

Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-10
Particle in a box: Uncertainty Principle - Continued

(Refer Slide Time: 00:24)

Uncertainty in position

$$\langle x \rangle = \frac{L}{2} \quad \psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad \sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

$$\langle x^2 \rangle = \int_0^L x^2 [\psi_n(x)]^2 dx = \frac{2}{L} \int_0^L x^2 \sin^2 \frac{n\pi x}{L} dx = \frac{1}{L} \int_0^L x^2 \left[1 - \cos \frac{2n\pi x}{L} \right] dx$$

Integration by parts:

$$= \frac{L^2}{3} - \frac{L}{2n^2\pi^2} \left[\int_0^L x \cdot \frac{d}{dx} \left(\cos \frac{2n\pi x}{L} \right) dx \right]_{L1}^{L2} \quad u \frac{dv}{dx} = [u \cdot v]_{L1}^{L2} - \int_{L1}^{L2} v \frac{du}{dx} dx$$

$$= \frac{L^2}{3} - \frac{L}{2n^2\pi^2} \left[L - 0 - \int_0^L \left(\cos \frac{2n\pi x}{L} \right) dx \right] = \frac{L^2}{3} - \frac{L}{2n^2\pi^2} [L - 0 - 0]$$

$$= \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$

$$\sigma_x = \sqrt{\frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - \frac{L^2}{4}} \quad \sigma_x = L \sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}} \quad \sigma_x = \frac{L}{2n\pi} \sqrt{\frac{n^2\pi^2}{3} - 2}$$

This is where we stopped in the last module. We worked out an expression for uncertainty in position and that turns out to be L^2 by 3 - L^2 by $2n^2\pi^2$. Well to be very honestly not worked out the uncertainty in position yet. What we have worked out is the average value of x^2 which is the first in the linear combination under square root sign in the expression for uncertainty in position.

Saving grace to already know the average value of x from previous model that is $L/2$. Now let us work out the expression under the square root sign average value of x^2 minus square of the average value of x this is what we need to work it out and then put under square root sign the final answer that we get is L multiplied by square root of $1/12 - 1/2n^2\pi^2$. I strongly recommend that all those were taking this course should work this out by themselves.

Because it is impossible to understand it completely or we convinced just listening to me and seeing me work this out especially as you not writing on a board we are using electronic media.

please workout this expression by yourself. Then only I think you are going to be convinced. Ok. So crux of the matter is we have this expression for uncertainty in position that we had looked for. Now let us see expression for uncertainty in linear momentum and that is going to be much easier than uncertainty in position.

(Refer Slide Time: 02:04)

Uncertainty in momentum

$$\langle p_x \rangle = 0 \quad \psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad \sigma_{p_x} = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} \quad \therefore \sigma_{p_x} = \sqrt{\langle p_x^2 \rangle}$$

$$\langle p_x^2 \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \cdot \hat{p}_x^2 \left[\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \right] dx \quad \hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \quad \hat{p}_x^2 = -\hbar^2 \frac{d^2}{dx^2}$$

$$\langle p_x^2 \rangle = -\hbar^2 \int_0^L \frac{2}{L} \sin \frac{n\pi x}{L} \cdot \frac{d^2}{dx^2} \left[\frac{2}{L} \sin \frac{n\pi x}{L} \right] dx = \frac{n^2 \pi^2 \hbar^2}{L^2} \int_0^L \frac{2}{L} \sin \frac{n\pi x}{L} \cdot \left[\frac{2}{L} \sin \frac{n\pi x}{L} \right] dx$$

$$= \frac{n^2 \pi^2 \hbar^2}{L^2} \quad \therefore \sigma_{p_x} = \frac{n\pi\hbar}{L}$$

=1

This is the expression that we have got and now uncertainty in momentum. What is it? Let us see. Well we already know that out of these two terms under the square root that we need to find for uncertainty in momentum. We already know that average value of p_x is actually equal to 0 so then this expression becomes little simple it turns out to be square root of average value of p_x square. Please do not think that the square root of average value of p_x square, square root and square will take care of each other and it will turn out to be average value of p_x it will not.

