Now the question is that whether you can solve this problem exactly. And it turns out that it's not a difficult problem to solve. You just have to complete the square. So if you add and subtract some terms such that you can write this as some x plus x naught whole squared, then it still looks like a harmonic oscillator with these energies given by n plus half h cross omega, excepting that now the oscillator will no longer execute oscillation about x equal to 0, but that point, the equilibrium point now would be shifted to some x naught. So, that is the only change—you have a shift in the equilibrium point—but other than that, the problem remains identical. So, even if you have a charged oscillator in an electric field, you can still treat it as an uncharged one, except that the equilibrium point shifts. Now, let us move on to the Schrödinger equation in 3D, where we will again encounter degeneracy and so on. This problem is significantly complicated as compared to the 1D problem because of one is in 3D, second it is in this there are r theta phi coordinate system or the spherical polar coordinate systems that needs to be considered and why it's important to consider a spherical polar coordinate system, why can't we do with Cartesian coordinate system and the reason is simple that we have to abide by the symmetries of the problem. If you have spherical symmetry—because the hydrogen atom is the simplest atom—this is what is being said here. So, it has a nucleus at the center, which is what we have learned from Rutherford scattering.

It is the simplest of all atoms, made up of a positively charged proton with a rest mass equal to the proton mass, and an electron with a mass that is three orders of magnitude smaller. It is the only atom composed of just two particles, and this makes the analytic solution of both classical and quantum mechanical dynamics of the hydrogen atom straightforward and tractable. All other atoms are composed of a nucleus and more than one electron. Still, we can handle, for example, the helium atom either exactly or through variational calculations, which we will see later. So, in any case, the Schrodinger equation for this case looks like this Laplacian of Psi, which is del square Psi plus 2 m0 by h cross square e minus V of Psi. And so on. And this m naught is same as mu. You would see that, you know, most often it is written as mu, which is the effective mass, which is written as the mass of the proton multiplied by the mass of the electron divided by their total mass. So that's called as a reduced mass or effective mass, whichever you want to call it. And this r is nothing but equal to r theta phi, okay?

# Solution of Schroedinger equation in 3D : Hydrogen atom

The simplest of all atoms is the Hydrogen atom, which is made up of a positively charged proton with rest mass $m_p = 1.6726231 \times 10^{-27}$ kg, and a negatively charged electron with rest mass $m_e = 9.1093897 \times 10^{-31}$ kg. Therefore, the hydrogen atom is the only atom which consists of only two particles. This makes an analytical solution of both the classical as well as the quantum mechanical dynamics of the hydrogen atom possible. All other atoms are composed of a nucleus and more than one electron.

The Schroedinger equation is written as, $\qquad m_0 \equiv \mu$

$$\nabla^2 \psi(\vec{r}) + \frac{2m_0}{\hbar^2} (E - V(\vec{r})) \; \psi(\vec{r}) = 0 \qquad m_0 = \frac{m_p \cdot m_e}{m_p + m_e}$$

And, you know, r is the radial variable, theta is the angular variable or the polar variable, and phi is the azimuthal variable. And what is V of r here? V of r is some e square, which is a charge. In this particular case, it is simply e square because the proton has a charge e and the electron has a charge minus e. So it is minus e square by 4 pi epsilon 0 r. And this r that you see in the denominator is the distance between the proton and the electron. So this is the form of the Laplacian. That's the del square operator in a spherical polar coordinate system. That's the R part, and the theta phi parts are combined. In fact, a lot of books or texts that you would come across do the angular momentum problem ahead of the hydrogen atom. We took a different stance because we thought of solving the Schrödinger equation for different kinds of potentials. But nevertheless, the reason angular momentum is done ahead of this is that the thing you see in the bracket here is the angular momentum or the square of the angular momentum operator, apart from some constant, okay. So, first, if you solve this and know the eigenstates of the angular momentum operator, then of course it becomes easier to introduce, then we really need to solve for the r part or the radial part because the theta phi part is already solved. And these have a solution known as the Y lm functions, which are functions of theta and phi. They are called spherical harmonics.

