13.3: Uncertainty and Superposition- Wavefunctions as Waves

The uncertainty principle, "you can't know where something is and how fast it is going," is one of the most important aspects of quantum mechanics. In our explanation of this phenomenon, we will study bell-shaped wavefunctions that are centered inside a box that goes from $0 \leq x \leq L$:

\[\frac{1}

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e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\ \nonumber \]

We will analyze two different wavefunctions, a narrow one that we call "localized" and a wide one that we call "delocalized". Hopefully it is intuitively clear that there is more certainty in the position of the localized wavefunction compared to the delocalized state.

In the previous chapter we introduced the idea that an eigenfunction ψ of one operator can be expressed as a linear combination of the eigenfunctions $\mathit{\Phi}_n$ of a different operator. This is called a superposition:

$$\psi = \sum_n c_n \cdot \mathit{\Phi}_n$$

and for our purposes we will make all the $\mathit{\Phi}_n$'s freewave states:

$$\mathit{\Phi}_n = e^{ik_n x}$$

were the wavevector k is defined so that the freewaves fit in the box: $k_n = \frac{n\pi}{L}$ and n = ±1, ±2, ±3, etc. The bell-shaped wavefunctions and the freewaves are all graphed in Figure 13.10.

An example of a superposition is shown in Figure 13.11, where we see that the wider delocalized bell-shaped state can be equated to a sum of wave states weighted by an appropriate constant. Here only three waves are needed to create a superposition that appears identical to the delocalized function as shown in Figure 13.11. A very different result is observed with the localized state shown in Figure 13.12. Here, it is necessary to sum at least 5 wave states to provide a reasonable representation of the localized function. Even then the overlap isn't as good as observed with the delocalized state in Figure 13.11 despite the fact that more functions were used!

Now you are probably asking- what any of this has to do with the uncertainty principle? To answer, let's now measure the momentum of the localized and delocalized states. The measurements require us to do an experiment, and we will be repeat the experiment several times to statistically quantify the average value and standard deviation which is the uncertainty. This is necessary because it is reasonable to expect some variation in the measurements from experiment to experiment. In fact, we contend that each measurement will return the momentum of one of the wave states, which is $\hbar k_n = \hbar \cdot \frac{n\pi}{L}$, with a probability $c_n{}^2$. Thus, measuring the momentum from the delocalized state will return one of the three composing wave state's momenta with corresponding probabilities of $c_1{}^2$, $c_2{}^2$, or $c_3{}^2$. We can also calculate the expectation value of the momentum via:

$$\langle p \rangle = {|c_1|}^2 \cdot \hbar k_1 + {|c_2|}^2 \cdot \hbar k_3 + {|c_3|}^2 \cdot \hbar k_5$$

In contrast, when the same experiment is repeated on the localized state, each measurement returns one of five values of wave momenta with corresponding probabilities of $c_1{}^2$, $c_2{}^2$, $c_3{}^2$, $c_4{}^2$, or $c_5{}^2$.

Do you have more or less confidence in the measurement of the momentum of the delocalized vs. localized state? Of course, there is greater certainty for the delocalized state since each measurement returns one of just three values, and probably we won't have to make too many measurements before we are comfortable with the average. However, measuring the localized state is problematic since the result varies more from experiment to experiment! This is due to the fact that the experiment samples from five different wave states, and thus we will have to make more measurements to have the confidence in the result. We conclude that the certainty in position is anticorrelated to the certainty in momentum. This is in fact the Heisenberg uncertainty principle, "you can't know where something is and how fast it's going at the same time." Mathematically, this is expressed by the variance in the function, the square root of which is the standard deviation (\sigmaup) you may recall from your introduction into statistics; more on this later.

