

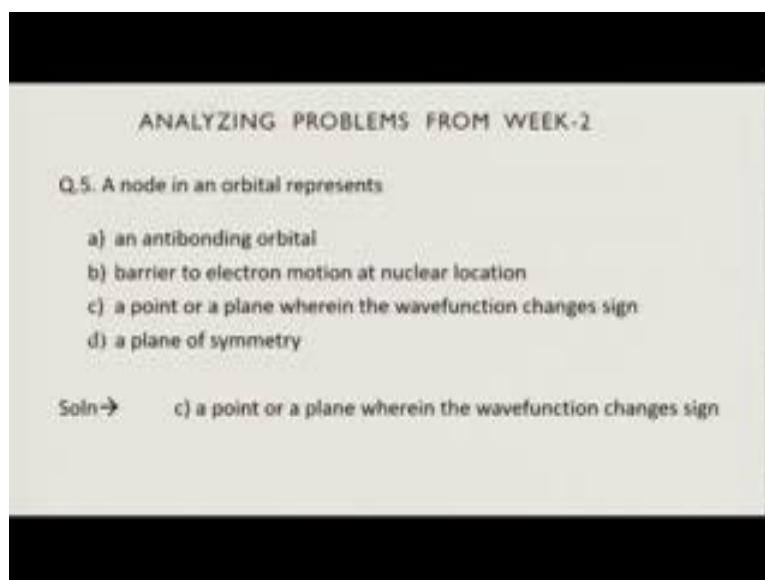
Implementation Aspects of Quantum Computing
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Lecture – 26
Reviewing Concepts and Clarifying Problems – II

Welcome to these lectures where we are reviewing our concepts that we have been utilizing all through this period for understanding how you are able to implement the quantum computing aspects. In doing so we are going back to the problems that we had given to you and based on their solutions and the understandings we are going ahead with our implementation problems.

Once again reviewing, let us see where we stand as of now. In this reviewing concepts that we have been doing let us look back to week 2 which we have been doing earlier.

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ANALYZING PROBLEMS FROM WEEK-2

Q.5. A node in an orbital represents

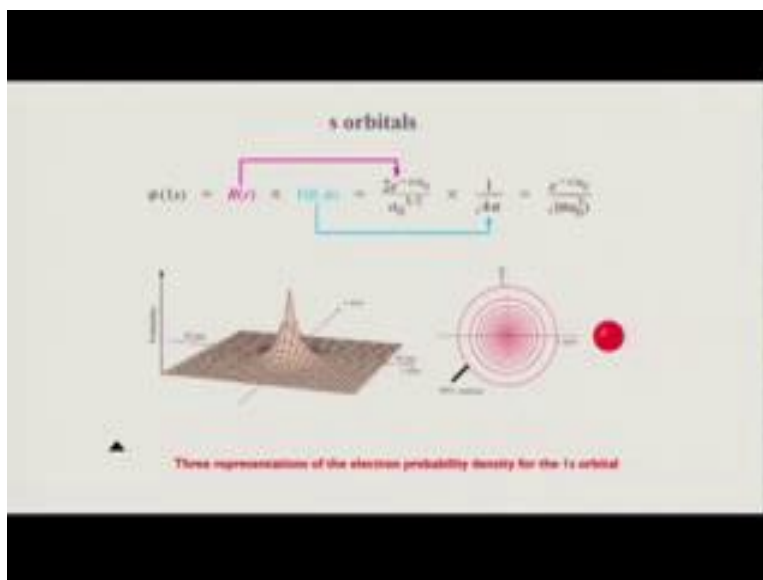
- a) an antibonding orbital
- b) barrier to electron motion at nuclear location
- c) a point or a plane wherein the wavefunction changes sign
- d) a plane of symmetry

Soln → c) a point or a plane wherein the wavefunction changes sign

And in this we have been analyzing the problems that we have been doing there. We have finished four of them earlier. So, let us look at the fifth one where, it was looking at the concept of the orbital. Now in the principle of analyzing the orbital the question which was probing was to see how the node in orbital is understood. So, the question is

essentially asked to what a node of orbital represents and it is a point or a plane where in the wave function changes sign that was the solution given. So, let us revisit the concept of the orbital and its nodes.

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So, in order to do that let us look at this simplest of the orbital which is the s orbital where the s orbital wave function has the form where the radial part corresponds to the distance the angular part corresponds this. Now the angular part for the s orbital as we know is constant because, there is no change along a spherical symmetrical, so the angular part is going to be constant.

So, we get a spherical there are three possible representations that are possible for looking at these orbital's; one is to look at the probability along the different axis, another one is to look at it is contour along the two dimensions, and finally it is to look at the probability density in terms of dots or colors.

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Wavefunctions and orbitals
Orbital: defined by the quantum numbers n , l and m ,
Orbital is a wavefunction
Orbital is a region of space occupied by an electron
Orbitals has energies, shapes and orientation in space

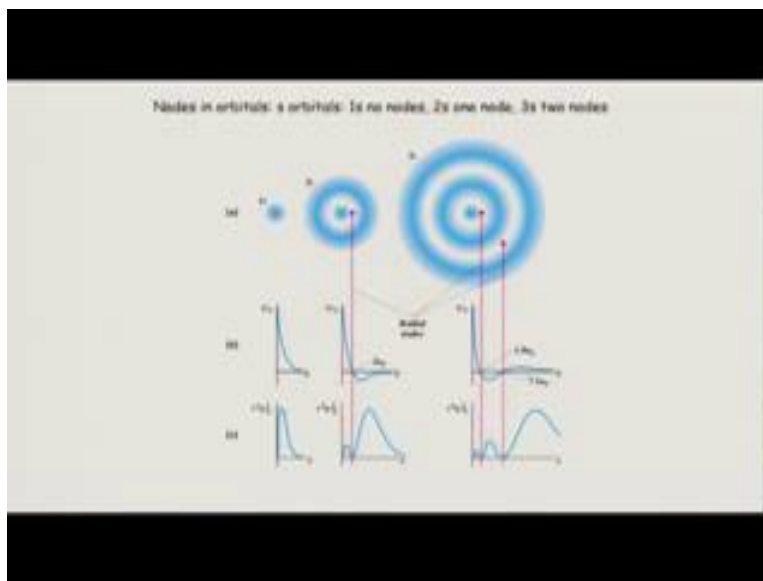
Thus, orbital is defined as one electron wavefunction

Size, Shape, and orientations of orbitals
 n determines size; l determines shape;
 m determines orientation

Generally speaking wave functions in orbital's are defined by their quantum numbers n , l and m 's of l . Orbital is a wave function, it is a region of space where the electronic exist and it has energy shapes and orientations in space. Thus, an orbital is defined as one electron wave function. So, here at the 3 s orbital's which are all spherical symmetric, but as you can see the sizes shapes and orientations of the orbital depends on the quantum numbers. So, n determines the size, l determines the shape and m 's of l determines the orientation.