Coulomb potential (between the electron and the proton:

$$V(\vec{r}) = -\frac{e_0^2}{4\pi\varepsilon_0\,|\vec{r}|}$$

$$\nabla^2\psi = \underbrace{\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}}_{\text{r-part}} + \underbrace{\frac{1}{r^2}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial\psi}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2\psi}{\partial\varphi^2}\right]}_{\vartheta\text{-}\varphi\text{ part}}$$

$\downarrow$ $Y_{\ell m}(\vartheta,\varphi)$ Spherical harmonics

Assume:   $\psi(r,\vartheta,\varphi) = \underline{R(r)\ \theta(\vartheta)\ \phi(\varphi)}$ .

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left(\frac{2m_0E}{\hbar^2} + \frac{m_0e_0^2}{2\pi\varepsilon_0\hbar^2 r} - \frac{\alpha}{r^2}\right)R = 0$$

$e^{\pm im\phi}$

$$\frac{1}{\sin\vartheta}\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\theta}{d\vartheta}\right) + \left(\alpha - \frac{m^2}{\sin^2\vartheta}\right)\theta = 0 \qquad\qquad \frac{d^2\phi}{d\varphi^2} + m^2\phi = 0$$

Once again, we will not solve elaborately, but this r, theta, and phi can get decoupled, and you can write down the solution in terms of r of r, theta of theta, and phi of phi. And this is the radial equation, and this is the theta equation. The phi equation is very simple, which gives a solution like exponential plus minus i m phi, while the other two are a little more complicated. These are, these Pl functions are Legendre polynomials. They come out as solutions of this, and for the theta part, and what we get is the Laguerre polynomials for the R part. So now the r part is in terms of the Laguerre polynomials. We do not go into details of the solution, and the theta and phi parts, when put together, correspond to this Ylm or the spherical harmonics. And we just have to multiply the Laguerre polynomials with the spherical harmonics to get the different bound state eigenfunctions for the problem. And again, we have to solve by solving this Schrödinger equation that you see there, or rather solving all three of them. We should be able to construct the eigenfunctions and get the energy eigenstates. And of course, we would get the bound states with negative eigenfunctions.

Energies for the reason that the electron is really bound to the nucleus or to the proton because otherwise it would just fly away, and that does not happen because there is a very large binding energy between the electron and the proton, and that is what we want to find out. So, as I said, this is the radial solution and the Y lm solutions. At times, the Y lms are written as this, and in some texts, they are written as Y l with a, but they are identical, okay. So, this is m. And as I said, they are functions of theta and phi. And this

R n l is simply a function of r, the radial variable. This R is a scalar variable which goes from 0 to infinity. Theta goes from 0 to pi, and phi goes from 0 to 2 pi. So, we do not go into the details but want to reflect upon the first few eigenfunctions of this. So, this eigenfunction, the ground state, is called the ground state. And the ground state eigenfunction looks like 1 by root over pi a0 cube exponential minus r over a0, where a0 is called the Bohr radius, okay. So this falls off, unlike the harmonic oscillator; it falls off as an exponential fall-off, you know. We will show the pictures schematically; we will show these wave functions and also talk about these quantum numbers. So n is a quantum number, l is a quantum number, m is a quantum number, and these three quantum numbers actually denote the energies of the system or the degeneracies.

Skipping details of the calculations, the stationary states are:

$$\psi_{nlm}(r, \vartheta, \varphi) = \underline{R_{nl}(r)} \ \underline{Y_l^m(\vartheta, \varphi)}. \qquad Y_{\ell m} \ \text{or} \ Y_\ell^{m.}$$

The first 4 eigenfunctions are written as:

$$\psi_{100}(r, \vartheta, \varphi) = \frac{1}{\sqrt{\pi}\sqrt{a_0^3}} e^{-r/a_0} \qquad \longrightarrow \text{Ground state} \qquad a_0 : \text{ Bohr radius.}$$

$$\psi_{200}(r, \vartheta, \varphi) = \frac{1}{4\sqrt{2\pi}\sqrt{a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$n, \ \ell, \ m$$

$$\psi_{210}(r, \vartheta, \varphi) = \frac{1}{4\sqrt{2\pi}\sqrt{a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos\vartheta$$

$$\psi_{21\pm1}(r, \vartheta, \varphi) = \frac{1}{8\sqrt{\pi}\sqrt{a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin\vartheta e^{\pm j\varphi},$$

$$\psi_{300}(r, \vartheta, \varphi) = \frac{1}{81\sqrt{3\pi}\sqrt{a_0^3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$$

