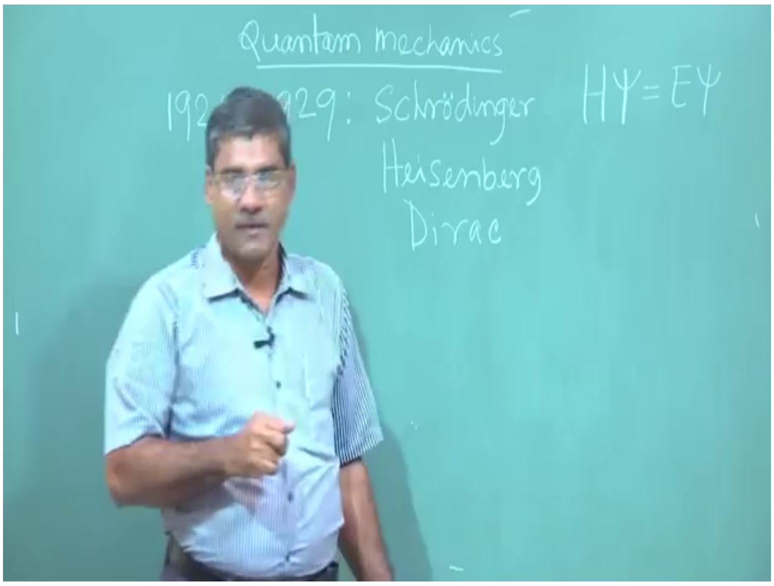
Atomic and Molecular Physics
Prof. Amal Kumar Das
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture - 27
Quantum mechanical treatment

So, for today, I will start quantum mechanical treatment or atomic and molecular physics.

(Refer Slide Time: 00:30)



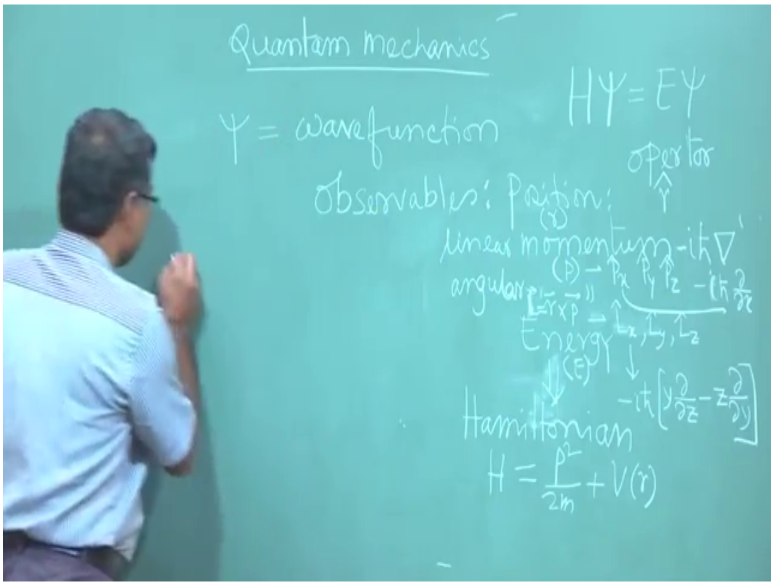
So, one has to use quantum mechanics ok. So, so far we have explained, the atomic spectra based on the basically old quantum theory it is not actually not the quantum mechanics it is just; that can be treated as a as a these between the classical mechanics and the quantum mechanics. So, from classical concept, we are going towards the mechanical concept quantum mechanical concept and in between this all quantum theory, that is the basically from classical to quantum that is the development and on ad hoc basis lot of assumption was made.

So, actually this quantum mechanics, it is realized that this for small system like atoms molecules and many other things which are in size is very small. So, for that classical mechanics is not is not the appropriate one. So, one needs new mechanics So that is the idea for quantum mechanics. So, that quantum mechanics actually, it was developed, during this 1926 to 1929.

