Quantum Chemistry of Atoms and Molecules
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Lecture – 26
Hydrogen Atom: Quantum Numbers

We are discussing hydrogen atom, we have talked about a couple of quantum numbers and now, we are going to discuss the quantum number that we are perhaps most familiar with and that is principle quantum number.

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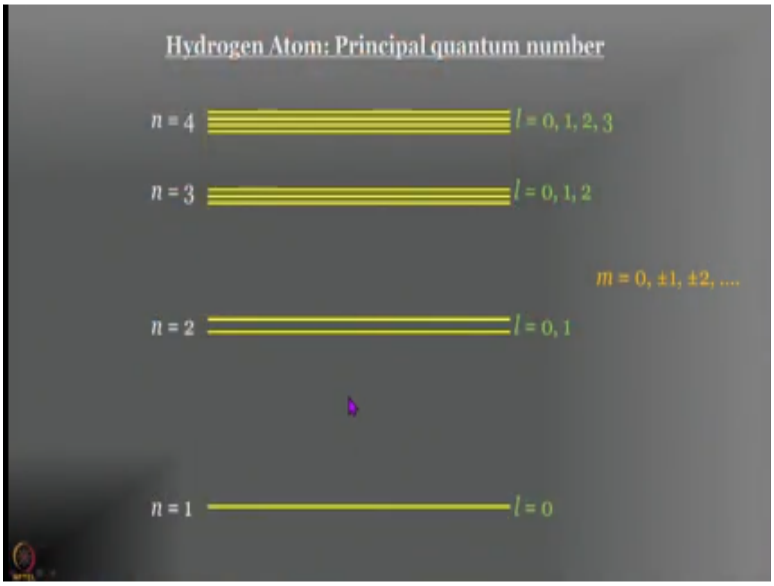

Hydrogen Atom: Principal quantum number

Remember all the discussion of not just hydrogen atom but also quantum mechanics, one of the beginnings of quantum mechanics is this transitions from one level to the other of hydrogen atom which showed up as line spectra of hydrogen atom and from there, different experiments reveal different features of the spectrum and that is what led to the idea of quantum mechanics anyway.

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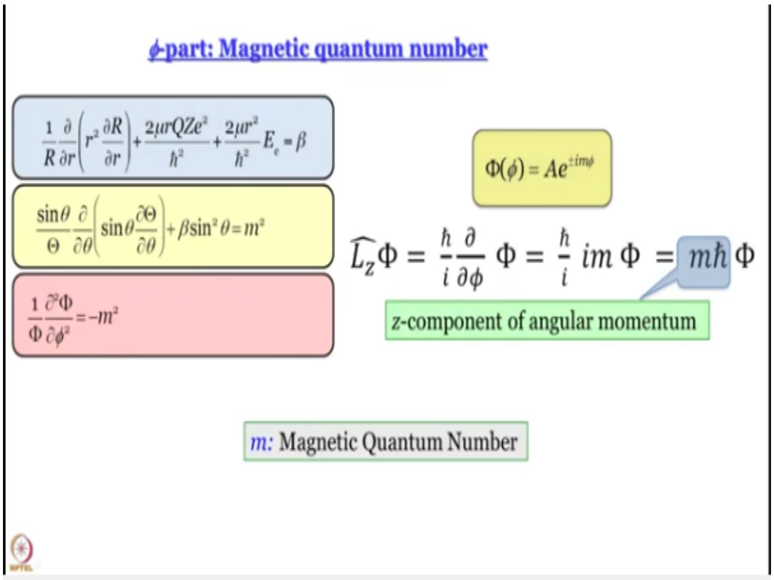

ϕ-part: Magnetic quantum number

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

$$\Phi(\phi)=Ae^{\pm im\phi}$$

$$\widehat{L_z}\Phi=\frac{\hbar}{i}\frac{\partial}{\partial\phi}\Phi=\frac{\hbar}{i}im\Phi=m\hbar\Phi$$

z-component of angular momentum

m: Magnetic Quantum Number

So, today we talk about principle quantum number but before that let us do a quick recap as usual what we have done so far in hydrogen atom is that we have been able to write Schrodinger equation and separate; for separation of variables and hence generate 3 different equations; one in r, one in theta, one in phi and we have solved the phi part and we said that it is exactly the same as our treatment of rigid rotor and from the phi part we got this wave function 1 by root over 2 pi e to the power plus minus im phi.