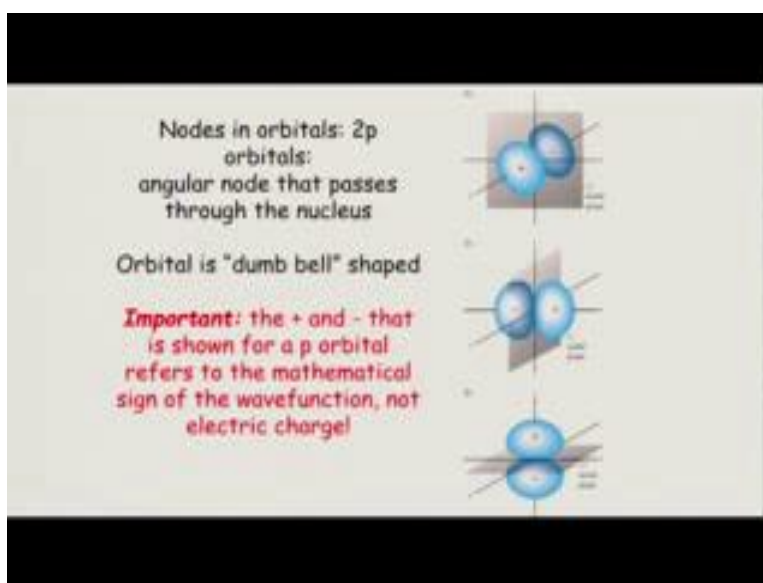
So, given the nodal plane as we show here the orientation and the presence of the system is being shown here. Now the p_x , p_y , p_z are the once which have angular dependence, so they are non-symmetric along the nodal plane, whereas in terms of the s orbital they are always going to be symmetric.

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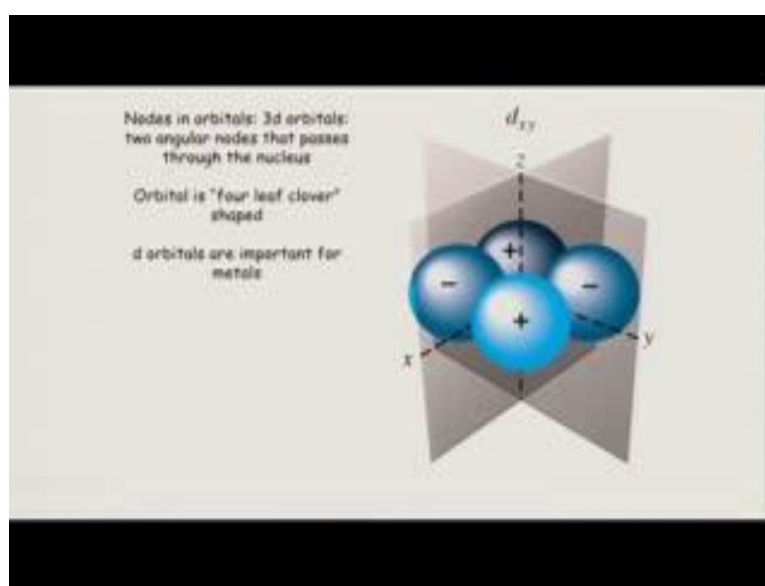
However nodes can exist irrespective of the symmetry and other issues. In terms of s orbitals the nodes exist in the radial part. So, 1 s has no nodes, 2 s has one node, and 3 s has two nodes. So, typically in terms of these are radial nodes which are represented in terms of $n - 1$ kind of nodes that you always get. And the first one does not have any node.

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Nodes in the p orbital's are of different kind because, they are angular nodes that passes through the nucleus and the orbital therefore becomes a “dumb bell” shaped because, it is no longer symmetric. And in this case it is important to note: that the plus and the minus sign is shown for the p orbital refers to the mathematical sign of the wave function and not anything to do with a electric charge, because the we are essentially looking at only the electrons. So, there is no charge aspect associated with it, it is the mathematical sign of the wave function, it is something to do with the symmetry of the system.

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The nodes in the orbitals for example, here we show the 3D orbitals. There are two angular nodes that pass through the nucleus the orbital is “four leaf clover” shaped and the d orbital's are important for metals and so and so forth. But, generally speaking these as some ways of how to visualize these orbital's and to know that these nodes are the places where the sign changes are occurring or the symmetry aspects are changing as you go across in terms of the orbital's. And that is why these are important in terms of the nodes and how they are represented in each of these representations.

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Q.6. In case of the He atom, it is not possible to solve the Schrödinger equation exactly as it is a three-body problem. The main difficulty arises from the


- a) electron-nuclear attraction term
- b) inter-nuclear repulsion term
- c) electron-electron repulsion term
- d) none of the above

Soln → c) electron-electron repulsion term

So, with that let us now look at the case of the Schrodinger equation which in terms of more than multi-electron system it is known that it cannot be solved exactly and the critical problem for that remains in what form was the question. And the electron electron repulsion term has been pointed out as the main issue.

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· He atom consists of a nucleus with atomic number $Z=2$ and two electrons


$$r_{12}^2 = |\vec{r}_1 - \vec{r}_2|^2 = r_1^2 + r_2^2 - 2r_1r_2\cos\alpha$$

So, in order to know this let us first look at the helium atom picture and understand that it has a one nucleus with two protons and it two electrons, so there are this three body problem and the two electrons can exist around the nuclei two different directions which gives raise to this condition where we have three coordinates to worry about r_1 , r_2 and r_{12} .

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• the state of the electrons is given by the wavefunction $\psi(r_1, r_2)$
 • the potential energy:

$$V = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}} \right)$$

 • operator of the kinetic energy:
 (center of mass system, $\mu \approx m_e$)

$$T = -\frac{\hbar^2}{2\mu} (\nabla_1^2(r_1) + \nabla_2^2(r_2))$$

The state of the electron is given by the wave function which depends on r_1 and r_2 , and the potential energy is a function of both r_1 , r_2 as well as r_{12} . So, the kinetic energy at the center mass of the system would be also dependent on two of them, but the potential energy part is the one which has the difficulty because, the electron electron repulsion part the is dependent on the r_{12} coordinate which is the one which is the couple coordinate system in this case.

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· Schrödinger equation:

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

· because of the last term from the potential energy, the potential isn't any more spherically symmetric (it depends on the angle between r_1 and r_2)

→ the Schrödinger equation can't be solved analytically

So, if you write the Schrodinger equation in this form, and the complete Schrodinger equation it turns out that it depends on three coordinates here; r_1 , r_2 and r_{12} , because of the last term which is coupled between r_1 and r_2 the coming from the potential energy the potential is not any more spherically symmetric and it depends on the angle between r_1 and r_2 . And so the Schrodinger equation cannot be solved analytically. So, the way it has been looked at this has been done has been is to approximate the problem and that will deal it later, but generally the Schrodinger equation has the electron electron repulsion term which needs to be taken care if this has to be solved. So, that was the part of the question which is asked.