During this period this quantum mechanics was developed by Schrodinger, then Heisenberg and Dirac. So, they developed this quantum mechanical formalism for small particles like atom or electron and for; so first basically this very useful formalism, that is the Schrodinger equation. So, Schrodinger equation, it is we write this equation H psi equal to E psi. So, that is the equation is call Schrodinger equation.

Now, what is H? What is psi? What is E? So, for that one has to one has to go through the some postulates. So, this equation or this quantum mechanics also this based on some postulates is 5, 6 postulates. So, I will not I will not tell in details, but I will try to explain whatever; I will use in quantum mechanics. So, the psi is wave function wave function.

(Refer Slide Time: 04:57)



So, wave function of what; psi wave function or wave function of what. So, so wave function of our problem of our system the system, which you want to study, right. So, say electron; electron it may be free electron, it may be electron in a in a potential well or electron in a in a central potential central force right, as like in case of hydrogen atom. So, these are the system these are the our problem we want to study the system. So, in quantum mechanics the system is expressed our all problem is expressed ok.

So, our study material is expressed, in terms of wave function; that is psi ok. So, so psi basically con should contain all information about the about the about the system, which we are want to study right. So, this psi have all information about the particle about the system and psi it have to follow some rules it has to follow some rules. So, if I want to; so about system or information is in psi, now what we want to study; about a system we want to we want to say we want to know the position of our of our particle or system we want to know the momentum we want to know the angular momentum, we want to know the energy of the of the system ok.

So, these are the properties or these are the observables in quantum mechanical language is called observables; what we want to observe what we want to study that property. So, these are observables. So, observable is it is position say momentum ok. So, linear momentum and angular momentum, angular momentum we want to know the want to know the energy of the system.

So, how to know how to know these observables; so that is why; in quantum mechanics; so for each observable there is there will be operator it is called operator like position it is operator corresponding operator it is so we write r caps A or cap. So, it is a operator position operator. Now we want to observe the position is to observables. So, observables is basically if it is a position r it is r, right, so it is corresponding operator r cap.

Now idea is in quantum mechanics. So, if I apply this operator on the wave function, then we will get output, we will get that is the; that is the observables, we will get the position operator we applied on this wave function. So, I will get the position, if I apply linear momentum. So, there is the there is the basically P linear momentum P ok. Since corresponding operator so P has different components it is corresponding operator, it is write minus i h cross del minus i h cross del.

So, for P has three component P x, P y, P z P x, P y, P z so for corresponding operator, generally, we also write P cap x, P cap y, P cap z, and it is and this we write minus i h cross del by del x for P x del by del x for P y i h cross I this complex number psi equal to square root of minus 1. So, P y that will be I minus i h cross del by del y other one del by del z ok.

So, this is the; this is the operator for position operator, sorry; linear momentum operator. Now, if I apply this operator on the way function. So, then I will get the momentum linear moment of the of the system. So, so achieve this the psi have all the information, and in quantum mechanics there is of the operators they are they corresponds to some observables whatever the it is; it is related with the property of the system ok. So, this corresponding operator, if I apply on the wave function I will get the; I will get the information that particular that information.

