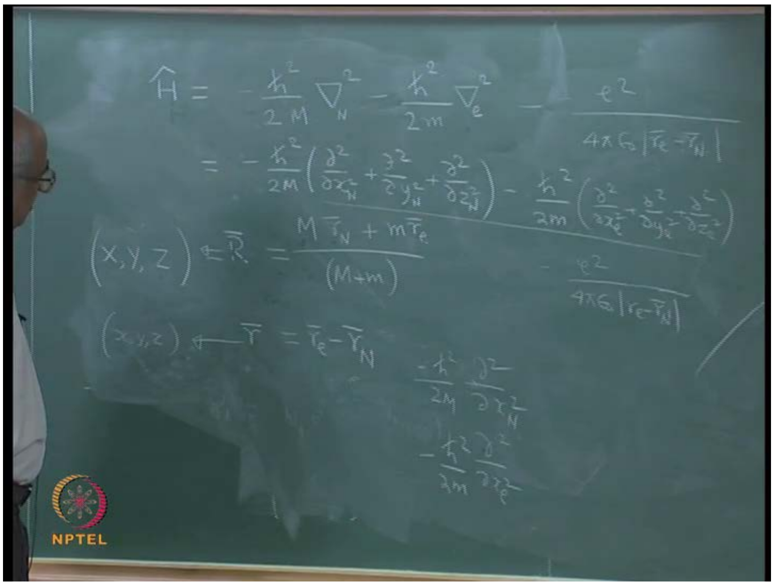
Introductory Quantum Chemistry
Prof. K. L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 21
Hydrogen Atom: Separating Centre of Mass Motion and Internal Motion

Today we are going to discuss the most important problem as per as a chemist is concerned, that is; the problem of the hydrogen atom. So, if you think of the hydrogen atom, it is very clear that there are two particles; one is the nucleus and other is electron. And therefore, if you wrote the Hamiltonian for the system, how would it look like?

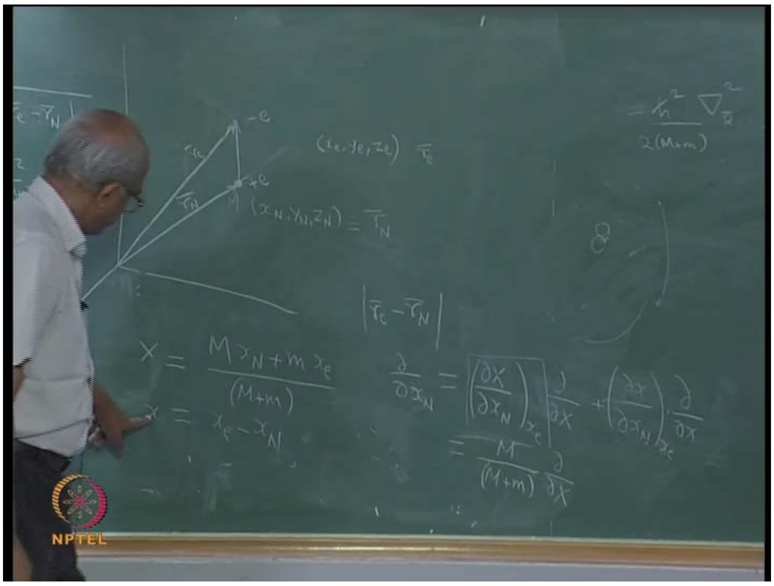
(Refer Slide Time: 00:47)



When the Hamiltonian for the system will have kinetic energy of the nucleus, the nucleus is moving definitely; so, it would have the kinetic energy of the nucleus. Of course, when I say kinetic energy there is going to be an operator as far as quantum mechanics is concerned. So, that is going to have minus h cross square divided by 2 times the mass; that is what happens with the Hamiltonian all the time. So, if you have the nucleus the mass may be M right. And then there is nuclear kinetic energy operator; so that, you will have to write as del square. But you should remember that this differentiation involves differentiation with respect to the position coordinates of the nucleus right.

That is what will happen; I mean, will have 2 particles in a system both will have kinetic energy. And when you switch over to quantum mechanics from each one you are going to get a del square; because it has kinetic energy. So, the del square that is going to occur here; is going to be del square and I will say subscript N, to indicate that it is coming from the nucleus. And then you will have the electron minus h cross square divided by 2 m; why m? Because whenever I am concerned with the electron and you will, I will have a del square. But this will come from this del square, will have differentiation with respect to the coordinates of the electron, 3 coordinates. So, del e square right. So, nuclear kinetic energy operator, electronic kinetic energy operator and then in addition to this, I would have interaction between the nucleus and the electron; how is that interaction? It is columbic interaction. The interaction energy will depend only upon the distance between the nucleus and the electron.

