Chapter 5

Need a smoke. . .need a drink. . .no money. . .shirt reeks. . .shoes soaked. . .feet cold. . .two hours with this stupid shadow on my tail. . . Other than that, things are swell, just swell. Time to meet this clown. Yeah, the train station. . .past this marble corner. . .a moment. . .another moment. . . about right, turn. . . . The timing was perfect—face to face with the"shadowman." "Hey buddy, can I bum a smoke?" The shadow fumbled through his overcoat, then his jacket finally producing a pack of cigarettes. "Got a light?" He was quicker finding a lighter, but he was still so shaky that it took five tries to produce fire. Maybe send a signal to his boss. . .whoever that is. . . "Hey, buddy, let me tell you about Rutherford. They say he named the alpha particle. . ."

The Infinite Square Well

An atom in a molecule, an electron in an atom, and a nucleon in a nucleus are examples of particles confined to limited regions. Each demonstrates energy quantization while confined. Each limited region can be considered to be a "box" with "soft walls" formed by electrical or nuclear forces. The first step toward describing such realistic systems is to examine a one dimensional box with the simplest possible geometry and infinite or "hard walls". The potential energy function goes from zero in the region of confinement to infinity at each edge. This bit of unrealism makes the mathematics most tractable. The second step is to model "soft walls" by examining a one dimensional box where the potential energy function goes from zero in the region of confinement to a finite value at each edge. Both illustrate energy quantization. In fact, a particle subject to any type of confinement exhibits energy quantization.

Energy quantization is revealed in the form of allowed energy levels that are eigenenergies, or energy eigenvalues. These are the observable energies. Each eigenenergy has a corresponding eigenfunction, eigenstate, or eigenvector. A general wavefunction or state function may be an eigenfunction but will generally be a linear superposition of eigenfunctions.

As in the last two chapters, the postulates of quantum mechanics are not necessarily obvious in this development. The differential equation form of the time independent Schrodinger equation in position space dominates the discussion. Remember that it is simply a convenient form of the sixth postulate. Any eigenstate or any linear combination of eigenstates can comprise the state vector, as described by the first postulate. Measurements yield eigenvalues per the third postulate. We can attain probabilities for eigenstates or linear combinations of the eigenstates using the fourth postulate, and so on. The postulates are ever present.

As you work through this chapter, notice how the techniques of boundary value problems are used. Notice the mathematics used to attain eigenenergies and eigenfunctions. These things are useful and recurrent. Notice that position space is only one of many representations. Energy and momentum space representations are illustrative in this problem to further assimilate the idea that different representations may be more useful in other problems. Notice the impact of state vectors or wave functions that are linear combinations of eigenfunctions. Notice that results in two or three dimensions are generalizations of results in one dimension. The three dimensional problem may be pleasing because it is what we might first picture when we hear the phrase "particle in a box," which is the informal name of a square well.

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1. Derive the eigenenergies of a particle in an infinite square well.

The potential energy function for an infinite square well is

$$\begin{aligned} V(x) &= \infty\,, \quad x \le -a \;\text{ and }\; x \ge a\,, \\ V(x) &= 0\,, \qquad -a < x < a\,, \end{aligned}$$

pictured at the right in an energy versus position plot. All space is divided into three regions. A consequence of the walls being of infinite height and thickness is that the wavefunction is zero in regions 1 and 3. The general solution to the time-independent Schrodinger equation is

$$\psi(x) = \begin{cases} 0 & x \le -a\,, \\ Ae^{-ikx} + Be^{ikx} & -a < x < a\,, \\ 0 & x \ge a\,, \end{cases}$$

where $k = \lambda/2\pi$ is the wave number, and λ is the de Broglie wavelength. This is a free particle within the region of confinement. The eigenvalues of a free particle were found in chapter 3 to be

$$\frac{p^2}{2m} = E \quad \Rightarrow \quad E = \frac{\hbar^2 k^2}{2m}\,.$$

The eigenenergies are then expressed in terms of the parameters of the given potential using the condition of continuity of the wavefunction per chapter 4.

Continuity of the wave function at the left boundary means $\psi(-a) = 0$, or

$$A\,e^{-ik(-a)} + B\,e^{ik(-a)} = 0 \quad \Rightarrow \quad A\,e^{ika} + B\,e^{-ika} = 0$$

$$\Rightarrow \quad A\cos(ka) + A\,i\sin(ka) + B\cos(ka) - B\,i\sin(ka) = 0\,, \tag{1}$$

and at the right boundary $\psi(a) = 0$, so $A\,e^{-ika} + B\,e^{ika} = 0$

$$\Rightarrow \quad A\cos(ka) - A\,i\sin(ka) + B\cos(ka) + B\,i\sin(ka) = 0\,. \tag{2}$$

Adding equations (1) and (2),

$$2A\cos(ka) + 2B\cos(ka) = 0 \quad \Rightarrow \quad 2(A+B)\cos(ka) = 0 \quad \Rightarrow \quad \cos(ka) = 0$$

$$\Rightarrow \quad ka = \frac{n\pi}{2}, \quad n = 1,\,3,\,5,\ldots \quad \Rightarrow \quad k = \frac{n\pi}{2a}\,, \quad n = 1,\,3,\,5,\ldots \tag{3}$$

Subtracting equations (1) and (2),

$$2A\,i\sin(ka) - 2B\,i\sin(ka) = 0 \quad \Rightarrow \quad 2i\,(A-B)\sin(ka) = 0 \quad \Rightarrow \quad \sin(ka) = 0$$

$$\Rightarrow \quad ka = \frac{n\pi}{2}, \quad n = 2,\,4,\,6,\ldots \quad \Rightarrow \quad k = \frac{n\pi}{2a}, \quad n = 2,\,4,\,6, \tag{4}$$

Equations (3) and (4) can be summarized in one relation,

$$\Rightarrow \quad k = \frac{n\pi}{2a}, \quad n = 1,\,2,\,3,\,4,\ldots$$

These are related to energies of the free particle

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{2a}\right)^2 \quad \Rightarrow \quad E_n = n^2\,\frac{\pi^2\hbar^2}{8ma^2}\,.$$

Postscript: The confined particle, though it is free within the region of confinement, can possess only allowed energies that depend upon the geometry of the region of confinement. Allowed energies are discrete and are pictured only at discrete heights above the floor of the potential. Energies of a confined particle are **quantized**. The eigenenergies, or eigenvalues, are subscripted because they depend on the index n called the **quantum number**. A quantum number is simply an integer index. Since n can be any integer, there are an infinite number of eigenenergies for a particle in an infinite square well.

The free particle is not quantized and can have any energy. A free particle can be at any height above the floor of the potential. Confinement is not a consideration for a free particle or a scattering state so energy quantization was not encountered in chapters 3 or 4. Confinement, or forced localization, is the physical condition that results in energy quantization.

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2. Find the normalized eigenfunctions for a particle confined to an infinite square well.

Eigenfunctions are also found using continuity of the wavefunction at the boundaries.