And we showed that when z; Lz operator operates on phi, it gives an Eigen value of mh cross, so phi is what; phi contains information about the z component of angular momentum okay and from here by using cyclic boundary condition, we get the magnetic quantum number. Magnetic quantum number takes the values of 0, plus minus 1, plus minus 2, plus minus 3 and so on and so forth.

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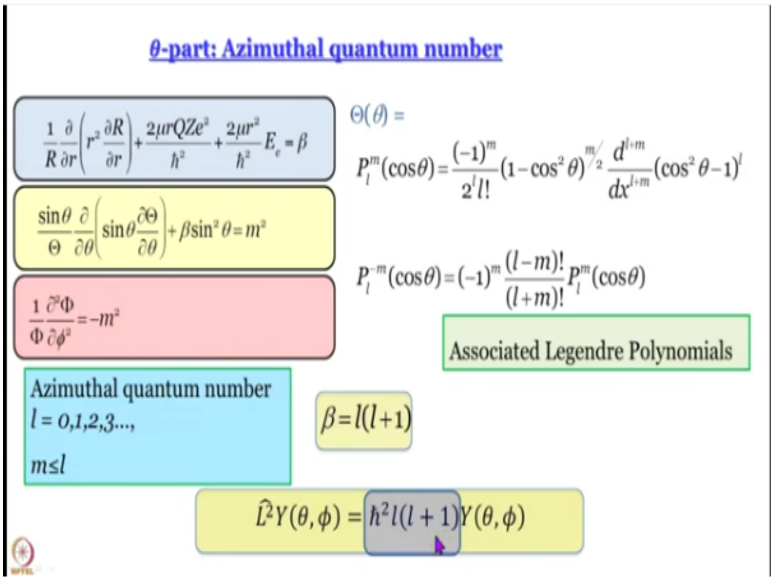

θ-part: Azimuthal quantum number

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r QZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

$\Theta(\theta)=$

$$P_l^m(\cos\theta)=\frac{(-1)^m}{2^l l!}(1-\cos^2\theta)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(\cos^2\theta-1)^l$$

$$P_l^{-m}(\cos\theta)=(-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(\cos\theta)$$

Associated Legendre Polynomials

Azimuthal quantum number
$l = 0,1,2,3\ldots,$
$m\leq l$

$\beta=l(l+1)$

$$\hat{L}^2Y(\theta,\phi)=\hbar^2 l(l+1)Y(\theta,\phi)$$

And what we not solved explicitly but given you the results is a solution of the theta part which yields another quantum number l, the solution of theta part; capital theta turns out to be an Associated Legendre polynomial in cos theta and what we see is that this beta turns out to be l into l + 1 and when l square operator operates on the angular part of the wave function, we get h cross square multiplied by l multiplied by l + 1 multiplied by the same wave function.

So, it is an eigenvalue equation, this is the value of square of angular momentum and hence we had worked out that the value of total angular momentum of electron in hydrogen atom is square root of l into l + 1 multiplied by h cross.

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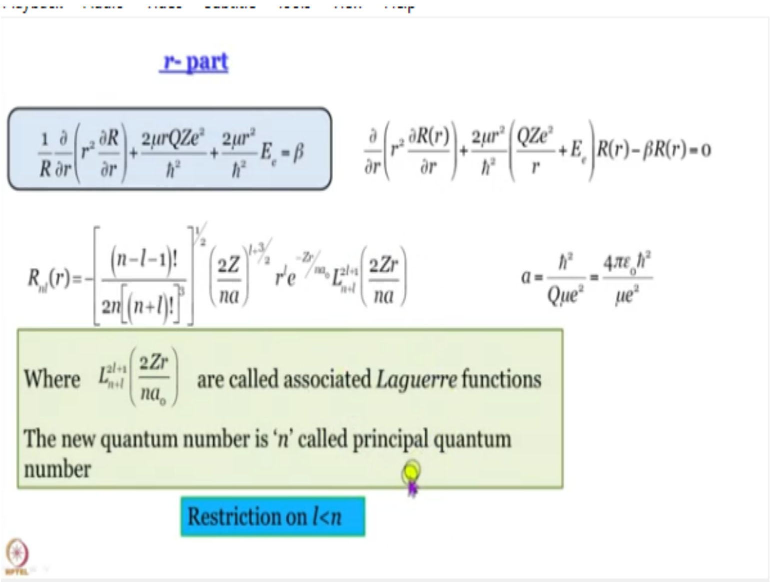

