Atomic and Molecular Physics
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Lecture - 28
Quantum mechanical treatment (Contd.)

So, up let us consider some problem, which you want to study earlier in Quantum mechanics. We start with Schrodinger equation.

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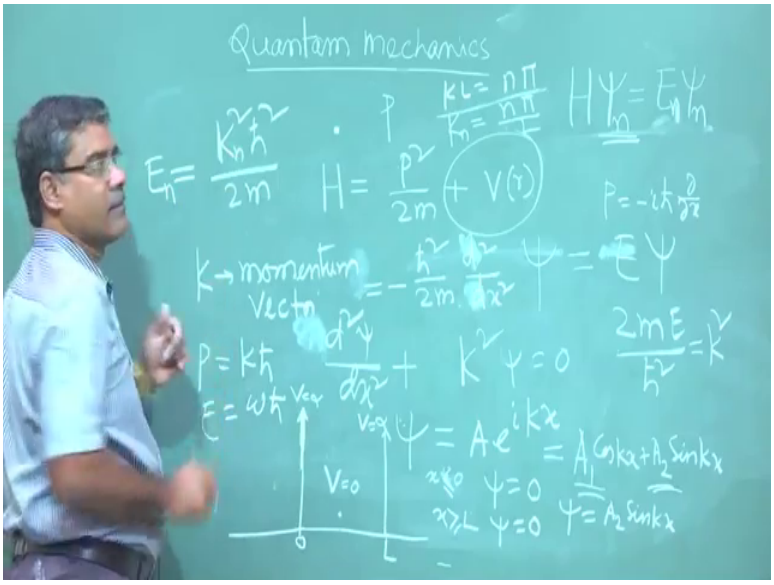

So, this is the Schrodinger equation ok, very famous Schrodinger equation. So, to study any problem to study any problem, we start from the Schrodinger equation because, see we have to starting from this equation, it is like your Newton equation in classical mechanics, right, then Maxwell equation in electricity magnetism ok. So, in quantum mechanics, this equation, we start from this equation. And then we proceed to develop the wave function for our system ok, for our problem whatever we want to study, what are the problem; we want to study? So, let us say 1 electron or 1 particle; forget electron, 1 particle, it is free particle, it is free particle, it is momentum P, it moves it moves ok. it moves so, fine.

So, then for this for this system for this P particle, I have to develop I have to develop Hamiltonian H. So, H is P square by 2 m plus potential energy ok. So, here for this system this is 0 this is 0, right potential energy 0 because, this is free particle that is no potential ok. So, H is P square by 2 m, and if it is if we consider for simplicity this linear means one dimensional motion of this particle, P particle one dimensional motion. So, then I can write, that time I I wrote something. So, H is P is basically minus I h cross del by del x and P square is minus minus plus and, then I square that is minus minus, yes. So, that time, I did mistake, I make it last earlier minus h cross square by 2 m h square by 2 del 2 by del x square, right. Since it is one dimensional ok; so, I can write d 2, I can write d 2 by d x square, right.

So, this is my problem Hamiltonian. So, as per my as per my problem of as per my system, I have to first I have to the Hamiltonian. And then this Hamiltonian; it will be put on this psi psi and, then I have to write. So, so then what you are getting from here, you are getting h cross I can write d 2 psi by d x square ok, then minus 2 m E by h cross square means this side, when it will come plus 2 m E by h cross square this psi equal to 0 ok.

So, this I can write I can write say some constant, 2 m E by h cross square 2 m E by h cross square. So, let us say some k square constant 2 m E by h cross square equal to some constant I am writing. So, K K square so, this is equation this is the equation this you know second order differential equation, second order differential equation, it is a homogeneous equation solution is A E to the power i k psi k x sorry k x this x here. So, function will be like this ok. So, this the this the wave function it is it is nothing, but it can also return the A 1 A 1 cos k x plus A 2 sin k x ok, this also equation this solution return the this the this solution is called plane wave solution, plane wave solution ok, and it is tell it is the your particle is free.

So, from where; from here; here I have written it is interestingly, if they tell that tell that E equal to from their I can write K square h cross square by 2 m and, you know this is nothing, but P square, you know, K square h cross square is nothing, but the P square ok. So, this k is basically called the momentum vector this k is called the basically momentum vector k is called momentum vector because, E is energy it is basically P square by 2 m equivalent to P square by 2 m. So, K K is cross h P. So, that you move probably, earlier I have discussed this P equal to k h cross and E energy equal to I think omega h cross ok.