Using the wavenumber in terms of quantum number at the right boundary,

$$A\,e^{-ika} = -B\,e^{ika} \quad \Rightarrow \quad A = -B\,e^{i2ka} = -B\,e^{i2\left(\frac{n\pi}{2a}\right)a} = -B\,e^{in\pi}.$$

Now $\quad e^{in\pi} \;=\; \cos(n\pi) \,+\, i\sin(n\pi) \;=\; \begin{cases} -1 & n \text{ odd} \\ 1 & n \text{ even} \end{cases} \quad \Rightarrow \quad A \;=\; \begin{cases} B & n \text{ odd} \\ -B & n \text{ even.} \end{cases}$

The result is the same at the left boundary. The wavefunction within the well for odd n is

$$\begin{aligned}\psi(x) &= A\,e^{-ikx} + B\,e^{ikx} = A\,e^{-ikx} + A\,e^{ikx} = A\Big(e^{-ikx} + e^{ikx}\Big) \\ &= A\Big[\cos(kx) - i\sin(kx) + \cos(kx) + i\sin(kx)\Big] = 2A\cos(kx)\end{aligned}$$

$$\Rightarrow \quad \psi_n(x) = C\cos\left(\frac{n\pi}{2a}\,x\right), \quad n \text{ odd}, \tag{1}$$

where $C = 2A$ is the "updated" normalization constant. For even n,

$$\begin{aligned}\psi(x) &= A\,e^{-ikx} + B\,e^{ikx} = A\,e^{-ikx} - A\,e^{ikx} = A\left(e^{-ikx} - e^{ikx}\right) \\ &= A\Big[\cos(kx) - i\sin(kx) - \cos(kx) - i\sin(kx)\Big] = -2A\,i\sin(kx)\end{aligned}$$

$$\Rightarrow \quad \psi_n(x) = D \sin\left(\frac{n\pi}{2a}\, x\right), \quad n \text{ even} \tag{2}$$

where $D = -2Ai$ is the "conglomerate" normalization constant. The normalization condition is

$$<\psi(x)\,|\,\psi(x)> = 1 \quad \Rightarrow \quad \int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx = \int_{-a}^{a} \psi^*(x)\,\psi(x)\,dx = 1\,.$$

For odd n this is

$$\begin{aligned}
1 &= \int_{-a}^{a} C^* \cos\left(\frac{n\pi}{2a}\, x\right)^* C \cos\left(\frac{n\pi}{2a}\, x\right)\, dx = C^* C \int_{-a}^{a} \cos^2\left(\frac{n\pi}{2a}\, x\right)\, dx \\
&= |\,C\,|^2 \left[\frac{1}{2}\, x + \frac{2a}{4n\pi} \sin\left(\frac{n\pi}{a}\, x\right)\right]_{-a}^{a} \\
&= |\,C\,|^2 \left[\frac{1}{2}\, a - \frac{1}{2}\,(-a) + \frac{a}{2n\pi}\left(\sin\left(\frac{n\pi}{a}\, a\right) - \sin\left(\frac{n\pi}{a}\,(-a)\right)\right)\right] \\
&= |\,C\,|^2 \left[a + \frac{a}{2n\pi}\Big(\sin(n\pi) + \sin(n\pi)\Big)\right] = |\,C\,|^2 \left[a + \frac{a}{n\pi} \sin(n\pi)\right]\,.
\end{aligned}$$

But $\sin(n\pi) = 0$ for all integral n, so $a\,|\,C\,|^2 = 1 \;\Rightarrow\; C = \dfrac{1}{\sqrt{a}}$. A similar calculation for even n yields $D = \dfrac{1}{\sqrt{a}}$. Using these results in equations (1) and (2), we have

$$\psi_n(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi}{2a}\, x\right), \quad n = 1, 3, 5, \ldots, \qquad \text{and} \qquad \psi_n(x) = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi}{2a}\, x\right), \quad n = 2, 4, 6, \ldots$$

Postscript: The derivations of problems 1 and 2 are based on the width of the infinite square well being $2a$ with the origin in the center. Other conventions exist. Since the width of the well appears in the eigenenergies, the normalization constants, and the arguments of the trigonometric functions, the exact form of the eigenenergies and eigenfunctions is dependent on the convention used. An infinite square well of width a with the origin at the center has

$$E_n = n^2\, \frac{\pi^2 \hbar^2}{2ma^2} \qquad \text{and} \qquad \psi_n(x) = \begin{cases} \sqrt{\dfrac{2}{a}} \cos\left(\dfrac{n\pi}{a}\, x\right), & n \text{ odd}\,, \\ \sqrt{\dfrac{2}{a}} \sin\left(\dfrac{n\pi}{a}\, x\right), & n \text{ even}\,. \end{cases}$$

An infinite square well of width a with the origin at the left edge has

$$E_n = n^2\, \frac{\pi^2 \hbar^2}{2ma^2} \qquad \text{and} \qquad \psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}\, x\right)\,.$$

All three conventions provide the same numerical values for the eigenenergies and identical graphs of the eigenfunctions. See problems 3 and 4, for example.

Notice that $n = 1$ is the lowest energy state, or the **ground state**, of the eigenenergies for the infinite square well. A system of zero energy is non-physical so $n = 0$, which would describe zero energy for an infinite square well, is not allowed and quantum numbers start at $n = 1$. In

contrast, the simple harmonic oscillator, addressed in the next chapter, uses $n = 0$ for the ground state. The eigenenergies of the simple harmonic oscillator (SHO) are non-zero when $n = 0$, so $n = 0$ suitably describes the ground state energy of the SHO.

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3. (a) What is the ground state energy of an electron in a one–dimensional infinite square well of "radius" one half Angstrom?

(b) Find the eigenenergies of the first three excited states.

A "one–dimensional radius" of one half Angstrom means use $a = 0.5$ Å in the result of problem 1. It is often convenient to describe the energy of excited states in terms of the ground state energy. If E_g is the ground state energy, $n^2 E_g$ describes all eigenenergies of the infinite square well.

(a)
$$E_1 = E_g = (1)^2 \frac{\pi^2 \hbar^2}{8ma^2} = \frac{\pi^2 h^2}{(2\pi)^2\, 8ma^2} = \frac{h^2 c^2}{(4)\, 8mc^2 a^2}$$
$$= \frac{(1.24 \times 10^4\, eV \cdot \text{Å})^2}{32 \left(0.511 \times 10^6\, \dfrac{eV}{c^2}\right) c^2\, (0.5\, \text{Å})^2} = \frac{1.54 \times 10^8\, eV^2 \cdot \text{Å}^2}{4.09 \times 10^6\, eV \cdot \text{Å}^2} = 37.65\ eV\,.$$

(b)
$$E_2 = 2^2\, E_g = 4\left(37.65\, eV\right) = 150.60\ eV\,,$$
$$E_3 = 3^2\, E_g = 9\left(37.65\, eV\right) = 338.85\ eV\,,$$
$$E_4 = 4^2\, E_g = 16\left(37.65\, eV\right) = 602.40\ eV\,.$$

Postscript: The diameter of a small atom is on the order of one Angstrom.

Converting quantities from CGS or MKS units is inconvenient by comparison to using constants such as $hc = 1.24 \times 10^4\, eV \cdot \text{Å}$ and the electron mass $= 0.511\ MeV/c^2$.

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4. Given an infinite square well of width $2a$, graph the first four eigenenergies on an energy versus position plot and superimpose the the first four eigenfunctions on corresponding eigenenergies on the same plot. Plot the probability densities of the first four eigenfunctions in the same manner.

Examine the two graphs below.

Eigenenergies and Eigenfunctions Eigenenergies and Probability Density

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Postscript: There is a lot of information contained in these two graphs. It is conventional to graph energy versus position for the eigenenergies. The vertical is actually amplitude for the eigenfunctions. The eigenfunctions all have an amplitude of zero at the boundaries. They should, therefore, all be located on the horizontal axis that denotes zero amplitude. They are, however, conventionally located at the level of the corresponding eigenenergies where each horizontal line represents zero amplitude for that eigenfunction. Energy is usually scaled $E_1 = E_g$, $E_2 = 4\,E_g$, $E_3 = 9\,E_g$, $E_4 = 16\,E_g$, etc., but the vertical scale for amplitudes is qualitative.

