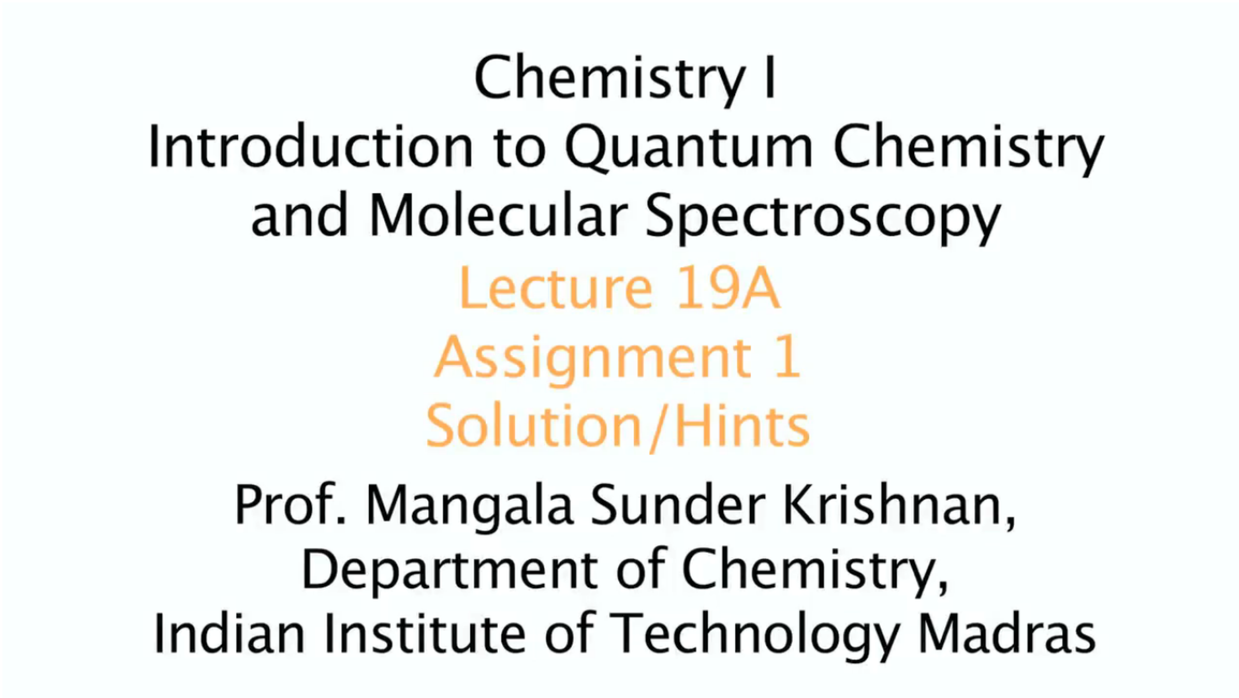
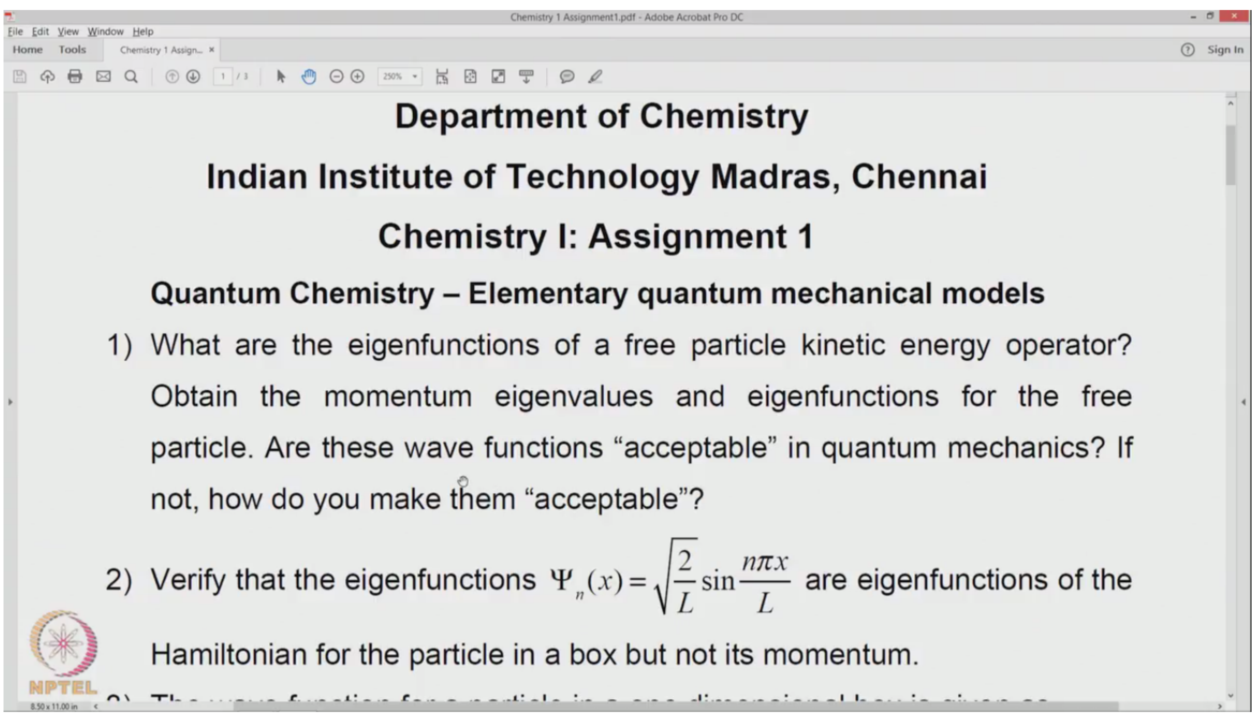