So, this comes; the standard relation so, this momentum vector. So, this way one can proceed, one can proceed. Now it is free particle, it is free particle, but it cannot go it cannot go outside of a box in a box it is free so, but it cannot go outside the box. So, then we tell in terms of potential (Refer Time: 08:51) means this boundary, or this space of this of this box ok. So, it is the barrier is the barrier to the electron, or to the particle this particle cannot overcome this barrier this wall this is barrier. So, if tell in terms of potential it is a barrier potential. So, it is the huge potential at the wall at the surface at the boundary of the box ok. So, then we write in terms of so, we put that condition, what condition ok. So, there are two regions basically we say so, so this box one dimensional box ok, one dimensional box ok.

So, here this is the particle is here in this box. So, it is free to move so; that means, it is potential is here 0, but at this position so, if it is 0 position and this is L position, L position. So, at 0 this V is very high V is very high this particle cannot go out so, we tell V equal to infinity here and, here V equal to infinity V equal to infinity here also V equal to infinity ok. So, this way, one has to model this problem like this ok. So, this particle free within this box, but at the surface of the box it is potential is very high it cannot go here this ok. So, so, you have you have now you have to you have to you have to choose psi we have to choose psi in such a way that it should it should satisfy this condition here is called boundary condition, one has to apply it is in quantum mechanics called boundary condition. What is the condition? So, psi is as I told. So, psi should not exist should not exist at the boundary of the of the box ok.

So, condition is that at when x equal to 0 x is this way x is less than x is less than equal to 0 means this side psi has to be 0 because, there it may be exit of the particle in this side there is no possibility ok. So, psi has to be 0 and x is greater than equal to L psi has to be equal to also 0 ok. If this partition is not their so, particle go can go anywhere, if there one can find. So, this solution is this solution ok.

Now, if just problem, if we restrict if we restrict this particle, within this box outside it cannot go so, then one has to put boundary condition, realistic boundary condition, this the boundary condition and for this so, this is your solution and this solution is having you see this is the 2 unknown constant. Now if you put this boundary condition. So, k equal to 0 k equal to 0 psi has to be 0 k equal to 0 psi has to be 0 means not k x x equal to

0. So, this is 1 this is 1 and this is 0 this is 0 ok. So, psi has to be 0 equal to 0. So, this equal to 0 so, A 1 equal to 0 then ok.

So, then after this condition what I will get, psi I will get psi I will get this A1 is 0. So, I will get a 2 sin k x that is the solution A 2 sin k x. Now second 1 I have to apply so, when x equal to L psi equal to 0. So, when x equal to L ok; that means, A 2 cannot be 0 this is clear because, then there will not be exist of the solution. So, A 2 cannot be 0, but sin k L has to be 0, right. So, sin k L has to be 0 when it will be 0 ok. So, this k L when k L will be will be 0, will be pi will be 2 pi will be 3 pi, will be 4 pi, then it will be 0 it will be 0 ok.

So; that means, this is giving k L equal to n pi kind of condition n equal to 0 1 2 3 right. So, this k I can k L. So, it has to follow this relation ok. So, it is it is giving restriction it is giving restriction on k value you know k value. So, k will be momentum vector. So, it depends so, it is now discrete value n equal to 1 2 3. So, we write k n k n equal to n pi by L n pi by L ok, n equal to 1 2 3. So, k 1, k 2, k 3 and corresponding I can write n k n ok. Now these are basically different states, it will give different states and, for each state I will set momentum I will get energy, I will get corresponding wave function psi 1, psi 2, psi 3 momentum k 1, k 2, k 3 energy E 1, E 2, E 3. So, this system now system wave function for the system is known to me now on that wave function, if I just apply different operator I will I will I will get it is basically it will get different Eigen equation, Eigen value ok, either for momentum or for energy ok. So, I will get this all information about the about my system ok.

So, so final psi will be now A 2; A 2 cannot be 0, A 2 it is constant ok. So, one has to normalized this one, then one will get the value of A 2. So, psi psi star equal to A A A square basically you know. So, either I think one can find out within this limit it is the one, within 0 to L; one has to psi psi star indication 0 to L d x psi psi star d x. So, one can find this one. So, normalized wave function for your problem you can find out, you will get the energy momentum ok.

So, this way one has to proceed for different. So, one has to go one after one another different kind of problem. So, now our problem in atomic molecular physics our problem let us go there, our problem is; what is our problem. What is our system? Our system is our system is hydrogen like atom, hydrogen like atom means.