(Refer Slide Time: 03:15)



So, if the way we are proceeding, we are saying we have the nucleus which is rather massive and then we have the electron. And what we are saying is at this as a mass M this as mass m. And this is located at (x N, y N, z N); that is what we are actually saying, nucleus is located at this location. While the electronic is located at (x e, y e, z e); right. These are the coordinates that we are using fine. And then what will happen? The distance between the 2; how will you write it? Well, we will have to adopt some short hand notation because it is difficult to write x N, y N, z N and x e, y e, z e. So, therefore; what I will do is, I will use the position vector. Position vector actually may be written as r N; that is just a short hand notation which says that this is equivalent to r N. The components of r N are (x N, y N, z N). I mean, this is just convenience; I could have written (x N y N z N), but it would have been difficult to keep on writing it again and again.

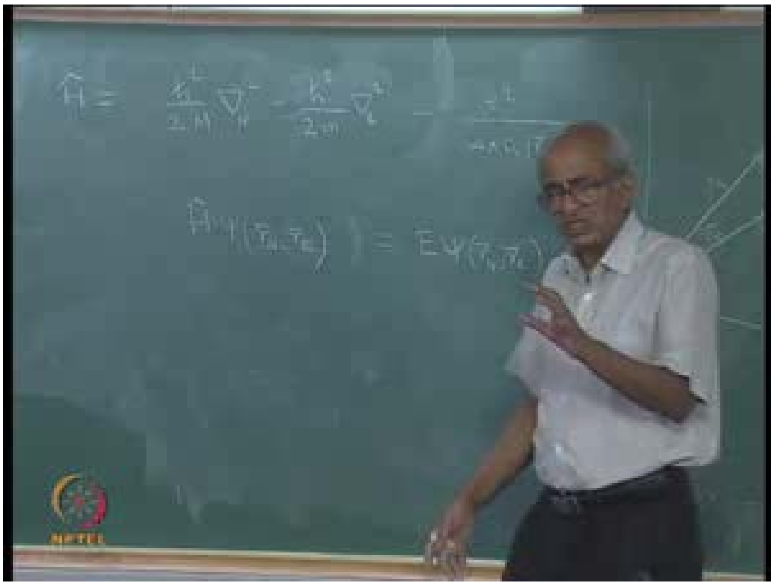
And, similarly; the position coordinate of the electron would be noted as r e. This is essentially means, that you see I have some coordinate system somewhere here; with the respect to this coordinate to origin. This vector is r N; that is the electron. And this position vector is r e, that is all; fine. And if you wanted the distance between these 2 how will you write the distance in terms of these vectors. Well, the distance is actually r e; vector r e minus vector r N, what is this? This is the vector that will connect the nucleus with the electron; it is this vector. And its magnitude will give me the distance between the 2 particles; that is all, correct.

So, therefore; is the interaction energy will be actually equal to; how much will be the interaction energy; is the nucleus as a plus e charge. Because I am assuming that it is a proton. And the electron has I mean, I should not be putting the plus e here, but it is at the nucleus. So, therefore; the nucleus has a plus e charge and the electro has a charge which is equal to minus c. If I am saying that my nucleus is a proton, but the way the treatment is done actually, you can have 2 positive charge on the nucleus or 3 positive charges on the nucleus; but only 1 electron. So, if you say you have 2 positive charges, this actually will correspond to helium ion. If you say there are 3 positive charges it will correspond to lithium 2 plus di positive iron.

But to keep things in simple I shall only be considering the hydrogen atom. But the same the derivation everything will actually go through; even if you had helium ion over lithium 2 plus ion. So, the interaction potential energy, if you say this is positive plus e and if you that is minus e; then, the interaction energy will depend upon the product of these 2.

So, therefore; you are going to have minus e square right; minus e square divided by 4 phi epsilon 0. This is happening because you are using SI units for phi epsilon 0 and the distance r e minus r N. So, this is the full Hamiltonian for the system; both the particles are accounted for, so what will happen? I would have a wave function which will depend upon the coordinates of all the 2 particles. So, the wave function is going to be a function of how many variables? It is going to be a function of 6 variables. I am thinking of the time independent wave function not the time dependent one. Why because I am thinking of the statutory states of the system. So, I want to solve the equation H psi is equal to E psi. And here you have 6 variables which I may denote as r N and r e.

(Refer Slide Time: 06:56)



Now, you say we have difficulties even in solving ordinary differential equations. And so if you say that you have a partial differential equation involving 6 variables, it seems, extremely difficult to solve, correct. But then you see if a problem mathematically appears difficult, what you should do is; one should think of a physical situation. From the physical situation, you may able to say something about the nature of the solution. And once you have some idea about the nature of the solution, you may be able to actually find a way of showing that, that is a solution.

So, let us look at this physically I mean, after all what is a system? It is a nucleus proton; actually in this case and an electron. And we know that this proton and the electron what do they do? They usually form the hydrogen atom. Even though you are saying there are 2 particles; actually what happens they form a hydrogen atom. And then if you think of hydrogen atom, what can the hydrogen atom do? I mean, if you had hydrogen atom in this room it can execute translation motion. What is translation motion? Translation motion in which there is no relative motion like. Translation motion means, the relative motion, motion of the electron with the respect to the nucleus is not important at all. What you have is, a system comprising of the electron and the nucleus both travelling together as one entity, right.