r- part

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r QZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(\frac{QZe^2}{r}+E_e\right)R(r)-\beta R(r)=0$$

$$R_{nl}(r)=-\left[\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right]^{1/2}\left(\frac{2Z}{na}\right)^{l+3/2}r^l e^{-Zr/na_0}L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$$

$$a=\frac{\hbar^2}{Q\mu e^2}=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

Where $L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$ are called associated *Laguerre* functions

The new quantum number is '*n*' called principal quantum number

Restriction on $l<n$

Now, let us start talking about the r part, once again this is a differential equation solution to which was already known by the time people started working on Schrodinger equation of a hydrogen atom, so there was no need for them to really work it out, I mean from the beginning. So, I mean in the present day with this COVID 19 outbreak one term that has become very familiar with many of us is repurposing of drugs, inventing a new drug is not so easy; it takes many, many years.

So, what people are trying to do is that they are trying to use already existing drugs and explore whether they have any efficacy against this novel coronavirus. So, similarly already existing equation, so I sort of; if I may use the same term, repurposed to get the solution right, little bit of digression but I mean let us not forget the times we live in okay.

So, this equation; solution of this was already known and the solution was when put in context of this hydrogen atom problem, solution turned out to be R; it was a function of 2 quantum numbers n and l; l we know about already, n is the new quantum number that we are going to talk about that is a constant, the constant is factorial n - l – 1 divided by 2n into n + l factorial to the power 3, the whole thing under square root sign that multiplied by 2Z divided by na.

What is a; a is 4pi epsilon 0 h cross square by mu e square, if you remember or if you just go back and have a look at what we had said while discussing Bohr theory in very brief, this is the expression that we had got for the radius of the atom, right. So, this is essentially Bohr radius and very soon it will boil down to Bohr radius of hydrogen atom. Now, this is a constant, we do not really have to remember all this, all we need to know is that this is a constant.

Then the next part is important, you have r to the power l, so r is the radius that will be raised to the power l, so for if l equal to 0 that will just be 1, l equal to 1 it will be r, l equal to 2 it will be r square and so on and so forth. So, something that increases as a function of r that is multiplied by e to the power -Zr by na0 so that is an exponential decay in terms of r, so you have unless l equal to 0, you have an increasing function of r multiplied by a decreasing function of r.

But that is not all you also have that multiplied by a, once again another kind of polynomial, the solutions are all sort of power series solutions we always end up getting these polynomials and this polynomial that we get here, these are called Associated Laguerre functions. So, Associated Laguerre functions you do not really need to know their form but just remember that this Associated Laguerre functions are functions of r multiplied by some constant, that constant is 2Z divided by na0 but we do not need to remember all that.

All we need to know is some constant multiplied by r to the power l, this I would like you remember constant multiplied by r to the power l e to the power minus constant into r multiplied by Laguerre function in constant into r that is what that is the general form of the r part of the wave function. Now, let us have a look at this function by function but before that let us also state something that we have said already that n takes up values of 1, 2, 3, 4 so on and so forth it can go up to infinity.

It also puts a restriction on the value of l, remember beta is the bridge between the r dependent part and the theta dependent part and theta dependent part gives rise to the values of l anyway, so restriction on l and the restriction essentially is l has to be less than n that comes from applying the boundary conditions here.