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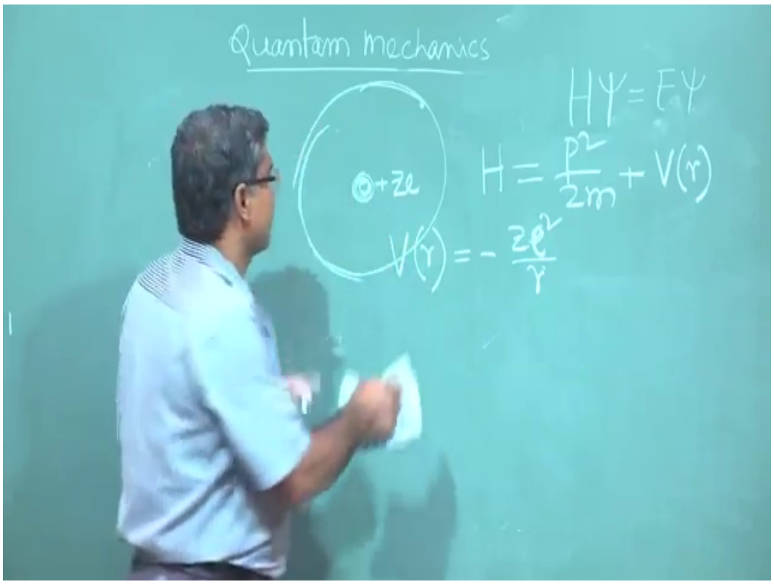

There is a nucleus there is a nucleus positive charge plus z e positive charge ok. Now, so now there is a electron there is electron, now this electron is in this central in this in this central field ok, central field of nucleus central field of nucleus. So, now this electron or in this system; so, central field electron central field of this of a nucleus having positive charge plus z e. Now electron is moving in this field in this potential ok.

So now, I want to study this system ok, I want to study this system ok. So, actually a particle that is electron it has negative charge, now it is in motion in a central field, it is in motion in a central field of a nucleus ok. So, this here I have to I have to. So, this will we will start from the Schrodinger equation. So, for this I have to I have to develop this Hamiltonian for this problem. So, for this problem Hamiltonian is all the time P square by 2 m kinetic energy plus potential energy, when particle was free particle. So, we took it 0 ok.

When particle is in a constant field a constant potential ok, potential is not varying with distance or time ok. So, then we just write the V 0. Now in our in this problem V r potential V r is minus z e square by r ok. And this potential is basically spherical symmetric potential spherically symmetric potential because, potentially ius z e is same on a for a particular radius r. So, spherically symmetric potential central field we tell central field central force ok. So, in our problem this is the potential this is the kinetic energy P square by 2 m this is the kinetic energy or potential energy is this one ok.

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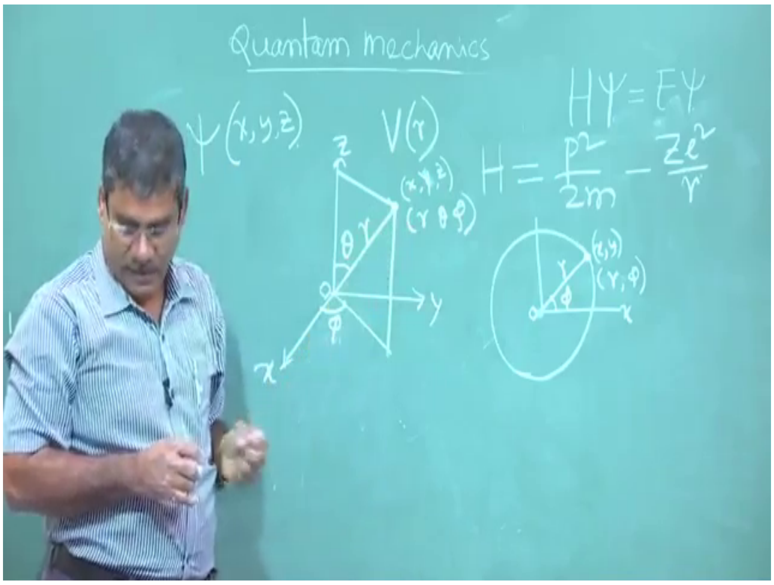

So, for hydrogen like problem whatever we want to study. So, here our problem is basically z e square by r. So, now we have to so, these are Schrodinger equation Hamiltonian is this hm. So, what we want to do? We want to we want to study the system and, we want to we want to so, we want to solve this quantum mechanically and, so here what so, I have to consider psi for this problem. Now is not one dimensional problem, it is the three dimensional problem is the three dimensional problem. So, this psi will be function of x y z ok.