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Q.7. The electronic Hamiltonian for He atom in atomic units is:

a) $H = -\frac{1}{2} \nabla^2 - \frac{1}{r}$

b) $H = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$

c) $H = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{r_{12}}$

d) $H = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2}$

Soln → b) $H = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$

The very next question however, asks about the electronic Hamiltonian of the helium atom in atomic units, which means that all the aspects of the mass and those are all taken as unity in terms of the atomic units as we know. So, it simplifies and becomes a form which only depends on the differential parts as well as the distances. And so this is the actual form which I just showed you earlier in atomic units in terms of the Hamiltonian, and that is the one which is shown here.

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Q.8. The electronic wavefunction of He atom in its ground state is:

a) $\psi_{total}(1,2) = 1s(1)1s(2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$

b) $\psi_{total}(1,2) = 1s(1)1s(2)\alpha(1)\beta(2)$

c) $\psi_{total}(1,2) = 1s(1)1s(2)\alpha(1)\alpha(2)$

d) $\psi_{total}(1,2) = 1s(1)2s(2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$

Soln → a) $\psi_{total}(1,2) = 1s(1)1s(2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$

So, there is nothing more to discuss in that. So, we come to the next question which was asked which is the electronic wave function of the helium atom in its ground state. Now, this is done under some approximation as I have been discussing when we looked at the Hamiltonian before that we can only solve this under the condition that we assume that the r^{-12} term is not going to create a problem. So, let us look at how this is done.

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APPROXIMATE MODEL

Independent electron approach

- because of the repulsion of the two e⁻
- $\vec{r}_1 > \vec{r}_2 = \vec{r}_1$
- e⁻-e⁻ repulsion term in the Hamiltonian can be neglected
- now we can use the product function:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1) \cdot \psi_2(\vec{r}_2)$$

- the Schrödinger equation is separated into two equations, one for each e⁻:

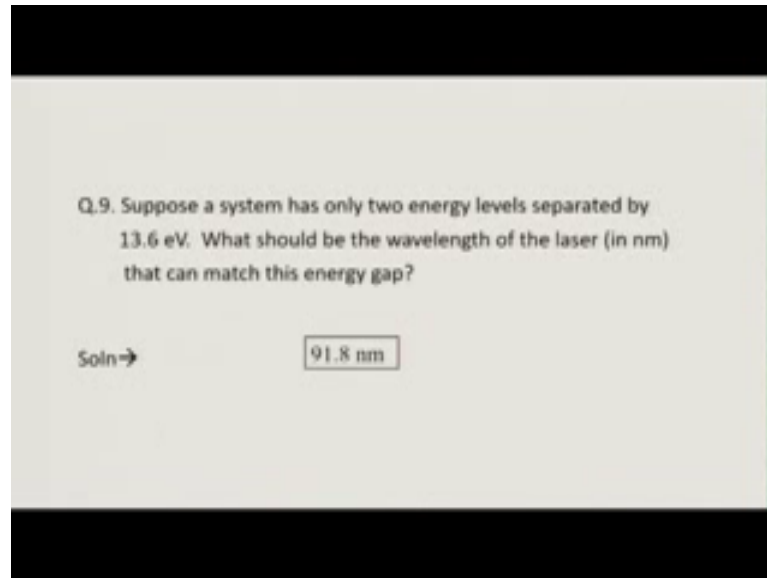
$$\psi_{\text{total}}(1,2) = 1s(1)1s(2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

And the approximate model essentially is an idea which is assuming that it is an independent electron approach. The electron-electron repulsion term is going to be ignored and then the product of the two functions can be used as then the problem essentially depends only on r_1 and r_2 . The Schrödinger equation is then separated into two equations and each one of the electrons in the helium atom is independent of each other. Now, this is an approximation as I have been mentioning because, there is an interaction between the two electrons, but the interaction is at a first-order level it can be ignored to at least solve it as two independent electrons. And that is the solution which has been shown here. Except that in this particular case the spins of the two have been taken into consideration, and alpha and beta represent the plus and minus signs or the right circularly rotating versus left circularly rotating electrons spin which is being combined here to the wave function to give it the total wave function.

Whenever a total wave function is given for a multi-electron system the individual spins of the electrons are also to be considered. That is what is being done here, alpha beta so the spin of 1 alpha and the spin of the other beta is being considered and the possibility of one being of one kind and the other and their linear combination is something which is being looked at. Since, this spin function due to Pauli exclusion principle is anti-symmetric. So, when you change sign, when the spin flips for one to the other the sign changes. And

therefore, we have this anti symmetric relationship between them. This sought out this model includes, the Pauli exclusion principle in terms of this spin

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Q.9. Suppose a system has only two energy levels separated by 13.6 eV. What should be the wavelength of the laser (in nm) that can match this energy gap?

Soln →

Now finally, we also looked at some problems which were just looking at if it was possible to understand how the energy transfers was been looked at. So, it is very simple questions which ask as to if there only two energy levels separated by say the ionization potential and hydrogen atom which is 13.6 electron volt what should be the wavelength of the laser in nanometer that can match these energy gaps? Now this is been asked because, it is sought of like unit transformation.

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$$E = h\nu = \frac{hc}{\lambda}$$
$$\lambda = \frac{hc}{E} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{13.6 \times 1.602 \times 10^{-19}} = 91.8 \times 10^{-9} \text{m}$$

And the simple equation in this case is to recognize that the energy can be written in many different terms and units and this is one of the ways of looking at it. Now, this is another condition that this is all under vacuum at the velocity that we are considering is the speed of light in vacuum and therefore, this is written in this term. Typically if it is matter is involved in this then a refractive index term will come into the picture, but as if now if you consider the simplest possible case then the lambda can be simply calculated in this form which turns out to be 91.8 nanometers. And so after this mathematics this is what it comes out to.

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Now, after having done all of this I also realize that it is time perhaps that we look at how to solve the hydrogen atom to at least some level so that all these understanding is put to in the right place. So, the hydrogen atom is the simplest physical system containing interaction potential that is not just an isolated particle. Before coming to the hydrogen atom problem we basically solve our Schrodinger equation problems in terms of particle in a box or rotating system rigid rotor or simple harmonic oscillator.

In doing so we basically ensure that we are looking at potentials which are independent and they are not interacting potentials here. Hydrogen atom is a complete problem in some sense and this also a good problem, because it can be solve completely using the Schrodinger equation. So, that is the reason why we can look at it.

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The hydrogen atom is the simplest physical system containing interaction potentials (i.e., not just an isolated particle).

Simple: one proton, one electron, and the electrostatic (Coulomb's) potential that holds them together.

The potential energy in this case is just $V = -\frac{e^2}{4\pi\epsilon_0 r}$

(the attractive potential between charges of $+e$ and $-e$, separated by a distance r).

