# 5.61 Fall 2017
# Problem Set #3 Solutions

## 1

**A.** McQuarrie, page 120, #3-3 Show $\hat{A}f(x) = \lambda f(x)$, for $\lambda$ constant. Find the eigenvalue $\lambda$.

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Solution:

**(a)**

$$\hat{A} = \frac{d^2}{dx^2} \tag{1.1}$$

$$f(x) = \cos(\omega x) \tag{1.2}$$

$$\frac{d^2}{dx^2}\cos(\omega x) = -\omega^2 \cos(\omega x) = -\omega^2 f(x) \tag{1.3}$$

$$\implies \lambda = -\omega^2 \tag{1.4}$$

**(b)**

$$\hat{A} = \frac{d}{dt} \tag{1.5}$$

$$f(t) = e^{i\omega t} \tag{1.6}$$

$$\frac{d}{dt}e^{i\omega t} = i\omega e^{i\omega t} = i\omega f(t) \tag{1.7}$$

$$\implies \lambda = i\omega \tag{1.8}$$

**(c)**

$$\hat{A} = \frac{d^2}{dx^2} + 2\frac{d}{dt} + 3 \tag{1.9}$$

$$f(x) = e^{\alpha x} \tag{1.10}$$

$$\left(\frac{d^2}{dx^2} + 2\frac{d}{dx} + 3\right)e^{\alpha x} = \frac{d^2}{dx^2}e^{\alpha x} + 2\frac{d}{dx}e^{\alpha x} + 3e^{\alpha x} \tag{1.11}$$

$$= \alpha^2 e^{\alpha x} + 2\alpha e^{\alpha x} + 3e^{\alpha x} \tag{1.12}$$

$$= (\alpha^2 + 2\alpha + 3)f(x) \tag{1.13}$$

$$\implies \lambda = \alpha^2 + 2\alpha + 3 \tag{1.14}$$

**(d)**

$$\hat{A} = \frac{\partial}{\partial y} \tag{1.15}$$

$$f(x, y) = x^2 e^{6y} \tag{1.16}$$

$$\frac{\partial}{\partial y}(x^2 e^{6y}) = 6x^2 e^{6y} = 6f(x, y) \tag{1.17}$$

$$\implies \lambda = 6 \tag{1.18}$$

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**B.** McQuarrie, page 120, #3-4

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Solution:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{1.19}$$

$$\nabla^2[\cos ax \cos by \cos cz] = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)[\cos ax \cos by \cos cz] \tag{1.20}$$

$$= -a^2 - b^2 - c^2[\cos ax \cos by \cos cz] \tag{1.21}$$

$$\implies \lambda = -a^2 - b^2 - c^2 \tag{1.22}$$

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**C.** McQuarrie, page 182, #4-11

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Solution:

**(a)** The Commutator $[\widehat{A}, \widehat{B}] = \widehat{A}\widehat{B} - \widehat{B}\widehat{A}$ operates on $f(x)$.

$$\left[\frac{d^2}{dx^2}, x\right] f = \frac{d^2}{dx^2}(xf) - x\frac{d^2}{dx^2}f \tag{1.23}$$

$$= \frac{d}{dx}(f + xf') - xf'' \tag{1.24}$$

$$= f' + f' + xf'' - xf'' \tag{1.25}$$

$$= 2f' \tag{1.26}$$

$$\implies \left[\frac{d^2}{dx^2}, x\right] = 2\frac{d}{dx} \tag{1.27}$$

**(b)**

$$\begin{aligned}
\left[\frac{d}{dx}-x,\frac{d}{dx}+x\right]f &= \left(\frac{d}{dx}-x\right)\left(\frac{d}{dx}f+xf\right)-\left(\frac{d}{dx}+x\right)\left(\frac{d}{dx}f-xf\right) && (1.28)\\
&= \left(\frac{d}{dx}-x\right)(f'+xf)-\left(\frac{d}{dx}+x\right)(f'-xf) && (1.29)\\
&= \frac{d}{dx}(f'+xf)-x(f'+xf)-\frac{d}{dx}(f'-xf)-x(f'-xf) && (1.30)\\
&= (f''+f+xf')-(xf'+x^2f)-(f''-f-xf')-(xf'-x^2f) && (1.31)\\
&= 2f && (1.32)\\
\Rightarrow \left[\frac{d}{dx}-x,\frac{d}{dx}+x\right] &= 2 && (1.33)
\end{aligned}$$

**(c)**

$$\begin{aligned}
\left[\int_0^x dx,\frac{d}{dx}\right] &= \int_0^x dx\frac{df}{dx}-\frac{d}{dx}\int_0^x f\,dx && (1.34)\\
&= \int_0^x df - f && (1.35)\\
&= f(x)-f(0)-f(x) && (1.36)\\
&= -f(0) && (1.37)\\
\Rightarrow \left[\int_0^x dx,\frac{d}{dx}\right] &= \text{``}\,-(\quad)|_{x=0}\,\text{''} && (1.38)\\
&= -\int dx\delta(x) && (1.39)
\end{aligned}$$

(There's no particularly good notation for this type of operation.)