Remember the task that I gave you in the last module take a set of numbers workout the average of squares and then work out the average of numbers themselves take square and you see that they are not the same. So, it has to be written as square root of average value of p_x square is a root mean square quantity analogous to what we studied when we talked about say speeds of gas molecules in kinetic theory.

There we talked about root mean square velocity is it not this is also a root mean square expression. Do not think that the square and square root will take care of each other. They will

not but the good thing is all we need to do is we need to find this average value of p^2 . How do you do it like this? We know already how to find expectation value so we write the wave function and in this case we are working with the real wave function.

So $\langle p^2 \rangle$ is equal to $\int_0^L \psi^* \hat{p}^2 \psi dx$ divided by $\int_0^L \psi^* \psi dx$. Because you are still have to take a square root. So, what is \hat{p} that we know $\hat{p} = -i\hbar \frac{d}{dx}$. What is the operator for p^2 that would be making the same operator operate twice that is the meaning of operator p^2 .

So, make it operate twice what do you get \hbar^2 multiplied by \hbar^2 that gives minus \hbar^2 and then $\frac{d^2}{dx^2}$ so this might ring a bell actually because when I talk about Schrodinger equation because something very similar to this remember the Hamiltonian operator the first term kinetic energy operator was minus \hbar^2 by $2m$, why? Because kinetic energy is p^2 by $2L$, so on our discussion is in sync.

So, \hat{p}^2 operator is minus $\hbar^2 \frac{d^2}{dx^2}$. So, now what we have to do is to take this expression for the operator plug it in the expression for the plug into the integral. Let us do that this is what we have minus \hbar^2 comes out of the integral sign $\frac{d^2}{dx^2}$ root over 2 by $L \sin n \pi x$ by L . I am intentionally not taking this root 2 by L and this root 2 by L out because if I can keep the wave function when there will I know what the integral is the limits are 0 to L integral for $\psi^* \psi dx$ is equal to 1.

Now and also the good thing is here, is we have a sine function. So, what happens when I take second derivative of sine I get back the same sine function. You only think that here is that you have to take care of $n \pi$ by L . For every differentiation this $n \pi$ by L will come and we can take it outside the bracket so this is what we get $n^2 \pi^2 \hbar^2$ divided by L^2 integral 0 to L root over 2 by $L \sin n \pi x$ by L multiplied by root over 2 by $L \sin n \pi x$ by $L dx$.

What just happened? Where did I get n square and pi square and L square well because remember we differentiated twice. So first derivative of sin kx is equal to k multiplied by -k multiplied by cos kx right that is why minus sign also came out the first differentiation and that took care of the minus sign that was already there and then when you differentiate cos kx function again one k comes out, so that is why you get k square outside and you get back your sin kx so far so good.

What about this integral as you said a few seconds earlier this integral is equal to 1 because we are working with a normalised particle in a box wave function, this is equal to 1. So the expression for the mean of square of Linear Momentum turns out to be n square pi square h cross square divided by L square. What is Sigma px? Sigma px is just a square root of this, whereas find out it comes out to be a very simple expression n pi h cross by L. So earlier, we have determined the uncertainty in position now, we have determine uncertainty in momentum.

(Refer Slide Time: 07:35)

Uncertainty Principle

$$\sigma_x = \frac{L}{2n\pi} \sqrt{\frac{n^2\pi^2}{3} - 2} \quad \sigma_{p_x} = \frac{n\pi\hbar}{L}$$

$$\sigma_x \cdot \sigma_{p_x} = \frac{n\pi\hbar}{L} \cdot \frac{L}{2n\pi} \sqrt{\frac{n^2\pi^2}{3} - 2} = \frac{\hbar}{2} \sqrt{\frac{n^2\pi^2}{3} - 2}$$

Even for the smallest value of n, $\sigma_x \cdot \sigma_{p_x} > \frac{\hbar}{2}$



Then next task is to multiply them together multiply them with each other and see whether uncertainty principle is satisfied by the system of particle in a box that we are talking about. Sigma x remember is L by 2 n pi square root of n square pi square by 3 - 2 sigma p x is equal to n pi h cross by L just multiply them cricket this is what we get. What happens here L and L cancel each other n pi and n pi cancel each other so you are left with h cross by 2 outside the square root sign.

