Time Dependent Quantum Chemistry
Professor. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangaluru
Lecture 08 Module 02
Meaning of Probabilty Density

Welcome to module 2 of the course Time Dependent Quantum Chemistry. In this module we will try to find out classical mechanical viewpoint in quantum dynamics. The reason we would like to try to find out in the beginning of this course the classical mechanical flavor is that all the motion we see in our daily life is actually classical motion and it would be an good idea to correlate what we see classically and what does it mean by the motion in quantum mechanics. So, trying to find out these two connections can help us understand quantum dynamics quickly.

So, the problem of thinking about this, or trying to find out the classical mechanical flavor in quantum dynamics is that in quantum mechanics the particle will be represented by the wave function and the first question which is important in quantum mechanics and quantum dynamics is written here, how can I delocalize mathematical function?

So, when I think about a classical particle moving, I always draw some kind of ball and show this arrow to present the movement of the particle, but in quantum mechanics this picture is not valid anymore, there is no particle concept in quantum mechanics at least in the standard interpretation of quantum mechanics, it has to be presented in terms of the wave function and wave function is always delocalized in nature.

This is something which we have learned from the previous module, it is the density distribution, the wave function is delocalized as nature and because it is delocalized there is a possibility that particle can be here, there is a possibility the particle can be here, there is a possibility the particle can be here, here, here all these possibilities are there. There can be higher possibility of finding the particle at a particular position as compared to the other position that is possible but still there is a possibility.

And this possibility, this idea of possibility makes us very difficult to understand the motion of a particle in quantum dynamics when you think about the classical picture. So, the first question in this module is that how can a delocalized mathematical function, which is wave function represent a particle which is supposed to be localized according to our classical consensus?

Classically we think that the particle should be localized, but quantum mechanically there is no way I can represent a local function, I only have the wave function which is delocalized or global in nature. So, this question is important and we have seen that quantum mechanics only provides a probabilistic answer to this question in terms of probability density which I have plotted here this is called probability density.

Once I get ψ which is the wave function of the particle from ψ I get this probability density and the probabilistic answer to this question is given with respect to this probability density for finding the particle at a particular point x and time t. So, this is a point which will be illuminating here.

A quantum particle is defined by its wave function, the wave function can be complex function but probability density is always going to be real because probability density is nothing but $\psi^*\psi$ which is the absolute value we take and then square it and that is why it is always going to be real. So, quantum mechanics can give me imaginary wave function but in the in from the wave function the probability density what we get is real.

In this figure a typical example of probability density distribution of a particle at a given time t is presented and the way we interpret this graph, probability distribution graph is following this $\rho(x,t)\mathrm{dx}$ at a particular time t this is representing area under the curve for dx interval.

So, for example here I have this distribution function for this interval and this is the area associated at a particular position A, and at position B this is the area I represent and probability of finding the particle, so this is something which I should write down, this is called probability of finding the particle at time t and in space between x and x + dx interval.

So, this is actually giving me probability of finding the particle at time t and in the space between x and dx interval that is the probability of finding the particle and this is nothing but the area. It is quite clear that because this area is larger than this area, this area near this point A is much larger than point B that is why there is a higher probability of finding the particle at position A as compared to position B.

So, this is the basic interpretation of a distribution function, probability distribution function. Now question is how we get this probability distribution function function, experimentally, we get this distribution function experimentally that something which I will discuss in the next slide.

Let us first consider a hydrogen atom problem and hydrogen atom I have nucleus here, we will not use Bohr atomic model, we will use more appropriate model for this and this is nucleus and electron. According to Bohr atomic model, electrons is orbiting like this, an electron particle is orbiting like this, but quantum mechanically we do not have any particle, so all we have is a cloud.

So, what we will do? Electrons are present like cloud this dots I am representing the density and there will be a point where there will be higher density. So, what we see is that if I consider this to be (0,0) position and if I move in space along the r direction I will see that lower density to higher density, so that is the way I am getting change in density. We see that it is more like a cloud around this nucleus and there is a higher density of cloud and the entire cloud is representing one classical particle.

The particle does not exist anymore in quantum mechanics it behaves like a wave, but still it is one single particle. So, to find out the meaning, what we have drawn here a possible probability distribution of the electron, this is the probability distribution of the electron assuming that nucleus is sitting at the (0,0) position. So, question is what does it mean by this probability distribution?