**(d)**

$$\begin{aligned}
\left[\frac{d^2}{dx^2}-x,\frac{d}{dx}+x^2\right] &= \left[\frac{d^2}{dx^2},\frac{d}{dx}\right]+\left[\frac{d^2}{dx^2},x^2\right]-\left[x,\frac{d}{dx}\right]-[x,x^2] && (1.40)\\
&= 0+x\left[\frac{d^2}{dx^2},x\right]+\left[\frac{d^2}{dx^2},x\right]x+\left[\frac{d}{dx},x\right]-0 && (1.41)\\
&= x\left(2\frac{d}{dx}\right)+\left(2\frac{d}{dx}\right)x+1 && (1.42)\\
&= 2x\frac{d}{dx}+2x\frac{d}{dx}+2+1 && (1.43)\\
&= 3+4x\frac{d}{dx}. && (1.44)
\end{aligned}$$

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## 2 McQuarrie, pages 121-122, #3-11. Continuity of $\psi'$

<u>Solution:</u>

Beginning with the Schrödinger equation

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi(x), \tag{2.1}$$

we integrate both sides from $a - \varepsilon$ to $a + \varepsilon$ (taking the limit $\varepsilon \to 0$), where $a$ is some arbitrary fixed value of $x$,

$$\lim_{\varepsilon \to 0} \left[ \int_{a-\varepsilon}^{a+\varepsilon} \frac{d^2\psi}{dx^2} dx \right] = \frac{2m}{\hbar^2} \lim_{\varepsilon \to 0} \left[ \int_{a-\varepsilon}^{a+\varepsilon} [V(x) - E]\psi(x) dx \right] \tag{2.2}$$

$$\lim_{\varepsilon \to 0} \left[ \left. \frac{d\psi}{dx} \right|_{a+\varepsilon} - \left. \frac{d\psi}{dx} \right|_{a-\varepsilon} \right] = \frac{2m}{\hbar^2} \lim_{\varepsilon \to 0} [(V(a) - E)\psi(a) 2\varepsilon]. \tag{2.3}$$

If the left side of Eq 2.3 is 0, then by definition $d\psi/dx$ is continuous at $x = a$. The right side of Eq 2.3 is obtained by noting than in the limit that $\varepsilon \to 0$, the integral about $x = a$ is just equal to the integrand evaluated at $x = a$ (if the integrand is continuous) times the width of the integration limits, which is simply $2\varepsilon$. Since this first case assumes $V(x)$ is continuous, and since $\psi(x)$ is always continuous, we can perform this "rigorous limiting approximation." (Apologies if that sounds like an oxymoron). Since $(V(a) - E)\psi(a)$ is just some constant number, the limit on the right hand side of Eq 2.3 is equal to 0. Therefore, the condition for continuity of $d\psi/dx$ at $x = a$ is satisfied. Since $a$ was an arbitrary value for $x$, $d\psi/dx$ must be continuous everywhere.

If $V(x)$ is not continuous at $x = a$, then we need to split up the integral into two parts

$$\begin{aligned}
\frac{2m}{\hbar^2} \lim_{\varepsilon \to 0} \left[ \int_{a-\varepsilon}^{a+\varepsilon} [V(x) - E]\psi(x) dx \right] &= \frac{2m}{\hbar^2} \lim_{\varepsilon \to 0} \left[ \int_{a-\varepsilon}^{a^-} [V(x) - E]\psi(x) dx \right] && (2.4)\\
&= \frac{2m}{\hbar^2} \lim_{\varepsilon \to 0} \left[ \int_{a+}^{a+\varepsilon} [V(x) - E]\psi(x) dx \right] \\
&= \frac{2m}{\hbar^2} \lim_{\varepsilon \to 0} [(V(a^-) - E)\psi(a^-)\varepsilon + (V(a^+) - E)\psi(a^+)\varepsilon] && (2.5)\\
&= \frac{2m}{\hbar^2} \lim_{\varepsilon \to 0} [(V_\ell + V_r - 2E)\psi(a)\varepsilon] && (2.6)
\end{aligned}$$

In the last step, we replaced $V(a^-)$ with the limiting value of $V(x)$ on the left side of the discontinuity $V_\ell$ (and similarly for $V(a^+)$). Since $\psi(x)$ is continuous, both limits are equal to its value at $x = a$. Examining this limit, we see that even though $V_\ell \neq V_r$, both are still finite numbers. Therefore, the limit (which is $\propto \varepsilon$), still goes to 0. Thus the left side of Eq 2.3 is still zero, and $d\psi/dx$ is continuous even at finite discontinuities in $V(x)$.

In the case that $V(x)$ has an *infinite* discontinuity at $x = a$ (e.g. a particle in a box potential), then either $V_\ell$ or $V_r$ is infinite. The limit as $\varepsilon \to 0$ of Eq 2.6 won't be zero, but some finite number ("$0 \times \infty \sim$ finite"). Therefore, by Eq 2.3, $d\psi/dx$ will have different limiting values depending on which direction you come from. Thus, we've shown that the derivative of the wavefunction is discontinuous at infinite boundaries.