Probability density is also conventionally placed at the level of the corresponding eigenenergy where the vertical is probability density amplitude using an arbitrary scale. Notice that probability density is non-negative and that there are points where the probability density is zero. The pertinent non-classical feature is that there are regions of maximal and minimal probability. Remember that probability is $|\,\psi\,(x)\,|^{\,2}\,dx$ so probability density is $|\,\psi\,(x)\,|^{\,2}$ with units of $1/\sqrt{\text{length}}$.

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5. Compare the probability of locating a particle in its ground state in an infinite square well of width $2a$ between $\pm a/10$ at the center of the well and an interval of equal length at the right edge.

This is an application of the fourth postulate in position space. Integrate probability density for a particle in its ground state between $\pm a/10$, then integrate probability density between $8a/10$ and a, and compare the numerical results. Classically, the probabilities would be identical.

$$\text{Using}\quad \psi_1\,(x) = \frac{1}{\sqrt{a}}\,\cos\left(\frac{\pi}{2a}\,x\right)\quad \text{in}\quad P\,(x_1 < x < x_2) = \int_{x_1}^{x_2} \psi^*\,(x)\,\psi\,(x)\,dx\,,$$

$$\begin{aligned}
P\,(-a/10 < x < a/10) &= \int_{-a/10}^{a/10} \left(\frac{1}{\sqrt{a}}\right)^* \cos^*\left(\frac{\pi}{2a}\,x\right)\left(\frac{1}{\sqrt{a}}\right)\cos\left(\frac{\pi}{2a}\,x\right)dx \\
&= \frac{1}{a}\int_{-a/10}^{a/10} \cos^2\left(\frac{\pi}{2a}\,x\right)\,dx = \frac{1}{a}\left[\frac{1}{2}\,x + \frac{2a}{4\pi}\,\sin\left(\frac{\pi}{a}\,x\right)\right]_{-a/10}^{a/10} \\
&= \frac{1}{a}\left[\frac{1}{2}\left(\frac{a}{10} - -\frac{a}{10}\right) + \frac{a}{2\pi}\left(\sin\left(\frac{\pi}{a}\frac{a}{10}\right) - \sin\left(\frac{\pi}{a}\frac{-a}{10}\right)\right)\right] \\
&= \frac{1}{a}\left[\frac{a}{10} + \frac{a}{2\pi}\,2\sin\left(\frac{\pi}{10}\right)\right] = \frac{1}{10} + \frac{1}{\pi}\,\sin\left(\frac{\pi}{10}\right) \approx 0.198\,.
\end{aligned}$$

For an interval of equal length at the right edge of the well,

$$\begin{aligned}
P\,(8a/10 < x < a) &= \frac{1}{a}\int_{8a/10}^{a} \cos^2\left(\frac{\pi}{2a}\,x\right)\,dx = \frac{1}{a}\left[\frac{1}{2}\,x + \frac{2a}{4\pi}\,\sin\left(\frac{\pi}{a}x\right)\right]_{4a/5}^{a} \\
&= \frac{1}{a}\left[\frac{1}{2}\left(a - \frac{4a}{5}\right) + \frac{a}{2\pi}\left(\sin\left(\frac{\pi}{a}\,a\right) - \sin\left(\frac{\pi}{a}\frac{4a}{5}\right)\right)\right] \\
&= \frac{1}{a}\left[\frac{a}{10} - \frac{a}{2\pi}\,\sin\left(\frac{4\pi}{5}\right)\right] = \frac{1}{10} - \frac{1}{2\pi}\,\sin\left(\frac{4\pi}{5}\right) \approx 0.00645\,.
\end{aligned}$$

The probability of finding the particle near the center is approximately 30 times greater than the probability of finding the particle near the edge when comparing intervals of length $a/5$.

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6. Calculate the momentum space wavefunctions, $\widehat{\psi}_n(p)$, for an infinite square well of width $2a$. Write the eigenfunctions for $\widehat{\psi}_n(p)$ for $n = 1,\ 2,\ 3,$ and 4, and then sketch them.

The momentum space wave functions are attained from the position space wave functions using

$$\widehat{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} e^{-ipx/\hbar}\, \psi(x)\, dx\,. \qquad \text{Do the integral for odd } n \text{ which is}$$

$$\widehat{\psi}_n(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-a}^{a} e^{-ipx/\hbar}\, \frac{1}{\sqrt{a}}\, \cos\left(\frac{n\pi x}{2a}\right) dx \qquad \text{and then for even } n\text{, where}$$

the wavefunction will include a sine. The limits of the integral reflect the fact that all eigenfunctions are zero outside the potential well. Recall angle sum formulas from trigonometry and the expressions for cosine and sine in terms of complex exponentials. You should get

$$\widehat{\psi}_n(p) = \frac{1}{\sqrt{2\pi\hbar a}}\, \frac{(-1)^{\frac{n+1}{2}}}{\left(\frac{p}{\hbar}\right)^2 - \left(\frac{n\pi}{2a}\right)^2}\, \frac{n\pi}{a}\, \cos\left(\frac{p}{\hbar}\, a\right) \qquad \text{for n odd.}$$

By the way, $\sin(n\pi/2) = (-1)^{\frac{n-1}{2}}$ for odd n. $\widehat{\psi}_n(p)$ for even n is of similar form though not the same. Ignore the factor of i in the momentum space wavefunctions for the n even sketches.

Calculating the Fourier transforms of the position space wavefunctions starting with odd n,

$$\widehat{\psi}_n(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-a}^{a} e^{-ipx/\hbar} \frac{1}{\sqrt{a}}\, \cos\left(\frac{n\pi x}{2a}\right) dx \qquad \text{Let } c = p/\hbar \text{ and } b = n\pi/2a\text{. Then}$$

$$\sqrt{2\pi\hbar a}\ \widehat{\psi}_n(p) = \int_{-a}^{a} e^{-icx} \cos(bx)\, dx = \int_{-a}^{a} e^{-icx} \left(\frac{e^{ibx} + e^{-ibx}}{2}\right) dx\,,$$

$$\begin{aligned}
\Rightarrow\quad 2\sqrt{2\pi\hbar a}\ \widehat{\psi}_n(p) &= \int_{-a}^{a} \left(e^{-i(c-b)x} + e^{-i(c+b)x}\right) dx \\
&= \left[\frac{1}{-i(c-b)}\, e^{-i(c-b)x} + \frac{1}{-i(c+b)}\, e^{-i(c+b)x}\right]_{-a}^{a} \\
&= \frac{i}{c^2 - b^2} \left[(c+b)\, e^{-i(c-b)x} + (c-b)\, e^{-i(c+b)x}\right]_{-a}^{a} \\
&= \frac{i}{c^2 - b^2} \left[(c+b)\left(e^{-i(c-b)a} - e^{i(c-b)a}\right) + (c-b)\left(e^{-i(c+b)a} - e^{i(c+b)a}\right)\right] \\
&= \frac{i}{c^2 - b^2} \left[(c+b)(-2i)\sin\Big((c-b)\,a\Big) + (c-b)(-2i)\sin\Big((c+b)\,a\Big)\right] \\
&= \frac{2}{c^2 - b^2} \left[(c+b)\Big(\sin(ca)\,\cos(ba) - \cos(ca)\,\sin(ba)\Big)\right] \\
&\qquad + \frac{2}{c^2 - b^2} \left[(c-b)\Big(\sin(ca)\,\cos(ba) + \cos(ca)\,\sin(ba)\Big)\right] \\
&= \frac{4}{c^2 - b^2} \left[c\sin(ca)\,\cos(ba) - b\cos(ca)\,\sin(ba)\right] \\
&= \frac{4}{c^2 - b^2} \left[c\sin(ca)\,\cancel{\cos\left(\frac{n\pi}{2}\right)} - \frac{n\pi}{2a}\,\cos(ca)\,\sin\left(\frac{n\pi}{2}\right)\right].
\end{aligned}$$