Very importantly, they would define the degeneracies and so on. So, these n, l, m that you see here are the three quantum numbers. They are called as principal quantum number for L. L is called as azimuthal quantum number and M is called as a magnetic quantum number. And because of this, you know, there are n can take values from 1, 2, 3, etc., integer values, l will take values from 0 to n minus 1, and m can take values minus l to plus l, so these two l plus 1 values. And we'll see that how these different, you know, interlinked sort of dependencies, they would give rise to the degeneracy. So, this first few things, eigenfunctions, one is, this is simply exponential minus r by a0 with some normalization, which is 1 by root over pi a0 cube. And then we have, again, polynomial

multiplied by these exponential functions. So, this is 2 0 0 and 0 0s that is whenever l equal to 0 and m equal to 0, they do not have any theta or phi dependence. They only come when you have, you know, the l or m or both of them to be finite. So, you see that psi 2 1 0. So, there is a ground state and all these are excited states. In fact, you see that these three, they are degenerate first excited state, which means that they have the same energy. However, they correspond to three different distinct eigenfunctions and which all are orthogonal to each other. They kind of are orthonormal, you know, sort of eigenstates.

And then there's a psi 300 that's shown there. And so these are different eigenstates or the bound states of the system. And what about the, you know, the bound state energy spectrum? The bound state energy spectrum is given by this minus m 0 e to the power 4. We were writing it E0, but it is just the electronic charge and then 8 epsilon 0 square H square by 1 by n square. And there is nothing but equal to minus 13.6 by n square. And n is called as a principal quantum number. So that tells you that the energy level of a hydrogen atom is minus 13.6 by n square electron volt. So, if you give 13.6 electron volt, when the electron is in the ground state of the hydrogen atom, it will escape. That means the hydrogen atom will lose that electron and will become an ion. So, that is called as the ionization energy of hydrogen.

The bound state energy spectrum is written as

$$E = -\frac{m_0 e^4}{8\,\varepsilon_0^2 h^2}\frac{1}{n^2} \qquad = -\frac{13.6}{n^2} \qquad$$

$n$ is called as the

principal

number

quantum

The ionization energy of Hydrogen is 13.6 $eV$.

$$E_n = -\frac{13.6}{n^2}\,eV$$

So let me show the pictorially how the radial wave functions look like. So these are s states and so on. So you see the S state is this is the R10 state and this is the R20 state and

this is the R30 state. And these are the P states, which are, again, this is like R11 state, and so this one, and then this is R21 states, and this is R31 states. And this nomenclature and it's plotted, this is the radial part, that is Rnl multiplied by R is plotted as a function of r, okay, in terms of the Bohr radius, which you can call as a0. So, it's r over a0 and so on. Okay, so s and p states, so s states correspond to l equal to 0, okay, and these p states correspond to l equal to 1. So the s and p states are shown.
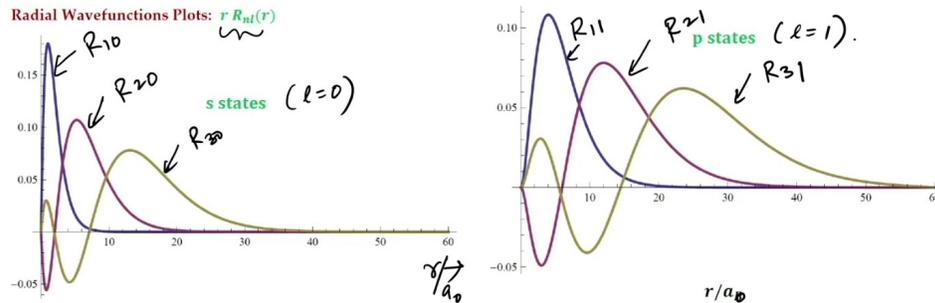