Inside the square root sign you have n square pi square by 3 - 2 this is what you get. Let us try to see whether we can get a simpler expression here. What is the value of the n square pi square by 3? For the smallest value of n, what is the smallest value of n? Smallest value of n is 1, we are talking about particle in a box. So, if the smallest value of n is 1 then what is the value that we expect here? Pi square Pi is 3.142 in fact so square root of that is going to be; square of that is going to be more than 9.

You do not need to remember exactly so more than 9 divided by 3, what is that? That is more than 3 so more than 3 - 2 is more than 1. So, what you have under the square root is a real number which is more than 1. Does not that prove that for any value of n this product is always going to be greater than h cross by 2? You see in this expression h cross by 2 is multiplied by this quantity under square root which we are shown is always more than 1.

That is why the product of uncertainties is of position and Momentum for particle in a box and turns out to be always greater than it was h cross by 2 which is nicely in agreement with uncertainty principle.

(Refer Slide Time: 10:04)

Uncertainty Principle

$\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \quad \psi = e^{\pm ikx}$ <p style="text-align: center;">Linear momentum, $p_x = \pm k\hbar$</p> <p style="text-align: center;">Position, $x = \text{any value}$</p> $\psi = Ae^{ikx} + Be^{-ikx} = \cos kx \text{ or } \sin kx$	$\hat{p}_x \psi = \frac{\hbar}{i} \frac{d}{dx} e^{\pm ikx} = \pm k\hbar \cdot e^{\pm ikx}$ <p style="text-align: center;">Sign: Direction of motion</p> <p style="text-align: center;">Linear momentum: Two values, $p_x = \pm k\hbar$; Position: Maximum probability occurs periodically</p>
$\psi = \sum_j A_j e^{ik_j x} + B_j e^{-ik_j x} = \sum_j C_j \cos k_j x \text{ or } \sum_j C_j \sin k_j x$	<p style="text-align: center;">Linear momentum: Highly uncertain; Position: Well defined</p>

NPTEL

So we have demonstrated that uncertainty principle is obeyed for a particle in a box. Remember non conformity with Uncertainty Principle sounded the death Snell of the Bohr Theory. So, it is

comforting to know that the first system that was studied using the wave mechanical treatment of Schrodinger conforms with Uncertainty Principle. So, a very major problem that was there in Bohr Theory is not there at least so far.

So, next question you want to ask you that is this a specific case is the only for particle in a box uncertainty principle is valid or do we expect for the mechanical treatment? But it is not going to be it is going to be valid for everything. Is there a General way in which we can look at Uncertainty Principle itself? So this discussion might sound to be a little bit of digression because after all, the topic under which we are performing discussion is particle in a box, but this digression you can call it digression is definitely worth it.

So, bear with me. So, let us see, let us understand Uncertainty Principle a little bit better. To do that let us revise what kind of wave functions we have for your p_x . So, p_x again, you know is \hbar cross by i d/dx and good wave function for this Ψ equal to e to the power plus minus ikx the wave function is an imaginary wave function but it is important to note that the eigenvalue is not imaginary, eigenvalue is definitely real because when you differentiate e to the power plus minus ikx with respect to x you are going to get plus minus ik multiplied by the same function.

So that i and this i are going to cancel each other. So, p_x operating on Ψ gives you plus minus $\hbar k$ cross e to the power plus minus ikx we have touched upon this in one of the previous modules, but let us make sure that once again, everybody is on the same page. So this as you see is an eigenvalue equation with e to the power plus minus ikx as eigen function, is it normalized? We are not try to normalise yet maybe normalised will not be normalised. Let us not worry at the moment.

