Quantum Chemistry of Atoms and Molecules
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Lecture-9
Particle in a box: Uncertainty Principle

In the last module we have said that we are going to discuss what happens when there are finite variants, but then I had a second thought and so in this module let us see what happens or how uncertainty principle is manifested by this wave function that we are now familiar with in particle in a box.

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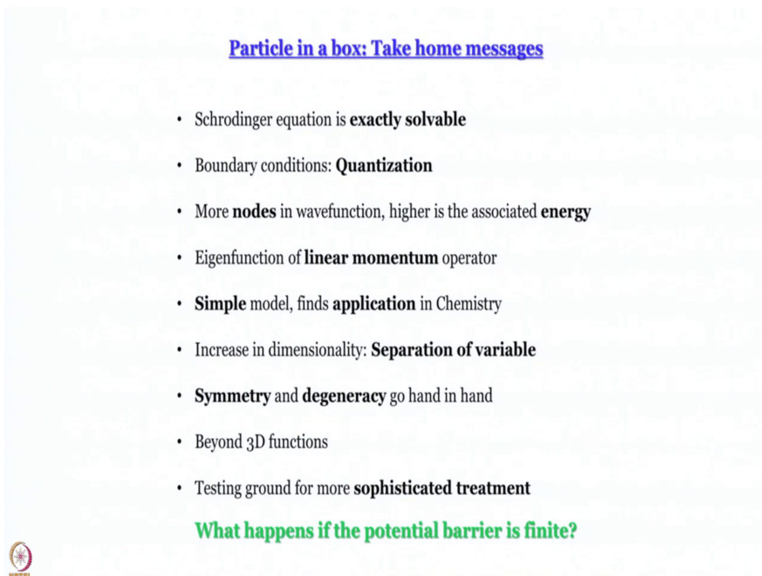

Just to recapitulate this are the things that we have learnt so for. The Schrodinger equation is exactly solvable. Boundary conditions lead to quantization this is the most important lesson that we have got in the last three modules and the other useful rule of thumb that has a reason is that more nodes we have in the wave function higher is the associated energy. This is going to come handy time and again, especially when we talk later about atomic and Molecular wave function.

Then we talked little bit about eigenfunction of the linear momentum operator. We are going to revise that once again today and the reason why particle in a box is interesting. And the reason why it is taught in chemistry is that even though it is so simple it starts as it act as or serves as a very good first approximation for some rather complicated chemical systems as we have seen already. One more lesson that we got is that when we have more than one dimension then we have to perform separation of variable like what we are done between spatial and temporal variables earlier.

This is again going to come very handy when we talk about hydrogen atom. Symmetry and degeneracy go hand in hand. This lesson goes a long way in understanding systems like d-orbitals degenerate in a bare metal Ion but get classified into two groups inter territorial and octahedral field as split further upon the things like John-Teller distortion. One way of thinking of it is that we are going from more symmetric to a less asymmetric system progressively and that leads to decrease in degeneracy.

As we have seen in particle in two dimensional box the moment we go from a square box to rectangular box level that will be generated earlier no longer remains so. Also, we talked about 3 dimensional box we understood that we need a 4 dimensional function xyz for the dimensions of the box and the dimension of the wave function itself. How is one supposed to draw it? We were exactly the same problem later on when you talk about things like orbital's, but let us wait until then

So to conclude this part of the discussion particle in a box model has provided ground for provided testing ground for more sophisticated treatment that we are going to see once again later on when talk about approximation method. And the question is stopped within the last module is at what happens if the potential barrier is finite instead of being infinite. But we said in this module we are taking a rain check on that and rather than we are going to focus on something that we all know very well, but perhaps I have do not understand all that well the Uncertainty Principle.

The product of uncertainties in Position and Momentum for example has to be greater than or equal to h cross by 2. Let us see how this is manifested nicely using the wave functions of particle in a box and then we will diverse a little bit and we will talk about how we will talk little more about general aspects of Uncertainty Principle, so here goes. Now we have already learnt what the expectation values of position and linear momentum are for particle in a box for nth level.