## 3

**A.** McQuarrie, page 123, #3-17

Solution:

For a particle in a box of extent $[0, a]$, we have the normalized eigenfunctions

$$\psi_n = \sqrt{\frac{2}{a}} \sin(n\pi x/a). \tag{3.1}$$

The expectation values, $\langle x \rangle$ and $\langle x^2 \rangle$, for the state $\psi_n$ are

$$\begin{aligned}
\langle x \rangle &= \int_0^a \psi_n^* x \psi_n dx & (3.2)\\
&= \frac{2}{a} \int_0^a x|\psi_n|^2 dx & (3.3)\\
&= \frac{2}{a} \int_0^a x \sin^2(n\pi x/a) dx & (3.4)\\
&= \frac{a}{2}
\end{aligned}$$

$$\begin{aligned}
\langle x^2 \rangle &= \int_0^a \psi_n^* x^2 \psi_n dx & (3.5)\\
&= \frac{2}{a} \int_0^a x^2|\psi_n|^2 dx & (3.6)\\
&= \frac{2}{a} \int_0^a x^2 \sin^2(n\pi x/a) dx & (3.7)\\
&= \frac{a^2}{6} \left(2 - \frac{3}{n^2\pi^2}\right). & (3.8)
\end{aligned}$$

This yields

$$\begin{aligned}
\sigma_x &= \left(\langle x^2 \rangle - \langle x \rangle^2\right)^{1/2} & (3.9)\\
&= \left[\frac{a^2}{6}\left(2 - \frac{3}{n^2\pi^2}\right) - \frac{a^4}{4}\right]^{1/2} & (3.10)\\
&= a\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}} < a. & (3.11)
\end{aligned}$$

Therefore, the uncertainty $\sigma_x$ is always less than $a$, the width of the box. Since we know the particle cannot be outside the box (where $V = \infty$), it makes physical sense that the uncertainty in position can never be larger than the width of the box.

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**B.** McQuarrie, page 127, #3-36

Solution:

In this problem, we apply the de Broglie hypothesis to standing waves in the particle in a box potential. We posit that the waves in the allowed region must satisfy

$$\frac{n\lambda}{2} = a \tag{3.12}$$

$$\Rightarrow \lambda = \frac{2a}{n} \tag{3.13}$$

so that nodes occur at the end points and there are an integral number of half-wavelengths within the box. Using the de Broglie hypothesis to solve for the corresponding momenta, we obtain

$$p_n = \frac{h}{\lambda_n} = \frac{nh}{2a} \tag{3.14}$$

$$\Rightarrow E_n = \frac{p_n^2}{2m} \tag{3.15}$$

$$= \frac{n^2h^2}{8ma^2}. \tag{3.16}$$

The resulting energies match the energy eigenvalues obtained from solving the Schrödinger equation.

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## 4 Particle in an infinite 1-D Well

**A.** McQuarrie, page 122, #3-12. Answer this problem qualitatively by drawing a cartoon for $n = 2$ and $n = 3$ states.

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Solutions: The solutions for a particle in an infinite box of length $a$ are

$$\psi_n(x) = (2/a)^{1/2} \sin\left(\frac{n\pi x}{a}\right).$$

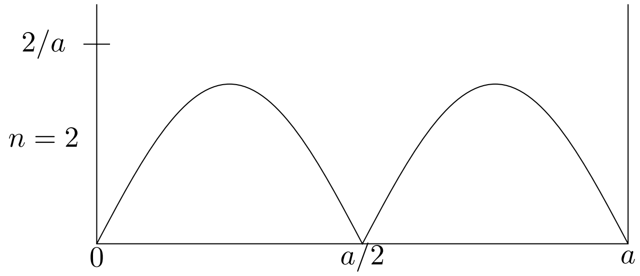
The number of internal nodes is $n - 1$. The nodes are equally spaced.

There is an equal probability of the particles being in each of the lobes of $\psi(x)$.

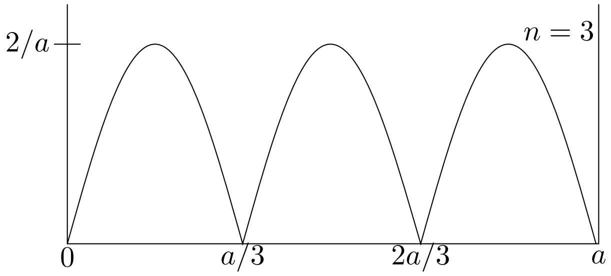
| n | # nodes | probabilities in each lobe |
|---|---|---|
| 1 | 0 | 1 |
| 2 | 1 | 1/2 |
| 3 | 2 | 1/3 |
| 4 | 3 | 1/4 |
| 5 | 4 | 1/5 |

The probabilities in the four equal regions are not equal, which is illustrated by the sketch for $n = 2$ and $n = 3$.

The cartoons that show the difference in probability for regions of width $a/4$ for $n = 2$ and $n = 3$.



Probability is 1/4 in all 4 regions because each contains exactly 1/2 of a lobe



Probability is larger than 1/4 in two regions because there is no node in those regions and smaller than 1/4 in two regions because there is a node in those regions.

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**B.** Is there a simple mathematical/physical reason why the probabilities are not 1/4 for all four regions: $0 \leq x \leq a/4$, $a/4 \leq x \leq a/2$, $a/2 \leq x \leq 3a/4$, and $3a/4 \leq x \leq a$?

[**HINT**: where are the nodes in $\psi_n(x)$?]