What is more important is that it is eigenfunction of the linear momentum operator and the eigenvalue is a real eigenvalue $\hbar k$ cross. Well, we were written it plus minus $\hbar k$ cross. What does it mean? It means that the linear momentum associated with this system associated with wave function is plus minus $\hbar k$ cross, plus minus $\hbar k$ cross is the value of the linear momentum. No Surprise Root over 2 $m v$ divided by \hbar cross that would better be the linear momentum.

Now see what does this plus or minus sign signify? $\hbar k$ cross is magnitude understand fine? Plus means that direction of motion is along positive x and minus means the direction of motion is along negative. Sign of the wave function specifies the direction of the motion of the particle remember we are right now talking about one dimensional space, right? So if it is just plus minus ikx then direction of motion. If it is plus ikx class momentum is define very, very well. If it is minus ikx then you know you have 0 and uncertainty in momentum.

Let us say I am not saying plus minus let me say it is a $+ ikx$ then what is the value of linear momentum $+\hbar k$ cross one value no deviation this is not average value every time you do this experiment you are going to get this eigen value $\hbar k$ cross. So, for this wave function e to the power ikx no matter whether sign is plus or minus momentum is defined very nicely is defined precisely. What about position? Position x can take up any value because you work out the expectation value of position also here what will it be?

Position is x multiplied by the wave function exact operator x multiplied by wave function what you get? You get x , x is a variable. So, the uncertainty in position is infinite is defined with boundaries. So what we see here is that the moment the momentum is specified precisely in the wave function. Position becomes infinitely answered this is the philosophy of uncertainty principle. But let us go ahead and before we make that statement.

Let us see what happens if we can get a situation where position is better define what happens to your ah Momentum there. To do that let us use this wave function very familiar with this wave function $\cos kx$ $\sin kx$ is sort of box like wave function that as we know can be written as a linear combination of exponential imaginary terms. Let us say we chosen A and B in such a way that we get either $\cos kx$ or $\sin kx$.

Actually the diagram is that we are going to show you we are going to use $\cos kx$ little more convenient but let us not forget $\cos kx$ and $\sin kx$ are basically same. The only difference is the phase shift right where $\cos kx$ is equal to 0 $\sin kx$ equal to 1 but the shape is the same. See that we have to give an offset $2x$ then \sin can become \cos . So let us say we work with this wave function. If this is wave function then what does it mean?

It means that your linear momentum either can be ik or $-ik$. So there is little bit of uncertainty in linear momentum two values are there p_x can be plus $\hbar k$ or minus $\hbar k$ sorry, I said ik that was the mistake plus $\hbar k$ or minus $\hbar k$. What about position? Position we can understand position while looking at the probability. Probability is mod of $\Psi(x)$ square, so if you plot this function mod of $\Psi(x)$ square here is $\Psi(x)$ square.

What do we get? We get some regions of more a greater probability density, some regions of zero probability density some points at zero probability density. So if you just take a small slice dx then in this position, and this position and this this this and wherever there is a maximum in this plot of $\Psi(x)$ square you get maximum probability of occurrence. So that is the position. So what we say is that position gets a little better defined at least we can say that the particle is more probable to be here and here and less probable to be here.

Earlier position could happen anything all values of x had the same probability when you took one of the exponential terms. So, we demonstrated that if we introduce a little bit of uncertainty in momentum position becomes more precisely defined. Let us now go way further let us take a large number of e^{ikx} and e^{-ikx} for different values of k and let us add them up like this. Let now work with sum over j $A_j e^{ik_j x} + B_j e^{-ik_j x}$ coefficient A_j and B_j are chosen in such a way that you get $C_j \cos k_j x$ that kind of a wave function.

Right now we are just making wave function so everything is in our hands. What happens then? What happens to Momentum now? There are many values that j I have not saying how many j are there. May be there are 1 lakh values of j in the expression that I am going to show you have taken a combination of about 10 values of j . So, momentum has become more uncertain depending on how many values of j we are working with? k_1, k_2 so what is momentum, $\hbar k$ can have $+\hbar k_1$ or $-\hbar k_2$ so on and so forth.