And say we are we are going to study the static is not dynamic 1 it is not the function it is a function of the time ok. So, we are not taking that these function of time. So, x y z only we are taking for stationary cases. So, this is psi fine, but here what we saw this potential V r so, these are it has spherical symmetry, it has spherical symmetry. So, since it has spherical symmetry. So, one has to choose go for coordinates system, you know this; this is the Cartesian coordinate, this is the Cartesian coordinate, this the x y z Cartesian coordinate. So, coordinate system used to fixed to locate to locate the position of the of the particle ok.

So, for in space, we need three coordinate. So, we have to choose coordinate system this it is the origin and what is x, what is y, and what is z so, basically this along the x and, then along x amount, along the y deduction y amount along the z deduction z amount. So, this it will be x y z x y z ok. So, this the Cartesian coordinate one can use it, but here since a people use also this you know polar coordinate, in two dimensional where will take r psi remember this two dimension ok, this point is x y in Cartesian coordinate, but we can also fix this point defining the distance this from origin it is r, I have to fix this one, if I just tell this distance from origin is r, then we cannot fixed because keeping the distance same, it can it can be any point on the circle, it can be any point on the circle it can be any point on the circle ok.

So, you cannot fix this one. So, now if I because aim of this of using this coordinate system to fix the point at a definitely. So, it can be any point on this ok. Now if I define, no, no, it is the phi. So, these distance are and this with x axis this angle is phi, then it is not this point it cannot move because, then angle will change. So, that I fixed. So, either you can use x y Cartesian coordinate, or we can use r phi r phi in polar coordinate ok.

Now, when it is three dimension, when it is three dimension, then Cartesian coordinate fine x y then another dimension is z, but now polar coordinate there is 2 type of coordinate are there, spherical polar coordinate and cylindrical polar coordinate ok. So, if it is cylindrical symmetry cylindrical cylindrical symmetric. So, then we use cylindrical polar coordinate, or if it is spherical symmetric, then we use the spherical coordinate ok.

So, so in this case since v r is having the spherical coordinate, spherical symmetric. So, it is called convenient to use the spherical polar coordinate. So, in spherical polar coordinate you know this what we do. So, I have to fix this point. So, I can pass I can take this r the distance is r. Now when distance is r now in three dimensional taking keeping this r constant so, it will any point on a on a sphere ok, it is not a point. So, all point on the sphere is satisfy this condition, this distance is r ok.

Now, then I can to fix this point, I can define this angle with the z axis say theta ok. Now it can only now so, r is fixed now theta angle also fixed. Now what it can do so? It can be it can be see, it can be any point on the circle ok.

So, without changing r and theta, without changing with z axis keeping theta and r phase so, it can be any point on this circle, any point on this circle. So, that also I do not want. So, I have to fix this one, I have to fix this one. So, any point on this on this circle. So, what so if I just take projection of this one projection on the on the on the x y plane, x y plane ok. This is the projection on the x y plane. So, this height is basically I think yes projection on this plane, right.

Now so, basically yes it is rotating as I told so, I think with respect to this this this as a whole this is rotating ok. Now if I fixed if I apply angle here say phi. So, this projection it is it is having angle with the x axis is phi, then now it cannot rotate. So, it will be it will have to be here, it will have to be here, this is the only point which we can define by r theta phi r theta phi define r theta phi ok. So, this the spherical coordinate system, spherical coordinate system and you know this they have relation, it is the same point same x axis y axis z axis in space or in same, now either using r theta phi or x y z one can define the position ok.

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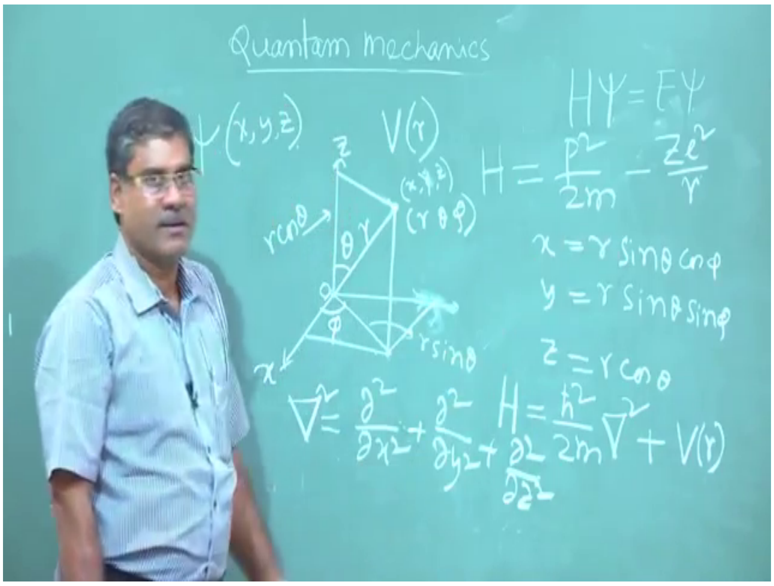