This is a stationary state potential (no time dependence). We could just plug it in to Schrödinger's equation to get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} \left[E - \left(-\frac{e^2}{4\pi\epsilon_0 r} \right) \right] \psi = 0$$

It is a simple one proton one electron and the electrostatic coulomb potential that holds them together; so simple enough problem. The potential energy in this case is just e squared over $4\pi\epsilon_0 r$ at the attractive potential between the charged of the proton and the electron is separated by distance r , so it is all columbic. And this is the stationary state potential with node time dependence we could just plug it in to the Schrodinger's equation a time dependent equation to get the form as which is been shown here.

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The potential looks quite simple, but it is a function of r not x or (x,y) . What can we do about that?

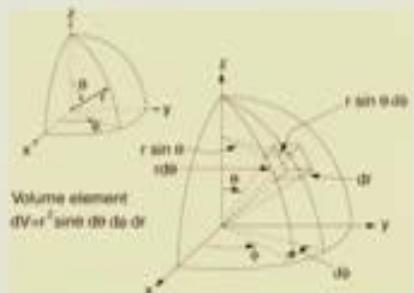
$$x^2 + y^2 + z^2 = r^2 \Rightarrow r = \sqrt{(x^2 + y^2 + z^2)}$$
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} \left[E - \left(\frac{e^2}{4\pi\epsilon_0 \sqrt{(x^2 + y^2 + z^2)}} \right) \right] \psi = 0$$

We need to let the symmetry of the problem dictate our mathematical approach.

At the potential looks quite simple, but it is a function of radial part r and not of x or x y z . So, what can we do about that? So, what we have to do is we have to recognize that we have to actually use the radial potential means, we are going to use this in this form where we have to put back the x y z in this form. And we need to use the help of symmetry of the problem to use our mathematical approach.

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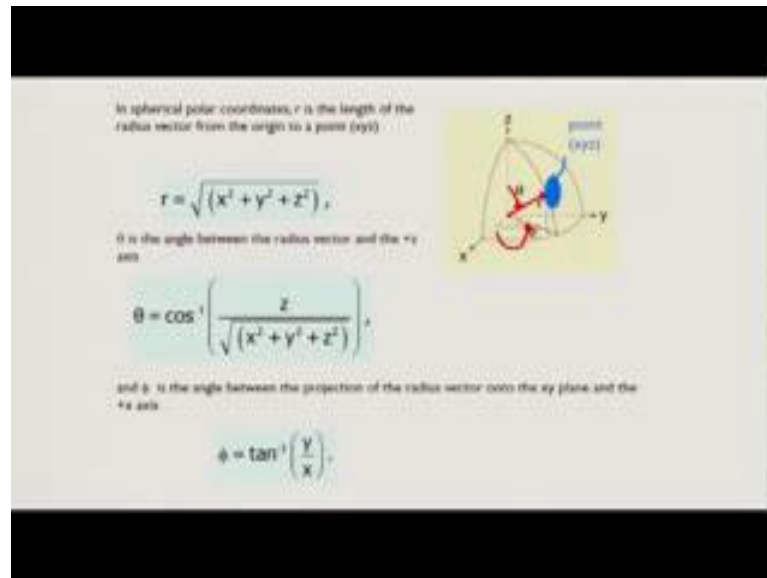
The spherically symmetric potential "tells" us to use spherical polar coordinates!



Volume element $dV = r^2 \sin \theta dr d\theta d\phi$

The spherical symmetry potential in this case tells us that we can use spherical polar coordinates just like what we have done for 3D rigid rotor for instance, the only difference is here it is not a rigid rotor the r can also change; so as before we can look at it and define the volume element as $r^2 \sin \theta \, d\theta \, d\phi \, dr$.

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And in the spherical polar coordinates r is the length of the radius vector from origin to the point, that we are looking at in x y z dimension. θ is the angle between the radius vector and the z plus axis. And ϕ is the angle between the projection of the radial vector on to the x y plane and the plus x axis. So, ϕ is $\tan^{-1} y$ over x .

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The equations on the previous slide tell us how to express (r, θ, ϕ) in terms of (x, y, z) . We can also express (x, y, z) in terms of (r, θ, ϕ) .

$$x = r \sin(\theta) \cos(\phi), \quad y = r \sin(\theta) \sin(\phi), \quad z = r \cos(\theta).$$

Now we can rewrite the 3D Schrödinger equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

in three dimensions, and in spherical polar coordinates, as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0.$$

The equation on the previous slide tells us how to express r, θ, ϕ in terms of x, y, z . We can also express x, y, z in terms of r, θ, ϕ . So, we can take advantage of that and we can write it out in the individual terms and then we can rewrite the 3D Schrödinger equation in this form where it is a function of x, y, z the energy. In three dimensions and in spherical polar coordinates we can rewrite this, because we know how to convert Cartesian coordinates into spherical polar coordinates in this form as we show here.

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If we plug in our potential V and multiply both sides by $r^2 \sin^2 \theta$, we get

$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) \psi = 0.$$

This equation gives us the wave function ψ for the electron in the hydrogen atom. If we can solve for ψ , in principle we know "everything" there is to know about the hydrogen atom.

Now, if we plug in our potential V , which we had discussed before and multiply, both sides by r squared \sin square theta we get this form. Now this equation gives us the wave functions ψ for the electron in the hydrogen atom. If we solve for ψ in principle we know everything that is to know about the hydrogen atom. So, that is the main part of about it, because it is a one electron system and that is what it is.

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When we solved Schrödinger's equation in one dimension, we found that one quantum number was necessary to describe our systems.

For example, in the Bohr atom, the electron moves in an orbit, but we need only one parameter to specify its position in the fixed orbit, so we only need one quantum number.

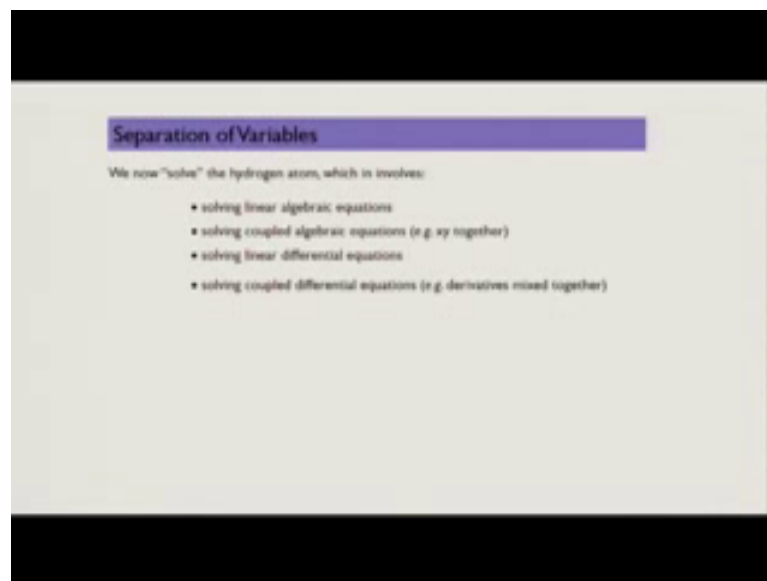
Now, in three dimensions and with three boundary conditions, we will find that we need three quantum numbers to describe our electron.