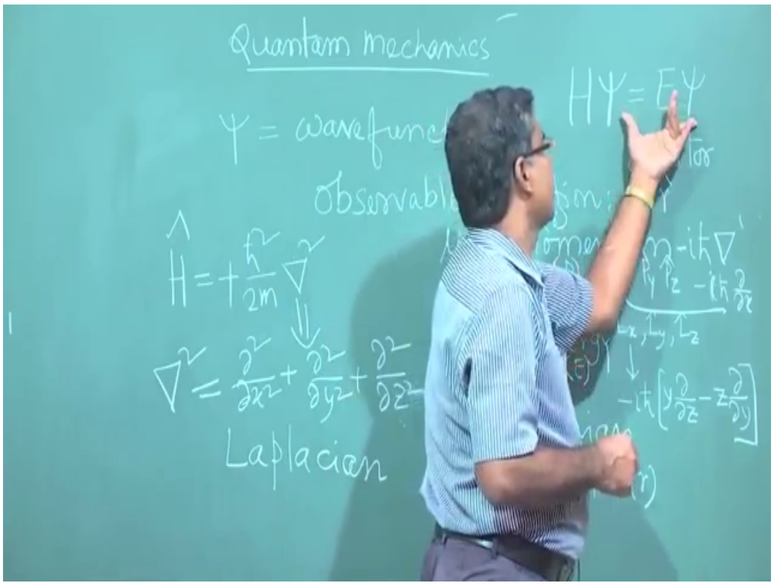
Similarly, angular momentum it is basically r cross P r cross P right; r cross P. So, it is nearly right in times of l l angular momentum l equal to r cross P and corresponding operator l x, one can write l x, l y, l z, l x, l y, lx, ly (Refer Time: 12:34) we write capital L (Refer Time: 12:36) we write capital L as the operator say l l.

So, it is three component L x, L y, L z L x, L y, L z and it has some form. So, actually this r cross P we can is cross product. So, it is component that L x operator is the from here itself one can if you know this r and P operator. So, from there here one can find out. So, this basically it will be minus i h cross minus i h cross. So, this x means y del by del z minus z del by del y right (Refer Time: 12:48).

Similarly, L y, y component, z component so one can write one can write right. So, y it will be minus i h cross, y mean z del by del x minus x del by del z. So, so this is the angular momentum operator. Now, if I apply angular momentum on this I should get the information about the about the angular momentum of the of the system. Similarly, energy operator E, energy operator E; so E energy it is corresponding it is operator is called Hamiltonian, it is operator is called Hamiltonian and that is basically H say energy operator H and this H is that H H psi equal to E psi.

So, energy it is of observable E, corresponding operator is operator is H. So, H is basically energy operator is kinetic energy plus potential energy plus potential energy ok.

(Refer Slide Time: 15:38)



So, this P square by 2 m P square you know from here one can so H one can write basically H is the yeah; these are observable, these are observable potential and this momentum; so corresponding operator in terms of operator. So, that will get Hamiltonian operator energy operator. So, this if you, if you take this one so, one can write minus I think is; so that will be minus plus plus. So, minus h cross square by 2 m h cross square by 2 m, and then one can one can write del square ok.

So, del square this dot this P x square or this as a whole. So, this way one can write this del square equal to; basically del 2 by del x square plus del 2 by del y square plus del 2 by del z square right .

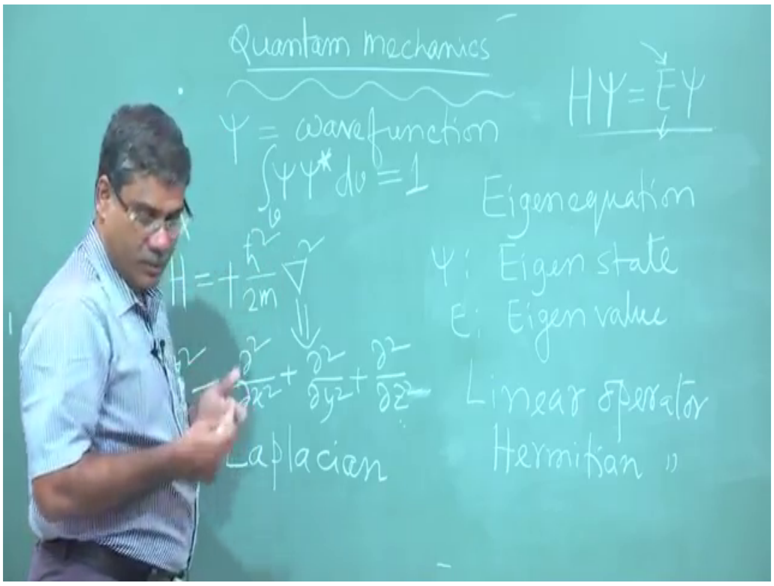
So, del square; so from here itself if it right component, then you will get this rather whole if you take this. So, P a P square means this dot this so h cross square minus minus 1 and this is plus 1. So, it should be plus h cross square by 2 m, then it is del square. So, del square is called Laplacian del square is also called also Laplacian. So, this del square. So, the del square is this del square is this it is called Laplacian Laplacian ok.