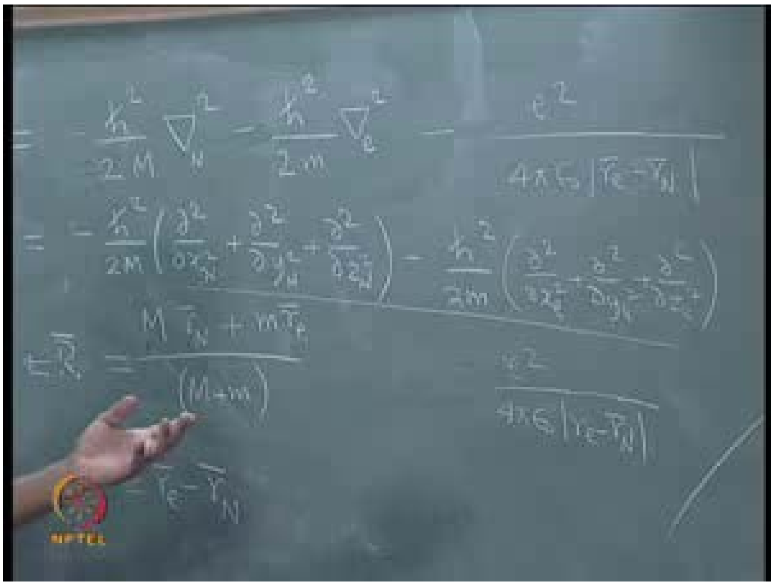
So, therefore; what I would expect, this is; the Schrodinger equation. But physically what it what I expect is that this should describe definitely at the translation motion of the whole thing. In addition to that, it is possible also for the electron to move with respect to the nucleus. That is the relative motion; the distance of the electron from the nucleus can change. That is something that I can referred as relative motion, motion of the electron relative to the nucleus. And that is what is actually more interesting for the chemist translation motion; we understand I mean there is nothing great about translation motion. So, the translation motion is motion as a whole and what will happen that translation motion of course; will have only kinetic energy.

But the relative motion is the one that is of interest, but both are actually contained in here, in this equation. And so I have to get out this translational motion and then look at the internal motion; I have to get rid of the translational motion. How would I do that is the question; fine. So, how will you describe translation motion of the hydrogen atom as a whole? See, when you say translation motion; actually, what you are saying is that the central of the mass of the system is moving, translational motion is motion in which center of mass is moving. And when you say the relative motion; actually, then in the in that case the position of the electron with respect to the nucleus is changing.

So, the effectively; that means, r e minus r N is changing, right. So, therefore; what I will do is I will change over to what are known as center of mass coordinates and relative coordinates. Why? If I had center of mass coordinates, what will happen? That will be best for the description of translational motion. And relative coordinate will be best for the description of the motion of the electron with respect to the nucleus. So, how will you define the center of the mass of the system is the first question, that you would have.

So, I have an electron which is located at r e and I have a nucleus which is located at r N; fine. Now, this has a mass which we denote as M; that is the mass of the nucleus and this as a mass which we denote as m. So, where would be the center of mass of the system? The way you define center of mass is you would multiply r N by the mass of that particle which is M. You will multiply r e by the mass of that particle which is m and that adds that together and divided by the total mass of the system. This is the center of mass of the system, right. Now, I mean you can think about it, if you like. You see suppose the nuclear was very heavy, the center of mass will be very close to the nucleus because the electron is very light.

(Refer Slide Time: 12:34)



So, this one is our, one of our new variables. And what do I want to call it, I will denote it by symbol R. R will stand for (X, Y and Z); do not be confuse this with this coordinate system, coordinate axis right. This is R, is a vector. What is it? I mean, this is; very physical. You have a coordinate with origin, here is your hydrogen atom; you want to specify the center of mass of the hydrogen atom. So, you have to use a vector, which is denoted by the symbol R and its components you denote by (X, Y and Z). Why did I use capital letters because R itself is capital; so, it is common and it is better, so, I use capital letters.