We are really solving Schrödinger's equation for the electron in a hydrogen atom. Nevertheless, we talk about solving the "hydrogen atom," because our solution will provide us with much of what we need to know about hydrogen.

When we solve the Schrodinger equation in one dimension we found out that one quantum number was necessary to describe our systems. For example, in the Bohr atom, the electron moves in an orbit, but we need only one parameter to specify its position and the fixed orbit, so we need only one quantum number. Here, in three dimensions and with three boundary conditions, we will find that we need three quantum numbers to describe our electron.

So, this is what we are getting to. So, we are really solving Schrodinger equation for the electron in the hydrogen atom. However, we talk about solving the “hydrogen atom,” because our solution will provide us with much more what we need to know about the hydrogen. Thus, because for one electron system coulombic interaction one you know particle then we have been essentially solved the whole thing.

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So, in order to solving linear algebraic equations as we have been taking about solving coupled algebraic equations for example, x y together and solving linear differential equations and solving coupled differential equations example with derivatives mix together that is what we have in this case. So we need to separate the variables.

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We have a coupled linear differential equation to solve, maybe if you are clever; like when we were doing with the earlier calculations in some cases we can make the problem easier. A big improvement would be to uncouple the variables. Stated more mathematically, when we have an equation like the one that we are discussing we would like to see if we can "separate" the variables; or "split" the equation into different parts, with only one part of variable in each part.

So, our problem will be much simplified if we can write the wave function which is a function of r θ ϕ in terms of three different functions r which is dependent only on r , θ which is capital θ which is dependent on the angle θ , and capital ϕ which is dependent only on the ϕ .

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Let's assume $\psi(r, \theta, \phi) = R \Theta \Phi$ and see where it takes us.

If our assumption works, in the orderly world of mathematics we know it must have been right.

With this assumption, the partial derivatives in Schrödinger's equation become

$$\frac{\partial \psi}{\partial r} = \Theta \Phi \frac{dR}{dr} = \Theta \Phi \frac{dR}{dt}$$
$$\frac{\partial \psi}{\partial \theta} = R \Phi \frac{d\Theta}{d\theta} = R \Phi \frac{d\Theta}{dt}$$
$$\frac{\partial \psi}{\partial \phi} = R \Theta \frac{d\Phi}{d\phi} = R \Theta \frac{d\Phi}{dt}$$

The partial derivatives become full derivatives because R , Θ , and Φ depend on r , θ , and ϕ only.

So, that is what we are after. So, let us assume that it is possible to break it up into a these parts and see what happens. If our assumption works, then the orderly world of mathematics will know that it will be right. So, we can rewrite this six, we are the original expression in this form three different terms founds where we have taken them. So, with this assumption the partial derivatives in the Schrodinger equation become like this, where the partial derivatives become full derivatives because now they depend only one on each coordinate at one point of time.

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To separate variables, plug $\psi = R(r)\Theta(\theta)$ into Schrodinger's equation and divide by $R\Theta$. The result is

$$\frac{\sin^2\theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} - \frac{2mV^2 \sin^2\theta}{\hbar^2} \left(\frac{e^i}{4\pi\epsilon_0 r} + E \right) = 0.$$

We have separated out the ϕ variable! The term

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2}$$

is a function of ϕ only. Let's put it over on the right hand side of the equation. This gives us...

To separate the variables what we need to do is, to plug in the wave function in to the Schrodinger equation and divide by them assuming that they are non 0 and the result is what is now shown here. Once we do this it immediately separates the phi variable and the term one over phi d squared phi d phi is the function of phi only. So, let us put this over to the right side of the equation.

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$$\frac{\sin^2\theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{2mV^2 \sin^2\theta}{\hbar^2} \left(\frac{e^i}{4\pi\epsilon_0 r} + E \right) = - \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2}$$

This equation has the form

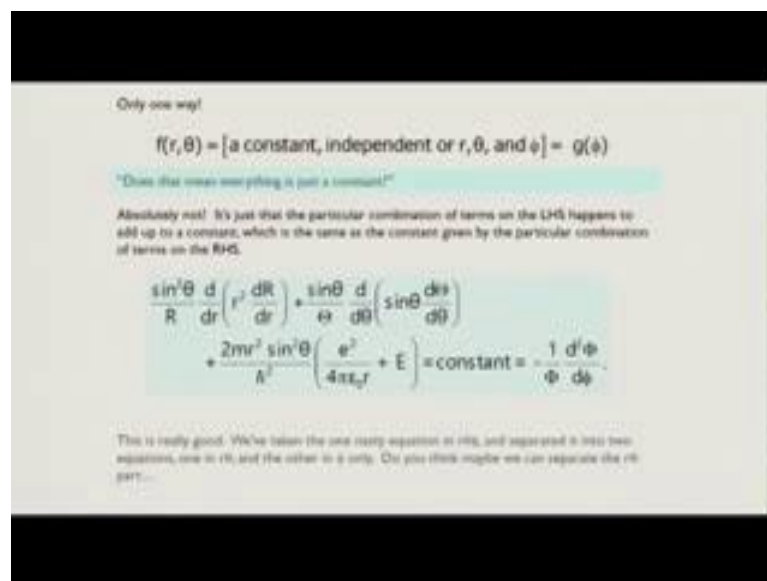
$$f(r, \theta) = g(\phi)$$

f is a function of r and θ only, and g is a function of ϕ only.

"How can this be? The RHE has only θ in it (but no r and ϕ), and the LHE has only r and θ in it (but no ϕ)! And LHS=RHS!"

And this gives us this form where we have already separated out the phi part. So, this equation has the form f of r theta which is equal to g of phi; f is a function of r and theta only, where g is a function of phi only. So, how can this be the, that is the natural question which may sometimes arise the right hand side only has phi in it, but no r and theta where as the left hand side only has r and theta in it but no phi; and at left hand side and right hand side is equal.

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This is only possible, its only one way when you have a constant independent of r theta and phi which is equivalent to g of phi. So, does that mean everything is just a constant that is not true, it just means that the particular combination of terms in the left hand side happens to add up to a constant which is the same as the constant given by the particular combination of terms in the right hand side. So, when we use this idea that the left hand side has this kind of a form then we can write it in this kind of an expression where we have equated both the sides to a constant.

Now this is really good because, we have taken one nasty equation in r theta phi and separated out into two equations; one in r theta and the other one in phi only. Now, the question is can we actually separate out the r and theta part also.

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$$\frac{\sin^2\theta}{R} \frac{d}{d\theta} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\theta}{d\theta} \right) + \frac{2m^2 \sin^2\theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = \text{constant} = \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2}$$

It turns out (although we won't do the math here) that the "constant" must be the square of an integer.

If not, our differential equations have no solution.