$R_{10}, R_{20}, R_{30}$                                    $R_{11}, R_{21}, R_{31}$

Similarly, you can plot the d states and f states and so on, which are corresponding to l equal to 2 and l equal to 3 and other higher values. So, it is important to look at the probability density, you know, how the probability density and the wave function, they vary. So, this for the 1s state, it sort of quickly falls off. It is plotted in, you know, kind of Angstrom. The 2s, it goes down and then it sort of, you know, picks up and becomes mildly positive at large values of r, almost zero. And then you have a 3s and so on and so forth. So you see that the probability density behaves like this for the 1S state and then it has a 0 in between for the 2s state and it has two 0s in between for the 3s states and so on. This tells you that as you go to larger and larger the quantum number, the principal quantum number or associated with r, which is the principal quantum number, and these s values say that it's l value is equal to 0. There are more fluctuations, you know, as you go to larger and larger values of n. So, we are really talking about R nL square and this is R as a function of, you know, r in Angstrom. This is not, you know, scaled by the Bohr radius, whereas in the earlier figure, it was scaled by the Bohr radius.

**Wavefunction & Probability Density – s states**
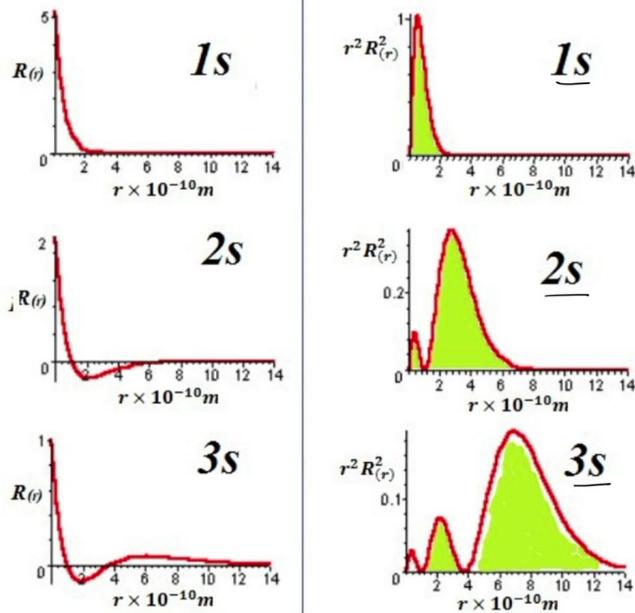


Similarly, for the p states and the d states, they look like this. So, the 2p state has a peak density close to, say, r equal to 3 Angstrom or something, and for the 3d, it peaks at about 5 Angstrom, and so on. This is how the p state and the d states, the 3d states, look like. The first one, as I said, corresponds to the value of n, and the second one corresponds to the value of l. So, this means n equal to 2 and l equal to 1. Similarly, this is n equal to 3 and l equal to 2. That's the depiction of the wave function and the probability. And if you plot the angular orbital, this is the s wave.

Wavefunction
& Probability
Density – $p$ states
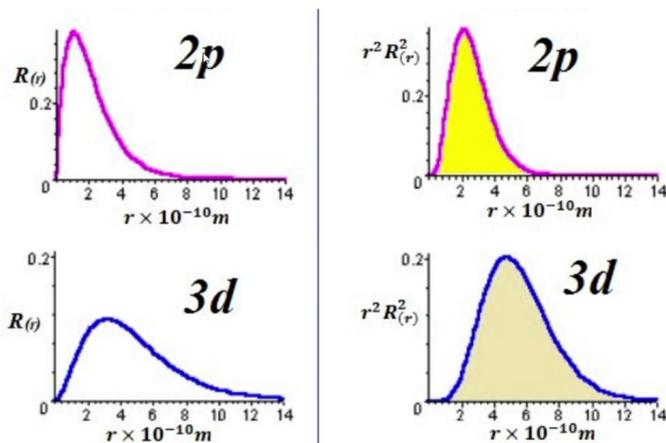