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Solution:

Compute the probabilities in the four equal length regions for any value of quantum number $n$.

Probability in region $c \leq x \leq d$

$$P(c,d) = \int_c^d \psi^*(x)\psi(x)dx = \left(\frac{2}{a}\right)\int_c^d \sin^2\left(\frac{n\pi x}{a}\right)dx$$

From integral table

$$\int \sin^2 x dx = \frac{x}{2} - \frac{\sin 2x}{4}.$$

Compute the probabilities

First Region: $0 \leq x \leq a/4 \qquad c = 0,\ d = a/4$

$$\begin{aligned}\sin\left(\frac{2n\pi d}{a}\right) - \sin\left(\frac{2n\pi c}{a}\right) &= \sin\left(\frac{n\pi}{2}\right) - \sin 0 \\ &= 0 \text{ for n even} \\ &= (-1)^{(n-1)/2} \text{ for n odd}\end{aligned}$$

Second Region: $a/4 \leq x \leq a/2 \qquad c = a/4, d = a/2$

$$\begin{aligned}\sin\left(\frac{2n\pi d}{a}\right) - \sin\left(\frac{2n\pi c}{a}\right) &= \sin(n\pi) - \sin\left(\frac{n\pi}{2}\right) \\ &= 0 - (-1)^{(n-1)/2}\ 0 \text{ for even n} \\ &= -(-1)^{(n-1)/2} \text{ for odd n}\end{aligned}$$

Third Region $a/2 \leq x \leq 3a/4 \qquad c = a/2, d = 3a/4$

$$\sin\left(\frac{3n\pi}{2}\right) - \sin(n\pi) = 0 \text{ for even, } -(-1)^{(n-1)/2} \text{ for odd-n.}$$

Fourth Region $3a/4 \leq x \leq a \qquad c = 3a/4, d = a$

$$\sin(2n\pi) - \sin\left(\frac{3n\pi}{2}\right) = 0 \text{ for even-n, } (-1)^{n-1/2} \text{ for odd-n.}$$

Overall we get probability

$$\begin{aligned}&\frac{1}{4} + \frac{1}{2n\pi}(-1)^{(n-1)/2} \text{ for 2 regions}\\ &\frac{1}{4} - \frac{1}{2n\pi}(-1)^{(n-1)/2} \text{ for 2 regions}\end{aligned}$$

The sum over all 4 regions is 1, but the probability is not 1/4 in each of the 4 regions as you saw from the cartoons in part **A**.

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## 5 Particle on a Ring

Solve for the energy levels of the particle confined to a ring as a crude model for the electronic structure of benzene. The two dimensional Schrödinger Equation, in polar coordinates, is

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2} + U(r,\phi)\right]\psi = E\psi.$$

For this problem, $U(r,\phi) = \infty$ for $r \neq a$, but when $r = a$, $U(a,\phi) = 0$.

**A.** This implies that $\psi(r,\phi) = 0$ for $r \neq a$. Why?

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Solution:

We begin with the two-dimensional Schrödinger equation in polar coordinates $(r,\phi)$,

$$\left[-\frac{\hbar^2}{2\mu}\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right\} + U(r,\phi)\right]\psi = E\psi, \tag{5.1}$$

where

$$U(r,\phi) = \begin{cases} \infty & r \neq a \\ 0 & r = a \end{cases} \tag{5.2}$$

Just like the particle in the box, wherever the potential is infinite, the wavefunction must be zero. Otherwise, the Schrödinger equation would diverge. Therefore $\psi(r,\phi) = 0$ for $r \neq a$.

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**B.** If $\psi(r,\phi) = 0$ for $r \neq a$, then $\frac{\partial\psi}{\partial r} = 0$. What is the simplified form of the Schrödinger Equation that applies when the particle is confined to the ring?

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Solution:

Since $\frac{\partial\psi}{\partial r} = 0$, the first term in the brackets of Eq. 5.1 is 0. Additionally, we can replace $r$ with $a$ everywhere else. Since $U(a,\phi) = 0$, this term also vanishes. We are left with

$$-\frac{\hbar^2}{2\mu}\frac{1}{a^2}\frac{\partial^2\psi}{\partial\phi^2} = E\psi. \tag{5.3}$$

---

**C.** Apply the "periodic" boundary condition that $\psi(a,\phi) = \psi(a,\phi+2\pi)$ to obtain the $E_n$ energy levels.

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Solution:

Eq. 5.3 can be rewritten as

$$\frac{\partial^2\psi}{\partial\phi^2} = -\frac{2\mu a^2 E}{\hbar^2}\psi, \tag{5.4}$$

which has solutions

$$\psi(\phi) = Ae^{im\phi}, \qquad m = \pm\left(\frac{2\mu a^2 E}{\hbar^2}\right)^{1/2}. \tag{5.5}$$

Applying the periodic boundary condition $\psi(\phi) = \psi(\phi+2\pi)$ gives us

$$\begin{align}
\psi(\phi) &= \psi(\phi+2\pi) \tag{5.6}\\
e^{im\phi} &= e^{im\phi}e^{im2\pi} \tag{5.7}\\
1 &= e^{im2\pi} \tag{5.8}\\
\Rightarrow m &= 0, \pm1, \pm2, \ldots \tag{5.9}
\end{align}$$

Now solving for $E$ in terms of $m$,

$$\begin{align}
m &= \pm\left(\frac{2\mu a^2 E}{\hbar^2}\right)^{1/2} \tag{5.10}\\
\Rightarrow E_m &= \frac{m^2\hbar^2}{2\mu a^2}, \quad m = 0, \pm1, \pm2, \ldots \tag{5.11}
\end{align}$$

The quantized energy levels are $\propto m^2$ and for $|m| \geq 1$ occur in degenerate pairs of $\{\pm m\}$.