The above demonstration involved some approximations and was meant to give you a graphical description of uncertainty in quantum mechanics. Now, we must slog through more rigorous mathematics. First, let's define uncertainty via the variance, and we will start with the variance in position:

$$\langle Var\left(\hat{x}\right)\rangle = \langle \frac{1}{N-1} \sum^N_{i=1} {\left(x-\underline{x}\right)}^2 \rangle = \langle {\hat{x}}^2 \rangle - {\langle \hat{x} \rangle}^2$$

You may be familiar with this formula from your first introduction to statistics, and also note that the expressions $\langle \hat{x} \rangle$ and $\langle {\hat{x}}^2 \rangle$ are expectation (average) values. Let's calculate the variance in the position for our bell-shaped wavefunction: $\frac{1}{\sqrt{2\pi\sigma}} e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{2\sigma^2}}$ using the $\hat{x}$ and ${\hat{x}}^2$ operators.

\[\langle \hat{x}\rangle =\int^{\infty }_{-\infty }{}{\psi }^*\cdot \hat{x}\cdot \psi \cdot \partial x=\int^{\infty }_{-\infty }{}{\left(\frac{1}

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e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\right)}^*\cdot x\cdot \frac{1}

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$$=\frac{1}{\sqrt{2\pi\sigma^2}}\int_{-\infty}^{\infty} x\cdot e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}}\cdot\partial x=\frac{L}{2}$$

Next: $\langle\hat{x}^2\rangle=\frac{1}{\sqrt{2\pi\sigma^2}}\int_{-\infty}^{\infty} x^2\cdot e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}}\cdot\partial x=\sigma^2+\left(\frac{L}{2}\right)^2$

As a result: $\langle\hat{x}^2\rangle-\langle\hat{x}\rangle^2=\sigma^2+\left(\frac{L}{2}\right)^2-\left(\frac{L}{2}\right)^2=\sigma^2$. This is a perfectly sensible result, and in fact it is a standard statistical definition that the variance of a bell-shaped curve is σ^2!

Let's determine the variance in momentum, $var\left(\hat{p}\right)=\langle p^2\rangle-\langle p\rangle^2$:

\[\langle \hat{p}\rangle =\int^{\infty }_{-\infty }{}{\psi }^*\cdot \hat{p}\cdot \psi \cdot \partial x=\int^{\infty }_{-\infty }{}{\left(\frac{1}

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e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\right)}^*\cdot \frac\hslash{i}\frac{\partial }{\partial x}\frac{1}

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e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\cdot \partial x= \nonumber \]

$$\frac{\hbar}{i\sqrt{2\pi\sigma^2}}\int_{-\infty}^{\infty} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}}\cdot\frac{\partial}{\partial x}e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}}\cdot\partial x=\frac{\hbar}{i\sqrt{8\pi\sigma^3}}\int_{-\infty}^{\infty}\left(x-\frac{L}{2}\right)\cdot e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}}\cdot\partial x=0$$

No average momentum, which shouldn't be interpreted as the particle not moving. Rather, the particle can move left or right equally averages out to 0. Next, calculating the average of the momentum squared takes a bit more effort:

\[\langle {\hat{p}}^2\rangle =\int^{\infty }_{-\infty }{}{\psi }^*\cdot {\hat{p}}^2\cdot \psi \cdot \partial x=-\hslash^2\int^{\infty }_{-\infty }{}{\left(\frac{1}

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e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\right)}^*\cdot \frac

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e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\cdot \partial x= \nonumber \]

\[\frac{-\hslash^2}{\sqrt{2\pi {\sigma }^2}}\int^{\infty }_{-\infty }{}e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\cdot \frac

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\cdot \partial x=\frac

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\cdot \partial x=\frac{\hslash^2}{4{\sigma }^2} \nonumber \]

As a result, the variance in momentum is: $\langle\hat{p}^2\rangle-\langle\hat{p}\rangle^2=\frac{\hbar^2}{4\sigma^2}-0^2=\frac{\hbar^2}{4\sigma^2}$

The results reveal that the uncertainty in position and momentum are anticorrelated; the position uncertainty scales as σ^2, however, the momentum uncertainty is inversely proportional to σ^2. Thus, if the particle is localized in position then there is an increasing uncertainty in momentum. This becomes clearer when we multiply the two variances:

$$Var\left(\hat{x}\right)\cdot Var\left(\hat{p}\right)=\sigma^2\frac{\hbar^2}{4\sigma^2}=\frac{\hbar^2}{4}$$

which results in a constant. This is, in fact, the mathematical version of the Heisenberg uncertainty principle.