So, this is quantum mechanical language. So, one has to the adapt; with these language. So, for; so this is the; so in quantum mechanics so one is wave function. So, here whatever I have written; so this wave function for a particular system is wave function contain it is a; it contain all information about this particle, now in quantum mechanics operators are there different kind of operators as I as I discussed. So, now, if you apply operator on that; so you will get the observables.

So, here if I energy operator I I apply on this. So, if I get, then I will get the energy of the system E and this equation is written like this. So, this E is called basically energy, because it has come out, because of application of energy operator Hamiltonian. So, and this kind of equation is called Eigen equation, this kind of equation is called Eigen equation.

So, it is a, it is if I apply operator on the wave function and it gives the observable gives the observable and relation is like this; so this equation is called Eigen equation Eigen equation and this Eigen equation.

(Refer Slide Time: 19:47)



So, this wave function then if it is follows this type of equation Eigen equation. So, then this psi is called Eigen state Eigen state and this; so when psi will be called Eigen Eigen state and E is will be called the Eigen Eigen value Eigen value Eigen value ok. So, there are many there are many basically there are many algebra one can draw rules regulation in quantum mechanics, then one has to learn and I think so you have to learn slowly slowly ok.

And I will just I will just briefly just mention whatever I need for this course. So, ; so if I yes; so ah; so, it is; so it is not the case always this happens; it is not the case always it happens ok. So, it depends on different condition. So, operator will tell this operators are linear have to be linear Hermitian. So, this kind of lot of conditions are there algebras are there I think that we have to if you do not know you have to learn slowly slowly ah, but I just I will I will I will briefly, I will tell and I will use those property. So, what is linear that you should you should learn linear operator which operator ok, Hermitian operator Hermitian operator and yes.

So, this two terms are very important. So, when it will be called linear operator, when it will be called Hermitian operator for real system for real observable. So, it has to be Hermitian ok. So, there are some definition. So, I will not going to just do the things just I just mention and we have to we have to be familiar with this; this terms and so for the system and also this the psi also the psi as I told this ; so psi about this psi is basically is; so a function.

So, wave function when we tell wave function it is the it is something like this varying when we tell particle when we tell particle; so as if this it. So, it indicates that is a you can you can you can locate you can locate the particle precisely and when we tell lower it is you cannot locate, you can locate you cannot locate like this ok.

So, there is a uncertainty there is a ah. So, where you cannot look at where you cannot tell definitely ok, then we tell above in terms of probability ok. So, what is the probability; what is the probability of something ok; so, that probability that probability to find either position or momentum or other things ok. So, then that we tell we define probability, it is in terms of psi star or psi star psi star ok.

So, we tell the psi we tell this to get to get the particle in a small volume dv in a small volume dv, in small volume dv; so what is the probability to find the particle in small volume dv ok. So, then it is the probability psi psi star dv, that is the probability to have to get the particle within this volume dv right. Now, as if as if this whole is particle, where it is I do not know, but it is inside a box of volume v ok, but if I want to look at the position of the particle. So, definitely I cannot tell.

So, only I can tell in terms of probability, but one things is clear or we define in that way; the wave function has to be such that; the probability to have the particle inside this box as a whole volume v it is 1, probability is 1. So then this to find the particle in this box of volume v; so we have to if I indicate over v.