$\cos\left(\frac{n\pi}{2}\right) = 0$ for odd n so is struck, and $\sin\left(\frac{n\pi}{2}\right) = (-1)^{\frac{n-1}{2}}$ so $-\sin\left(\frac{n\pi}{2}\right) = (-1)^{\frac{n+1}{2}}$, and

$$2\sqrt{2\pi\hbar a}\ \widehat{\psi}_n(p) = \frac{(-1)^{\frac{n+1}{2}}}{\left(\frac{p}{\hbar}\right)^2 - \left(\frac{n\pi}{2a}\right)^2}\ \frac{2n\pi}{a}\ \cos\left(\frac{p}{\hbar}a\right)$$

$$\Rightarrow \quad \widehat{\psi}_n(p) = \frac{1}{\sqrt{2\pi\hbar a}}\ \frac{(-1)^{\frac{n+1}{2}}}{\left(\frac{p}{\hbar}\right)^2 - \left(\frac{n\pi}{2a}\right)^2}\ \frac{n\pi}{a}\ \cos\left(\frac{p}{\hbar}a\right) \qquad \text{for odd } n\,.$$

For even n,

$$\widehat{\psi}_n(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-a}^{a} e^{-ipx/\hbar}\frac{1}{\sqrt{a}}\sin\left(\frac{n\pi x}{2a}\right)\,dx\,.$$ Again let $c = p/\hbar$ and $b = n\pi/2a$. Then

$$\sqrt{2\pi\hbar a}\ \widehat{\psi}_n(p) = \int_{-a}^{a} e^{-icx}\sin(bx)\,dx = \int_{-a}^{a} e^{-icx}\left(\frac{e^{ibx} - e^{-ibx}}{2i}\right)dx\,,$$

$$\Rightarrow \quad 2i\sqrt{2\pi\hbar a}\ \widehat{\psi}_n(p) = \int_{-a}^{a}\left(e^{-i(c-b)x} - e^{-i(c+b)x}\right)dx\,.$$

This is the same integral just evaluated, except for the minus sign in front of the second exponential term. Using essentially the same procedure,

$$\begin{aligned} 2i\sqrt{2\pi\hbar a}\ \widehat{\psi}_n(p) &= \frac{4b}{c^2 - b^2}\Big[\sin(ca)\cos(ba) - \cos(ca)\sin(ba)\Big] \\ &= \frac{2n\pi/a}{c^2 - b^2}\left[\sin(ca)\cos\left(\frac{n\pi}{2}\right) - \cos(ca)\cancel{\sin\left(\frac{n\pi}{2}\right)}\right] \end{aligned}$$

The $\sin\left(\frac{n\pi}{2}\right) = 0$ for all even n, and $\cos\left(\frac{n\pi}{2}\right) = (-1)^{\frac{n}{2}}$, so

$$2i\sqrt{2\pi\hbar a}\ \widehat{\psi}_n(p) = \frac{(-1)^{\frac{n}{2}}}{\left(\frac{p}{\hbar}\right)^2 - \left(\frac{n\pi}{2a}\right)^2}\frac{2n\pi}{a}\ \sin\left(\frac{p}{\hbar}a\right)$$

$$\Rightarrow \quad \widehat{\psi}_n(p) = \frac{i}{\sqrt{2\pi\hbar a}}\ \frac{(-1)^{\frac{n+2}{2}}}{\left(\frac{p}{\hbar}\right)^2 - \left(\frac{n\pi}{2a}\right)^2}\ \frac{n\pi}{a}\ \sin\left(\frac{p}{\hbar}a\right) \qquad \text{for even } n$$

The factor of i in the numerator accounts for the exponent of -1 being $(n+2)/2$ instead of $n/2$. The first four momentum space wave functions then are

$$\widehat{\psi}_1(p) = \frac{1}{\sqrt{2\pi\hbar a}}\ \frac{-1}{\left(\frac{p}{\hbar}\right)^2 - \left(\frac{\pi}{2a}\right)^2}\ \frac{\pi}{a}\ \cos\left(\frac{p}{\hbar}a\right),$$

$$\widehat{\psi}_2(p) = \frac{i}{\sqrt{2\pi\hbar a}}\ \frac{-1}{\left(\frac{p}{\hbar}\right)^2 - \left(\frac{\pi}{a}\right)^2}\ \frac{2\pi}{a}\ \sin\left(\frac{p}{\hbar}a\right),$$

$$\widehat{\psi}_3(p) = \frac{1}{\sqrt{2\pi\hbar a}} \frac{1}{\left(\frac{p}{\hbar}\right)^2 - \left(\frac{3\pi}{2a}\right)^2} \frac{3\pi}{a} \cos\left(\frac{p}{\hbar} a\right),$$

$$\widehat{\psi}_4(p) = \frac{i}{\sqrt{2\pi\hbar a}} \frac{1}{\left(\frac{p}{\hbar}\right)^2 - \left(\frac{2\pi}{a}\right)^2} \frac{4\pi}{a} \sin\left(\frac{p}{\hbar} a\right).$$

Sketches of these functions, ignoring the factor of i in the even n wavefunctions, are

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7. Draw graphs of the $n = 1$, $n = 2$, and $n =$ many wavefunctions in position space, energy space, and momentum space.

Examine the graphs below.

Position, Energy, and Momentum Space Wave Functions for $n = 1$

Position, Energy, and Momentum Space Wave Functions for $n = 2$

Postscript: The energy eigenfunctions, $\widetilde{\psi}(E)$, are the eigenvalues of energy so are discontinuous spikes. In momentum space, $\widehat{\psi}(p)$ versus momentum or wave number, the wavefunctions are sinc functions. Energy is related to momentum, $E = p^2/2m = \hbar^2 k^2/2m$, so energy proportional to the square of the wave number is on the horizontal axis of the momentum space graphs. The effect is that the spikes in energy space are "spread" in momentum space at the wave number that corresponds to the eigenenergy. Remember that the relation between position space and momentum space wavefunctions is that one is the Fourier transform of the other.

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8. Given $\Psi(x) = \sum_n c_n \psi_n(x)$, show that $c_n = \int \psi_n^*(x)\,\Psi(x)\,dx$.

This problem is a derivation of the procedure used to calculate Fourier coefficients in a quantum mechanical context and should also highlight some of the utility of the Dirac notation. Remember the techniques of inserting and resolving the identity, and forming position space functions by operating from the left with $<x|$. One thing that is appropriate to introduce at this point is the statement $<x|E_n> = \psi_n(x)$; the inner product of the continuum of position space with the energy eigenkets are the energy eigenfunctions in position space. These eigenfunctions have the independent variable of position and eigenvalues that are energy. For the infinite square well, they are the normalized sines and cosines found in problems 2.

$$
\begin{aligned}
|\psi> = \mathcal{I}\,|\psi> &= \sum_n |E_n><E_n|\psi> \\
\Rightarrow \quad <x|\psi> &= <x|\sum_n |E_n><E_n|\psi> = \sum_n <x|E_n><E_n|\psi> \\
\Rightarrow \quad \Psi(x) &= \sum_n \psi_n(x) <E_n|\psi>
\end{aligned}
$$

where the identity is inserted and resolved in the first line and we prepare to respresent the expression in the second line. The third line in the partial position space representation. Inserting and resolving the identity again preparing to represent the right side entirely in position space,

$$
\begin{aligned}
\Psi(x) &= \sum_n \psi_n(x) <E_n|\mathcal{I}|\psi> = \sum_n \psi_n(x) <E_n|\Big(\sum |x><x|\Big)|\psi> \\
&= \sum_n \psi_n(x) \sum <E_n|x><x|\psi> = \sum_n \psi_n(x) \sum \Big(<E_n|x>\Big)\Big(<x|\psi>\Big)
\end{aligned}
$$

where we have simply rearranged and regrouped. Representing the terms in parentheses,

$$\Rightarrow \quad \Psi(x) \longrightarrow \sum_n \psi_n(x) \int \left(\psi_n^*(x)\right)\left(\Psi(x)\right) dx$$

in the limit that the distance between $|x>$'s approaches zero. Comparing the last line with the given $\Psi(x) = \sum_n \psi_n c_n(x)$, $\Rightarrow \quad c_n = \int \psi_n^*(x)\, \Psi(x)\, dx$.