13.3.1 The Heisenberg Uncertainty Principle. There is a math theorem that can assist us with understanding the previous example called the Cauchy-Schwartz inequality. It is analogous to the fact that a dot product between two vectors: $\overrightarrow{a}\cdot\overrightarrow{b}=|a|\,|b|\,cos\left(\theta\right)$, is equal to or less that $|a|\,|b|$ due to the fact that the maximum $cos\left(\theta\right)$ can be is 1. This concept allows us to express the Heisenberg uncertainty principle as an equation:

$$Var\left(\hat{x}\right)\cdot Var\left(\hat{p}\right)\geq\frac{1}{4}|\langle[\hat{x},\hat{p}]\rangle|^2$$

where a new mathematical entity called the commutator appears on the right:

$$[\hat{x},\hat{p}]=\hat{x}\cdot\hat{p}-\hat{p}\cdot\hat{x}$$

The expectation value of the commutator is simply $\langle[\hat{x},\hat{p}]\rangle=\langle\hat{x}\cdot\hat{p}-\hat{p}\cdot\hat{x}\rangle=\langle\hat{x}\cdot\hat{p}\rangle-\langle\hat{p}\cdot\hat{x}\rangle$. Normally, expectation values have to be evaluated using specific wavefunctions. However, there is a simple and general way to evaluate $\langle[\hat{x},\hat{p}]\rangle$. This works by applying a "dummy" ψ on the right of the operators, allowing them to act on it and then dividing ψ out on the left:

$$\langle[\hat{x},\hat{p}]\rangle=\frac{1}{\psi}[\hat{x},\hat{p}]\,\psi$$

Inserting $[\hat{x},\hat{p}]=\hat{x}\cdot\hat{p}-\hat{p}\cdot\hat{x}$ and the definition of the momentum operator $\hat{p}=\frac{\hbar}{i}\frac{\partial}{\partial x}$ and $\hat{x}=x$ into the above yields:

$$\langle[\hat{x},\hat{p}]\rangle=\frac{1}{\psi}(\hat{x}\cdot\hat{p}-\hat{p}\cdot\hat{x})\,\psi=\frac{\hbar}{i}\frac{1}{\psi}\left(x\cdot\frac{\partial}{\partial x}-\frac{\partial}{\partial x}\cdot x\right)\psi=\frac{\hbar}{i}\frac{1}{\psi}\left(x\cdot\frac{\partial}{\partial x}\psi-\frac{\partial}{\partial x}\cdot x\cdot\psi\right)$$

Noting the need for the product rule on the right-hand side results in:

\langle \left[\hat{x},\hat{p}\right]\rangle =\frac\hslash{i}\frac{1}{\psi }\left(x\cdot {\psi }^'-x\cdot {\psi }^'+\psi \right)=\frac\hslash{i}\frac{\psi }{\psi }=\frac\hslash{i} \nonumber

This can be re-inserted into the expression from our previous formula: $\frac{1}{4}|\langle[\hat{x},\hat{p}]\rangle|^2=\frac{1}{4}\left|\frac{\hbar}{i}\right|^2=\frac{\hbar^2}{4}$ to yield:

$$Var\,(\hat{x})\cdot Var\,(\hat{p})\geq\frac{\hbar^2}{4}$$

13.3.1.1 Interpretation. The Heisenberg uncertainty principle states that once cannot know position and momentum, or speed, of a quantum mechanical object simultaneously. Better knowledge of position increases the uncertainty in momentum, and the only way the uncertainty in momentum can rise is for the average momentum to increase. To understand why, take for example a car going 10 miles per hour on average. Do you have more, or less uncertainty in its speed compared to a car going 100 mph on average? Of course, there must be greater uncertainty in the velocity of the faster moving car because it has considerably more leeway for its momentum to vary more. As a result, a greater uncertainty in momentum must be associated with greater momentum in general, which also means that the object must have greater kinetic energy. Thus, if a delocalized quantum mechanical particle, such as an electron in an aromatic ring, becomes localized on a single atom, then it's kinetic energy must increase. This is why quantum particles like to become delocalized if possible, and also describes why the energy of a particle in a box increases if the box is smaller: $E\propto\frac{1}{L^2}$. The Heisenberg uncertainty principle is often used to explain nanoscale phenomena including the size dependence of the emission of quantum dots shown in Figure 13.6.