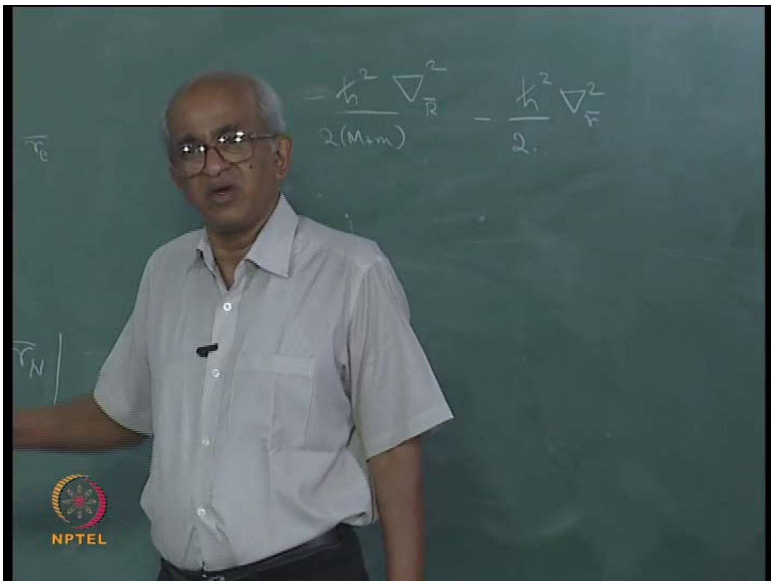
Then, I want to describe relative motion how will I do that? Relative motion is easy, all that I need to do is you see r e minus r N is changing correct. Relative motion means r e minus r N, that vector; I mean the electron is going away from the nucleus, all the distance between the 2 is changing. So, therefore this is my new coordinate which I will denote by the symbol r. And the components of that vector, I will denote as (x, y and z); these are the components. Now, we have a not very difficult, I mean somewhat easy change over. Change over means; I mean, see here differentiation is with respect nuclear coordinate and electronic coordinate. Differentiations are not with respect to (X, Y and Z), but what I want to do is I want to write down the Hamiltonian in terms of R and r; I do not want these r N and r e. Because of the reasons of that, I have already told you; I want to describe the center of mass, motion of the system as a whole. If I want to do that

I should express everything in terms of R which stands for center of mass motion and in terms of r which represents relative motion.

So, this Hamiltonian which is expressed in terms of nuclear and electronic coordinative you have to change over to center of mass and relative coordinate. So, how you will do that is the question. So, I will do that it is not difficult as I told you. The way I am going to proceed is; see this is Hamiltonian; let me rewrite it. Minus h cross square by 2 m, it would have dou square upon dou x N square that is this part. And then what happens is minus h cross square by 2 m e; no there is no e there m, dou square upon dou x e square plus dou square upon dou y e square plus dou square upon dou z e square. That is the kinetic energy and then of course; you would have minus e square divided by 4 phi epsilon 0 r e minus r N. correct.

So, this has differentiation with respect to (x N, y N, z N) (x e, y e, z e). But I said I am not going to use those coordinates anymore, I am going to change over to another system of variables which are (X, Y, Z) and (x, y, z); this is what I want to do. As far as the potential energy part is concerned, it is pretty straight forward. Because r e minus r N is my new variable right. r e minus r N is actually R and that is just (x, y, z). So, therefore, this is actually nothing but R; magnitude of R very easy, that part is straight forward. But I have to find out what this operator is, the kinetic energy operator is in terms of the new coordinates. But then without doing any calculation again I will actually do the calculation because I want you be to convinced. But without doing the calculation can we guess, what is going to be the answer? See, I told you the physical reasoning. I have the hydrogen atom, what can it do? It can execute translation motion as a whole. So, therefore; it will have translational kinetic energy and what will be the operator corresponding to that?

(Refer Slide Time: 19:08)



Definitely, you will have minus h cross square right. Translational motion, the center of mass is the thing that is moving. So, therefore; you will have a del square; what will that del square be? It will correspond to the center of mass motion right. So, it is going to be del square with respect to this R right. So, therefore, I am going to have del square; it be very specific, I will put R sorry R there to indicate that, this is; del with respect to center of mass coordinates. And what about the mass? What mass will you put in? Center of mass is moving; so, effectively the whole system is moving. So, therefore; you will have to put in the mass of the whole system.

So, therefore, you are going to have minus h Cross Square by 2 times M plus m right. Actually, this is the answer; I mean, I do not have to actually compute it is possible to compute and I will do it. But even before I do that, I will tell you that I can guess; this has to be the way it comes out. And then you look at the relative motion, what do you expect to happen with relative motion? See, the electron and the nuclear moving relative to one another. There must be a relation kinetic energy because of that relative motion. So, therefore, what is, what I would expect is I would have del square, where this del is carried out with respect to that r. So, maybe I will put a r here to be very clear that is to what is happening. And then I will have minus H cross square by 2.

Now, what mass will you put in here? Again, you can have physical reasoning. See, what is relative motion? The relative motion is motion in which you do not worry about center of mass motion. The you can say, even say center of mass is not moving; if you like. Relative motion involves motion of one particle with respect to the other and it does not involve any center of motion, right. So, you can say in relative motion, center of mass of the system does not move right. It is motion such that center of mass is unaffected effectively.