Department of Chemistry

Indian Institute of Technology Madras, Chennai

Chemistry I: Assignment 1

Quantum Chemistry – Elementary quantum mechanical models

1) What are the eigenfunctions of a free particle kinetic energy operator? Obtain the momentum eigenvalues and eigenfunctions for the free particle. Are these wave functions "acceptable" in quantum mechanics? If not, how do you make them "acceptable"?

2) Verify that the eigenfunctions $\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$ are eigenfunctions of the Hamiltonian for the particle in a box but not its momentum.

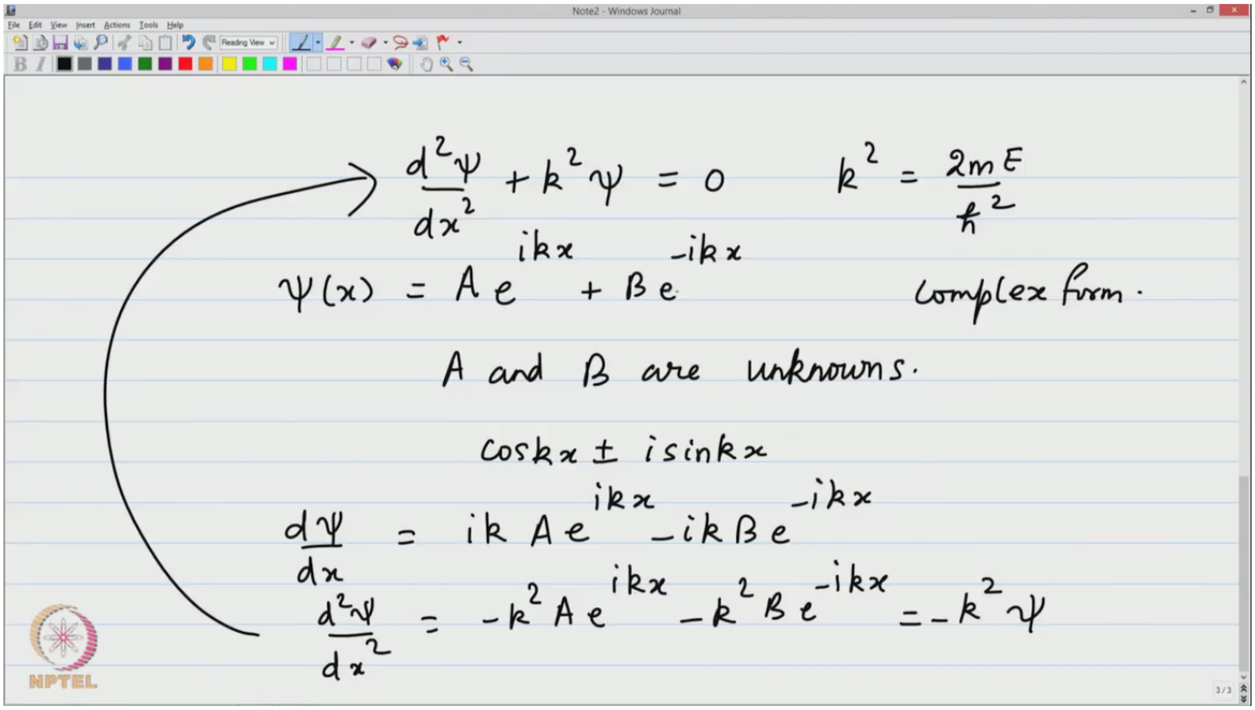
Welcome back to the course. Chemistry one which is an introduction to quantum chemistry and molecular spectroscopy. This is a lecture on the solutions to the assignment problems. Some of these problems I shall give the hints instead of going through the numerical detail. This will be in small bits maybe one or two problems for each of these lecture. This is useful to you.