Thus, we can write the RHS of this equation as

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = m_l^2$$

Kind of hard to see, but that's a lowercase script l .

Where did this m_l come from? It's an integer. We just "assumed" to give it that "name."

So, in order to do that let us examine that it turns out that although we do not want to do the detail math here that the constant has to be a square of an integer. So, this particular constant that we are taking about as to be particular constant like it has to be a square of an integer and once we do that then these equations would have solutions otherwise there are no solutions now this hunch we get from the fact that our left hand side is already well defined and well known.

So, we can write our right hand side equation of this it turns out that we will not do the math here, but the "constant" has to be a square of an integer, if not our differential equations have no solution. And we already know that the right hand side of the equation therefore, can be written simply as a part which is equivalent to a square of a constant. And I am highlighting the facts that the m actually depends on a l with the lower subscript. So, where did this m 's of l , well come from it is an integer.

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The LHS of our big Schrödinger equation also must equal m_l^2 . If we set the LHS equal to m_l^2 , divide by $\sin^2(\theta)$, and rearrange, we get

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right)$$

Once again we have separated variables. The LHS is a function of r only, and the RHS is a function of θ only.

Again, the only way to satisfy this equation is for LHS = constant = RHS.

Solution of the resulting differential equations will result in restrictions on the constant. In this case, the constant must equal an integer times the next larger integer ($l(l+1)$).

And we just happen to give it that name the left hand side of our big Schrodinger equation also must be equal to m_l^2 . Now, if we set the left hand side equal to m_l^2 divided by \sin^2 and rearrange this we get this kind of an expression, once again we have separated the variable the left hand side is a function of r only and the right hand side is a function of θ only.

Again the only way to satisfy this equation is for the left hand side is to be a “constant” which is equal to a right hand side. The solution of this resulting differential equation will result in restrictions of this constant. In this case, the constant must be equal to an integer times the next larger integer and that is one of the tricks that we find out as to how it is happening.

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We have taken our initial differential equation and split into 3. Here are the pieces, rewritten slightly:

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m_l^2 \quad \text{Equation (I)}$$

--- Angular equations

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta} \right] \Theta = 0 \quad \text{Equation (II)}$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad \text{Equation (III)}$$

--- Radial equation

Schrodinger equation has been separated into three ordinary second-order differential equations [Eq (I), (II), and (III)], each containing only one variable. Now solutions need to be found for the boundary conditions ...

No longer need of dealing with partial differentials !!
 Everything falls into place by boundary conditions, that wavefunction amplitudes need to go to zero at infinity, that they need to be single valued, ...

And what we find is that we have taken our initial differential equation and split into 3, here are the 3 pieces rewritten slightly differently. The first two parts of the angular equations where this double derivative of the phi function is a constant square. The second part is basically a part where the constant was 1 time's 1 plus 1 which we have utilized to write the second part which is our theta variable. And finally, the radial part is dependent only on the r function and that is why we get. The Schrodinger equation has been separated into three ordinary second order differential equations, equations 1, 2, and 3 each containing only one variable.

Now, the solutions need to be found for the boundary condition and we no longer need to be dealing with partial differentials, because everything now falls into place by boundary conditions that the wave function amplitude need to go to zero at infinity and that they need to be single valued and so on and so forth.

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SOLUTION OF THE RADIAL EQUATION

- The radial equation is called the **associated Laguerre equation** and the solutions R that satisfy the appropriate boundary conditions are called **associated Laguerre polynomials**.
- Assume the ground state has $l = 0$ and this requires $m_l = 0$.
Eq (III) becomes
$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2\mu}{\hbar^2} (E - V) R = 0$$
- The derivative of $r^2 \frac{dR}{dr}$ yields two terms (product rule).
Write those terms and insert the spherical electrostatic potential
$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} - \frac{2\mu}{\hbar^2} \left(E - \frac{e^2}{4\pi\epsilon_0 r} \right) R = 0$$

So with this background then the different parts of the equations can be solved the radial part of the equation is called the associated Laguerre equation. And the solutions R that satisfy the appropriate boundary conditions are called associated Laguerre polynomial.

Assuming that the ground state has l equals to 0 and that requires m of l equals 0 the equation 3 which is the radial part takes this form where the derivative of the r squared r $d r$ yields two terms based on the product rule, writing those terms and inserting the spherical electrostatic potential we get the final form.

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SOLUTION OF THE RADIAL EQUATION

Try a solution $R = Ae^{-r/a_0}$ $\frac{dR}{dr} = -\frac{1}{a_0}R$ $\frac{d^2R}{dr^2} = \frac{1}{a_0^2}R$

A is a normalized constant.
 a_0 is a constant with the dimension of length.
 On inserting the first and second derivatives of R

$$\left(\frac{1}{a_0^2} + \frac{2\mu}{\hbar^2}E\right) = \left(\frac{2\mu e^2}{4\pi\epsilon_0\hbar^2} - \frac{2}{a_0}\right)\frac{1}{r} = 0$$

Condition to satisfy for any r is for each of the two expressions in parentheses to be zero.
 So we set the second parentheses equal to zero and solve for a_0 : $a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$

And then we set the first parentheses equal to zero and solve for E :

$$E = -\frac{\hbar^2}{2\mu a_0^2} = -E_n$$

Both equal to the Bohr result !!
Backed up by spectral lines !!

Many often ignore the reduced mass refinement

We can then try a solution which is of the form a to the exponential minus r over a n ught a is the nomination constant a_0 is the constant with the dimension of length on inserting the first and the second derivative of r we are able to make the expression look much better and given the condition to satisfy for any of the r is for each of the two expression is parentheses has to be 0.

So, we can set the second parentheses to be zero to solve for a zero which happens to be the Bohr radius as we find it here and then we can said the first parentheses equal to 0 and solve for E which is what we get many often ignore the reduce mask and because it turns out to be essentially the mass of the electron. The difference of mass is so small where it is the smaller mass which comes.

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HYDROGEN ATOM RADIAL WAVE FUNCTIONS

- First few radial wave functions R_{nl}

n	l	R_{nl}
1	0	$\frac{2}{a_0} e^{-r/a_0}$
2	0	$\frac{1}{2\sqrt{2}} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$
2	1	$\frac{1}{2\sqrt{6}} \frac{r}{a_0} e^{-r/2a_0}$
3	0	$\frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2} \right) e^{-r/3a_0}$
3	1	$\frac{4}{81\sqrt{6}} \frac{r}{a_0} \left(6 - \frac{r}{a_0} \right) e^{-r/3a_0}$
3	2	$\frac{4}{27\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$

already normalized

- Subscripts on R specify the values of n and l
associated Laguerre polynomials

But both are equal to the Bohr results and which are backed by the spectral lines. So, the hydrogen atom radial wave functions of the first few are now that we have seen them we can write some of them from the books we can see it in any of the books around and they subscripts specify the values of n 's of l n and l .