Postscript: Notice that the derivation is independent of potential.

"In the limit that the distance between $|x>$'s approaches zero" is simply another way to say that x is treated as a continuous variable.

---

9. Calculate the uncertainty in position for a particle in an infinite square well of width $2a$.

Find (a) $<x>$, (b) $<x^2>$, and (c) $\triangle x$ for all n. The limits of integration for an expectation value for position become $-a$ and a because the wavefunction is zero outside those bounds. There are two integrations for each expectation value, one for n_{odd} and one for n_{even}. Realize $\sin(n\pi) = 0$ and $\cos(n\pi) = \pm 1$ for all n. Having found the expectation values, uncertainty is $\triangle x = \left(<x^2> - <x>^2\right)^{1/2}$. What is reasonable for $<x>$? Will it surprise you if the "average" is near the center of the box? The second moment, $<x^2>$, reflects the magnitude of position. Expect this to be a non-zero quantity.

(a) When n is odd,

$$<x>_{\text{n odd}} = \int_{-a}^{+a} \left[\sqrt{\frac{1}{a}} \cos\left(\frac{n\pi x}{2a}\right)\right]^* x \sqrt{\frac{1}{a}} \cos\left(\frac{n\pi x}{2a}\right) dx = \frac{1}{a} \int_{-a}^{+a} x \cos^2\left(\frac{n\pi x}{2a}\right) dx$$

$$= \frac{1}{a}\left[\frac{x^2}{4} + \frac{x \sin\left(\frac{n\pi x}{a}\right)}{\frac{2n\pi}{a}} + \frac{\cos\left(\frac{n\pi x}{a}\right)}{\frac{4n\pi}{a}}\right]_{-a}^{+a} .$$

The first and the third terms inside the brackets are zero, because they are even functions evaluated between symmetric limits, so

$$<x>_{\text{n odd}} = \frac{1}{a}\left[\frac{x \sin\left(\frac{n\pi x}{a}\right)}{\frac{2n\pi}{a}}\right]_{-a}^{+a} = \frac{a \sin(n\pi)}{2n\pi} - \frac{-a \sin(-n\pi)}{2n\pi} = \frac{a}{2n\pi}\left[\sin(n\pi) - \sin(n\pi)\right] = 0 .$$

For even n,

$$<x>_{\text{n even}} = \int_{-a}^{+a} \left[\sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{2a}\right)\right]^* x \sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{2a}\right) dx = \frac{1}{a} \int_{-a}^{+a} x \sin^2\left(\frac{n\pi x}{2a}\right) dx$$

$$= \frac{1}{a}\left[\frac{x^2}{4} - \frac{x \sin\left(\frac{n\pi x}{a}\right)}{\frac{2n\pi}{a}} - \frac{\cos\left(\frac{n\pi x}{a}\right)}{\frac{4n\pi}{a}}\right]_{-a}^{+a} .$$

Again, the first and third terms inside the brackets are even functions evaluated between symmetric limits so they are zero, and

$$<x>_{\text{n even}} = \frac{1}{a}\left[-\frac{x\,\sin\left(\frac{n\pi x}{a}\right)}{\frac{2n\pi}{a}}\right]_{+a}^{-a} = -\frac{1}{a}\left[\frac{x\,\sin\left(\frac{n\pi x}{a}\right)}{\frac{2n\pi}{a}}\right]_{+a}^{-a} = \frac{1}{a}\left[\frac{x\,\sin\left(\frac{n\pi x}{a}\right)}{\frac{2n\pi}{a}}\right]_{-a}^{a} = 0$$

$$\Rightarrow \quad <x> = 0 \quad \text{for all } n\,,$$

or notice that both integrals are odd functions evaluated between symmetric limits so are zero.

(b) The expectation value of position squared for odd quantum number is

$$<x^2>_{\text{n odd}} = \int_{-a}^{+a}\left[\sqrt{\frac{1}{a}}\cos\left(\frac{n\pi x}{2a}\right)\right]^* x^2\,\sqrt{\frac{1}{a}}\cos\left(\frac{n\pi x}{2a}\right)\,dx = \frac{1}{a}\int_{-a}^{+a} x^2\,\cos^2\left(\frac{n\pi x}{2a}\right)\,dx$$

$$= \frac{1}{a}\left[\frac{x^3}{6} + \left(\frac{x^2}{4\left(\frac{n\pi}{2a}\right)} - \frac{1}{8\left(\frac{n\pi}{2a}\right)^3}\right)\sin\left(\frac{n\pi x}{a}\right) + \frac{x\,\cos\left(\frac{n\pi x}{a}\right)}{4\left(\frac{n\pi}{2a}\right)^2}\right]_{-a}^{+a}.$$

Since $\sin(n\pi) = 0$ for all n, the middle term with a multiple of sine is zero at both a and $-a$,

$$\Rightarrow \quad <x^2>_{\text{n odd}} = \frac{1}{a}\left[\frac{a^3}{6} - \frac{(-a)^3}{6} + \frac{a\,\cos\,(n\pi)}{4\left(\frac{n^2\pi^2}{4a^2}\right)} - \frac{-a\,\cos\,(-n\pi)}{4\left(\frac{n^2\pi^2}{4a^2}\right)}\right].$$

Both the cosine terms are -1 for all odd n, so

$$<x^2>_{\text{n odd}} = \frac{1}{a}\left[\frac{a^3}{3} - \frac{2a^3}{n^2\pi^2}\right] = \frac{a^2}{3} - \frac{2a^2}{n^2\pi^2}\,.$$

For even n, the calculation is very similar except the integration is over sine squared,

$$<x^2>_{\text{n even}} = \frac{1}{a}\int_{-a}^{+a} x^2\,\sin^2\left(\frac{n\pi x}{2a}\right)\,dx$$

$$= \frac{1}{a}\left[\frac{x^3}{6} - \left(\frac{x^2}{4\left(\frac{n\pi}{2a}\right)} - \frac{1}{8\left(\frac{n\pi}{2a}\right)^3}\right)\sin\left(\frac{n\pi x}{a}\right) - \frac{x\,\cos\left(\frac{n\pi x}{a}\right)}{4\left(\frac{n\pi}{2a}\right)^2}\right]_{-a}^{+a}.$$

Again, the middle term vanishes at $x = \pm a$, and the cosine terms are $+1$ for all even n, so

$$<x^2>_{\text{n even}} = \frac{1}{a}\left[\frac{a^3}{3} - \frac{2a^3}{n^2\pi^2}\right] = \frac{a^2}{3} - \frac{2a^2}{n^2\pi^2}\,.$$

This is the same as the n odd case, so we conclude

$$<x^2> = \frac{a^2}{3} - \frac{2a^2}{n^2\pi^2}\,.$$

(c) $\qquad \triangle x = \left(<x^2> - <x>^2 \right)^{1/2} = \left(\dfrac{a^2}{3} - \dfrac{2a^2}{n^2\pi^2} \right)^{1/2}$ for all n.