Then there are three p waves, which look like dumbbells: px, py, pz. And then there are five d orbitals, which look like these blobs along the axis, and so on. And there are five of them called dxy, dyz, xz, dx square, minus y square, and dz square. These are the five orbitals. So, this is, you know, L equal to 2, this is l equal to 1, this is l equal to 0 and so on. So, the multiplicity is 2l plus 1 and that is why you get 5 for this, you get 3 for l equal to 1 and so on, okay. So, the s orbital is spherically symmetric; that is, the ground state is spherically symmetric for the theta and phi dependence. Finally, coming to the quantum numbers and degeneracies, we have stated that n corresponds to the principal quantum number. It can take values 1, 2, 3, etc.

l is called the azimuthal quantum number. It can take values from 0 to n minus 1. m corresponds to the magnetic quantum number. It takes values from minus l to plus l. So, if you need to calculate the degeneracy, you need to consider the degeneracy of m values. These m values can take 2l plus 1 values. And if you try to calculate this, it becomes equal to, so 2l equal to 0 to n minus 1, l plus 0 to n minus 1, 1. Now, this can be, it is like, so 2 into, so it is n into n plus 1 by 2 when you are summing numbers from 1 to n, but this is from 0 to n minus 1. It will be n minus 1 into n by 2, those many values, and then you are simply summing up 1 n times, so that gives you n. So, the 2 will cancel, and you have n squared minus n plus n. So, this becomes equal to simply this n will cancel; it is n-squared-fold degenerate. So, each of the states of the hydrogen atom is n-squared-fold degenerate. The ground state, which corresponds to n equal to 1, is non-degenerate. n

equal to 2 is four-fold degenerate. n equal to 3 is nine-fold degenerate. But here, of course, we have not taken into account the spin degeneracy. So, if you take into account the spin degeneracy, these are the degenerate states. So, this ground state is non-degenerate, but this degeneracy that we are now talking about is not 3; this is equal to 4. And this is equal to 9, and so on. So, there are nine states which are degenerate.

Angular plot of the H-orbitals.
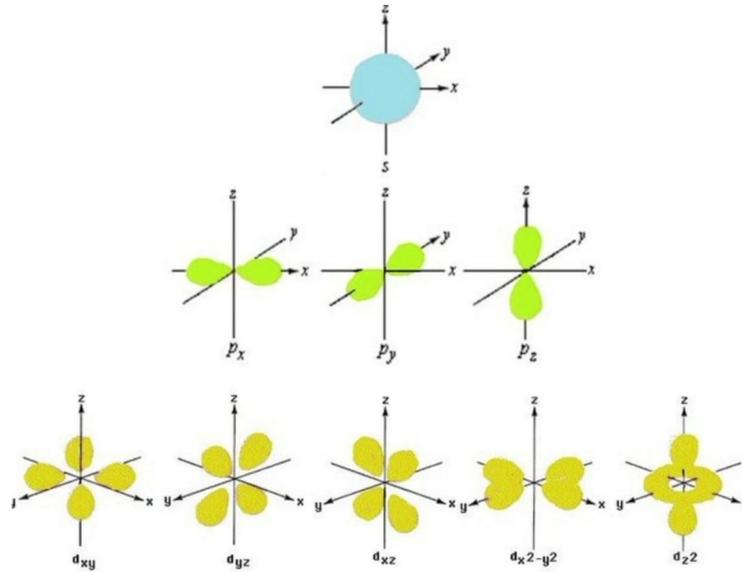


Then, as you go up to larger values of n, these degeneracies increase as n squared. So, including the spin degeneracy, we have this as 2n squared. Because the spin degeneracy brings in a 2s plus 1 factor, and since the electron has spin half, a factor of 2 comes out, so this becomes 2n squared. So, in fact, this degeneracy for the ground state is again non-degenerate, but then this is eight-fold degenerate, and this is 18-fold degenerate, and the next one would be 32-fold degenerate, and so on.