So, if you say that you have this nucleus and the electron; imagine I mean you think of may be the bore model where the electron is moving around the nucleus. So, to have a physical picture. So, if the electron is moving and if the nucleus is just sitting there, then is that fine? Is that center of mass motion sorry; is the center of mass not moving in that motion? It is moving, if you think about it. If you, if the electron is here see and if the nucleus was stationary; then, the center of mass of this system will be here. While, if the electron is come here right; then, the center of mass would have been here. And therefore, you see a situation where the nucleus is just held fixed and the electron is going around. That is, that will involve some motion of the center of mass. So, actually what should happen is that; when the electron moves, the nucleus also should move a little bit. So, that the center of mass of the system does not change; that is how the motion actually takes place.

So, how will it do that? Well, the answer is actually extremely simple. See, imagine this is the nucleus and here is the electron. Actually, in the case of the electron and the nucleus, the center of mass is very close to the nucleus actually; it is even inside the nucleus. But we will not worry about that. Well, it is not probably inside; I mean the nucleus too small to be the center of mass to be inside, but it is very close to the nucleus. So, you can say center of mass is here, right. Now, suppose this electron it is going and it is moving, it has come here and then what will happen? You want the center of mass to be still here. So, how is that possible? The nucleus should have moved to a new position which is something like that, correct. Then, only center of mass will remain unchanged.

So, when the electron is going around, the nucleus actually also will be going around by a little bit not by a large extent. But it has to move a little. So, therefore when I say relative motion, it involves motion of both the electron and the nucleus. So, therefore, the mass that I will have to put in has to depend upon both the mass of the nucleus as well as the mass of the electron. But then again if you look at this, you see it is the nucleus that is almost not moving, while the electron is doing all the work. The electron actually goes around quite a bit, but the nucleus; because it is heavy it does not move much correct.

So, if you walk out the algebra, what happens is that you will get here some effective mass of the system which you would be familiar; this effective mass is known as the reduced mass of the system. So, why is that you have reduced mass that is occurring here, because both the electron and the nuclei are involved in the motion. They are both involved, but the nucleus moves only a little bit; while the electron moves a lot, such that the center of mass of the system does not change. So, this will be your kinetic energy operator and then what will happen we have minus e square divided by 4 phi epsilon 0 R; where that will represent the potential energy of the system.

So, this is the actual answer that I shall get, physically I mean. This is quite interesting because you see in most problems or in many problems, you look at the system physically, you understand it and then you can say without actually doing the mathematic, most many a times you can say what is going to happen, how the solution should look like; many a times. If that is not obvious or you cannot guess it, then usually the Problem I would say will deserve a noble prize, if you solve it. I mean things which are not obvious and if you find a solution, then I mean it is difficult it is not so easy. But in many of these problems, the large number of problems actually, you can look at the situation physically and you can get some idea of the solution. And then look for a solution which satisfies that idea and that usually works. Now, how will I do this? You see the way I am going to do this is I have dou square upon dou x n square and I also have here; I mean, I have this, I also have dou square upon dou x e square, correct.

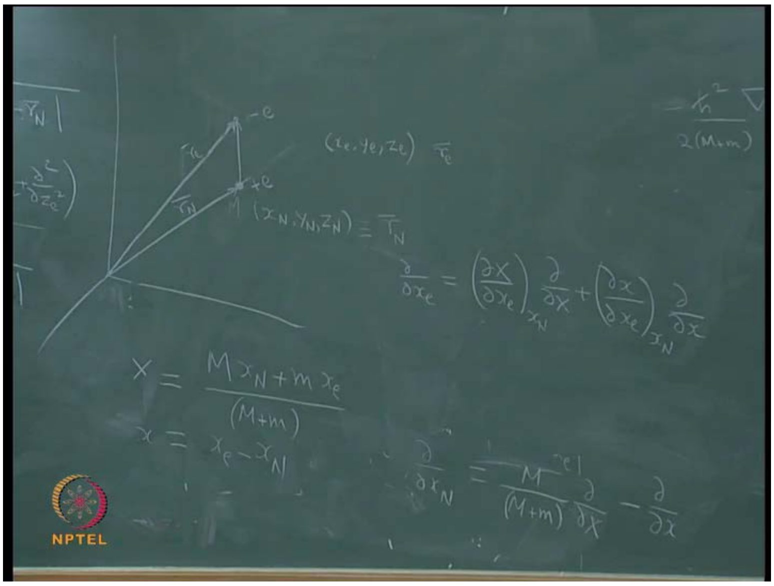
And, similarly, of course, I have the y m and z m; I will consider them, but let us just look at these two terms. So, this term is occurring with 1 by 2; sorry, no minus H cross square by 2 M, while this is occurring with minus H cross square by 2 m. Now, we have defined new coordinates X and x; what is the definition of X, what is the definition of x? It can be easily inferred from this definition. This is actually the vector; all that you have to do is, you have to think of the x component of R and x component of this r. So, if you think of the x component of the R, what is the expression? It is going to be M into x n plus m into x e divided by M plus m, right. That is X. What is x? It is going to be x e minus, where is it. See x is the x component of this vector. So, all that you need to do is you take the x component of right hand side. x component of R e is x e and x component of R n is x n. So, therefore, it is going to be x e minus x n. Fine.