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**D.** The C–C bond length in benzene is 1.397 Å. Thus a circle which goes through all 6 carbon atoms has a radius $r = 1.397$ Å. Use this to estimate the $n = 2 \leftarrow n = 1$ electronic transition for "benzene" treated as an electron on a ring. The longest wavelength allowed electronic transition for real benzene is at 2626 Å. Explain why the agreement is not perfect.

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Solution:

Approximating the electronic structure of benzene as a particle on a ring, with $a = 1.397$ Å, we calculate the $m = 2 \leftarrow m = 1$ transition to lie at

$$
\begin{aligned}
E_2 - E_1 &= (4-1)\frac{\hbar^2}{2m_e(1.397\ \text{Å})^2} && (5.12)\\
&= 3\frac{(6.626\times10^{-34}J\cdot s/2\pi)^2}{2(9.11\times10^{-31}kg)(1.397\ \text{Å})^2} && (5.13)\\
&= 9.38\times10^{-19}J && (5.14)\\
\Rightarrow \lambda = \frac{hc}{\Delta E} &= 2120\ \text{Å}. && (5.15)
\end{aligned}
$$

This is fairly close to the experimental value of 2626 Å, indicating that the particle on a ring is a qualitatively correct picture of benzene's electronic structure. There are various reasons for the discrepancy, however. First, the potential is not uniform with $\phi$, but has periodic wells near each carbon atom. Additionally, electron-electron repulsion will significantly change the multi-electron orbital energies (which we do not account for in this simple one-electron state model).

[Note: if you are confused why we use the $2 \leftarrow 1$ transition instead of the $1 \leftarrow 0$, consider how many "ring electrons" there are in benzene. What electronic states (i.e. orbitals) are filled? What transition corresponds to the longest wavelength?]

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## 6 1-Dimensional Infinite Wells with Steps

Consider the potential

$$
\begin{aligned}
V(x) &= \infty && x < 0, x > a\\
V(x) &= 0 && 0 \le x \le a/2\\
V(x) &= V_0 = \frac{h^2}{8ma^2}(2)^2 && a/2 < x \le a
\end{aligned}
$$

(This is the energy of $n = 1$ of an infinite well of width $a/2$.)

**A.**

Sketch $V(x)$ vs. $x$.

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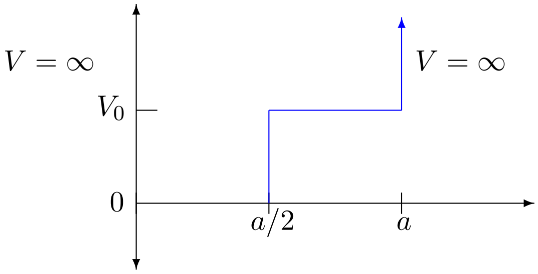
Solution:



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**B.** What are the boundary conditions for $\psi(x)$ at $x = 0$ and $x = a$?

Solution:

$\psi(0) = \psi(a) = 0$

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**C.** What requirements must be satisfied at $x = a/2$?

Solution:

$$\psi_{\text{left}}\left(\frac{a}{2}\right) = \psi_{\text{right}}\left(\frac{a}{2}\right) \qquad \text{continuity of } \psi$$

$$\frac{d\psi_{\text{left}}\left(\frac{a}{2}\right)}{dx} = \frac{d\psi_{\text{right}}\left(\frac{a}{2}\right)}{dx} \qquad \text{continuity of } \frac{d\psi}{dx}$$

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**D.** Solve for the $n = 2$ (one node) and $n = 3$ (two nodes) $\psi_n(x)$ eigenfunctions of $\widehat{H}$ and $E_n$ energy levels.

Hints:

(i) For $0 \leq x \leq a/2$, $\psi_{\text{I}}(x) = A \sin k_{\text{I}} x \qquad k_{\text{I}} = [2mE/\hbar^2]^{1/2}$

(ii) For $a/2 < x \leq a$, $\psi_{\text{II}} = B \sin k_{\text{II}}(a - x)$ $k_{\text{II}} = [2m(E - V_0)/\hbar^2]^{1/2}$

(iii) $\psi_{\text{I}}(a/2) = A \sin(k_{\text{I}} a/2)$

$\psi_{\text{II}}(a/2) = B \sin(k_{\text{II}} a/2)$

$\left.\frac{d\psi_{\text{I}}}{dx}\right|_{x=a/2} = Ak_{\text{I}} \cos(k_{\text{I}} a/2)$

$\left.\frac{d\psi_{\text{II}}}{dx}\right|_{x=a/2} = +Bk_{\text{II}} \cos(k_{\text{II}} a/2)$

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Solution:

The matching requirements at $x = a/2$ are

$$\begin{aligned} A\sin(k_{\mathrm{I}}a/2) &= B\sin(k_{\mathrm{II}}a/2) \\ Ak_{\mathrm{I}}\cos(k_{\mathrm{I}}a/2) &= Bk_{\mathrm{II}}\cos(k_{\mathrm{II}}a/2) \\ k_{\mathrm{I}} &= [2mE/\hbar^2]^{1/2} \\ k_{\mathrm{II}} &= [2m(E-V_0)/\hbar^2]^{1/2} \end{aligned}$$

$$\begin{aligned} \frac{A}{B} = \frac{\sin(k_{\mathrm{II}}a/2)}{\sin(k_{\mathrm{I}}a/2)} &= \frac{k_{\mathrm{II}}\cos(k_{\mathrm{II}}a/2)}{k_{\mathrm{I}}\cos(k_{\mathrm{I}}a/2)} \\ \frac{1}{k_{\mathrm{II}}}\tan(k_{\mathrm{II}}a/2) &= \frac{1}{k_{\mathrm{I}}}\tan(k_{\mathrm{I}}a/2) \end{aligned}$$

To simplify the algebra, let $k'_{\mathrm{I}} = k_{\mathrm{I}}a/2$, $k'_{\mathrm{II}} = k_{\mathrm{II}}a/2$

$$\boxed{\frac{1}{k'_{\mathrm{II}}}\tan(k'_{\mathrm{II}}) = \frac{1}{k'_{\mathrm{I}}}\tan(k'_{\mathrm{I}})} \tag{6.1}$$

$$\begin{aligned} k'^2_{\mathrm{I}} - k'^2_{\mathrm{II}} = \left(\frac{a}{2}\right)^2\left(k^2_{\mathrm{I}} - k^2_{\mathrm{II}}\right) &= \left(\frac{a}{2}\right)^2\frac{2m}{\hbar^2}V_0 \\ &= \left(\frac{a}{2}\right)^2\left(\frac{2m}{\hbar^2}\right)\left(\frac{h^2}{8m(a/2)^2}\right) \\ &= \pi^2 \\ k'^2_{\mathrm{I}} - k'^2_{\mathrm{II}} &= \pi^2 \end{aligned}$$

$$\boxed{k'_{\mathrm{I}} = \pm[\left[k'^2_{\mathrm{II}} + \pi^2\right]^{1/2}} \tag{6.2}$$

or

$$\boxed{k'^2_{\mathrm{II}} = \pm[\left[k'^2_{\mathrm{I}} - \pi^2\right]^{1/2}} \tag{6.3}$$

Combine Eqs. (6.1) and (6.3) and solve using Wolfram Alpha.

We get pairs of $k'_{\mathrm{I}}$ and $k'_{\mathrm{II}}$.

| $k'_{\mathrm{I}}$ | $k'_{\mathrm{II}}$ |
|---|---|
| 2.3236 | $2.1144i$ |
| 4.015838 | 2.50147 |
| 5.1920 | 4.13361 |
| 6.6964 | 5.91374 |

This $i$ means that $\psi_1(x)$ has an exponentially decreasing form in the $x > a/2$ region.

$$\begin{aligned} k_{\mathrm{I}} &= k'_{\mathrm{I}}(2/a) = \left[\frac{2mE}{\hbar^2}\right]^{1/2} \\ E &= \frac{k^2_{\mathrm{I}}\hbar^2}{2m} = \frac{k'^2_{\mathrm{I}}(2/a)^2\hbar^2}{2m} = \frac{k'^2_{\mathrm{I}}h^2}{2\pi^2a^2m} \end{aligned}$$

So we get the first three energy levels:

$$\begin{aligned}E_1 &= 0.2735(h^2/a^2m)\\ E_2 &= 0.8170(h^2/a^2m)\\ E_3 &= 1.3657(h^2/a^2m)\end{aligned}$$

We take these values of $E$ and input them to the original forms of $\psi_{\mathrm{I}}$, $\psi_{\mathrm{II}}$, $\frac{d\psi_{\mathrm{I}}}{dx}$ and $\frac{d\psi_{\mathrm{II}}}{dx}$ and solve for the values of A and B, and finally normalize the $\psi_i(x)$.

**E.** Compare your values of $E_2$ and $E_3$ to what you obtain from the de Broglie quantization condition

$$\begin{aligned}&(n/2) = \frac{a/2}{\lambda_{n,\mathrm{I}}} + \frac{a/2}{\lambda_{n,\mathrm{II}}}\\ &\lambda = h/p = 2\pi/k = h[2m(E - V(x))]^{-1/2}\end{aligned}$$

Solution:

The de Broglie quantization condition is based on the requirement that $\psi(0) = 0$ and $\psi(a) = 0$. We have two segments of the wavefunction which have

$$\lambda = h/p.$$

For $n = 2$ we expect one internal node, so there will be one full wavelength. For $n = 3$ we expect two internal nodes so there will be 3/2 wavelength. We calculate the accumulated phase in the $0 \leq x \leq a/2$ and $a/2 \leq x \leq a$ regions.