---

10. Calculate the uncertainty in momentum for a particle in an infinite square well of width $2a$.

Find (a) $<p>$, (b) $<p^2>$, and (c) $\triangle p$ for all n. The expectation values can be calculated in momentum space since the $\widehat{\psi}_n(p)$ are known from problem 6. It is easier to stay in position space and calculate expectation values using the P_{op} representation in position space, i.e.,

$$<p> = \int_{-\infty}^{+\infty} \psi^*(x)\, P_{op}\, \psi(x)\, dx \quad \text{where} \quad P_{op} = -i\hbar\nabla = -i\hbar \frac{d}{dx}$$

in one spatial dimension. The wavefunction is zero outside the box in position space so the limits of integration are $\pm a$. Find $<p^2>$ following the same procedures except using

$$P_{op}^2 = (-i\hbar\nabla)(-i\hbar\nabla) = \left(-i\hbar \frac{d}{dx}\right)\left(-i\hbar \frac{d}{dx}\right) = -\hbar^2 \frac{d^2}{dx^2}.$$

The answers that you should anticipate concern the fact that nothing prejudices momentum to the left or right. The magnitude of the momentum is non-zero, so will be reflected by non-zero expectation values in the second moment.

$$\begin{aligned}
\text{(a)} \quad <p>_{\text{n odd}} &= \int_{-\infty}^{\infty} \left[\sqrt{\frac{1}{a}} \cos\left(\frac{n\pi x}{2a}\right)\right]^* \left(-i\hbar \frac{d}{dx}\right) \left[\sqrt{\frac{1}{a}} \cos\left(\frac{n\pi x}{2a}\right)\right] dx \\
&= \frac{-i\hbar}{a} \int_{-a}^{a} \cos\left(\frac{n\pi x}{2a}\right) \frac{d}{dx} \cos\left(\frac{n\pi x}{2a}\right) dx = \frac{in\pi\hbar}{2a^2} \int_{-a}^{a} \cos\left(\frac{n\pi x}{2a}\right) \sin\left(\frac{n\pi x}{2a}\right) dx \\
&= \frac{in\pi\hbar}{2a^2} \left[\frac{2a}{2n\pi} \sin^2\left(\frac{n\pi x}{2a}\right)\right]_{-a}^{a} = \frac{i\hbar}{2a} \left[\sin^2\left(\frac{n\pi}{2}\right) - \sin^2\left(\frac{-n\pi}{2}\right)\right].
\end{aligned}$$

Since $\sin\left(\dfrac{\pm n\pi}{2}\right) = \pm 1$ for odd n, $\sin^2\left(\dfrac{\pm n\pi}{2}\right) = 1$, so $<p>_{\text{n odd}} = \dfrac{i\hbar}{2a}[1-1] = 0$.

$$\begin{aligned}
<p>_{\text{n even}} &= \int_{-\infty}^{\infty} \left[\sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{2a}\right)\right]^* \left(-i\hbar \frac{d}{dx}\right) \left[\sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{2a}\right)\right] dx \\
&= \frac{-i\hbar}{a} \int_{-a}^{a} \sin\left(\frac{n\pi x}{2a}\right) \frac{d}{dx} \sin\left(\frac{n\pi x}{2a}\right) dx = -\frac{in\pi\hbar}{2a^2} \int_{-a}^{a} \sin\left(\frac{n\pi x}{2a}\right) \cos\left(\frac{n\pi x}{2a}\right) dx \\
&= -\frac{in\pi\hbar}{2a^2} \left[\frac{2a}{2n\pi} \sin^2\left(\frac{n\pi x}{2a}\right)\right]_{-a}^{a} = -\frac{i\hbar}{2a} \left[\sin^2\left(\frac{n\pi}{2}\right) - \sin^2\left(\frac{-n\pi}{2}\right)\right].
\end{aligned}$$

$\sin\left(\dfrac{n\pi}{2}\right) = 0$ for all even n so both sine terms are zero,

$$\Rightarrow \quad <p>_{\text{n even}} = -\frac{i\hbar}{2a}[0-0] = 0 \quad \Rightarrow \quad <p> = 0 \quad \text{for all } n.$$

Alternatively, both integrals are odd functions evaluated between symmetric limits so are zero.

$$\text{(b)} \quad <p^2>_{\text{n odd}} = \int_{-\infty}^{\infty} \left[\sqrt{\frac{1}{a}}\cos\left(\frac{n\pi x}{2a}\right)\right]^* \left(-i\hbar\frac{d}{dx}\right)\left(-i\hbar\frac{d}{dx}\right)\left[\sqrt{\frac{1}{a}}\cos\left(\frac{n\pi x}{2a}\right)\right] dx$$

$$= -\frac{\hbar^2}{a}\int_{-a}^{a}\cos\left(\frac{n\pi x}{2a}\right)\frac{d^2}{dx^2}\cos\left(\frac{n\pi x}{2a}\right) dx = \frac{\hbar^2}{a}\left(\frac{n\pi}{2a}\right)^2\int_{-a}^{a}\cos^2\left(\frac{n\pi x}{2a}\right) dx$$

$$= \frac{n^2\pi^2\hbar^2}{4a^3}\left[\frac{x}{2}+\frac{2a}{4n\pi}\sin\left(\frac{n\pi x}{a}\right)\right]_{-a}^{a} = \frac{n^2\pi^2\hbar^2}{4a^3}\left[\frac{a}{2}-\frac{-a}{2}+\frac{2a}{4n\pi}\left(\sin(n\pi)-\sin(-n\pi)\right)\right].$$

Both sine terms are zero so $<p^2>_{\text{n odd}} = \dfrac{n^2\pi^2\hbar^2}{4a^2}$.

$$<p^2>_{\text{n even}} = -\frac{\hbar^2}{a}\int_{-a}^{a}\sin\left(\frac{n\pi x}{2a}\right)\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{2a}\right) dx = \frac{\hbar^2}{a}\left(\frac{n\pi}{2a}\right)^2\int_{-a}^{a}\sin^2\left(\frac{n\pi x}{2a}\right) dx$$

$$= \frac{n^2\pi^2\hbar^2}{4a^3}\left[\frac{x}{2}-\frac{2a}{4n\pi}\sin\left(\frac{n\pi x}{a}\right)\right]_{-a}^{a}$$

$$= \frac{n^2\pi^2\hbar^2}{4a^3}\left[\frac{a}{2}-\frac{-a}{2}-\frac{2a}{4n\pi}\left(\sin(n\pi)+\sin(-n\pi)\right)\right] = \frac{n^2\pi^2\hbar^2}{4a^2}$$

$$\Rightarrow \quad <p^2> = \frac{n^2\pi^2\hbar^2}{4a^2} \quad \text{for all } n.$$

$$\text{(c)} \quad \triangle p = \left(<p^2> - <p>^2\right)^{1/2} = \left(<p^2> - 0\right)^{1/2} = \left(<p^2>\right)^{1/2}, \quad \Rightarrow \quad \triangle p = \frac{n\pi\hbar}{2a} \quad \text{for all } n.$$

Postscript: It is easier to do this calculation in position space than momentum space because of the relative complexity of the $\widehat{\psi}_n(p)$'s and the relative difficulty of the resulting integrations.

---

11. Normalize the wavefunction

$$\Psi(x) = N(a^2 - x^2)$$

describing a particle confined in an infinite square well of width $2a$.

Problems 11 and 12 are intended to emphasize that wavefunctions are generally linear combinations of the eigenfunctions. A particle in an infinite square well can be in its ground state, any excited state, or any linear combination of its ground state and all of its excited states. Symbollically,

$$\Psi(x) = c_1\,\psi_1(x) + c_2\,\psi_2(x) + c_3\,\psi_3(x) + \cdots = \sum_{n=1}^{\infty} c_n\,\psi_n(x),$$

where the c_n are constants that describe the relative contributions of each eigenfunction. The relative magnitudes of the c_n are fixed by normalization. Limited only by the constraint of normalization, the c_n can be anything, meaning the linear combination $\Psi(x)$ can be any shape.