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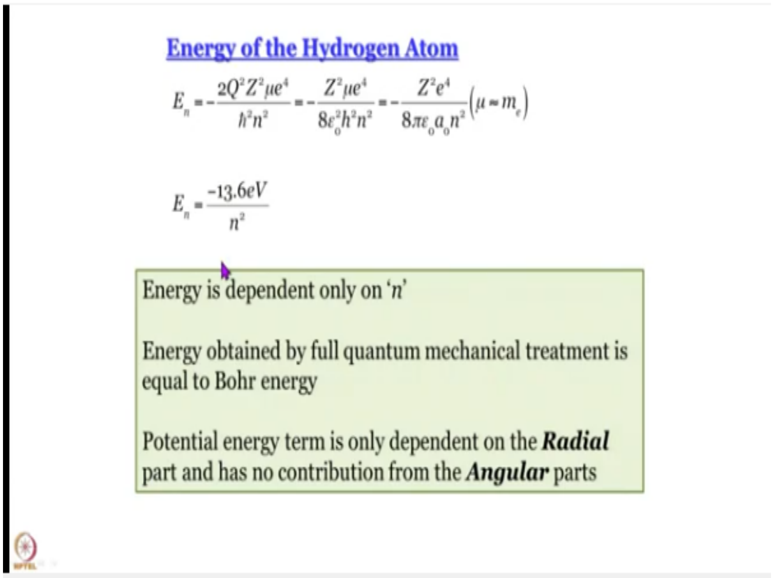

Energy of the Hydrogen Atom

$$E_n = -\frac{2Q^2Z^2\mu e^4}{\hbar^2 n^2} = -\frac{Z^2\mu e^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{Z^2 e^4}{8\pi\varepsilon_0 a_0 n^2} (\mu \approx m_e)$$

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

Energy is dependent only on '*n*'

Energy obtained by full quantum mechanical treatment is equal to Bohr energy

Potential energy term is only dependent on the ***Radial*** part and has no contribution from the ***Angular*** parts

One more thing; energy when you do the full quantum mechanical treatment turns out to be exactly the same as what was predicted by Bohr theory okay, does that mean that Bohr theory was correct and all these discussion that we are doing is rubbish not really, Bohr theory is not correct, it is just that it gives the right answer, gives the right answer because the physical assumptions and considerations in many cases are actually valid but we still cannot really use it.

Because it is a 100 percent classical theory, it violates uncertainty principle and also it uses classical and quantum, maybe it is not right to say it is 100 percent classical theory, it uses classical and quantum theories reversibly whenever whichever is more convenient that is not such a good thing to do most importantly, it violates uncertainty principle, so we cannot use it.

This quantum mechanical treatment is the way to go but the beauty is even though Bohr theory is not really correct, it gives the correct values of many physical quantities, energy being the most prominent of them, you might remember that one in one of our earlier modules we had said that the value of Rydberg constant that we can predict from Bohr theory turns out to be fairly accurate when compared with the Rydberg constant determined experimentally.

Why is that so? Because Rydberg constant essentially comes from difference in energies of energy levels, so that 1 by n square is there everywhere, so interestingly we get the same value of energy as that of Bohr theory okay but maybe it is not such a big surprise because you knew that Bohr theory does give the right value of energy anyway okay but let us not put too much of weight is to that let us move ahead.

One more thing that we should say is that interestingly in this expression for e, the only quantum number that makes a contribution is n and not l, remember what we are doing here; we are working out Schrodinger equation for a hydrogenic atom; hydrogenic atom means a one electron atom. So, for a one electron atom what we are saying is that l does not contribute to energy.

However, when we have more than one electrons in an atom, l is going to have a role to play, so we will talk about it when the time comes but for now, let us have no confusion about this that different l values for the same n value are associated with exactly the same energy minus 13.6 by n square electron volt for hydrogen atom and hydrogenic atoms, l comes in only when you have more than one electron and your phenomena like screening, shielding so on and so forth, okay. So, the only thing that is there is the radial; the radial part is the only part that makes contribution to total energy, okay.