Depending how many terms we have taken? So when we take this linear combination we get this kind of a wave function where your position your Momentum has become significantly more answered. What about position? To get position once again we are going to take square of this

sum. It is easier. If you take a square of this sum over j $C_j \cos k_j x$ square we when we do that we get a plot like this. Now see what has happened.

Now the other positions here there is a local maximum of probability density versus x so small. Same here the clear global maximum of $|\Psi|^2$ appears at this position of x where all the cosine functions are in step. For x equal to 0 for all cosine function value is 1 the maximum value that is why here all this cosine wave are in step. As you go further what happens if the phase difference between all right the waves start getting out of phase?

This is the phenomenon that is made use of in things like Fourier transform, time-domain Spectroscopy as well. You have waves of different frequency at one point they are all in step then they start getting out of step, you get destructive interference. So what you get finally is that your linear momentum in this case is highly uncertain as you have said position gets reasonably well defined. For the record this kind of situation where we have taken a large number of waves that are been step at a particular point this is called a wave packet.

And one can even experimentally generates wave packets and wave packet dynamics is something that has been of interest to physical chemist, spectroscopist, physicist, Quantum chemist for several decades now and then provide very important information about how things proceed in ultra short time scale in systems. We have discussed this in more detail in the NPTEL course on ultrafast Spectroscopy in chemistry that was offered last semester.

Whoever is more interested can have a look at those lectures. But for now what you got is at the moment we made linear momentum uncertain we generated a wave packet which had significantly better significantly more precise information about location of the particle. So what we have shown here is that in Uncertainty Principle if linear momentum is well define position becomes ill define automatically.

In situations where position is better defined Linear Momentum becomes ill define automatically. So the wave mechanical treatment here of Schrodinger is absolutely in line with uncertainty principle and using it we also need to realize that uncertainty principle is really the

threshold of nature beyond which we cannot go. Here let me knowledge my teacher who is Rupendranath Banerjee of Jadavpur University, who actually talk with this expression threshold of nature when I was in class eleven.

That is because of greater teachers like them students like me learnt certain things that perhaps would have not understood so well, otherwise. So it is not possible to make a better instrument? Do you think that we will make better instrument and will determine linear momentum and position correctly, it is not just going to happen is not about instruments. It is an inbuilt law of nature that in microscopic world position is well defined Momentum cannot be and vice versa. And it is not restricted to just position and Momentum also it is a feature that you see for all conjugate properties energy and time for example.

(Refer Slide Time: 24:04)

Uncertainty and Commutation

$$\sigma_x \cdot \sigma_{p_x} > \frac{\hbar}{2} \quad \hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \quad \hat{x} = x.$$

$$\hat{x} \hat{p}_x \psi = x \cdot \frac{\hbar}{i} \frac{d\psi}{dx}$$

$$\hat{p}_x \hat{x} \psi = \frac{\hbar}{i} \frac{d}{dx} [x \cdot \psi]$$

$$\hat{p}_x \hat{x} \psi = \frac{\hbar}{i} \left[x \cdot \frac{d\psi}{dx} + \psi \right]$$

$$\therefore \hat{p}_x \hat{x} \psi - \hat{x} \hat{p}_x \psi = \frac{\hbar}{i} \psi$$

$$(\hat{p}_x \hat{x} - \hat{x} \hat{p}_x) \psi = \frac{\hbar}{i} \psi$$

$$[\hat{x}, \hat{p}_x] = i\hbar$$

Operators do not commute: Properties cannot be determined simultaneously

Now since you talking about uncertain let us talk little more about the workings of quantum mechanics and let us make this statement and when operators do not commute properties cannot be determined simultaneously, what is it supposed to be, commutation means you have 2 operators let us say x and p x. You make p x operate first as a wave function you get another function make x operate on it to get some value.