The components of $\Psi(x)$, the eigenfunctions, must be orthogonal, otherwise, eigenfunctions would contain portion of other eigenfunctions, and the c_n, would not be unique. Without unique c_n, the expansion $\Psi(x) = \sum c_n \psi_n(x)$ is not unique, and thus, it is not useful. Problem XX of part 2 of chapter 1 demonstrated that sines and cosines are orthogonal. The eigenfunctions of a particle in an infinite square well are composed of sines and cosines so are orthogonal.

$$
\begin{aligned}
&<\psi|\psi> = 1 \quad \Rightarrow \quad \int_{-\infty}^{\infty} \psi(x)^* \psi(x)\, dx = 1 \\
\Rightarrow\ 1 &= \int_{-\infty}^{\infty} N^* (a^2 - x^2)^* N (a^2 - x^2)\, dx = |N|^2 \int_{-a}^{a} (a^2 - x^2)^2\, dx \\
&= |N|^2 \int_{-a}^{a} (a^4 - 2a^2x^2 + x^4)\, dx = |N|^2 \left(a^4 \int_{-a}^{a} dx - 2a^2 \int_{-a}^{a} x^2\, dx + \int_{-a}^{a} x^4\, dx \right) \\
&= |N|^2 \left[a^4 x - 2a^2 \frac{x^3}{3} + \frac{x^5}{5} \right]_{-a}^{a} \\
&= |N|^2 \left[a^4 (a - -a) - \frac{2a^2}{3} (a^3 - (-a)^3) + \frac{1}{5} (a^5 - (-a)^5) \right] \\
&= |N|^2 \left[2a^5 - \frac{4a^5}{3} + \frac{2a^5}{5} \right] = |N|^2 a^5 \left[\frac{2}{3} + \frac{2}{5} \right] = |N|^2 a^5 \left[\frac{10}{15} + \frac{6}{15} \right] = |N|^2 a^5 \frac{16}{15}
\end{aligned}
$$

$$
\Rightarrow \quad N^2 = \frac{15}{16a^5} \quad \Rightarrow \quad N = \frac{1}{4a^2}\sqrt{\frac{15}{a}} \quad \Rightarrow \quad \Psi(x) = \frac{1}{4a^2}\sqrt{\frac{15}{a}} \left(a^2 - x^2 \right).
$$

---

12. Expand the system described in problem 11 into its component eigenfunctions.

For the infinite square well,

$$
\Psi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \quad \text{means} \quad \Psi(x) = \sum_{n \text{ odd}}^{\infty} b_n \sqrt{\frac{1}{a}} \cos\left(\frac{n\pi x}{2a}\right) + \sum_{n \text{ even}}^{\infty} d_n \sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{2a}\right),
$$

where the c_n are written as b_n and d_n just to aid identification. The wavefunction is an even function because $\Psi(-x) = \Psi(x)$. Only even eigenfunctions, therefore, can contribute so $d_n = 0$ for all even n. (Do not confuse even/odd quantum numbers with even/odd functions. Cosines are even functions, and for the infinite square well, they correspond to the odd quantum numbers. Sines are odd functions, but correspond to even quantum numbers for the infinite square well). Odd eigenfunctions cannot contribute to an even $\Psi(x)$, otherwise $\Psi(x)$ would have at least one odd component and would be neither an even nor an odd function. The wavefunction reduces to

$$
\Psi(x) = \sum_{\text{n odd}}^{\infty} b_n \sqrt{\frac{1}{a}} \cos\left(\frac{n\pi x}{2a}\right).
$$

The b_n are then found using procedures similar to finding Fourier coefficients.

$$
\begin{aligned}
b_n &= \int_{-a}^{a} \psi_n^*(x)\,\Psi(x)\,dx = \int_{-a}^{a} \sqrt{\frac{1}{a}}\,\cos\left(\frac{n\pi x}{2a}\right)\,\frac{1}{4}\sqrt{\frac{15}{a^5}}\,(a^2-x^2)\,dx \\
&= \frac{\sqrt{15}}{4a^3}\int_{-a}^{a}\cos\left(\frac{n\pi x}{2a}\right)(a^2-x^2)\,dx = \frac{\sqrt{15}}{4a}\int_{-a}^{a}\cos\left(\frac{n\pi x}{2a}\right)dx - \frac{\sqrt{15}}{4a^3}\int_{-a}^{a}x^2\cos\left(\frac{n\pi x}{2a}\right)dx \\
&= \frac{\sqrt{15}}{4a}\left(\frac{2a}{n\pi}\right)\sin\left(\frac{n\pi x}{2a}\right)\Bigg|_{-a}^{a} \\
&\qquad - \frac{\sqrt{15}}{4a^3}\left[\frac{2x\,\cos\left(\frac{n\pi x}{2a}\right)}{\left(\frac{n\pi}{2a}\right)^2} + \frac{x^2}{\left(\frac{n\pi}{2a}\right)}\sin\left(\frac{n\pi x}{2a}\right) - \frac{2}{\left(\frac{n\pi}{2a}\right)^3}\sin\left(\frac{n\pi x}{2a}\right)\right]_{-a}^{a} \\
&= \frac{\sqrt{15}}{2n\pi}\sin\left(\frac{n\pi x}{2a}\right)\Bigg|_{-a}^{a} - \frac{\sqrt{15}}{4a^3}\left[\frac{8a^2x}{n^2\pi^2}\cos\left(\frac{n\pi x}{2a}\right) + \frac{2ax^2}{n\pi}\sin\left(\frac{n\pi x}{2a}\right) - \frac{16a^3}{n^3\pi^3}\sin\left(\frac{n\pi x}{2a}\right)\right]_{-a}^{a} \\
&= \frac{\sqrt{15}}{2n\pi}\left[\sin\left(\frac{n\pi}{2}\right) - \sin\left(-\frac{n\pi}{2}\right)\right] - \frac{\sqrt{15}}{4a^3}\left[\frac{8a^2a}{n^2\pi^2}\cos\left(\frac{n\pi}{2}\right) - \frac{8a^2(-a)}{n^2\pi^2}\cos\left(-\frac{n\pi}{2}\right)\right. \\
&\qquad \left. + \frac{2a\,a^2}{n\pi}\sin\left(\frac{n\pi}{2}\right) - \frac{2a\,(-a)^2}{n\pi}\sin\left(-\frac{n\pi}{2}\right) - \frac{16a^3}{n^3\pi^3}\left(\sin\left(\frac{n\pi}{2}\right) - \sin\left(-\frac{n\pi}{2}\right)\right)\right] \\
&= \frac{\sqrt{15}}{n\pi}\sin\left(\frac{n\pi}{2}\right) - \frac{\sqrt{15}}{4a^3}\left[\frac{16a^3}{n^2\pi^2}\cos\left(\frac{n\pi}{2}\right) + \frac{4a^3}{n\pi}\sin\left(\frac{n\pi}{2}\right) - \frac{32a^3}{n^3\pi^3}\sin\left(\frac{n\pi}{2}\right)\right].
\end{aligned}
$$

Remembering that the quantum number n is odd only,

$$
\cos\left(\frac{n\pi}{2}\right) = 0 \;\text{ for all } n, \qquad \text{and} \qquad \sin\left(\frac{n\pi}{2}\right) = (-1)^{\frac{n-1}{2}}.
$$