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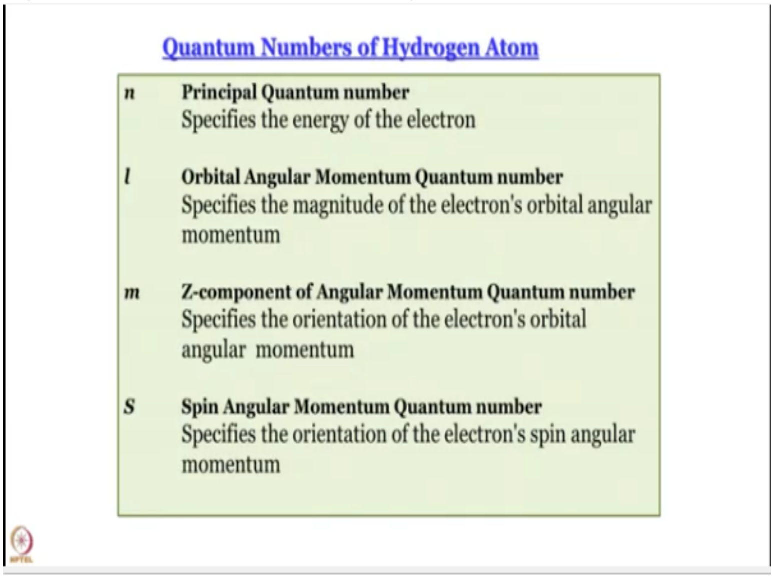

Quantum Numbers of Hydrogen Atom

n	**Principal Quantum number** Specifies the energy of the electron
l	**Orbital Angular Momentum Quantum number** Specifies the magnitude of the electron's orbital angular momentum
m	**Z-component of Angular Momentum Quantum number** Specifies the orientation of the electron's orbital angular momentum
s	**Spin Angular Momentum Quantum number** Specifies the orientation of the electron's spin angular momentum

So, now we have reached a stage where we have talked about 4 of the 3 quantum numbers that we know; n, l and m and we have come to a reconciliation with what we had said using old quantum theory that n specifies the total energy of the electron in the atom, l talks about orbital angular momentum, m talks about Z component of the orbital angular momentum. What we have not obtained and what we will not obtain at all from the Schrodinger treatment is the spin angular momentum quantum number.

Spin is something that arises out of relativistic quantum mechanics, dirac treatment, so that is something that has to be brought in externally, if you remember and we are going to say this again later on if you have a free electron then it is not associated with any n or l or m; n, l, m these quantum numbers arise due because the electron is in the field of a nucleus, however even for a free electron you do have s, you do have what is called ms; ms has values of plus 1/2 and minus 1/2.

Once again they denote the contribution of the spin angular momentum towards the z axis, so z component of spin angular momentum, we will talk about that in more detail when we discuss multi electron atoms okay. For now, let us move on to the next section with the understanding that we develop concepts of n, l and m interestingly in the opposite sequence, remember in Bohr theory n came first, then Sommerfeld modification brought in l.

And Zeeman effect necessitated bringing in m, in Schrodinger treatment however, m comes first followed by l followed by n because that is a sequence of a solution of Schrodinger equation, s comes from someplace else, right but with that understanding let us now continue with our discussion of the r dependent part, R.

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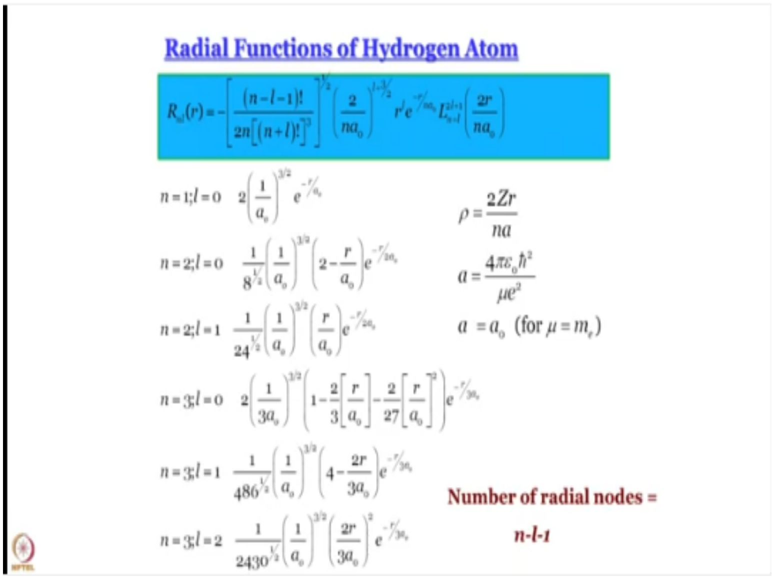

Radial Functions of Hydrogen Atom

$$R_{nl}(r) = -\left[\frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{l+3/2} r^l e^{-r/na_0} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$n=1; l=0$ $\quad 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