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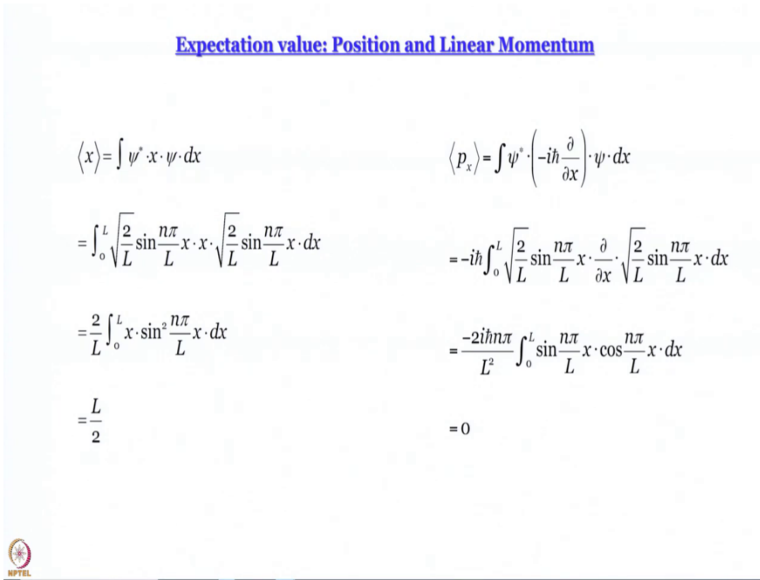

For position no matter what n is, the expectation value is L by 2 that mean if you perform a large number of experiments, we are going to find that the average of this experiment is going to lead to L by 2. Let us not forget that in each experiment to find we expect to find a different value of position it is just that the average values L by 2 and very soon we are going to define what average value means in a little more formal way.

And average value of Linear Momentum is 0, does it mean the particle is not moving not really, what it means is that the probability of the particle moving towards positive x direction is exactly equal to the to that of the particle move negative x direction. So, average value of momentum is 0. But before we go any further let us make sure that all of us are on the same page as far as the definition of average and standard deviation uncertainty in these things are concern. Then you are going to use. So, let us go back and let us talk about little bit of statistics.

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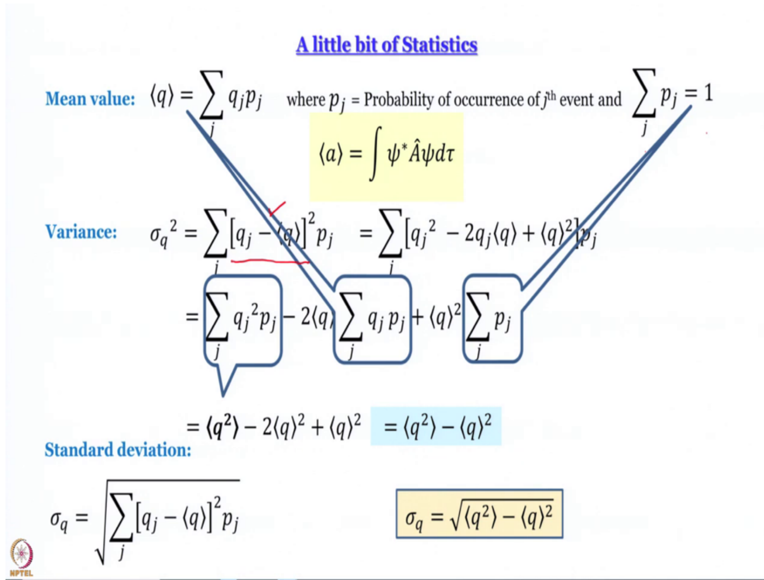

What is the meaning of mean value? Well we have learnt how to calculate mean value when we are in class 6 or class 7 maybe or may be earlier but a more formal definition using probability is this. The mean value is summation of j q j multiplied by p j which means to perform a large number of measurements of the quantity q? For each measurement we get some value. So, j is the identifier of the number of measurement. For first measurement j equal to 1 second j equal to 2, 12 measurement j equal to 12 and so on and so forth.