So let's go back to the first assignment problem that was posted on the website. If you recall the first problem asks you to calculate the eigenfunctions of a free particle kinetic energy operator. It also asks you to obtain the momentum eigenvalues and eigenfunctions for the free particles. Then the question is whether these wave functions are acceptable in quantum mechanics?

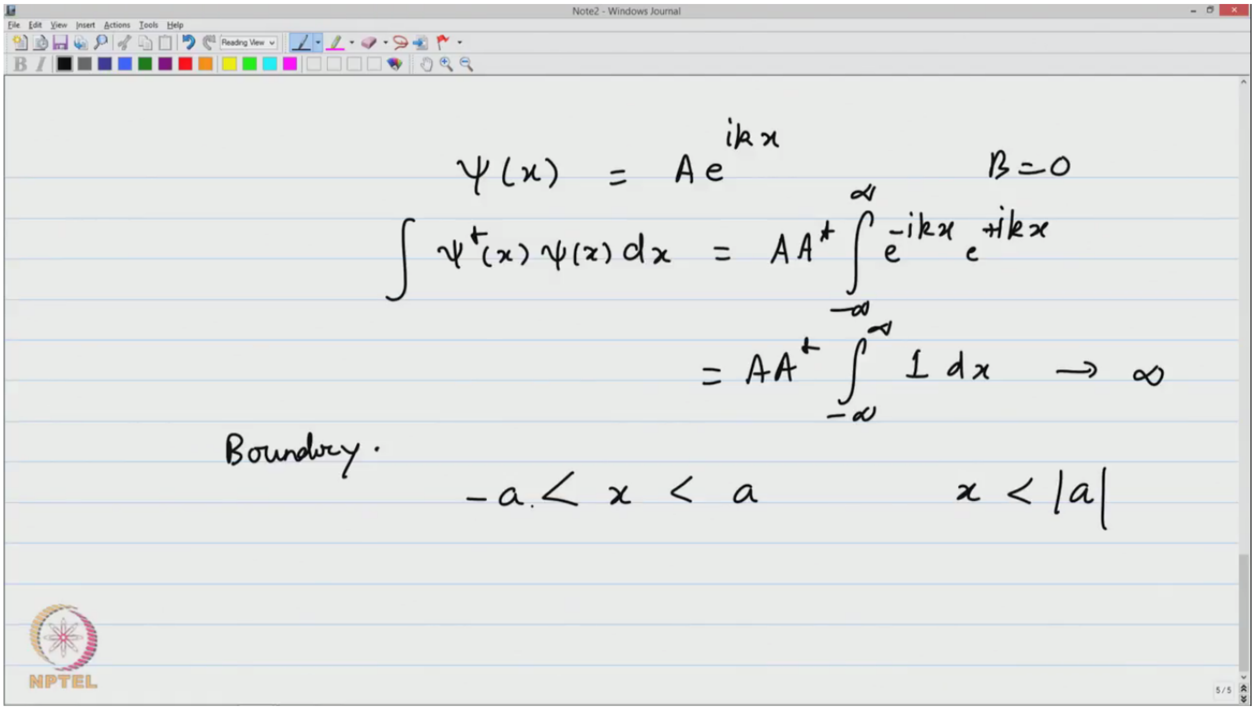
So we have to understand what is meant by acceptable wave functions and if they are not acceptable is it possible for us to make them acceptable. So that's what this problem is. These are all conceptual ideas when you are learning from mechanics for the first time. Therefore it is important to go through these details very carefully. So what are the wave functions for the free particle kinetic energy operator?