Directly it means that if I perform an experiment in one experiment I may find the particle to be present here, in second experiment I may find the particle to be here, in a third experiment I may find the particle here. So, there is a distribution, there is a possibility you can find the particle anywhere in this but there is a higher probability to finding the particle at this position as compared to this position. So, that is the meaning of this probability but in terms of measurement, in terms of experimental measurement what does it mean?

So, let us think about the thought experiment here and in this experiment let us assume that I have a device which can produce hydrogen atom, identical hydrogen atoms. Each atom if I magnify it each atom has a nucleus and its electronic cloud around it, electron cloud around this nucleus. So, I have a device which can produce identical hydrogen atom, why identical? Each experiment should encounter the same hydrogen atom or the same kind of hydrogen atom that is why identical hydrogen atom because I am going to perform experiment on each atom.

We will assume that there is a technique which which I have in the experiment, in that technique I can very precisely find out the position of the electron that also I can find out. If I can find out the exact position of the particle, electron with respect to the nucleus let us say my experiment is sensitive to find out the position of the electron with respect to nucleus, so if we do that then what will happen, if we perform that experiment, then this is one possibility that in the first experiment I have found the position of the electron with respect to nucleus is r1 at this position.

In the next experiment it is not necessary that i will get the position at the r1, position there is a possibility that I can get position something else always there is a possibility and that is the idea of quantum particle its distribution function. So, let us assume that in the second experiment I have found the electron to be at the r2 position. In the third experiment I have found r3, r3 does not need to be here, r3 can also be here, it is just an example; r3 can be here also it does not matter where r3 is, but I may get one r3 position.

Another experiment I have performed, I have got r4 position and so on. Like this way I will keep repeating the experiment and how many times I have to repeat the experiment? So this way if we repeat that experiment we will be able to find out different possible position and then what is our task? Our task is to find out how many times I have found a particular position r1, r2, r3, r4, r5, r6, r7, r8, and so on.

How many times I have found when I am repeating the experiment and how many times I am repeating the experiment? I am repeating the experiment that say avogadro number of times, 10^{23} times, many many times I have to repeat the experiment and if I repeat the experiment, I will be able to find out different position and I have to count how many times I have got that particular position.

Let us say r1, r2 and after counting what I am finding is that r1 position I have found in 10 experiments, r2 position I have found in 20 experiments, r3 position I have found in 40 experiments and so on. Like this way what we are seeing here is that these experimental counts after repetitive experiments are exactly going to show the distribution.

So, the meaning of probability distribution from an experimental viewpoint is that it is actually showing how the distribution would be, if I perform an experiment if I repeat the experiment several times that is the meaning we have. What we see is that in the experiment also maximum number of counts is associated with r4 position which is 50 counts I have got.

Similarly, in the distribution also r4 is the maximum of the distribution. Maximum of the distribution means there is a chance of getting that position many times in the experiment, so thats the primary meaning of this probability distribution function. So, probability distribution function does not tell that if I perform an experiment I will get this position directly probably distribution function does not mean that.

Probability distribution function shows that how different outcomes would be in a repetitive experiment. I can get this position, I can get this position, I can get this position, I can get this position, but finally if after repeating all these experiments if I try to count how many times I am getting the same value, same position then I will see that for this particular position I will get the maximum counts in the experiment, so that is the meaning of the entire distribution function.

So, it is sometimes very puzzling to accept that fact I am representing one particle this Psi x is a wave function of a single particle, but its meaning is related to ensemble of particle, many particles. Single particle it does not mean anything, so this becomes sometimes puzzling because I am dealing with a single particle, I am dealing with a wave function of a single particle.

But the meaning of that wave function which is carried forward through this probability distribution is actually considering an ensemble behavior. Many particles if I think of it how the overall distribution is going to be, so we have to remember this interpretation of this probability distribution.

Although I told you that probability distribution, it looks like this and this is just one example how in space probability distribution would look like and in quantum dynamics how the quantum dynamics is presented? This probability distribution should change as a function of time. So, this is at t equals 1 and this is at t equals 2 probability distribution function let us say this.

When there is a change in probability distribution function as a function of time, then only we get the quantum dynamics, otherwise if there is no change of the probability distribution as a function of time then there is no effective dynamics or observable dynamics we cannot observe the dynamics.

So, in order to have something which we call quantum dynamics, we need to have change in probability distribution, but we have to remember one thing this distribution function is representing one particle although it is representing, it has duality actually in a particular way when you think about it is representing single particle and there is a consequence for that.