$n=2; l=0$ $\quad \frac{1}{8^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$

$n=2; l=1$ $\quad \frac{1}{24^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}$

$n=3; l=0$ $\quad 2\left(\frac{1}{3a_0}\right)^{3/2}\left(1-\frac{2}{3}\left[\frac{r}{a_0}\right]-\frac{2}{27}\left[\frac{r}{a_0}\right]^2\right)e^{-r/3a_0}$

$n=3; l=1$ $\quad \frac{1}{486^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(4-\frac{2r}{3a_0}\right)e^{-r/3a_0}$

$n=3; l=2$ $\quad \frac{1}{2430^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{2r}{3a_0}\right)^2 e^{-r/3a_0}$

$$\rho = \frac{2Zr}{na}$$

$$a = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

$$a = a_0 \text{ (for } \mu = m_e)$$

Number of radial nodes =

n-l-1

So, let us have a look at the functions as we are said few minutes ago, this here is a general form, what we will do is; we will write rho for 2Zr by na because that is something that keeps arising everywhere, we will write a for this 4pi epsilon 0 h cross square by mu e square and since its hydrogen atom when mu equal to me, we are going to write a equal to a0 okay. Now, this is the wave function radial part that we get for n equal to 1, l equal to 0.

And just for the record it is the only part, remember when l equal to 0 then this l part and phi part are just constant okay, so that gets subsumed in the normalization constant and this is what we get, so it is a simple exponential decay in r. Remember l equal to 0, so r to the power l equal to 0 and this Lagurre function that also is a constant, so it is for n equal to 1, l equal to 0 that is a simple exponential decay in r.

Now, even though we have not written it in the slides we are going to, I think talk about it in the next module, let me just say something here, n equal to 1, l equal to 0 denotes an orbital, I think we know that, it denotes 1 is orbital, so even though I might be jumping the gun a little bit, let me pop this question right now, what is an orbital and let me give you the answer.

An orbital is an acceptable solution for Schrodinger equation for a one electron atom, some of us might be taken by surprise by this definition because in many textbooks especially, in 11 and 12 level, it is written in bold letters that an orbital is a region of space in which the probability of finding the electron is maximum, well that is a very popular wrong definition that region of space where probability of finding the electron is maximum can be worked out using the orbitals but they are not orbitals.

An orbital by definition, I will repeat is an acceptable solution of Schrodinger equation for hydrogenic atom which is a one electron atom, okay and these are solutions we can get directly like what we are getting okay, right now we are talking about only the r dependent part, we will come back to this orbital business in the next module okay, let us go ahead, n equal to 2, l equal to 0.

We get once again a constant multiplied by e to the power - r by 2a0, no harm done, multiply it by; now you see 2 - r by a0 okay, so this r to the power l; what would r to the power l be; l is still equal to 0, so r to the power l is 1. So, what is this 2 - r by a0, where does it come from? It comes from the Laguerre function, 2 - r by a0 into e to the power - r by 2 a0.

Now that brings us to an interesting something, you may just draw it even though we have talked about it a little later, let us say I want to plot this function, what will it look like; I can call it, I will call it R because it is only function of R, R for 1, 0. If I plot it as a function of R it is just some constant multiplied by e to the power - r by a0, so this is what it will look like and we have a better looking diagram in the next slide.

What will this look like? Here you have this same e to the power – r, this time by 2a0, so it will be a faster decay but multiplied by 2 – r by a0, so this 2 - r by a0 can become 0 somewhere, this whole thing where does it become equal to 0, where r is equal to 2a0, so this factor becomes 0 at r equal to 2a0 and then it does not matter what the value of e to the power - r by 2a0 is; the product will be a0.

So, if I try to plot R20 against okay, I forgot to write the x axis here, this is of course, r please believe me that I have written r, what will happen; at r equal to 2a0, this will become 0, so it will go down becomes 0 and become something like this, we are going to show this many,

many times, so please forgive my poor artistic skills for now, okay. So, the point is there is a node in the function, remember nodes.

What is a node? A node is where a wave function changes sign through a value of 0, so here the wave function changes sign, so this is plus, this is minus okay, of course plus and minus are related, so that is where a node is and what is the locus of that node r equal to 2a0; r equal to 2a0 is the equation of a sphere, is not it. So, in 3 dimensions this sphere is the node for the 2s orbital, okay.