$$\begin{aligned}&n = 2\\ &\qquad \lambda = \tfrac{h}{p} = \tfrac{h}{\sqrt{2m(E-V(x))}}\end{aligned}$$

$$\left.\begin{aligned}&\qquad \tfrac{n}{2} = \tfrac{a}{2}\tfrac{\sqrt{2m(0.817-0.500)\frac{h^2}{ma^2}}}{h} + \tfrac{a}{2}\tfrac{\sqrt{2m(0.817)\frac{h^2}{ma^2}}}{h} = 1.04 \approx \tfrac{2}{2}\\ &n = 3\\ &\qquad \tfrac{n}{2} = \tfrac{a}{2}\tfrac{\sqrt{2m(1.37-0.5)\frac{h^2}{a^2m}}}{h} + \tfrac{a}{2}\tfrac{\sqrt{2m(1.37)\frac{h^2}{ma^2}}}{h} = 1.48 \approx \tfrac{3}{2}\end{aligned}\right] \quad \text{pretty good agreement}$$

**F.** For the $n = 2$ and $n = 3$ energy levels, what are the probabilities, $P_2$ and $P_3$, of finding the particle in the $0 \leq x \leq a/2$ region?

Solution:

The relative probabilities of finding the particle in the $0 \le x \le a/2$ and $a/2 < x < a$ regions are proportional to the reciprocal of the momentum. The particle moves faster in Region I than in Region II.

The semi-classical (WKB) quantization condition may be expressed as an "action integral"

$$\int_{x_<(E_n)}^{x_>(E_n)} p_n(x)dx = (n - 1/2)h$$

where $p_n(x)$ is the classical momentum

$$p_n(x) = [2m(E_n - V(x))]^{1/2}$$

$n = 1, 2, \ldots$ is the integer quantum number, the number of internal nodes in $\psi_n(x)$ is $n-1$, the inner and outer turning points are $x_<(E_n)$ and $x_>(E_n)$, and $E_n$ is the n$^{\text{th}}$ eigenenergy. The quantity $p(x)dx$ is "action". The $-1/2h$ term on the right hand side corresponds to extra stabilization due to accumulation of action outside of the classically bounded region which is required to permit $\lim_{|x|\to\infty} \psi(x) = 0$. However, in the case of infinite vertical walls, the $-1/2h$ term is not present. The de Broglie relation, $\lambda = h/p$, becomes a basis for intuition. If $V(x)$ is piece-wise constant, then the fractional number of wavelengths in each constant $V(x)$ region is

$$\frac{\Delta x}{\lambda} = \frac{\Delta x}{h/p}$$

We are interested in the integer number of half-wavelengths between turning points. If $V(x)$ is piece-wise constant, then the number of 1/2-wavelengths in each constant–$V(x)$ region is

$$n = 2\frac{\Delta x}{h/p(x)}.$$

The $\psi_n(x)$ for the $n = 1, 2, 3$ levels have 1, 2, 3 half-wavelengths.

The two regions of the $V(x)$ are each of length $a/2$ and

$$\begin{aligned} p_{\text{I}} &= h[2mE_n]^{-1/2} \\ p_{\text{II}} &= h\left[2m(E_n - V_0)\right]^{-1/2} \end{aligned}$$

The relative probabilities are proportional to

$$\left.\begin{aligned} P_{\text{I}} &= [2mE]^{-1/2} \\ P_{\text{II}} &= [2m(E - V_0)]^{-1/2} \end{aligned}\right\} E = p^2/2m$$

$P_{\text{I}}^{\text{rel}} \propto 0.7820 \qquad P_{\text{II}}^{\text{rel}} \propto 1.256$

Normalize for $n = 2$:

$$\begin{aligned} P_{\text{I}} &= P_{\text{I}}^{\text{rel}}[(0.7820)^2 + (1.256)^2]^{-1/2} = 0.384 \\ P_{\text{II}} &= 0.616 \end{aligned}$$

For $n = 3$:

$$P_{\text{I}} = 0.444, \qquad P_{\text{II}} = 0.556$$

Notice that the probabilities in the two regions become more nearly equal as the energy increases. This illustrates how the effect of the step is felt less as $E$ increases, eventually becoming negligible at very high $E$.

**G.** (optional) Will the $n = 2$ and $n = 3$ energy levels of the $V_1(x)$ and $V_2(x)$ potentials (defined below) be identical, as suggested by part **E**? Why?

$$V_1(x): \quad \left.\begin{array}{ll} V_1(x) = \infty & x < 0, x > a \\ V_1(x) = 0 & 0 \leq x \leq a/2 \\ V_1(x) = V_0 & a/2 < x \leq a \end{array}\right] \text{barrier on right side}$$

versus

$$V_2(x): \quad \left.\begin{array}{ll} V_2(x) = \infty & x < 0, x > a \\ V_2(x) = 0 & 0 \leq x \leq a/4, 3a/4 \leq x \leq a \\ V_2(x) = V_0 & a/4 < x \leq 3a/4 \end{array}\right] \text{barrier in the center}$$

Solution:

This is the most important part of this problem. It asks you to create a cartoon that is built on all of the crucial insights of this problem:

1. The lowest energy level of any one dimensional problem has zero internal nodes.
2. Tunneling into a classically forbidden region always results in stabilization relative to a zero-tunneling situation.
3. The wavefunction in a classically forbidden region always has the form:

   $$\psi(x) = Ae^{\kappa x} + Be^{-\kappa x} \quad \text{where } \kappa \text{ is real and A,B are complex}$$

4. When the potential energy is stepwise-constant, $\kappa$ is independent of $x$

   $$\kappa = [(V_0 - E)2m/\hbar^2]^{1/2}$$

   and it is often convenient to assume that A and B are positive or negative real numbers.
5. A crucial point is that at every internal joining point, $x_{\text{join}}$, there are two requirements, continuity of the wavefunction and continuity of its derivative, $d\psi/dx$. At a boundary, at $x_{\text{step}}$, to a region where $V(x)$ discontinuously becomes infinite, there is only one requirement: $\psi(x_{\text{step}}) = 0$. There is no requirement on $d\psi/dx$. (You know this from the particle in an infinite well.)

For this specific problem, $V(x) = \infty$ for $x < 0$ and $x > a$, $V(x) = 0$ for $x \geq 0$ and $x \leq a$, with a barrier of width $a/2$ and height $V_0 = h^2/8m(a/2)^2$, $V_0$ is chosen to be the exact energy of the $n = 1$ level of a particle in an infinite well of width $a/2$ and the exact energy of the $n = 2$ level of an infinite well of width a. So the crucial issue is how does the location of the barrier within the box affect the energy of the $n = 1$ level. The problem is constructed so that you address the crucial question: which placement of the barrier, centered vs. right-side, results in the lowest energy?

This problem illustrates a shortcoming of a semiclassical "accumulated phase" method for estimating eigen-energies, which involves complete neglect of joining-point matching requirements. You might have guessed that the key insight is the existence of two (centered barrier) vs. one (right-side barrier) internal matching points.

6. **Cartoons provide key insights**

   *First insight*: if, upon entry into the $E < V_0$ barrier region, $\psi(x)$ and $d\psi/dx$ have the same sign, the absolute value of the wavefunction will increase exponentially. This means that, for the barrier in the center, it will be impossible to satisfy the continuity of derivative requirement at the midpoint of the barrier region, and for the barrier on the right it will be impossible to satisfy the requirement that $\psi(a) = 0$. For the barrier in the center, the energy of the $n = 1$ level must be larger than $V_0$. If $E_1 < V_0$, both $\psi$ and $d\psi/dx$ will have the same signs at both $x = a/4$ and at $3a/4$. Continuity of $d\psi/dx$ at $x = a/2$ cannot be satisfied. So the $n = 1$ level of the barrier in the center will be shifted to above the top of the barrier. For the $n = 1$ level of the barrier on the right, in order to satisfy the $\psi_1(a) = 0$ boundary condition, it is necessary for $\psi_1$ and $d\psi_1/dx$ to have opposite signs at $x = a/2$. The lowest energy at which this could occur is for $E_1$ slightly larger than $V_0/4$ (which is the energy of $n = 2$ of the barrier-free infinite well of width $a$)! This demonstrates that the location of the barrier has an enormous effect of the energy of the $n = 1$ level.

   *Second insight*: For the barrier in the center, $E_{n=1} > V_0$, and so this will be a simple 3-region problem and $E$ must be determined (iteratively) so that $\psi(a) = 0$. For the right side barrier, $\psi(x)$ will be decreasing exponentially and $E$ must be chosen so that $\psi(a) = 0$.

   *Major insight about tunneling*: For all symmetric wells with a barrier in the center, the $n = 1$ level (no internal nodes) will be shifted upward from the no barrier energy by a large amount, the $n = 2$ level (one node at the center) will be shifted upward by a very small amount, and the $n = 3$ level (two nodes, neither at the center) will be shifted upward by an amount much larger than that for the $n = 2$ level but much smaller than that for the $n = 1$ level. Level staggering is the signature of tunneling!

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**H.** Solve for $n = 1$ $\psi_1(x)$ and $E_1$ for $V_1$.

HINTS: For $a/2 < x \leq a$,

$$\psi_{\text{II}}(x) = Be^{\kappa_{\text{II}}(a-x)} + Ce^{-\kappa_{\text{II}}(a-x)}$$
$$\kappa_{\text{II}} = [2m(V_0 - E)/\hbar^2]^{1/2}$$

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Solution:

From Part **D.**: $\boxed{E_1 = 0.2735\frac{h^2}{a^2m}}$

$$\psi(a) = 0$$
$$\psi_{\mathrm{II}}(a/2) = \psi_{\mathrm{I}}(a/2)$$

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**I.** *(optional)* Is $E_1$ for $V_1$ larger or smaller than $E_1$ for $V_2$? Why? A cartoon would be helpful.

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Solution:

The form of $\psi_{\mathrm{II}}$ in the classically forbidden region for $n = 1$ is a decreasing exponential. There can be no zero-crossing in the under-barrier region. For the symmetric barrier, $\psi(a/4)$ and $\psi(3a/4)$ are smaller than $\psi(a/2)$ for the case of the right-side barrier. The rate of exponential decrease of $\psi$ in the forbidden region depends on $V(x) - E$. This means that the probability in the forbidden region is larger for the right side edge barrier. This implies that the energy is higher for $n = 1$ of $V_1(x)$.

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