So for every time I get some value and then let us say we will perform a large number of measurements so 10 to the power 10 number of measurement. Then what will happen is not as for every measurement will get a different value. Some values will occur more time some values in less time. From the number of occurrences we can figure out the probability of a particular value q j to occur. Probability we might remember is nj divided by sum over j where n j is the occurrence of the jth event.

Probability is n j number of occurrence of jth event divided by sum over j n j that means the total number of measurements total number of occurrences. Show the average value q in angular brackets is equal to sum over j q j multiplied by p j this is exactly the same thing that you have learnt in school. If you have; if you make a measurement three times, I get 5 twice I get 7 once I get 2 what is the average?

Multiply each value by the number of occurrence sum them up and divide by the total number of occurrences, basically the same thing that we have written here pj there is probability of occurrence of the jth event and it replaces the j perhaps that sum over j p j has to be equal to 1 total probability must is equal to 1 and it follows quite easily. You keep on adding all the probabilities to get sum over j n j divided by sum over j which is equal to 1.

Now let us define something else. Let us define what we have called the expectation value. Expectation value in quantum mechanics of some quantity a is given by integral Psi star A Psi A hat Psi d tau. So does this expression and this expression do they mean the same. Actually they do, why? Because we can think that for every measurement of using and operator means using a particular measurement right doing a particular measurement.

For every experiment you make this operator operate on Psi you get some value. So, that will come eigen value equation for that measurement. So what will you be left with? Aj multiplied by Psi star Psi. So we add large number of that measurement. You get an integral of this sort. So essentially the operator operating on Psi star Psi that is what the average value of expectation value is this particular aspect is discussed very nicely in Atkins physical chemistry book. I recommend that we go through it and get our idea clear about expectation value is.

Of course wave function is not normalized we have to normalize it also by dividing by integral Psi star Psi this expression that have written is valid only for your normalised wave function in our assignments we do have some problems where we are required to normalise wave functions and find expectation values. Once we work them out I think will be very clear about this, let us move on. Right now we are concern not only with the mean value but also with uncertainty.

So, what is the meaning of uncertainty? Uncertainty is represented by a statistical quantity called standard deviation. And to arrive at standard deviation it is better to talk about what is called variance first. Variance is defined as sum over j q j - average value of q whole square multiplied by p j and it is written as Sigma q square why because ultimately will going to work with square root which is standard deviation.

So, let us make sure you understand what we have written here. Let us forget the summary for the time being let us only focus on what is there inside the bracket? Let us only focus on this part q j – q. So, q j – average value of q what is that? For every measurement the Jth measurement how much does the value differ from the average value that is q j minus mean value of q. Suppose I do summation of this q j minus mean value of q.

What do I expect to get? Let us say I do something like this sum over j q j - Mod well average value of q, excuse my bad handwriting especially as I am using stylus. Well we can also write p j here. Because you are performing large number of measurement we should write probability. So what we get is the mean value of deviation. What do we expect this to be, for a good distribution let us say I draw something like this. This is the mean value.

That is going to remain invariant for all measurements. On x axis I have j on y axis I have q j. What do I expect for one measurement I should get something like this for the next measurement I might get something like this and another measurement that it might be like this, this might be like this and so on and so forth. For large number of measurement q j - average value of q for any value of j is this. It can be positive it can be negative also. So, this summation we can expect that is going to be 0 for a good distribution of data that summation is going to be 0. But then that is going to be 0 for all measurements provided we have performed a large number of measurements so it is useless.

That is why we work with the square of it. How does it help if I make a square of it then this quantity let us say square of it is here and now use bigger circles? This negative quantity its square will also be positive. This will be positive this one will also be positive this will also be positive and I am I showing you that all divisions are less than 1. This is positive this is also everything is positive.

