

Problem 1 Score: _____. Prove the following three theorems:

- For normalizable solutions, the separation constant E must be real. *Hint: Write E (in Equation 2.7) as $E_0 + i\Gamma$ (with E_0 and Γ real), and show that if Equation 1.20 is to hold for all t , Γ must be zero.*
- The time-independent wave function $\psi(x)$ can always be taken to be real (unlike $\Psi(x, t)$, which is necessarily complex). *Hint: If $\psi(x)$ satisfies Equation 2.5, for a given E , so too does its complex conjugate, and hence also the real linear combinations $(\psi + \psi^*)$ and $i(\psi - \psi^*)$.*
- If $V(x)$ is an even function (that is, $V(-x) = V(x)$) then $\psi(x)$ can always be taken to be either even or odd. *Hint: If $\psi(x)$ satisfies Equation 2.5, for a given E , so too does $\psi(-x)$, and hence also the even and odd linear combinations $\psi(x) \pm \psi(-x)$.*

Solution: (a) Suppose $E = E_0 + i\Gamma$ for some real E_0 and Γ . Then the time-dependent wave function $\Psi(x, t)$ can be written as

$$\begin{aligned}\Psi(x, t) &= \psi(x)e^{-iEt/\hbar} \\ &= \psi(x)e^{-i(E_0+i\Gamma)t/\hbar} \\ &= \psi(x)e^{\Gamma t/\hbar}e^{-iE_0t/\hbar}.\end{aligned}$$

Thus,

$$\begin{aligned}\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx &= \int_{-\infty}^{\infty} |\psi(x)|^2 e^{2\Gamma t/\hbar} dx \\ &= e^{2\Gamma t/\hbar} \int_{-\infty}^{\infty} |\psi(x)|^2 dx,\end{aligned}$$

which varies with time, unless $\Gamma = 0$. Therefore, the separation constant E must be real.

- If $\psi(x)$ satisfies $\hat{H}\psi = E\psi$, then its complex conjugate $\psi^*(x)$ also satisfies $\hat{H}\psi^* = E\psi^*$. If $\psi_1(x)$ and $\psi_2(x)$ are two solutions of $\hat{H}\psi = E\psi$, then any linear combination $\psi_3(x) = c_1\psi_1(x) + c_2\psi_2(x)$ is also a solution. Thus for any complex solution $\psi(x)$, we can construct two real solutions $\psi_1(x) = \frac{1}{2}(\psi(x) + \psi^*(x))$ and $\psi_2(x) = \frac{1}{2i}(\psi(x) - \psi^*(x))$.

- If $\psi(x)$ satisfies $-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$, then

$$\begin{aligned}-\frac{\hbar^2}{2m} \frac{d^2\psi(-x)}{d(-x)^2} + V(-x)\psi(-x) &= -\frac{\hbar^2}{2m} \frac{d^2\psi(-x)}{dx^2} + V(x)\psi(-x) \\ &= E\psi(-x),\end{aligned}$$

which means $\psi(-x)$ is also a solution. Thus we can construct two solutions $\psi_1(x) = \frac{1}{2}(\psi(x) + \psi(-x))$, which is even, and $\psi_2(x) = \frac{1}{2}(\psi(x) - \psi(-x))$, which is odd. □

Problem 2 Score: _____. Show that E must exceed the minimum value of $V(x)$, for every normalizable solution to the time-independent Schrödinger equation. What is the classical analog to this statement? *Hint: Rewrite Equation 2.5 in the form*

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

if $E < V_{\min}$, then ψ and its second derivative always have the same sign—argue that such a function cannot be normalized.

Solution: Rewrite time-independent Schrödinger equation as

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

If $E < V_{\min}$, then $V(x) - E > 0$ for all x . Thus ψ and its second derivative always have the same sign, which means ψ cannot be normalized.