So when you say free particle define it which means that that is there is no potential energy acting on the particle. Therefore, it has only kinetic energy energy. The kinetic energy operator is of course classically it is momentum square by 2m for a particle traveling with a velocity speed velocity v and with the mass m and we assume that the mass m is a simple form and is a constant that this is a non-relativistic motion and the operator for that is in quantum mechanics minus h bar square by 2m d square dx square as you might recall.

So what is the solution for the free particle kinetic energy operator? We are looking at all solutions minus h bar square by 2m d square psi by dx square is equal to e psi. this is the h psi is equal to e psi, the Schrodinger equation for time independent quantum mechanics. There's no condition. It's free particle. We have not defined the boundary like we did in the particle in the box. Therefore we have to find out the general solution. So the general solution is if we rewrite this equation again d square psi by dx square plus k square psi is equal to 0 and k square is 2m e by h bar square. After rearranging the equation the general solution for this is usually written for complex form and the complex form for this is Ae to the ikx plus Be to the minus ikx where A and B are unknowns. You can also write them in terms of a coskx and the sinkx that would be very useful if you have a finite boundary because then it's possible for us to impose the the boundary conditions. We can't do that here simply because e to the ikx never goes to zero. It's coskx plus or minus isinkx. Therefore these two functions do not go to 0 for any single value of x or kx. Therefore the function is never 0. It's always oscillatory and it's also complex. So this is the general solution. You can substitute this solution here and you will see that if you take this d psi by dx then you will see that the ik coming down Ae to the ikx and the minus ik coming down from this term to Be to the minus ikx and this is not the same as the function that is a minus sign and therefore if you take this second derivative d square by dx square you would see that ik that is also another ik, so this becomes i square k square which is minus k square Ae to the ikx and this is a minus ik and there is a minus ik for one more derivative. Therefore it's also minus k square Be to the minus ikx and you see that this is immediately minus k square times psi. That's getting back the equation.



So the free particle kinetic energy operator is defined with these solutions that you have here Ae to the ikx and Be to the minus ikx. Is it acceptable? No. No. Not acceptable. Why? Not acceptable unless a boundary is defined. If you say so psi x is valid for all x meaning minus infinity less than x plus infinity if you do that then the integral psi star psi x minus infinity to plus infinity dx will now become even if you take only one of the terms Ae to the ikx this will become actually minus infinity to plus infinity Ae to the ikx. Let's write this is a complex because we don't know what A is. It's a constant and we have plus B star e to the minus iks this is psi star multiplied by psi which is Ae to the, sorry, psi star is the minus sign here and the plus sign here. And it is Ae to the ikx plus Be to the minus ikx dx. It's easy to show that this integral never again terminates at infinity. It keeps on oscillating and in fact it becomes infinite. This integral becomes infinite. So not acceptable. Not normalizable.