Using these in the last expression yields

$$
\begin{aligned}
b_n &= (-1)^{\frac{n-1}{2}}\frac{\sqrt{15}}{n\pi} - \sqrt{15}\left[(-1)^{\frac{n-1}{2}}\frac{1}{n\pi} - (-1)^{\frac{n-1}{2}}\frac{8}{n^3\pi^3}\right] \\
&= (-1)^{\frac{n-1}{2}}\frac{\cancel{\sqrt{15}}}{\cancel{n\pi}} - (-1)^{\frac{n-1}{2}}\frac{\cancel{\sqrt{15}}}{\cancel{n\pi}} + (-1)^{\frac{n-1}{2}}\frac{8\sqrt{15}}{n^3\pi^3} = (-1)^{\frac{n-1}{2}}\frac{8\sqrt{15}}{n^3\pi^3}.
\end{aligned}
$$

Then the expansion in terms of component eigenfunctions is

$$
\Psi(x) = \sum_{\text{n odd}}^{\infty}(-1)^{\frac{n-1}{2}}\frac{8\sqrt{15}}{n^3\pi^3}\sqrt{\frac{1}{a}}\cos\left(\frac{n\pi x}{2a}\right) = \frac{8}{\pi^3}\sqrt{\frac{15}{a}}\sum_{\text{n odd}}^{\infty}\frac{(-1)^{\frac{n-1}{2}}}{n^3}\cos\left(\frac{n\pi x}{2a}\right).
$$

---

13. Find the time-dependent wavefunction for the system described in problem 11.

Chapter 2 introduced time evolution for the case $\mathcal{H} \neq \mathcal{H}(t)$ using small matrix operators by first expanding $|\psi(t)>$ in the eigenstates of $\mathcal{H}$, and then using the fact that the eigenstates of $\mathcal{H}$

obey $i\hbar \frac{d}{dt} | E_n > = E_n | E_n >$ with the simple time dependence $| E_n (t) > = e^{-iE_n t/\hbar} | E_n >$. When the general wavefunction is a linear combination of eigenfunctions, the time-dependent wavefunction is the sum of the time evolved eigenfunctions, or

$$\Psi (x,t) = \sum_n c_n \psi_n (x) e^{-iE_n t/\hbar}.$$

The Hamiltonian of the infinite square well is $\mathcal{H} = p^2/2m$ inside the well and zero elsewhere. This Hamiltonian is time independent so these procedures apply to the infinite square well.

The eigenenergies of the infinite square well are given in problem 1, so the exponential terms are

$$e^{-iE_n t/\hbar} = \exp\left[-i\left(n^2 \frac{\pi^2\hbar^2}{8ma^2}\right)\frac{t}{\hbar}\right] = \exp\left(-i\,\frac{\pi^2 n^2 \hbar}{8ma^2}\,t\right).$$

Merging this with the normalized eigenstates calculated in problems 11 and 12,

$$\Psi (x,t) = \frac{8}{\pi^3}\sqrt{\frac{15}{a}} \sum_{\text{n odd}}^{\infty} \frac{(-1)^{\frac{n-1}{2}}}{n^3} \cos\left(\frac{n\pi x}{2a}\right) \exp\left(-i\,\frac{\pi^2 n^2 \hbar}{8ma^2}\,t\right).$$

---

14. Find the eigenenergies of a two-dimensional infinite square well of width $2a$ on each side.

This problem extends the discussion to higher dimension. It also introduces the method of **separation of variables** for partial differential equations (PDE). This method is used repeatedly in future chapters and it is often among the first techniques selected to try to solve a PDE. A variables separable PDE has a solution of the form $f(x,y) = g(x)\,h(y)$, meaning that the solution in two dimensions is the product of two one-dimensional solutions. The strategy is to assume the existence of such a solution, and if such a solution is found, the assumption was valid.

In two dimensions, wavefunctions in position space are $\psi = \psi(x,y)$. The time-independent form of the Schrodinger equation within a two-dimensional infinite square well is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi(x,y) = E\,\psi(x,y)$$

where the potential energy function is excluded because it is defined to be zero in the region of confinement. The wavefunction is zero elsewhere so other regions are not considered. Assume a solution of the form $\psi(x,y) = f(x)\,g(y)$. The Schrodinger equation becomes

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) f(x)\,g(y) = E\,f(x)\,g(y)$$

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\left(g(y)\frac{\partial^2}{\partial x^2} f(x) + f(x)\frac{\partial^2}{\partial y^2} g(y)\right) = E\,f(x)\,g(y)$$

$$\Rightarrow \quad \frac{1}{f(x)\,g(y)}\left(g(y)\frac{d^2}{dx^2}f(x)+f(x)\frac{d^2}{dy^2}g(y)\right)=-\frac{2mE}{\hbar^2}$$

$$\Rightarrow \quad \frac{1}{f(x)}\frac{d^2}{dx^2}f(x)+\frac{1}{g(y)}\frac{d^2}{dy^2}g(y)=-\frac{2mE}{\hbar^2}\,.$$

The variables x and y are linearly independent. The first term is dependent only on x and the second term is dependent only on y. Their sum is constant because the right side of the equation is constant. Except for trivial cases, the only way this can be true is if the first term is equal to a constant and the second term is equal to another constant. This means

$$\frac{1}{f(x)}\frac{d^2}{dx^2}f(x)=C_1\,, \qquad \text{and} \qquad \frac{1}{g(y)}\frac{d^2}{dy^2}g(y)=C_2\,.$$

The constants C_1 and C_2 must sum to $-2mE/\hbar^2$. We chose the **separation constants**

$$\frac{1}{f(x)}\frac{d^2}{dx^2}f(x)=-\frac{2mE_x}{\hbar^2}\,, \qquad \text{and} \qquad \frac{1}{g(y)}\frac{d^2}{dy^2}g(y)=-\frac{2mE_y}{\hbar^2}\,, \tag{1}$$

$$\Rightarrow \quad \frac{d^2}{dx^2}f(x)=-\frac{2mE_x}{\hbar^2}f(x)\,, \qquad \text{and} \qquad \frac{d^2}{dy^2}g(y)=-\frac{2mE_y}{\hbar^2}g(y)\,.$$

Both have the same form as the Schrodinger equation for the infinite square well in one dimension,

$$\frac{d^2}{dx^2}\psi(x)=-\frac{2mE}{\hbar^2}\psi(x)\,,$$

so necessarily both equations have the same solution. Therefore, the component eigenvalues are

$$E_x=n_x^2\frac{\pi^2\hbar^2}{8ma^2} \qquad \text{and} \qquad E_y=n_y^2\frac{\pi^2\hbar^2}{8ma^2}\,.$$

Total energy is the sum of the energies in the two degrees of freedom, so

$$E_{n_x,n_y}=E_x+E_y=\frac{\pi^2\hbar^2}{8ma^2}\left(n_x^2+n_y^2\right)\,.$$

Postscript: Do not confuse the method of separation of variables used for partial differential equations with the variables separable method used for ordinary differential equations (ODE). They both concern arranging equations so that the variables are within the same term. Separating the variables of a PDE is an effort to reduce the PDE to a series of ODE's. If the PDE can be separated, methods appropriate to ODE's may then be used to solve the ODE's individually and these individual solutions are recombined to attain the solution to the PDE originally sought.

Remember that $\psi(x,y)=f(x)\,g(y)$ is an assumption. A solution of this form was found for the two-dimensional infinite square well so the assumption proved to be valid. If such a solution cannot be found in attempting to solve a PDE, then the assumption $\psi(x,y)=f(x)\,g(y)$ is invalid and other means must be used to attain a solution.

The selection of separation constants, as in equation (1), is an art. Realize that we are guided by the literature in our selections.

Notice that there are two quantum numbers, n_x and n_y, for the two-dimensional problem. In general, there will be as many quantum numbers as there are degrees of freedom in the problem. For a three dimensional system, for instance, there will be three quantum numbers.

Probability and probability density in two dimensions are $|\psi(x,y)|^2\,dx\,dy$ and $|\psi(x,y)|^2$ respectively, and probability density has units of $1/\text{length}$.