In classical mechanics, this statement is analogous that if the total energy of a particle is less than the minimum potential energy, the particle's kinetic energy is negative, then the particle cannot exist in the system. \square

Problem 3 Score: _____. Show that there is no acceptable solution to the (time-independent) Schrödinger equation for the infinite square well with $E = 0$ or $E < 0$. (This is a special case of the general theorem in Problem 2.2, but this time do it by explicitly solving the Schrödinger equation, and showing that you cannot satisfy the boundary conditions.)

Solution: When $E = 0$, the time-independent Schrödinger equation for the infinite square well becomes

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = 0,$$

which leads to $\psi(x) = 0$, which is not normalizable.

When $E < 0$, the time-independent Schrödinger equation for the infinite square well becomes

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi,$$

where $\kappa = \frac{\sqrt{-2mE}}{\hbar}$. The general solution to this equation is

$$\psi(x) = Ae^{\kappa x} + Be^{-\kappa x},$$

then the boundary conditions $\psi(0) = \psi(a) = 0$ lead to $A = B = 0$, which means $\psi(x) = 0$, which is not normalizable. \square

Problem 4 Score: _____. Calculate $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, $\langle p^2 \rangle$, σ_x , and σ_p , for the n th stationary state of the infinite square well. Check that the uncertainty principle is satisfied. Which state comes closest to the uncertainty limit?

Solution: The expectation value of x is

$$\begin{aligned} \langle x \rangle &= \int_0^a x |\psi_n(x)|^2 dx \\ &= \int_0^a x \left(\sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \right)^2 dx \\ &= \frac{2}{a} \int_0^a x \sin^2\left(\frac{n\pi x}{a}\right) dx \\ &= \frac{1}{a} \left[\frac{1}{2}x^2 - \frac{a}{2n\pi}x \sin\frac{2n\pi}{a}x - \frac{a^2}{4n^2\pi^2} \cos\frac{2n\pi}{a}x \right]_0^a \\ &= \frac{a}{2}. \end{aligned}$$

The expectation value of x^2 is

$$\begin{aligned}
 \langle x^2 \rangle &= \int_0^a x^2 |\psi_n(x)|^2 dx \\
 &= \int_0^a x^2 \left(\sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \right)^2 dx \\
 &= \frac{2}{a} \int_0^a x^2 \sin^2\left(\frac{n\pi x}{a}\right) dx \\
 &= \frac{1}{a} \left[\frac{1}{3} x^3 - \frac{a}{2n\pi} x^2 \sin \frac{2n\pi}{a} x - \frac{a^2}{2n^2\pi^2} x \cos \frac{2n\pi}{a} x + \frac{a^3}{4n^3\pi^3} \sin \frac{2n\pi}{a} x \right]_0^a \\
 &= \frac{1}{a} \left(\frac{a^3}{3} - \frac{a^3}{2n^2\pi^2} \right) \\
 &= a^2 \left(\frac{1}{3} - \frac{1}{2n^2\pi^2} \right).
 \end{aligned}$$

The expectation value of p is

$$\begin{aligned}
 \langle p \rangle &= m \frac{d\langle x \rangle}{dt} \\
 &= 0
 \end{aligned}$$

The expectation value of p^2 is

$$\begin{aligned}
 \langle p^2 \rangle &= \int_0^a \psi_n^*(x) \left(\frac{\hbar}{i} \frac{d}{dx} \right)^2 \psi_n dx \\
 &= -\hbar^2 \int_0^a \psi_n^*(x) \frac{d^2 \psi_n}{dx^2} dx \\
 &= -\hbar^2 \left(-\frac{2mE_n}{\hbar^2} \right) \int_0^a |\psi_n(x)|^2 dx \\
 &= 2mE_n \\
 &= \frac{n^2\pi^2\hbar^2}{a^2}.
 \end{aligned}$$

The standard deviation of x is

$$\begin{aligned}
 \sigma_x &= \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \\
 &= a \sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}.
 \end{aligned}$$

The standard deviation of p is

$$\begin{aligned}
 \sigma_p &= \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \\
 &= \frac{n\pi\hbar}{a}.
 \end{aligned}$$