On the other hand if I think about the interpretation of the wave function represented by that single particle, the interpretation is actually considering ensemble of particles, the behavior of ensemble particles what will happen. So because it is associated with single particle, total probability, and probability of finding the particle in entire space is going to be 1, because we have only one particle, total one particle I have if it is normalized.

So, if the wave function is a normalized wave function, then total probability or total probability of finding the particle in the entire position space is going to be always 1, and this is called global conservation of probability because I have only one particle in the entire space. Let us say in the in the entire cloud, in the entire sky I have only one particle which is shown, appearing like cloud and because I have only one particle if I integrate the entire space I get only one particle present in the entire space.

But this needs to be fulfilled through the fact that the wave function has to be normalized, if it is not normalized we can make it normalized and there are characteristics of the wave function which can be acceptable in quantum mechanics, we will go over it in subsequent modules but for the time being we will consider that it has to be a normalized wave function.

So, a normalized wave functions as an acceptable solution to the TDSE. Question is how do we normalize a wave function at t equals 0 and second question, so I have this function and it is evolving let us say in quantum dynamics, so the second question is that if a wave function is normalized at t equals 0 does it remain at any later time? These are the two questions which are very important in terms of quantum dynamics.

I told you that probability distribution; the total probability of finding the particle in the entire space is going to be always 1 that has to be maintained. We can try to find out how to get the normalized wave function in the beginning of the time of the quantum evolution but then question is I am going to use this wave function and plug it into the TDSE to get the solution at different time.

And when I am getting the solution question is am I still preserving the normalization because I have only one particle that is evolving and if it is not preserved it will mean that if the total probability is changing, then it mean that I am creating the particle or I am destroying the particle and that is not possible one particle is evolving through quantum dynamics.

So, it has to be always 1, no matter what we do this integration has to be always one. If we start with a normalized wave function that is a one requirement of quantum dynamics which needs to be fulfilled all the time. This is the point which we are going to clarify in the next few slides.

First we will go over how to normalize a wave function this is something which can be done very easily using the normalization condition. Normalization condition is

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx = 1$$

that is the normalization constant and will assume that at t equals 0 in the beginning of the quantum evolution, a particle can be represented by this Gaussian form.

$$\psi(x,0) = Ae^{-\alpha x^2}$$

This is a Gaussian function, its amplitude is A and it is centered at x equals 0 that is the way the function will mean. This function is centered at x equals 0. So it is maximum at x equals 0 and the maximum amplitude is A and we will assume that at t equals 0 just before the quantum evolution of the particle; particle has started, we are not observing the quantum dynamics yet we are just starting at the initial point t equals 0 the particle can be represented by this Gaussian function.

This is just an assumption one simple example it can be represented by many other ways but it is just on one example and question is if I have this wave function how can I normalize it? Obviously here A and a are real constants, and positive constants. So, first thing what we need to do is that we have to find out the density distribution function at time equal 0 is going to be

$$\rho(x,0) = A^2 e^{-2\alpha x^2}$$

and this is nothing but the density which is $\rho(x,0)$. So, I have to integrate this equation-

$$\int_{-\infty}^{\infty} \rho(x,0)dx = 1$$

$$\int_{-\infty}^{\infty} A^2 e^{-2\alpha x^2} dx = 1$$

Now this is a standard Gaussian integration, many occasions we will be using this standard integral and part of the reason why in many occasions we will see that will begin with Gaussian function because it is much easier to deal with analytically. Analytical expression, analytical integrations are available for Gaussian function and that is why we start with it so that we can understand the basic idea and then we can move forward to more complicated functions as well.

So, this is the standard Gaussian integral which will be using many occasions in this course,

$$\int_{-\infty}^{\infty} e^{-ax^2+bx+c} dx = \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}+c}$$

This is the standard Gaussian integral and we can use this we do not need to derive this one. If we do that then

$$A^2\sqrt{\frac{\pi}{2a}} = 1$$

$$A = \left(\frac{2a}{\pi}\right)^{1/4}$$

and this is the normalization constant.

So, in the end at t equals 0 we can write down the normalized wave function as this, if the particle is represented by this Gaussian function. Now in the next module, not in this module in the next module we will understand how this initial Gaussian wave packet or function will evolve. We will find out $\psi(x,t)$ in the next module, but in this class we will not get into that we will continue with this function we have shown that normalized Gaussian function should have this form. We will continue this session in the next class.