If you take even one term for example if you say psi of x is Ae to the ikx and let's assume that B is 0 it's very clear that psi star psi x dx is A A star integral e to the ikx e to the minus ikx, sorry this is minus, this is plus psi star psi minus infinity to plus infinity which is A A star integral minus infinity to plus infinity 1 dx and that's infinite. And you can show the same thing for that that is same for the cross terms. Therefore a boundary is needed. Suppose the solution is valid for x less than a certain absolute value A. X is between minus A and plus A then it's possible to find the normalization constant because if you assumes psi of x to be Ae to the ikx then integral psi star x psi of x dx between the limits minus A to plus A because the function is defined only in that region and we assume that it is zero everywhere else then you can see that this is nothing other than minus A to plus A A star 1 dx and that's A A star times 2a and if that should be set equal to one for probability then the absolute A square is 1 by 2a and therefore the magnitude of A is 1 by square root of 2a. This is okay. Normalizable.

Therefore, free particle wave functions are acceptable only within certain defined boundaries and this was the reason why we did the particle in a one dimensional box with very clear L bounday, 0 to L boundary and even in the hydrogen atom also when we did not have a boundary that r goes all the way to infinity we ensure that the wave function goes to zero faster than any other function that multiplies it and therefore eventually that integral psi star psi is normalizable to a finite value that integral has a finite value therefore 1 by square root of the finite value is the normalization constant. So that's important for understanding this problem.

Second problem is of course is to state that the eigenfunctions sine of x that you have done for the particle in the box at the finite boundary they are eigenfunctions of the Hamiltonian for the particle in a box but not its momentum. That is the they are not eigenfunctions of the momentum operator. You can see that right way that the momentum operator is a derivative operator d by dx and therefore the operation d by dx on sine of X does not give u sine n π x by L back but it gives u cosine n π x by L multiplied by n π by L therefore it's not an eigenfunction of momentum operator but it's an eigenfunction of the momentum square operator. Question will come what does that mean? I mean if the Hamiltonian is only momentum square and the wave function is an eigenfunction of momentum square but not of the momentum itself it – please remember the square root of 2 by L sin n π x by L was arrived with specific boundaries with potential v is equal to infinity. If you recall when we solve this equation minus h bar square by 2m d square psi by dx square is equal to E psi for 1-D model we assume that V is infinity everywhere else and V is zero. Potential is there. There's no potential here but it's the finite – infiniteness of the potential that restricts this solution to be psi of x is equal to square root of 2 by L sin n π x by L. Therefore, the Hamiltonian does incorporate the boundary conditions through the infinite potential and that it's just not p square by 2m it's P square by 2m plus the boundary and that particular operator does not obviously commute with the operator P. Therefore, the eigenfunctions of the operator P and the eigenfunctions of the operator P square are not the same.

On the other hand if there is no particle finite boundary you remember psi of x is Ae to the ikx if we take this as an eigenfunction this is a solution of this operator also but in addition please remember this is also a solution of the momentum operator psi of x is equal to obviously minus h bar times d psi by derivative dx will give you plus ik and it will give you Ae to the ikx and therefore the answer is h bar k e to the ikx A and you can see that this is the wave function therefore you have h bar k times psi. Thus the operator without any finite potential boundary for a free particle has the same wave function as the wave function the eigenfunction for the kinetic energy operator. There P and P square can look at each other obviously and you can see that the wave function also is same for both. Subtle details are important. So that is what this particular problem is supposed to illustrate.