The uncertainty principle is

$$\sigma_x \sigma_p = a \sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}} \cdot \frac{n\pi\hbar}{a}$$

$$\begin{aligned}
&= \frac{\hbar}{2} \sqrt{\frac{n^2 \pi^2}{3} - 2} \\
&\geq \frac{\hbar}{2} \sqrt{\frac{\pi^2}{3} - 2} \\
&\geq \frac{\hbar}{2}.
\end{aligned}$$

□

Problem 5 Score: _____. A particle in the infinite square well has as its initial wave function an even mixture of the first two stationary states:

$$\Psi(x, 0) = A[\psi_1(x) + \psi_2(x)].$$

- Normalize $\Psi(x, 0)$. (That is, find A . This is very easy, if you exploit the orthonormality of ψ_1 and ψ_2 . Recall that, having normalized Ψ at $t = 0$, you can rest assured that it stays normalized—if you doubt this, check it explicitly after doing part (b).)
- Find $\Psi(x, t)$ and $|\Psi(x, t)|^2$. Express the latter as a sinusoidal function of time, as in Example 2.1. To simplify the result, let $\omega = \pi^2 \hbar / 2ma^2$.
- Compute $\langle x \rangle$. Notice that it oscillates in time. What is the angular frequency of the oscillation? What is the amplitude of the oscillation? (If your amplitude is greater than $a/2$, go directly to jail.)
- Compute $\langle p \rangle$. (As Peter Lorre would say, “Do it ze kweek vay, Johnny!”)
- If you measured the energy of this particle, what values might you get, and what is the probability of getting each of them? Find the expectation value of H . How does it compare with E_1 and E_2 ?

Solution: (a)

$$\begin{aligned}
1 &= \int_0^a |\Psi(x, 0)|^2 dx \\
&= A^2 \int_0^a [\psi_1(x) + \psi_2(x)]^* [\psi_1(x) + \psi_2(x)] dx \\
&= A^2 \int_0^a [|\psi_1(x)|^2 + |\psi_2(x)|^2 + \psi_1^*(x)\psi_2(x) + \psi_2^*(x)\psi_1(x)] dx \\
&= 2A^2,
\end{aligned}$$

$$\text{so } A = \frac{1}{\sqrt{2}}.$$

(b)

$$\begin{aligned}
\Psi(x, t) &= \frac{1}{\sqrt{2}} [\psi_1(x)e^{-iE_1 t/\hbar} + \psi_2(x)e^{-iE_2 t/\hbar}] \\
&= \frac{1}{\sqrt{2}} [\psi_1(x)e^{-i\omega t} + \psi_2(x)e^{-4i\omega t}] \\
&= \frac{1}{\sqrt{2}} \left[\sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) e^{-i\omega t} + \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right) e^{-4i\omega t} \right]
\end{aligned}$$

$$= \frac{1}{\sqrt{a}} e^{-i\omega t} \left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right) e^{-3i\omega t} \right].$$

$$\begin{aligned} |\Psi(x, t)|^2 &= \frac{1}{a} \left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right) e^{-3i\omega t} \right] \left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right) e^{-3i\omega t} \right]^* \\ &= \frac{1}{a} \left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right) e^{-3i\omega t} \right] \left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right) e^{3i\omega t} \right] \\ &= \frac{1}{a} \left[\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right) + \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi x}{a}\right) (e^{-3i\omega t} + e^{3i\omega t}) \right] \\ &= \frac{1}{a} \left[\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right) + 2 \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi x}{a}\right) \cos(3\omega t) \right]. \end{aligned}$$

(c)