So, let us now calculate when I need to have dou by dou x. No, that is not what I want, I want to have dou by dou x n. Why do you want that, because you see I want to express here I have partial differentiation with respect to x n, 2 times. So, I want to express this x this in terms of partial differentiation with respect to X and x. So, if you ask a mathematician, he will give you this expression dou by dou x n, you can write in terms of variables which will be dou x by dou x n. Let me be very clear; see the variable, the original variables were x n and x e. So, partial differentiation with respect to x n, means that I am keeping x e constant.

So, therefore, here I will have kept x e constant and then I will have dou by dou x plus I would have dou x by dou x n with x e being kept constant into dou by dou x. So, this is what the mathematician will tell you; see this is rule for changing variables as far as partial derivatives are concerned. So, the first question is what is this? What does it say, you have to keep x e constant, differentiate X with respect to x n; that is what it says. So, where is my expression for X? Here, is X, you have to keep x e constant. So, this term is going to be kept constant; you have to differentiate with respect to x n.

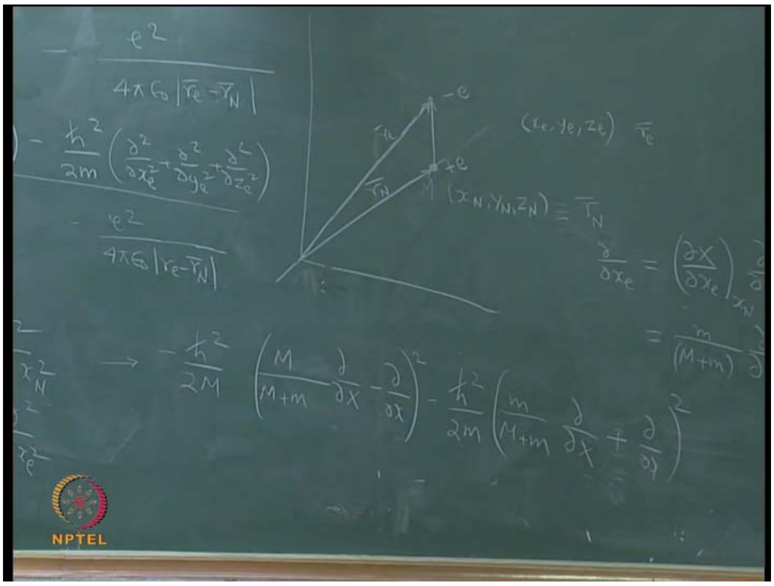
So, what is the answer? This is going to be kept constant; you are differentiating with respect to x n. So, the answer is M divided by M plus m. So, this is actually equal to M divided by M plus m into dou by dou x. What is the next step? See, here dou x by dou x n. So, this is to be differentiated with respect to x n keeping x e constant and this is minus 1. So, therefore, you will get minus dou by dou x, is that fine. So, dou by dou x n is just that. Similarly, I should express dou by dou x e in a similar fashion; let me try to do that.

(Refer Slide Time: 32:29)



dou by dou x e is equal to dou x by dou x e this is partial differentiation with respect to x e keeping x n fixed into dou by dou x. Where, is dou x by x e keeping x n fixed into dou by dou x fine. And what is this object? dou by dou X by dou x e; I will have to differentiate X with respect to x e keeping x n constant. So, the answer is actually m divided by M plus m into dou by dou x plus, what is the derivative there? This derivative if you evaluate, you will find out the answer is unity.

(Refer Slide Time: 34:32)



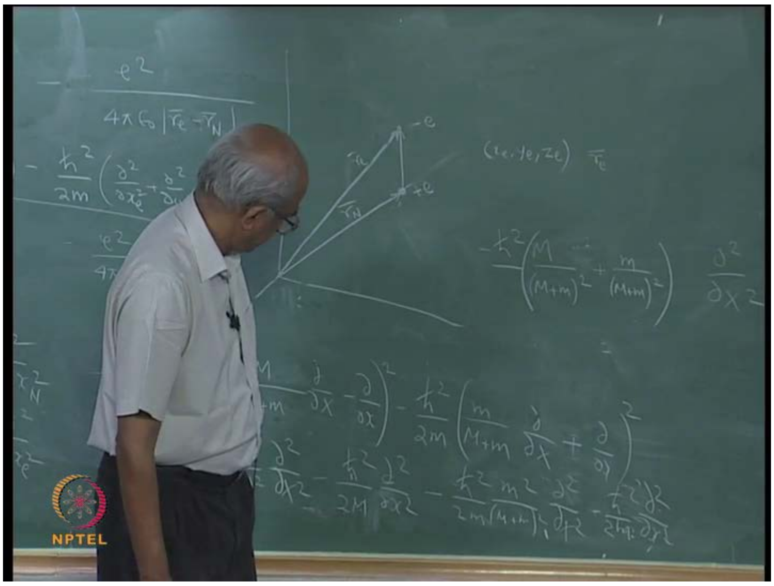
So, therefore, you will get dou by duo x, fine. And now to get this, what should I do? I will have to look at this expression. To get this expression, what I will have to do is I will have to take the square of it divided by 2 m and multiply by minus H cross square. And to get this I will have to take this square of this expression divided by 2 times m and multiplied by minus its cross square. So, let me just do that and look at the answer.

