12.5: The Freewave Potential

In the next few sections we will examine a few paradigms of systems that are good first examples. The first is called the “free wave” particle, which is a quantum mechanical object (let’s just say its an electron), that lives in a single dimension without end. Also, there is nothing to interact with. As a result, the Hamiltonian: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\left(x\right)$ of that particle is simply:

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

since V(x)=0 everywhere (no potential for interaction because there is nothing else to interact with). While this is a simple problem to work with, it has the unfortunate aspect of being highly unrealistic for describing the Universe with only one particle, and that the Universe doesn’t end (fyi ours does, thanks to the Big Bang).

You may have already figured out that we have been working with the free wave system for this entire chapter. As a result we already know that there are four wavefunctions, and that $\psi=N\cdot e^{ikx}$ is for a particle moving right, $\psi=N\cdot e^{-ikx}$ is for a particle moving left, and \(\psi =N\cdot

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cosleft(kx\right)) and \(\psi =N\cdot

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sinleft(kx\right)) are for particles that have no net momenta. Great, but here is something you may have not noticed. Let’s normalize the wavefunction by deriving the normalization constant that we already discussed is:

$$N=\frac{1}{\sqrt{\int\psi^2\partial\tau}}$$

And let’s use an unnormalized wavefunction $\psi=e^{ikx}$ (recall, that our purpose here is to calculate what “N” is). First let’s simply solve the integral

$$\int_{-\infty}^{\infty}\psi^2\cdot\partial x=\int_{-\infty}^{\infty}\psi^*\psi\cdot\partial x=\int_{-\infty}^{\infty}e^{ikx*}e^{ikx}\cdot\partial x=\int_{-\infty}^{\infty}e^{-ikx}e^{ikx}\cdot\partial x=\int_{-\infty}^{\infty}\partial x=\infty$$

To solve this we used the fact that $e^{-ikx}e^{ikx}=e^{-ikx+ikx}=e^0=1$. Thus, the normalized wavefunction is: $\psi=N\cdot e^{ikx}=\frac{1}{\sqrt{\infty}}e^{ikx}$. In case you are wondering, no this doesn’t make sense. You can’t have equations with ∞ in it, and the square root doesn’t “save” it in some miraculous way. This normalized wavefunction is absurd, so you may be wondering how you fix it.

The answer is, you don’t. You see, the problem itself is absurd, because this is a particle that is in an infinite universe and the particle may be found anywhere in it. Thus, the probability density for the normalized wavefunction $\psi^*\psi$ is:

$$\psi^*\psi=\frac{1}{\sqrt{\infty}}e^{-ikx}\frac{1}{\sqrt{\infty}}e^{ikx}=\frac{1}{\infty}=0$$

And this is exactly what you should get. In an infinite universe, the probability for a particle to be at any particular point in space is 0 because the particle has an infinite number of other places to be. So, the result is fine, just weird.

Example problems, the “particle in a box”. This paradigm is a bit more simple, which is that the free wave is in fact inside a finite universe. Inside the box there is no potential energy, so $\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. Outside the boundaries the potential energy is infinite, so the particle cannot leave the box. To make it interesting, we often make the particle have the mass of an electron and the box is 1×10^{-9} m (or 1 nm) big, which means that the electron displays quantum mechanical behavior. If the box was much bigger then the electron is just like a marble on a track, and we don’t really need quantum mechanics to describe it. This is a lesson that there are size regimes over which you observe quantum mechanical effects, and bigger ones where you don’t.

Shown on the right is the potential surface. Since the wavefunction $\psi\left(x\right)$ has to be$psi\left(0\right)=0$ at x=0, and$psi\left(L\right)=0$ at x=L, and have a double derivative that is equal to itself, the only mathematical entity that fits the bill for is $\psi=N\cdot sin(?)$. Now, we must design the argument of the function “?” to sure that \(

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sinleft(x=L\right)\ =0\). A sine wave always starts at 0, and it next crosses 0 at \piup. Thus, we know that:

$$\psi\left(x\right)=\left(\pi\frac{x}{L}\right)$$

works. Now, you might recall that we often found more than one solution to a problem; the free wave has four solutions for example. As you can see from the figure, the particle in a box also has more solutions because the sine wave has other 0’s, the first one at p and the next one at 2p. Thus, another solution to the particle in a box is \(\psi \left(x\right)=N\cdot

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sinleft(2\pi \frac{x}{L}\right)). And we can keep figuring out new solutions until we see that there is a general relationship \(\left(n\pi \frac{x}{L}\right)), where n=1, 2, 3…

While we have an infinite number of solutions for the particle in a box problem, how do we understand what they mean or represent? First, let’s figure out how to normalize them. As we have already shown many times that the normalization constant is $N=\frac{1}{\sqrt{\int\psi^2\partial\tau}}$, let’s simply calculate the integral:

$$\int_0^L\psi^2\cdot\partial x=\int_0^L\psi^*\psi\cdot\partial x=\int_0^L sin\left(n\pi\frac{x}{L}\right)^*sin\left(n\pi\frac{x}{L}\right)\cdot\partial x=\int_0^L sin^2\left(n\pi\frac{x}{L}\right)\cdot\partial x$$

To solve this we simply look up a table of standard trigonometric integrals to find:

$$\int\left(ax\right)partialx=\frac{x}{2}-\frac{1}{4a}sin(2ax)$$

and thus: $\int\left(n\pi\frac{x}{L}\right)partialx=\frac{x}{2}-\frac{L}{4n\pi}sin(2n\pi\frac{x}{L})$. When placed into a definite integral:

\[\int^L_0{}{sin}^2\left(n\pi \frac{x}{L}\right)\cdot \partial x={\frac{x}{2}-\frac{L}{4n\pi }sin(2n\pi \frac{x}{L})]}^{x=L}_{x=0}=\frac{L}{2}-\frac{L}{4n\pi }

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sinleft(2n\pi \right)\ =\frac{L}{2} \nonumber \]

because \(

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sinleft(2n\pi \right)\ =0\) since n is a whole number integer, i.e. since n=1, 2, 3… then \(

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sinleft(2n\pi \right)\ =

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sinleft(4\pi \right)=

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sinleft(6\pi \right)\ =0).