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Some Associated Legendre Polynomials $P_l^m(\cos \theta)$

$P_0^0 = 1$

$P_1^0 = \cos \theta$

$P_1^1 = \sin \theta$

$P_2^0 = \frac{1}{2}(3\cos^2 \theta - 1)$

$P_2^1 = 3\cos \theta \sin \theta$

$P_2^2 = 3\sin^2 \theta$

$P_3^0 = \frac{1}{2}(5\cos^3 \theta - 3\cos \theta)$

$P_3^1 = 3\cos \theta \sin^2 \theta$

$P_3^2 = 3\sin^2 \theta \cos \theta$

$P_3^3 = \sin^3 \theta$

Remember: l and m , were constant used to separate the Schrodinger equation in spherical coordinates, they were cleverly chosen and will become quantum numbers

Solutions to the Angular equation

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{df}{d\theta} \right) + \left[l(l+1) - \frac{m^2}{\sin^2 \theta} \right] f = 0$$

To be normalized for usage

And these are the associated Laguerre polynomials they are already normalized. Similarly, some of the associated Laguerre polynomials are given here with respect to the p l m 's of l l and m 's of l are constant which were used to separate the Schrodinger equation in spherical coordinates they were cleverly chosen and will become quantum numbers. Eventually that is what the whole story is about. And for general cases these have to be normalized for usages. Solutions to the angular equations are given in this form as we have to talk about.

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PRODUCT OF SOLUTION OF THE ANGULAR AND AZIMUTHAL EQUATIONS

- The general solutions for wave equation: $\frac{d^2 g}{d\phi^2} = -m_l^2 g$
- are $e^{im_l\phi}$ or $e^{-im_l\phi}$
- Solutions to the angular and azimuthal equations are linked because both have m_l .
- Group these solutions together into functions:

$$Y(\theta, \phi) = f(\theta)g(\phi) \quad \text{--- spherical harmonics}$$

The product of the solutions of the angular and the azimuthal equations can also be found from the other parts of the two expressions which turn out to be as I mentioned before this spherical harmonics we with which we started the whole problem, and these group solutions can be given into two functions.

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NORMALIZED SPHERICAL HARMONICS

l	m	Y_{lm}
0	0	$\frac{1}{\sqrt{4\pi}}$
1	0	$\frac{\sqrt{3}}{2} \cos\theta$
1	±1	$\pm \sqrt{\frac{3}{2}} \sin\theta e^{\pm i\phi}$
2	0	$\frac{3}{2\sqrt{5}} (3\cos^2\theta - 1)$
2	±1	$\pm \sqrt{\frac{15}{2}} \sin\theta \cos\theta e^{\pm i\phi}$
2	±2	$\pm \sqrt{\frac{15}{8}} \sin^2\theta e^{\pm 2i\phi}$
3	0	$\frac{7}{2\sqrt{14}} (5\cos^3\theta - 3\cos\theta)$
3	±1	$\pm \sqrt{\frac{21}{2}} \sin\theta (5\cos^2\theta - 1) e^{\pm i\phi}$
3	±2	$\pm \sqrt{\frac{105}{4}} \sin^2\theta \cos\theta e^{\pm 2i\phi}$
3	±3	$\pm \sqrt{\frac{35}{8}} \sin^3\theta e^{\pm 3i\phi}$

Already normalized

And they can be normalized and looked at in this form theta and phi dependent spherical harmonics.

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SOLUTION OF THE ANGULAR AND AZIMUTHAL EQUATIONS

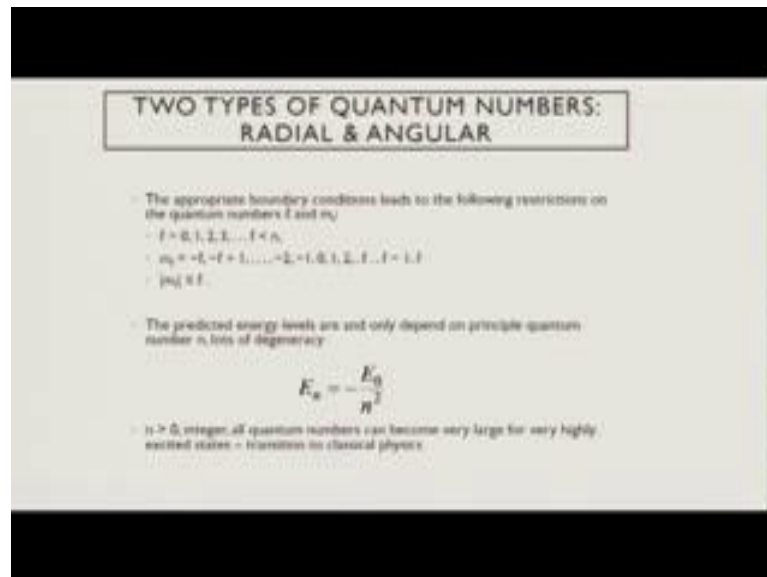
The radial wave function R and the spherical harmonics Y determine the probability density for the various quantum states. The total wave function $\psi(r, \theta, \phi)$ depends on n, l and m . The wave function becomes

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

The solution of the angular and azimuthal equations therefore, give rise to the entire full picture the radial wave function r and this spherical harmonics determine the probability

density of the various quantum states that total wave function $\psi(r, \theta, \phi)$ depends on n, l and m of l the wave functions therefore, become product function of the two cases, the radial part as well as the angular part.

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There are therefore, two types of quantum numbers radial and angular they appropriate boundary conditions needs to the following restrictions on the quantum numbers l and m of l , l can take any values going from zero to l as long as it is less than n m of l can take any values from minus l through zero to plus l and mode of m of l should be less than equal to l . So, the predicted energy levels are only depended on the principle quantum number n have with a lots of degeneracy E of n equal to minus e naught over n squared.

So, basically there are n square d generate when n is greater than 0 for hydrogen atom n is always greater than 0 and it is an integer all quantum numbers can become very large for very highly excited state transition to classical n can take any values from one to any integer all large values of possible all quantum numbers can become very large for very highly excited states.

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PRINCIPAL QUANTUM NUMBER N

Because only $R(r)$ includes the potential energy $V(r)$.

The result for this quantized energy is

$$E_n = -\frac{\mu}{2} \left(\frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \frac{1}{n^2} = -\frac{E_0}{n^2} \quad \text{just as in the Bohr model}$$

The negative sign means the energy E indicates that the electron and proton are bound together.

As energy only depends on n only there will be a lot of degeneracy due to the high symmetry of the potential (a 3D sphere has the highest symmetry that is possible in 3D)

And which can transit to the classical physical conditions the principle quantum number n is critical in terms of defining the energy, because only r radial part includes the potential energy V of r . The result of this quantized energy is e of n minus μ over 2 this form which is equivalent to e naught over n squared which is just like what was predicted in Bohr's model the negative sign means that the energy indicates, energy e indicates that the electron and the proton are bound together. As the energy only depends on n only, there will be lot of degeneracy due to the high symmetry of the potential at 3D sphere has the highest symmetry and that is possible in 3D.