So, when I do this summation now, what do I get, I get a sum of all this positive quantities essentially the area under curve. So, that is why it is better to work with sum of squares rather than the deviations themselves. Let me erase this so that it looks a little neater. Now we all set I hope you understood what the significance of variances is. Variance would give me a positive number is a sum of positive numbers and smaller the variance better is; better it is.

I mean thinner is the spread but then it is still the square of the deviations want to come down to square root. So, to do that let us expand this. Here q j - average value of q whole square is of the form of a - b whole square that anybody can see very clearly. You may know that a - b whole square is equal to a square - 2ab + b square, so let us write that what will be sum be the summation over j will be summation over j q j square minus 2 into q j multiplied by average value of q plus average value of q square whole thing multiplied by p j right.

Now the summation of sum, well summation of a linear combination is a linear combination of summations that is very easily understood instead of writing sum over j q j square - 2 q average value of q plus average value of q square multiplied by p j. I can write it as sum over j q j square p j – 2 sum over j q j into average value of q and when I do that average value of q is a constant quantity so that average value can come outside the summation.

And the third term will be again since square of average of q is constant quantity can come out and the third term will be square of average value of q multiplied by sum over j p j let us write it, this is what it is, sum over j q j square p j comes from the first term here -2 average value of q the constant quantity will come outside the summation sign. Average value of q multiplied by q j multiplied by p j plus again square of average value is also constant quantity come outside the summation square of average values of square of means multiplied by sum over j p j.

Now see we can simplify this without much of a hassle because we have defined already that sum over j q j p j is equal to the mean value of q. So, second term immediately becomes - 2 mean value of q multiplied by mean value of q or in other words minus 2 into square of the mean value of q what about the third term? Sum over j p j equal to 1 so the third term reduces to square of mean value of q. What about the first term? The first term is sum over j q j square p j.

Now look at this definition of mean value of any quantity that it is sum over j q j multiplied by p j p now instead of q if I use q square then the summation would be sum over j q j square p j and that is exactly what we have here. So this turns out to be the mean of squares of q. The difference between this and this is to be understood. What we have here is square of means. What we have here is mean of squares. They are not one and the same. It is trivial for us to workout take any set of numbers 2 3 5 6 7 why we eliminate 4; 2 3 4 5 6 7 work out the mean and take it square.

On the other hand take squares of each numbers and work out the mean of these squares of numbers. They are not going to be the same ok and that forms the basis of the definition we are hearing. So now let us write the expression for sigma q square what does it reduces to. The first term reduces to mean of squares of q. Second term reduces to minus 2 square of mean value of q. Third term reduces to square of mean value of q.

So, we are going to get mean of q square - 2 multiplied by square of mean value of q plus square of mean value of q of course - 2 + 1 is equal to -1 so this reduces to a very simple expression difference between the mean of squares and square of mean that is variances. Standard deviation is the square root of variance so that then turns out to be square root of mean of q square minus. Square of mean value of q. So, that is what we have arrived at something that is pretty well known and one can study this from any textbook Macquarie and Simon is physical chemistry textbook that has discussed it in some details one can actually look at that.

So now the stages set for us to go into the study of; to understand. What is the uncertainty? Uncertainty now means and deviation in position, what is the uncertainty in momentum linear momentum for a particle in a box? I think what will do it will talk about uncertainty in position and then will take a break in the next module perhaps we you are going to talk about uncertainty in momentum and continue from there.

Let us see depends entirely on how much time you spend on the next part of the discussion. What is uncertainty in position by the definition that we have just constructed?