So, this will become minus H cross square divided by 2 m, M divided by M plus m dou by dou x minus dou by dou x the whole square; that is one term. And the other term is minus H cross square by 2 m; we can remove this. This is going to be put there. m by M plus m dou by dou x plus dou by dou x the whole square. So, this is your kinetic energy operator, just the; when I say the kinetic energy operators the only part from the x coordinates are there. Well, you should also notice that there is a negative sign here and while positive sign there.

So, when you take this square, what is going to happen? If you look at the expression, you will see that the negative term from here and the positive term from there, because of that there will be some cancellation. Let me write the expression. It is going to be minus H cross square divided by 2 m square of this, if you evaluate m square divided by M plus m the whole square dou square upon dou x square, that is step number one. I will make from the square of this and coming from square of that you would have minus H cross square divided by 2 m dou square upon dou x square. there is a cross term coming from these two. But as I told you there is a cross term there and if you do the calculation, you will see that they two cancel each other nicely. So, let me write the remaining terms.

From here you will get minus H cross square by 2 M m square divided by M plus m the whole square, this right. duo square upon dou x square plus the last term will be a dou square upon minus H cross square divided by 2 m dou square upon dou x square. So, that is the, there is a say cross term involving the dou by dou x and dou by dou X; that too together. But that will be cancelled by the same kind of term at the other side. So, what is the net answer? Well, it involves dou square upon dou X square and dou square upon dou x square.

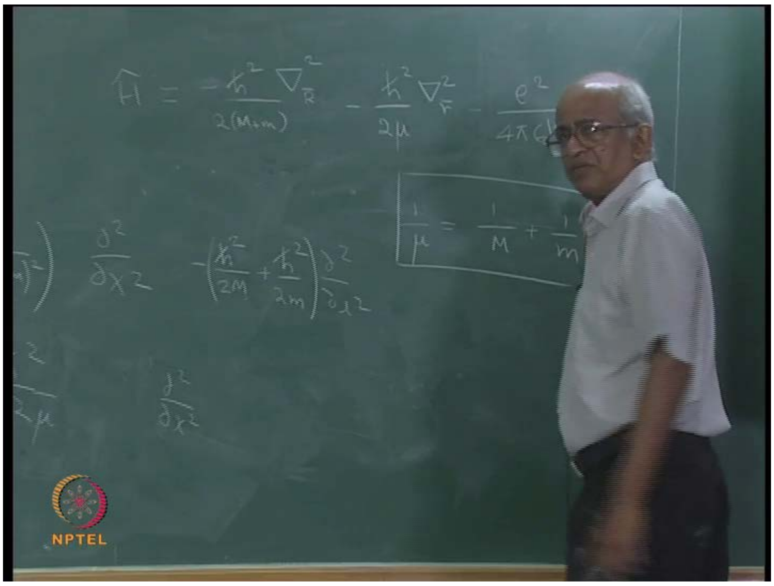
(Refer Slide Time: 38:00)



So, as far as this term is concerned you will have minus H cross square, see minus H cross square by 2 M and H cross square by 2 times m. So, the terms involving dou square upon dou x square are just these, fine. You have 1 by M here and 1 by m there, correct. And what are the terms involving dou square upon dou x square? The first term is this one and that I can look at it, it is actually equal to minus H cross square. Well, maybe I should write it here; minus H cross square divided by 2 M is there, but there is an m square in the numerator.

So, you are going to get M divided by M plus m the whole square; that is the first term. What about the second term? Coming from here, it is similar and it is going to be m divided by M plus m the whole square. So, this is what happens, right. See, what has happened is, where is it? Yes, there is an m square, that m square and this m will cancel. So, you will be left with an m and that m is the one that is occurring there, will be divided by M plus m the whole square.