As a result, the proper normalized particle in a box wavefunctions are:

$$\left(n\pi\frac{x}{L}\right)$$

Now for their interpretation, first we can calculate the energy. We will use the eigenvalue expression $\hat{H}\psi_n(x) = E\cdot\psi_n(x)$ since this is usually the fastest way if you know you are dealing with the eigenfunctions of the operator (here, the Hamiltonian).

$$\hat{H}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(n\pi\frac{x}{L}\right) \;\; = \frac{n^2\pi^2}{2mL^2}\left(n\pi\frac{x}{L}\right)$$

As a result we see that the energy is $E_n = \frac{n^2\pi^2}{2mL^2}$. Since n=1, 2, 3… then the n=1 state is the ground state and all the others are excited states, as these have higher energies than the ground state.

We can also figure out the average position of the particle in a box via the expectation value, which is always necessary when using the operator. Note that you must use normalized wavefunctions to properly evaluate expectation values.

\langle \hat{x}\rangle =\int^{upper}_{lower}{}{\psi }^*_{n^'}{\hat{x}\psi }_n\cdot \partial \tau =\int^L_0{}{\left(\left(n\pi \frac{x}{L}\right)right)}^*\cdot x\cdot \left(n\pi \frac{x}{L}\right)cdot \partial x \nonumber

Of course we know that sine functions are not complex, so $sin(x)^* = sin(x)$, and we can do some factoring to simplify the above into:

$$\langle\hat{x}\rangle = \frac{2}{L}\int_0^L x\cdot\left(n\pi\frac{x}{L}\right) cdot\partial x$$

Use of a table of trigonometric identities yields:

\langle \hat{x}\rangle =\frac{2}{L}\int{}x\cdot \left(n\pi \frac{x}{L}\right)cdot \partial x=\frac{2}{L}\left\{{\frac{x^2}{2}-\frac{xL}{4n\pi }{{sin}}sinleft(2n\pi \frac{x}{L}\right)\ -\frac{x^2}{4}-\frac{L^2}{8n^2{\pi }/

Inputting the limits and using the normalizer gives:

\[\langle \hat{x}\rangle =L-\frac{L}{2n\pi }

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sinleft(2n\pi \right)\ -\frac{L}{2}-\frac{L}{4n^2{\pi }^2}

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cosleft(2n\pi \right)\ +\frac{L}{4n^2{\pi }^2} \nonumber \]

Since \(

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sinleft(2n\pi \right)) and \(

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cosleft(2n\pi \right)) are always 0 and 1, respectively, for n=1, 2, 3… then we are left with:

$$\langle\hat{x}\rangle = L - \frac{L}{2} = \frac{L}{2}$$

And thus $\langle\hat{x}\rangle = \frac{L}{2}$, the middle of the box, for every state of the particle in the box since there is no dependence on the quantum number n in the equation above.

Let’s do one last example, problem, which is the average momentum:

\langle \hat{p}\rangle =\int^{upper}_{lower}{}{\psi }^*_{n^'}{\hat{x}\psi }_n\cdot \partial \tau =\int^L_0{}{\left(\left(n\pi \frac{x}{L}\right)right)}^*\cdot \frac\hslash{i}\frac{\partial }{\partial x}\left(n\pi \frac{x}{L}\ri

Several steps of simplification yield:

\[\langle \hat{p}\rangle =\int^{upper}_{lower}{}{\psi }^*_{n^'}{\hat{x}\psi }_n\cdot \partial \tau =\frac{2}{L}\frac\hslash{i}\frac{n\pi }{L}\int^L_0{}\left(n\pi \frac{x}{L}\right)cdot

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cosleft(n\pi \frac{x}{L}\right)cdot \partial x \nonumber \]

Since \(\int{}

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sinleft(ax\right)cdot cos(ax)\partial x=-\frac{1}{4a}cos\left(2ax\right)\) we find that:

\[\langle \hat{p}\rangle ={\frac{2\hslash n\pi }{iL^2}\left\{-\frac{L}{4n\pi }cos\left(2n\pi \frac{x}{L}\right)\right\}]}^{x=L}_{x=0}=-\frac\hslash{2iL}

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cosleft(2n\pi \right)\ +\frac\hslash{2iL} \nonumber \]

And since \(

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cosleft(2n\pi \right)\ =0\) for n as a whole number we find that $\langle \hat{p} \rangle = 0$. Does this make sense? Very much so, because if the particle had some net momentum then it could escape the box. But, it can't, so every time it starts to move left it must hit the wall and move right. The net of the left- and right- motion cancel out completely, so the particle is stuck.

Conclusion. This is your first introduction to basic quantum theory. The most important things to learn are that models that describe particles use the same equations that describe vibrating strings, which is why quantum is often called wave mechanics. Operators are the questions and eigenvalues are the answers, whereby the answers come from the wavefunction models. In the next chapter you will learn a few more complex models and review the uncertainty principle, which is the most important implication of quantum mechanics. Good luck with that.