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Uncertainty in position

$$\langle x\rangle = \frac{L}{2} \qquad \psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad \sigma_x = \sqrt{\langle x^2\rangle - \langle x\rangle^2} \qquad \cos(2\theta) = 1 - 2\sin^2\theta$$

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

Integration by parts:

$$\int_{L1}^{L2} u\frac{dv}{dx}dx = [u.v]_{L2} - [u.v]_{L1} - \int_{L1}^{L2} v\frac{du}{dx}dx$$

$$= \frac{1}{L}\int_0^L x^2 dx - \frac{1}{L}\int_0^L x^2.cos\frac{2n\pi x}{L}dx$$

$$= \frac{1}{L}.\frac{L^3}{3} - \frac{1}{L}.\frac{L}{2n\pi}\int_0^L x^2.\frac{d}{dx}(sin\frac{2n\pi x}{L})\, dx \; = \frac{L^2}{3} - \frac{1}{2n\pi}[(0-0) - 2\int_0^L x.sin\frac{2n\pi x}{L}\, dx\,]$$

$$= \frac{L^2}{3} + \frac{1}{n\pi}\left[\int_0^L x.sin\frac{2n\pi x}{L}\, dx\right] \qquad = \frac{L^2}{3} - \frac{L}{2n^2\pi^2}\left[\int_0^L x.\frac{d}{dx}(cos\frac{2n\pi x}{L})\, dx\right]$$

Uncertainty in position is square root of the difference between mean square position and square of mean position. Out of these two quantities we know one already, we know that we mean position which is this mean value of x for particle in a box is L by 2 that is established previously already. Now let us work out what is this average value of squares that will take a little bit of time and when to use integration in parts since we do not know who is there on the other side of the camera, what is the level of mathematical preparation? I am going to go slow in this part and we are going to show you every step of this.

Actually used integration by parts already, but that time I have perhaps I have went little fast let us makeup for that by showing every step in this one derivation, later on when we use integration by parts, I am going to jump steps. So, average value of square x square is equal to 0 to L x square multiplied by this square of Psi nx dx this is from the same expectation value that we have got that we operate here is x square which simply means multiplied by x square is a simple as that.

To go further we are going to use the expression for the wave function and this is what it is Psi n of x is equal to root over 2 by L multiplied by sin n Pi x divided by L this is something that we know very well already. Let us plug in the expression then this is what we get 2 by L with Psi square right. So, since Psi square root 2 by L multiplied by root 2 by L - 2 by L comes outside integration integral 0 2 L x square sin square x divided by L dx.

Now when we have an integration like this then usually we like to simplify it by going from the square of trigonometric term to something that does not have a square and the formula that one can use very easily in this case and once again going back to class 11 mathematics is formula that we want to use is cos of 2 theta is equal to 1 - 2 sin square theta I think all of us would actually know this formula cos 2 theta equal to 1 - 2 sin square theta.

So what is sin square theta then sin square theta is not very difficult to see Is half multiplied by 1 - cos 2 theta so here what is theta? Theta is n pi x by L so by substituting we get something like this. The integral becomes integral x square 1 - cos 2 n pi x by L this was n pi x pi by L so 2 n pi x pi by L and there is a half outside that half has cancelled this 2 in the numerator. So, this is what we have got.

Now let us simplify this a little bit will write it as a linear combination of two integrals. First one is very simple 1 by L integral x square between limit 0 and L second one is -1 by L integral 0 to L x square multiplied by cos 2 n pi x by L dx. What I can do is, work out the first one quickly that is very simple I do not even have to say x square integrates to give you L cube by 3 between limit 0 and L and then of course in the next step L cube by L will be written as a square.

This first integral essentially becomes L square by 3. What about the second one? We write the second one as minus 1 by L 2 n pi multiplied by integral 0 to L x square d dx of sin 2 n pi by L dx. Now why did you do that? First of all it is convince our self that this is correct. What is d dx of sin 2 n pi x by L? we except 2 n pi by L outside we do not have it that is why we have written L by 2 n Pi that part is fine. But why do we have to write it in this manner in the first place because formula for this integration by parts is this.

Integral well since you doing a standard integration written the formula for standard integral also well not standard definite integration we are use the formula for definite integral as well integral between limits L1 and L2 u dv dx into dx right dv dx that is why we have to write it as dv dx, u into dv dx into dx is equal to product of u and v substituting the limit L2 minus product of u and v for the limit in L1 ok minus integral L1 to L2 V du dx dx.