(Refer Slide Time: 40:25)



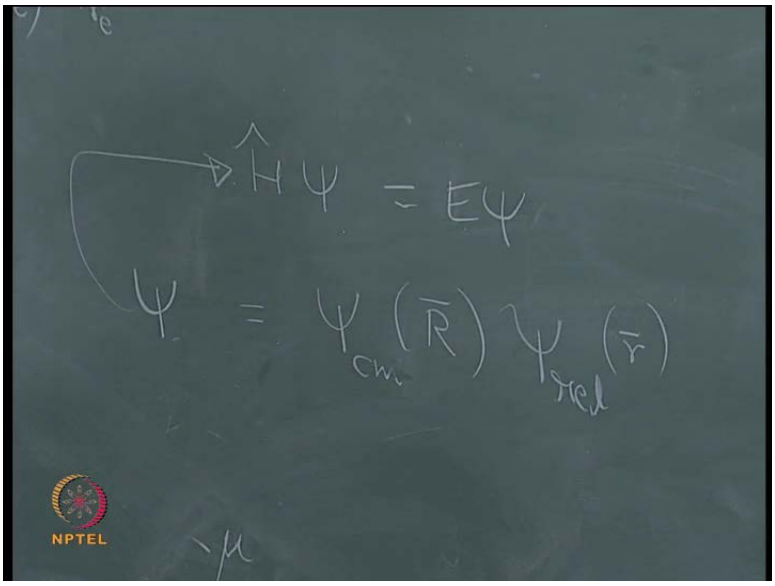
So, what is the answer that you are going to get? Well, the answer is extremely simple. It is just what we had written physically, get minus H cross square this may be combined; you will get M plus m. That is M plus m the square in the denominator. So, effectively this will become M plus m into 2; there is a 2 that I have missed out. So, there is a 2 here. So, here again you will get a 2, then this term will be minus H cross square divided by 2 into 1 by M plus 1 by m right; dou square upon dou x square, right.

Now, when you look at the expression; this is basically very meaning full. If the particle is very massive, then it does not move much, as I told you nucleus does not move much. And therefore, the kinetic energy corresponding to its motion will be very small; if m is large, you have 1 by M. So, the more mass of the particle is, see it makes more contribution into this relative motion; that is what this equation says, right. We have already seen the physical reason for that. So, therefore, if I now say that I am going to define an effective mass, how will I define an effective mass? This whole thing let me say is equal to 1 by mu. This sum if it is equal to 1 by mu, it will have the nice appearance. What will be the nice appearance? you see the nice appearance will be minus H cross square divided by 2 mu into dou square upon dou x square.

Where, what is the definition of mu? I have defined it in such a fashion that 1 by mu is equal to 1 by M plus 1 by m; this is known as the reduced mass of the system. Well, I had been a little bit careless here; because I should have, I should not have forgotten to put the dou square upon dou X square, right. That is the kinetic energy operator will be there. So, here I have demonstrated this for just x motion; you can do exactly the same thing for y motion as well as z motion. And therefore, what will happen? You will have this Hamiltonian right. The Hamiltonian would be actually equal to this.

So, you see this Hamiltonian that I had, which was written in terms of the coordinates of the particles, that was not very convenient. But I have changed over to center mass and relative coordinate and then I find that the Hamiltonian has this form. Now, this is quite convenient. Why do I say that? While first of all we have written it using our physical infusion. The second thing is, if you look at the potential energy of the system; potentially depends only upon relative coordinates right. Therefore, if you look at this Hamiltonian operator, you will see that this part depends only upon relative motion. While this part, is the one that describes translation motion. And what does it say? It says that there is just kinetic energy due to translational motion; that is what this term actually tells to you. While the other terms has of course, kinetic term as well as potential energy terms, because it is a relative motion.

(Refer Slide Time: 44:51)



So, if you have such a Hamiltonian and if you wanted to solve disoriented equation, what will you do? You will say that H psi is equal to e psi, is the equation that I want to solve. But what I will then do is, I will say that the psi which is the wave function may be written as psi center of mass right. The psi that describes the center of mass; this is the essentially the method of separation of variables. Remember, our psi the wave function will depend upon all the 6 coordinates, right and then we physically set that there is a center of motion and there is a relative motion and we were able to use that idea to write the Hamiltonian as a sum of two separate Hamiltonians in a sense. The first term is the kinetic energy of mass motion and the second term is relative motion. So, this is Hamiltonian for relative, for center of mass motion and that Hamiltonian for relative motion. So, we were able to write the original Hamiltonian as a sum of essential two separate Hamiltonian.

And, therefore, what I expect to happen is that, my wave function also should be possible to do the similar thing. My wave function must be a psi product; a product of a center of mass motion and relative motion. So, therefore, this psi center of mass will be a function of R and then I would else, I relative it which will be a function of r. So, this is essentially the method of separation of variables and what will I do, I will take this assumption for this unsets, put it into the Schrodinger equation. And use the method of separation of variables. And then you will find that the equation can be nicely separated; I will do it in the next lecture. It can be nicely separated into two separate equations; one will describe the center of mass of motion as a whole and the other will describe relative motion of the electron with respect to the nucleus. And then the center of mass motion is very easy. It is just simply the free particle moving in space, right very easy. And the other one is little bit more difficult; because it involves the motion of the electrons with respect to the nucleus. And we, I will tell you how to solve it eventually; it will give me the atomic Orbitals eventually.

So, thank you, thank you for listening.