So, along this spherical surface, the 2s orbital changes sign, goes from plus to minus okay, so remember 1s orbital has no node, 2s orbital does have a node and since the node arises from equating the radial part to 0, this is called a radial node okay, more about that in a while, for now let me show you n equal to 2, l equal to 1, here there is a theta phi part okay. In fact, phi parts will be for m equal to 1, 0 - 1 okay.

But if you look at only the radial part then what we have is once again some constant multiplied by r by 2a0 multiplied by e to the power -r by 2a0, what will this look like; r by 2a0 that is increasing in r obviously is a straight line multiplied by e to the power – r by 2a0 that is a decreasing function, so what you get here is essentially a function that goes through a maximum.

So, if we plot R for 2,1, n equal to 2 and l equal to 1, so that is a 2p orbital, you remember against r, what you get; it never at r equal to 0 what do you get; at r equal to 0 obviously, it is 0 e to the power – r by 2a0 is 1 but r equal to 0, so at r it is 0, at sorry; at r equal to 0 the function is 0, at r equal to infinity also it is 0, so it goes through a maximum. What is the value of r, where the maximum arises, well you just differentiate this and equate to 0, you will find what is the value of r, where this; horrible handwriting sorry, where this function goes through a maximum, it is very simple differentiation.

Let us move on, n equal to 3, l equal to 0 now, see we have here things are getting a little more interesting, again r to the power l right, r to the power l; l equal to 0, so r to the power 0 is equal to 1, here r to the power 1. So, here we have 1 - 2 by 3 r by a0 - 2 by 27 r by a0 to the power 2, so a second order polynomial multiplied by e to the power - r by 3a0, what will this function look like; if I plot against r, what is this function going to look like.

I am plotting R30 against r, now see this is a second order polynomial, if you equate that to 0 you will get a quadratic equation and that quadratic equation is going to have 2 roots, okay and just believe me when I say the roots are going to be real, so in two places for 2 values of R, the wave function will become 0. So to start with if it is plus then it should come down become 0 here, become negative but again it has to become 0 here, so it will increase like this becomes zero here, becomes positive.

Then of course, it has to go down somewhere and become equal to 0 asymptotically, what is this point, what is this point, what is this point, these 2 can we obtain from the quadratic equation and this point and this point you can find out by differentiating the function, the whole function and equating to 0 okay, not very difficult thing to do. Hence we can go ahead and we can write down different functions.

So, by looking at it and I leave you to figure this out we get something, well this is absolutely empirical, just by looking at the functions we see that the number of radial nodes turns out to be n – l – 1, so when n goes up number of radial nodes actually goes up but then when l goes up, it goes down because it is minus l that is why you have this alternate, not alternate you have this functions going through a node and then not going through a node also as you increase n.

So, this is the number of radial nodes and this expression is again something that we know from our high school days right, so this then is a brief discussion of the radial functions of hydrogen atom.

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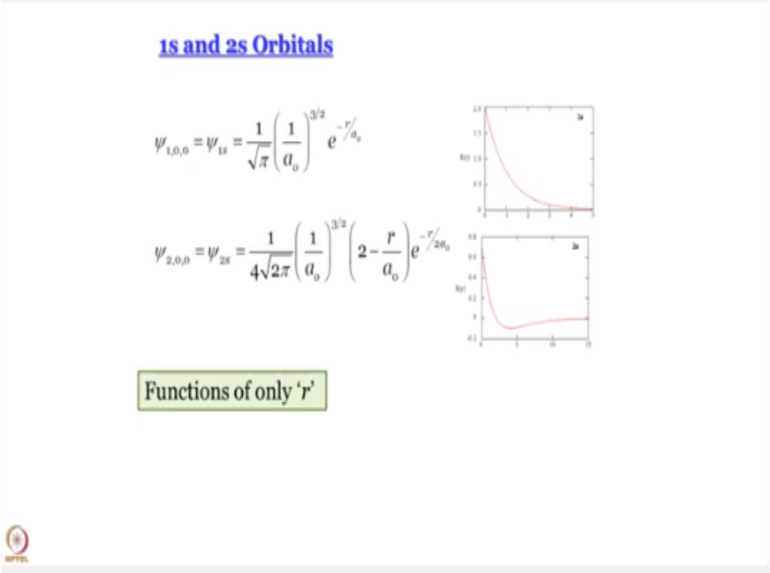

1s and 2s Orbitals

$$\psi_{1,0,0} = \psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\psi_{2,0,0} = \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$$

Functions of only 'r'

Here, now this slide has become not very important, I am going to show some prettier pictures of this and we talk about contour representations of orbitals just remember, 1s and 2s orbitals are functions of r only.