So as you see we will have to do it in one more step that will come to later on. Right now what do we have the first term has become L square by 3 and using which formula we can expand the second term by using integration by parts. What do you have your integral x square ddx of sin 2 n pi x by L dx so u is equal to x square v equal to sin 2 n pi x by L. There is definite recommended order of priority when one performs integration by parts.

Algebraic terms polynomials have highest priority for being used as u. The trigonometric function comes second. That is why we have used u is equal to x square not v equal to x square alright that is well 11, 12 mathematics. So let us go ahead let us work out. What is u v at limit L2 - uv at Limit L1. What is the limit L1? 0 so what is the value of u; u equal to x square so for the limit L0 this uv is going to be 0, so the 2nd term first term is going to be 0.

First term is u multiplied by v for L2, for L2 x equal to L x square is L square no problem with that but v is sin 2 n pi x by L that is sin 2 n pi what is that? 0, so this uv at L2 – uv at L1 essentially becomes 0 – 0. What about the second integral v equal to x square and well sorry u equal to x square du dx becomes 2x and v is simply sine time here. So, this is what we get -2x sin 2 n pi x by L dx. So clearly once again we have to do integration by parts.

So we try to do that so that we can clean it up the little bit and we get L square by 3 + 1 by n Pi integral 0 to L x sin 2n pi x by L dx and now it simple because it once already so I leave it for you to do it yourself and convince yourself that this is the result we get.

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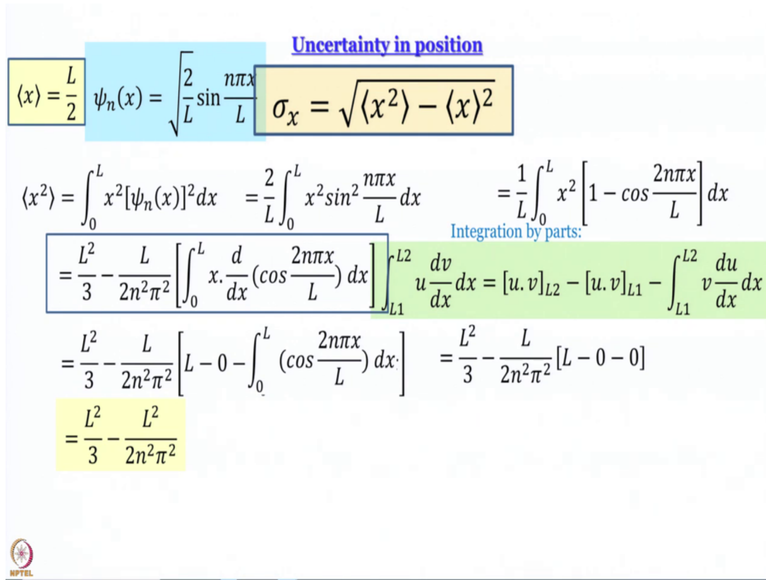

Go to the next one. So when we do integration by parts again this is what we get integral 0 to L x d dx Cos of 2 n pi x by L dx go to the next step again this time what will happen is v is equal to a cos term right v is equal to cos term and Cos at x equal to L cos 2 n pi x by L is actually equal to 1 and x equal to L there so for the first time is not 0, first time is L. In the second term is still 0 because you are multiplying by x which is 0 and then we get this integral cos 2 n pi x by L dx which is now everybody knows how to works this out and will do it and we use the conditions that you learnt already.

That at the boundaries the wave function is equal to 0 remembering the wave function is essentially the sine term to get L - 0 inside the bracket and we get L cube by 3 - L square by 2 n square pi square. This is the; what have we worked out there then let us not forget that will work out the average value of x square. What are we looking for? We are looking for the Uncertainty of standard deviation square root of average value of x square minus square of the average value of x this is what we are looking for.

Let us stop here in the next module we are going to start from here and then will get the final expression after that will work out the expression for the uncertainty in momentum and we will convince ourselves that the product is indeed greater than h cross by 2.