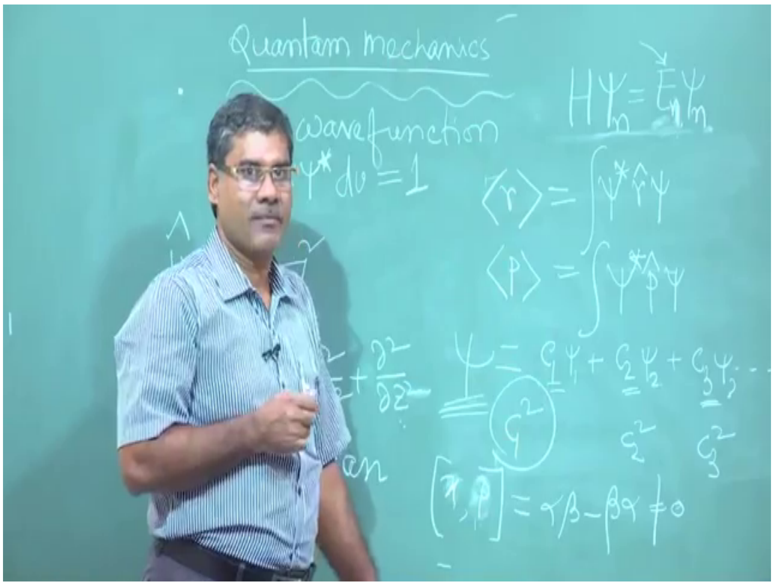
So, then we will definitely we will get the particle in the box so probability is 1. So, maximum probability that is the; that is the 1, and if you if you want to find out the position of the particle or to find out the particle within the box at some places. So, then this probability will be different less than 1 ok. So, so this is the probability and this we tell this is, then if finding the particle within this box, then probability is 1. So, that way if we if we if we form the wave function. So, then that wave function we tell this is a normalized wave function, this wave function is normalized ok. If it is if it is like this that; the probability to find the particle inside the box is not 1 .

So, it may have some value it is 4 say ok. So, then wave function is not normalized wave function, then we divided by 4, we divide this wave function we divide by basically not 4 by yeah; divide by 4, then 2, 2 psi psi star are there ok. So, basically half psi half psi and this is the other one also half psi ok. So, this that; way we normalize this wave function so that half factor is coming, because of this normalization. So, that way generally we normalize the wave function in such way the total probability to find the particle that is 1 ok.

So, this way we define wave function we develop wave function, we develop wave function and yeah, then there as I told this inside the box particle are there total probability the probability to find the particle inside the box is a 1 that is find, but if I if I just divided the box if I divided the box and makes small small cell imagine small small cells ok. Now, if I want to know that; now the particle where it is in which box it is in which cell it is. So, now, it is difficult to tell where it is ok. So, only we tell that, what is the probability to have the particle in this cell say cell number 6 or cell number 5 ok?

So, then we have to find out the we have to find out the that probability to get the position of the particle. So, in that case; so generally this probability find the or average value of the position average value of the position this kind of language we use.

(Refer Slide Time: 30:12)



So, average position of the particle if it is r or average momentum of the particle average energy of the particle, ecetera ok. So, that one can find out you say it is the psi psi star your operator is psi, then apply on psi ok. So, this will be the definition of this one r this is the average value of r ok. So, if I want to find out the average value of r; this average value of momentum. So, one has to define like this psi star P psi ok. So, that way we can one can find out the probability average value of these of the of the observable parameter.

So, that is ah, but difference when, but in case of in case of Eigen function in case of Eigen function wave equation Eigen, if this wave function satisfy this wave equation, then this energy or this observable definitely it has only we can definitely we can we can tell; what is the energy it is its not average energy it is not average energy ok. So, wave function one has to form one has to developed.