And so, they have they have relation it is not independent. So, what is then x y z? So, z equal to so z is basically nothing, but this height right this height this height. So, this height; so if it is r, if it is r; so r r cos theta will be z r cos theta will be z. So, this is r cos theta, r cos theta and this will be this will be r sin theta, this will be r sin theta because, this angle 90 minus theta. So, this r sin theta means this also r sin theta, fine.

Now, this 1 achieve in two dimensional we saw this this is r and this phi, then you can take r cos phi this r cos phi here r is r sin theta so, cos phi will be x. So, it is a cos phi will be x and this will be this ok. So, this x x; this is r sin theta cos phi x is r sin theta as this one and, then then x component cos phi and then y component along this r sin theta into sin phi r sin theta sin phi ok. So, one can get the relation between Cartesian coordinate and the polar coordinate right.

So, now in Hamiltonian what is there so, this in terms of kinetic energy and potential energy, I have written and in three dimensional H H is what is H H is h cross square by 2 m Laplacian for three dimension right plus it is potential energy V r. So, V r is basically this, but just let us write V r and we know this is a spherical it has spherical symmetric. And so, now basically del square you know del square you know del square you know that del 2 by del x square plus del 2 by del y square by del 2 by del z square so, in Cartesian coordinate. Now this I have to find out in polar coordinate.

So, it is not difficult one has to so, you know this relation here ok, but one has to sit and do it so, I actually I will tell the step but I will avoid calculation is so, it will take time long time. So, now I know the relation I have to I have to I have to get in terms of r theta phi and, if you do that, if you do that. What you will get; Laplacian?

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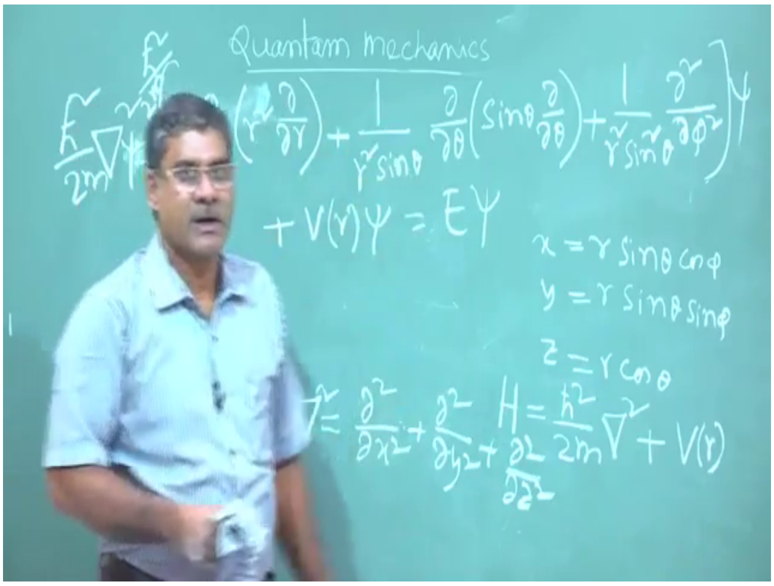

You will get del square Laplacian; you will get basically 1 by r square r square del by no no I think I have to see r square del by del r ok, r square del by del r, then here r square del by del r ok.

So, this plus 1 by r square sin theta 1 by r square sin theta, then del by del theta, sin of this the sin theta del theta sin theta del del theta and, then plus 1 by r square sin square theta ok, then del 2 by then del 2 by del phi square, yes del 2 by del phi square ok.

So, the Laplacian form; this is Cartesian coordinate and this is the in spherical coordinate Laplacian. So, if Laplacian if you know then your Hamiltonian will be h cross square h cross square divide by 2 m; that means, we have to multiply with h cross square by 2 m right and, then you have take psi you take psi; that means, you have to take psi, you have to take psi and then your plus plus V r psi equal to E psi. This is the Schrodinger's equation in spherical polar coordinate ok.

So, for our problem electron is in motion, we want to study the motion of an electron in a central field of a nucleus ok. So, for this problem now we have set the suitable Schrodinger equation ok. So, now in next class, I will continue discussion on it.

Thank you.