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ORBITAL ANGULAR MOMENTUM QUANTUM NUMBER l AND SPECTROSCOPIC NOTATION

- Use letter names for the various l values. When reference is to an electron

$l = 0$	1	2	3	4	$5 \dots$
Letter s	p	d	f	g	$h \dots$

- electronic states are referred to by their n and l .
- A state with $n = 2$ and $l = 1$ is called a $2p$ state.
- The boundary conditions require $n > l$.
- When referred to the H atom S, P, D...

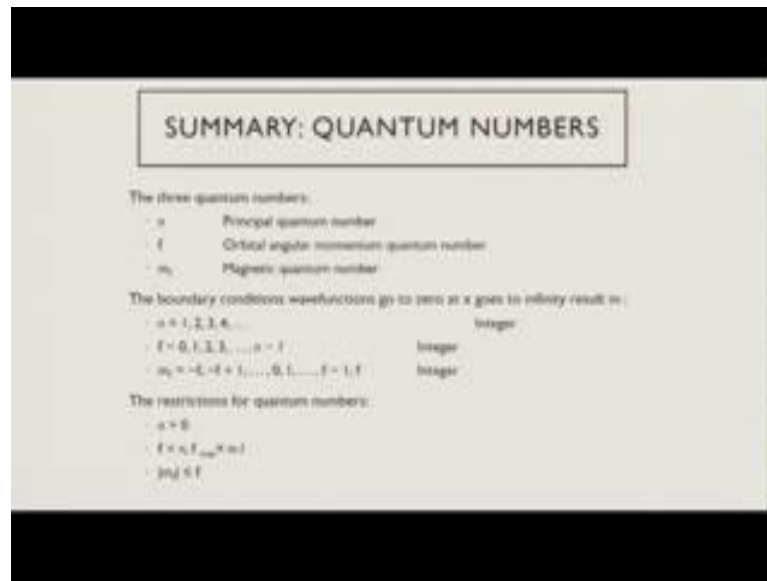
Spectroscopic Notation for Atomic Shells and Subshells

	Shell filled	Subshell filled	Subshell filled
1	1s		
2	2s	2p	
3	3s	3p	3d
4	4s	4p	4d
5	5s	5p	5d
6	6s	6p	6d
7	7s	7p	7d

The orbital angular momentum quantum number l and the spectroscopic notations can be also looked at in this same way in as we are now doing this, the letter names are given for the various l values when the reference is two n electrons. So, the l 's of value of 0 is letter notation is s 1 is p 2 is d 3 is f 4 is g 5 is h the electronic states are refer to by their n and l a state with n equal to 2 and l equal to 1 is called a 2 piece state. The boundary conditions required that n is always greater than l when refer to the hydrogen atom we therefore, have S, P, D kind of the shells and the spectroscopic notation involves the capital access where as the orbital's are always represented by the small letters.

The spectroscopic notations for the atomic shells and the sub shells are as we have been showing here has been given in terms of k l m n o p , whereas the shell symbol has been given as s p d f g and h .

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So, in summary the quantum numbers which we have used at the three main ones which are the principal quantum number, orbital angular momentum quantum number, magnetic quantum number m_l of l , the boundary conditions of the wave functions to go to zero at x goes to infinity result in; n values can go anywhere can take any integer $1, 2, 3, \dots$, l can go from 0 to $n-1$, m_l of l can go from minus l through 0 to plus l and the restrictions for the quantum numbers are such that n has to be greater than 0 , l has to be less than n and less than maximum is $n-1$, m_l of l mode is less than equal to l .

With this summary let us sought out finish on the idea of the hydrogen atom because, anything more than this would require the solution to the relativistic part of the Schrodinger equation which we are not doing the idea of the spin was introduced by Pauli in a different manner of symmetry and which we will be looking at later.

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Q.10. The common and contrasting factors for the Born-Oppenheimer approximation (BO) and the Frank-Condon principle (FC) are (mark True or False for each of the following statements) :

	Soln.
a) BO is for molecules, while FC is for atoms	False
b) BO is for generating molecular orbitals, while FC is for spectroscopic transitions	True
c) Both rely on the fact that the nuclear mass is extremely large compared to that of electrons	True
d) Both are gross approximations and mostly fail	False

The final question in the problem that we are looking at in week 2 was concerning the approximations that are very importantly done are very useful, and this is what the statement was being discussed the common and contrasting factors for the Born-Oppenheimer approximation and the Frank-Condon principle are tested in terms of true false which is what is being talked about Born-Oppenheimer is for molecules while Frank-Condon is for atoms.

Now, the fact of these are the fact is not true because as we will. So, the more important part to realize up as a questioning of this is to revisit the idea of Born-Oppenheimer approximation and the Frank-Condon principle which we will just now do, but let us read through the problem which have been looked at which is that Born-Oppenheimer is for generating molecular orbital's whereas, Frank-Condon is for spectroscopic transitions both relay which is a true statement. Both relay on the fact that the nuclear mass is extremely large compared to that of the electrons which is also true and both are gross approximations and mostly fail is a wrong statement because, amazingly this these two approximations work wonderfully truly for most of the time.

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In quantum chemistry and molecular physics, the **Born-Oppenheimer (BO) approximation** is the assumption that the motion of atomic nuclei and electrons in a molecule/atom can be separated.

$$\Psi_{\text{total}}(r, \theta, \phi) = R_{\text{el}}(r)Y_{l,m}(\theta, \phi)$$

The **Frank-Condon principle** is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy.

And the basic points of these two approximations are at in quantum chemistry and molecular physics, the Born-Oppenheimer approximation is the assumption that the motion of the atomic nuclei and electrons in a molecule or an atom can be separated based on the fact that mass difference between the two is extremely large which means that the motion of the electron is extremely fast as compare to that of the molecule, and the separation of variables that which we just discussed in terms of the hydrogen atom is in fact, true due to the Born-Oppenheimer approximation. The Frank-Condon principle on the other hand, is the transition condition for any spectroscopic rule and as we have been discussing the both were discussed in this particular lecture in both saying token and this is a rule in spectroscopy and Condon chemistry that explains the intensity of vibronic transitions.

Vibronic transitions are simultaneously change in the electronic and vibrational energy levels for molecule due to the absorption emission of a photon or the absorption of energy and there in it can only occur through vertical transition, that is because once again the nuclear coordinate motion is extremely sluggish as compare to the motion of the electrons and that is the basic idea behind all of these studies that we have been discussing until now. And they form the basis of most of the implementation aspects in

quantum computing and quantum information processing that we are actually dealing with in this entire course.

And therefore, I tell it was extremely important that we revisit and understand these basic concepts once more to make sure that whatever we have discussing currently in terms of implementations do not become faded because of the logical understanding and these things are not clear. With this let us end the lecture today and I look forward to meeting you in the next round.

Thank you.