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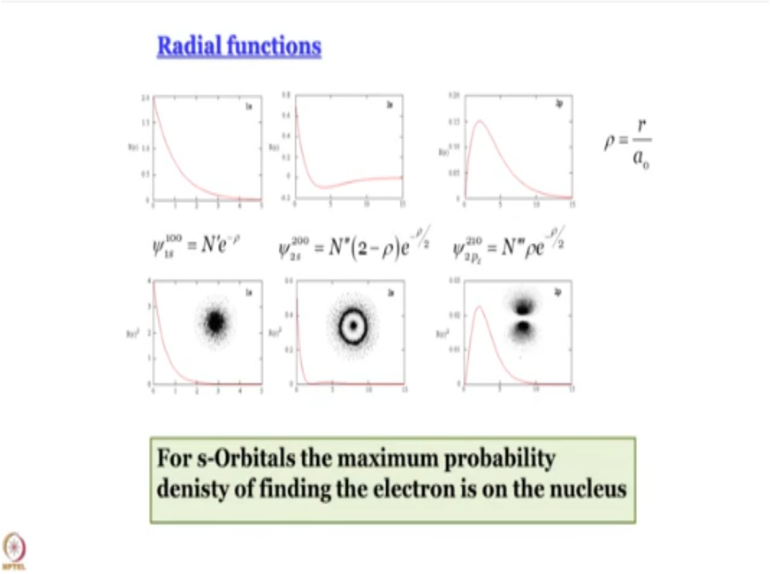

Radial functions

$$\rho = \frac{r}{a_0}$$

$\psi_{1s}^{100} = N'e^{-\rho}$ $\psi_{2s}^{200} = N''(2-\rho)e^{-\rho/2}$ $\psi_{2p_z}^{210} = N'''\rho e^{-\rho/2}$

For s-Orbitals the maximum probability denisty of finding the electron is on the nucleus

And now, we come to this interesting question that you take the s orbitals okay, look at say 1s orbital or 2s orbital, 2pZ has a value of well, psi of 2pZ has a value of 0 when r equal to 0 but what about 1s, what about 2s, what about 3s, for all of them the maximum value of psi is at r equal to 0, so the maximum value of psi square is a real functions of course, maximum value of psi square is also equal to r equal to 0.

What is the meaning of r equal to 0; r equal to 0 is the position of the nucleus, so are we saying that the maximum probability for finding an s electron is at the nucleus because if we do, then we are back to square 1, square 0 because once again if the maximum probability of finding the S electron is at the nucleus, then it is very similar to Rutherford situation where the electron and nucleus would be at the same position.

So, plus and minus charges would annihilate, right the atom sort of gets short-circuited that cannot be the case, so to the fallacy here, actually we do not, it is very important to remember that psi psi star is not probability, psi psi star gives us probability density, so it is true that s orbitals have maximum probability density in the nucleus at the nucleus that does not mean that probability is also maximum.

Because you might remember well and you do remember that see if I ask you a question, what is heavier; iron or cotton wool, what would your answer be? The correct answer would be that the question is incomplete, makes no sense, well iron is more dense than cotton wool that is true but suppose, I drop an iron pin from a fifth floor and then I drop 5 kg of cotton, which one will have more impact on anybody or anything that it falls upon; definitely cotton.

So, density of cotton is much less but then we are using a higher volume that is why the mass is more, density of iron is more but we are using a smaller volume, so mass is less, so let us not confuse the extensive quantity, extrinsic quantity, probability with the intrinsic quantity probability density, for s orbitals it is true that maximum probability density of finding the electrons is at the nucleus but volume is 0 as we are going to see in the shortest next module that we are going to have.