Now, I told this you have box now inside box particle somewhere in this within this box, but inside this box I have many cells, I have divided many cells ok. Now particle can stay in any of the cell, but it is not that it is it is staying only in one cell so, if you see this particle; now in this cell exactly in this cell or particle exactly in this cell ok.

So, that way it is the; if it is the case particle is in the cell ok. So, then it will follow it will follow like this ok, it will follow this wave function will be such so n equal to 1, 2, 3, 4, 5. So, different cell different cell ok, so in different cell, so, different cell have different position are in this case different energy ok. So, what is the energy of this; when particle will be in one of the cell? So, it will be that particle energy ok.

So, it can be in any cell. So, what are the energies of those cell ok. So, that can be find out that can be if we get like, this if we get like this. So, this system will have many wave function psi 1, psi 2, psi 3, psi 4 and then it is E 1, E 2, E 3, E 4 there corresponding energy and then complete psi; so this is the basically ah. So, system have face set of psi and we tell their orthogonally if they are they have to be orthogonal if they are orthogonal.

So, these are the quantum mechanical term ok. So, this complete this psi complete psi for the system, it can be retained in terms of this their Eigen wave function. So, wave function as I told this it is basically square of the wave function is the basically probability of anything ok. So, this is retained in terms of lay C 1 psi 1 plus C 2 psi 2 plus C 3 psi 3 etcetera ok up to n up to n.

So, this will be the complete wave function for the system and their each one is the basically individual they have. So, they this system have this have this set of wave function set of Eigen wave function one can say so. So, now, here if I; so this wave function contain this information that; what is the probability to have the system one of in one of the state ok.

So, that is basically we tell is this coefficient are basically the; the weightage of this of this of this wave function weightage of this wave function; so, or the probability to have in the state 1, state 2, state 3.

So, that is expressed it is a square of this C 1 C 2 star is the is the weightage C 1 square, C 2, square C 3 square ok. So, these are the weightage of our each state ok. So, system have many states many states ok; it have possibility to have many states; Now system; so as a whole to describe the system if form a wave function combining taking the linear combination linear or this called super position of this all individual waves, yeah, wave function and this coefficient basically tells the weightage of this of this of each wave function and that that weightage is basically C 1 square, C 2 square, C 3 square of different states.

So, the complete wave function the complete wave function for the system and this can be developed. So, task is for any problem task is to harm to develop the appropriate wave function for the system ok. So, that as I told wave function contain all information about the; should contain all information about the about the system.

So, adopting with the system one has to develop the wave function, then this work is done. So, that wave function, what it is that is by system, because it contain all information and what I want to know? I want to know position, if I know the wave function just I will apply position operator on that momentum operator on that energy operator on that, and then I will get the observables, I will get the properties of the system; what you want to study? What you want to know ok? So, then another since are there are commutator commutator and non commutator ok.

So, commutator is basically is write in square bracket. So, like if two operator say alpha and beta two operator, if this we write alpha beta commutator means alpha beta minus beta alpha ok. This commutator means is this ok. So, if it is 0, then we tell that alpha and beta communicates with each other in quantum mechanical language, if two operator follows this equal to 0, then we tell this two parameter this two operator means is corresponds to two parameter. So, this like position and momentum ok.

So, if that is equal to 0, then we tell that this two parameter can we majored simultaneously, can be majored simultaneously and accurately ok. If it is not 0, then we tell alpha beta is a non commutator they do not communicate with each other. So, one cannot major this two parameter alpha and beta simultaneously this happens for x and P, if alpha is x if alpha is x and this P say it is not equal to 0 basically ok, it is not equal to 0 minus i h cos it is equal to minus i h cos ok.

So, it is not equal to 0. So, in quantum mechanizes, which parameters are observables can major simultaneously and accurately and which parameter simultaneously we cannot major accurately ok. So, that is expressed in this language commutator and non commutator ok. So, this is the this is the preliminary language of this quantum mechanics just I try to told ok. So, in next class I will I will elaborate more ah.

Thank you.