Then we were; invert the sequence of operation. If you get the same quantity then x hat dot p x hat - p x hat dot x at would be equal to 0 which means the commutator is equal to 0 we will see

it right now. So, these are the wave function we are working with let us do $\hat{x} \hat{p} \Psi$, which means when you write like this \hat{p} operate on Ψ first then \hat{x} operate on it. So $\hat{x} \hat{p} \Psi$ what is it? It is x multiplied by \hbar cross by $i \frac{d}{dx} \Psi$.

Now we are not using particle in a box wave function. It is a General statement x multiplied by \hbar cross by $i \frac{d}{dx} \Psi$. Let us do the commutation, let us invert the sequence of operation $\hat{p} \hat{x} \Psi$ what would that be? \hat{x} operating on Ψ is just x multiplied by Ψ . So now your to make this is \hbar cross by i , \hbar cross by $i \frac{d}{dx}$ operate on the product of x and Ψ . You all know what $\frac{d}{dx} (uv)$ is, it is this $\hat{p} \hat{x} \Psi$ gives us \hbar cross by $i \frac{d}{dx} \Psi + \Psi$ very simple I am not going to do this time.

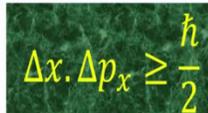
So now what is $\hat{p} \hat{x} \Psi - \hat{x} \hat{p} \Psi$ it is not zero it is \hbar cross by i and we can write it is an eigenvalue equation. We can write it like $\hat{p} \hat{x} \Psi - \hat{x} \hat{p} \Psi$ is equal to \hbar cross by $i \Psi$. In fact this operator is often written like this that \hat{x}, \hat{p} in third bracket that means the commutation, commutator of \hat{x} and \hat{p} that is equal to $i \hbar$ cross. So what we say is that it is not equal to zero.

And then the postulate of quantum mechanics says that when operator is not commute properties cannot be determined simultaneously. We will some examples of operators that do commute in the assignment. So this is what we have discussed so far. We have considered a very simple model of particle in a box. We started with particle in one dimensional box and then we extend it D2 dimensions and D3 dimensions.

(Refer Slide Time: 27:10)

Particle in a box: Take home messages

- Schrodinger equation is **exactly solvable**
- Boundary conditions: **Quantization**
- More **nodes** in wavefunction, higher is the associated **energy**
- Eigenfunction of **linear momentum** operator
- **Simple** model, finds **application** in Chemistry
- Increase in dimensionality: **Separation of variable**
- **Symmetry** and **degeneracy** go hand in hand
- Beyond 3D functions
- Testing ground for more **sophisticated treatment**


$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$$



And from this very simple model we will learn so many things last 4 module I think we have even learnt how we can see that wave mechanical treatment in general is in keeping with Uncertainty Principle. Sometimes students complain that whenever we try to study Quantum Mechanics and Quantum chemistry this particle in a box model keeps coming back and taught many times there is good reason for it. In fact even in this course we are going to refer to the particle in a box model once again, when we talk about the variation principle.

This provides a good testing ground for sophisticated treatment as we have said. But for now we are done with that discussion of particle in a box where the particle is confined within a box where the well the walls are infinitely high. Potential energy outside v is equal to infinity. Let us now move on to a variant and let us now finally take up a question what happens if the potential barrier is not infinite.

What happens if the potential barrier is finite? When I put it like this perhaps it sounds like a question that has a reason out of just curiosity from doing so much of theory that is not completely true. In fact this question arose out of an experiment. Very early days of quantum mechanics early 20 century it was found that will people worked out the and not taking the name of the people workout itself if it involves people like a Gemo and Rutherford and others stalwarts.

The kinetic energy of Alpha particle emitted from radioactive nucleus was worked out. And the potential barrier immediately outside the nucleus was also worked out and it turned out that will first of all will that potential is fine. I turn out that the energy kinetic energy of Alpha particle is actually lower than this potential barrier. So, now the question came how does this come? It appears that when the potential barrier is finite. The particle can somehow come out of that. Overcome the barrier even though its energy is less than the energy associated with the barrier.

How does it happen? Question of finite potential energy barrier arose from here and that is what we will discuss in the next module.