The commutator $[\hat{x},\hat{p}]=\hat{x}\cdot\hat{p}-\hat{p}\cdot\hat{x}$ can be interpreted in a way that makes sense out of the uncertainty principle. Since $[\hat{x},\hat{p}]\neq 0$, then $\langle\hat{x}\cdot\hat{p}\rangle\neq\langle\hat{p}\cdot\hat{x}\rangle$, and as a result measuring the position of a particle, and then its momentum, would yield a different result than if you first measured momentum and then position! However, there is no "right" way to do this, so the result is arbitrary depending on what order the experimentalist happened to use when making measurements on small, quantum mechanical particles. Thus, there is uncertainty.

13.3.1.1 Generalization. The Heisenberg uncertainly principle simply states that, at best, the product of the position and momentum variances is no more than $\frac{\hbar^2}{4}$. If one has a specific system with a known wavefunction then one has to evaluate the product of $var\,(\hat{x})$ and $var\,(\hat{p})$ directly. In fact we did so in the previous section using the bell-shaped wavefunction and found that the equality held for the uncertainty principle: $var\,(\hat{x})\cdot var\,(\hat{p})=\frac{\hbar^2}{4}$. These Gaussian functions are considered special as a result and are often referred to as "minimum uncertainty" wavefunctions. In some of the problem set questions at the end of this chapter you will find that the products of the variances in position and momentum for various particle in a box wavefunctions are indeed greater than $\frac{\hbar^2}{4}$.

It is important to realize that, while the position / momentum uncertainty principle is "famous", there are in fact a very large number of other examples. For any two operators $\widehat{\Omega}_1$ and $\widehat{\Omega}_2$ the uncertainty principle states:

$$Var\left(\widehat{\Omega}_1\right)\cdot Var\left(\widehat{\Omega}_2\right)\geq\frac{1}{4}\left|\langle\left[\widehat{\Omega}_1,\widehat{\Omega}_2\right]\rangle\right|^2$$

and as a result there is uncertainty if $\left[\widehat{\Omega}_1\ ,\widehat{\Omega}_2\right]\neq 0$. We will find examples using quantum rotational motion and when describing the spin angular momentum of electrons. Here is one you can try on your own; determine the uncertainty between the position $\hat{x}=x$ and kinetic energy operators $\widehat{KE}=\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. If you evaluate the uncertainty principle by simplifying the commutator using: $\left[x,\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\psi$ one finds that: $Var\,(\hat{x})\cdot Var\left(\widehat{KE}\right)\geq\frac{\hbar^2}{4m}|\langle\hat{p}\rangle|^2$

This at first may appear hard to interpret as the commutator is an operator rather than a constant. What is meant here is that the uncertainty between position and kinetic energy is dependent on the expectation of momentum. Thus, if the particle has no momentum then there is a potential for there to be no uncertainty between position and kinetic energy. However, the uncertainty increases as the particle is moving faster and faster.

There is one last implication of the uncertainty principle, which is that the eigenfunctions of one operator $\widehat{\Omega}_1$ cannot be the same as the other operator $\widehat{\Omega}_2$ if $\left[\widehat{\Omega}_1\ ,\widehat{\Omega}_2\right]\neq 0$. This is generally a topic that one encounters when studying more advanced quantum mechanical phenomena such as rotation, spin angular momentum and the spin-orbit effect discussed in latter chapters.

Conclusions. In this chapter we showed how increasing the complexity of model systems through their potential energy surfaces reveals new quantum phenomena. Specifically, how a particle may bounce off a wall even if it is higher than it. Also, quantum particles can tunnel through barriers like they have a negative kinetic energy. Furthermore, the kinetic energy of a particle increases if we trap it, which is why we can change the color of a quantum dot by changing its size. While this chapter discusses most of the basic principles of quantum mechanics, in the next few chapters we are going to move away from one dimensional example problems and discuss real systems leading up to the hydrogen atom. To do so we have to understand how quantum mechanics works in 3D and how to deal with rotational motion.