Quantum Numbers and Degeneracies

$n$: Principal Quantum Number, can take values 1,2,3....
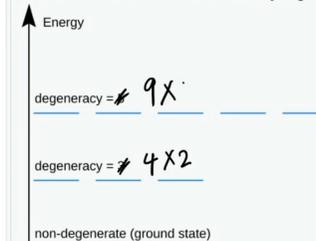
$l$: Azimuthal Quantum Number, can take values $0 \dots n-1$

$m$: Magnetic Quantum Number, can take values $-l \dots +l$

Degeneracy: $\sum_{l=0}^{n-1}(\text{degenracy of } m) = \sum_{l=0}^{n-1}(2l+1) = 2\sum_{l=0}^{n-1} l + \sum_{0}^{n-1} 1$

$$= 2 \cdot \frac{(n-1)n}{2} + n$$

$$= n^2 - n + n = n^2.$$

Including the spin degeneracy.

$2n$

$(2s+1)$

Energy

degeneracy = $9 \times$

degeneracy = $4 \times 2$

non-degenerate (ground state)

Okay, so we are there with this angular momentum. So, the angular momentum is defined as r cross p. So, this is written as x. It means it's r cross p, a cross product of the moment of the linear momentum. And now, with this, the Hamiltonian that we have for the hydrogen atom commutes with all of these three. But the problem is that each of these angular momentum components, or the operators corresponding to them, do not commute. And because they do not commute, you cannot use all of them as, or rather, you cannot find the eigenstates of H to be the same with all of them. So, rather, we choose L squared, which the H commutes with. That's the Hamiltonian for the hydrogen atom commutes with L squared, the angular momentum squared, and it also commutes with Lz. L squared commutes with Lz, of course. L squared commutes with Lx as well, but that is not so important. So, we take these two as the basis for constructing the eigenstates.

## Angular momentum and the spherical harmonics

$$L^2 Y_{\ell m}(\theta, \phi) = \ell(\ell+1)\hbar^2 Y_{\ell m}(\theta, \phi)$$

$$L_z Y_{\ell m}(\theta, \phi) = m\hbar Y_{\ell m}(\theta, \phi)$$

## Raising and Lowering operators

$$L_\pm = L_x \pm iL_y$$

$$L_\pm Y_{\ell m} = \hbar\sqrt{\ell(\ell+1) - m(m \pm 1)}Y_{\ell(m\pm 1)}$$

And this gives you these Ylm functions, which are functions of theta and phi. Okay, so this is exactly what we said earlier that this is the radial part. And we have written this radial wave function as UE because E corresponds to the principal quantum number, since energy is quantized as minus 13.6 by n squared. And there's again the wave function that is written there. That's not important. What's important for us is that the L square acting on Ylm gives you l into l plus 1 h cross square and returns you these Ylm functions. So, Ylm functions or the spherical harmonics are nothing but they are eigenstates of the L square and the LZ operator. And we have chosen it that way. We need two operators as preferred ones. So, we could have chosen L² and Lx or L² and Ly, but then the simultaneous eigenstates of L² and Lx would have to be determined. This is much easier because Lz acting on Ylm gives you mℏ Ylm(θ, φ). You can also use the raising and the lowering operators and which finally gives you these, of course, these raising and the lowering operators, which are Lx plus i Ly or Lx minus i Ly, which are L plus and L minus respectively. For them, of course, because Lx doesn't commute with Lz, these are not eigenfunctions. So, they actually raise the magnetic quantum number by one unit or lower it by one unit, depending on whether you're talking about the raising operator or the lowering operator for angular momentum.

In fact, we have introduced angular momentum, but we wish to do a little more and specifically talk about spin angular momentum, which has a different name for spin-half particles. These are called the Pauli spin matrices, and we will see some of their

properties. But that pretty much concludes one important task in quantum mechanics: the solution of the Schrödinger equation in a variety of potentials, including constant potentials, potential discontinuities, potential wells, delta-function potentials, harmonic oscillators, and finally the hydrogen atom, which is a 3D problem solved in spherical polar coordinates. In each of those cases, we have calculated the energy eigenstates and the corresponding eigenfunctions. That makes the solution complete. Of course, you can do many things with the eigenstates. Eigenstates allow you to calculate probabilities by taking the modulus squared, compute the probability current density, etc., and verify that the equation of continuity is satisfied for each case. We will see a little more on that before moving on to perturbation theory. We will stop here for today. Thank you.