$$\begin{aligned} \langle x \rangle &= \int_0^a x |\Psi(x, t)|^2 dx \\ &= \frac{1}{a} \int_0^a x \left[\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right) + 2 \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi x}{a}\right) \cos(3\omega t) \right] dx \\ &= \frac{1}{a} \int_0^a x \left[\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right) \right] dx + \frac{2}{a} \cos(3\omega t) \int_0^a x \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi x}{a}\right) dx \\ &= \frac{1}{a} \left[\frac{a^2}{4} + \frac{a^2}{4} \right] + \frac{1}{a} \cos(3\omega t) \int_0^a x \left[\cos\left(\frac{\pi x}{a}\right) - \cos\left(\frac{3\pi x}{a}\right) \right] dx \\ &= \frac{a}{2} + \frac{1}{a} \cos(3\omega t) \left[\frac{a}{\pi} x \sin\left(\frac{\pi x}{a}\right) + \frac{a^2}{\pi^2} \cos\left(\frac{\pi x}{a}\right) - \frac{a}{3\pi} x \sin\left(\frac{3\pi x}{a}\right) - \frac{a^2}{9\pi^2} \cos\left(\frac{3\pi x}{a}\right) \right]_0^a \\ &= \frac{a}{2} + \frac{1}{a} \cos(3\omega t) \left[-\frac{a^2}{\pi^2} - \frac{a^2}{\pi^2} + \frac{a^2}{9\pi^2} + \frac{a^2}{9\pi^2} \right] \\ &= \frac{a}{2} - \frac{16}{9\pi^2} a \cos(3\omega t) \\ &= \frac{a}{2} \left[1 - \frac{32}{9\pi^2} \cos(3\omega t) \right], \end{aligned}$$

where the angular frequency of the oscillation is $3\omega = \frac{3\pi^2\hbar}{2ma^2}$ and the amplitude of the oscillation is $\frac{16a}{9\pi^2} \approx 0.18a$.

(d)

$$\begin{aligned} \langle p \rangle &= m \frac{d\langle x \rangle}{dt} \\ &= m \frac{d}{dt} \left[\frac{a}{2} \left(1 - \frac{32}{9\pi^2} \cos(3\omega t) \right) \right] \\ &= \frac{16ma}{9\pi^2} 3\omega \sin(3\omega t) \\ &= \frac{8\hbar}{3a} \sin(3\omega t). \end{aligned}$$

(e) The possible values of energy are $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$ and $E_2 = \frac{2\pi^2\hbar^2}{ma^2}$, with the probability of getting each of them being $\frac{1}{2}$. The expectation value of H is

$$\langle H \rangle = \frac{1}{2} E_1 + \frac{1}{2} E_2$$

$$= \frac{5\pi^2\hbar^2}{4ma^2}.$$

□

Problem 6 Score: _____. Although the overall phase constant of the wave function is of no physical significance (it cancels out whenever you calculate a measurable quantity), the relative phase of the coefficients in Equation 2.17 does matter. For example, suppose we change the relative phase of ψ_1 and ψ_2 in Problem 2.5:

$$\Psi(x, 0) = A [\psi_1(x) + e^{i\phi}\psi_2(x)],$$

where ϕ is some constant. Find $\Psi(x, t)$, $|\Psi(x, t)|^2$, and $\langle x \rangle$, and compare your results with what you got before. Study the special cases $\phi = \pi/2$ and $\phi = \pi$. (For a graphical exploration of this problem see the applet in footnote 9 of this chapter.)

Solution:

$$\begin{aligned} 1 &= \int_0^a |\Psi(x, 0)|^2 dx \\ &= A^2 \int_0^a [|\psi_1(x)|^2 + |\psi_2(x)|^2 + e^{i\phi}\psi_1^*(x)\psi_2(x) + e^{-i\phi}\psi_2^*(x)\psi_1(x)] dx \\ &= 2A^2, \end{aligned}$$

$$\text{so } A = \frac{1}{\sqrt{2}}.$$

$$\begin{aligned} \Psi(x, t) &= \frac{1}{\sqrt{2}} [\psi_1(x)e^{-iE_1t/\hbar} + e^{i\phi}\psi_2(x)e^{-iE_2t/\hbar}] \\ &= \frac{1}{\sqrt{2}} [\psi_1(x)e^{-i\omega t} + e^{i\phi}\psi_2(x)e^{-4i\omega t}] \\ &= \frac{1}{\sqrt{2}} [\psi_1(x)e^{-i\omega t} + e^{i\phi}\psi_2(x)e^{-4i\omega t}] \\ &= \frac{1}{\sqrt{2}} \left[\sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) e^{-i\omega t} + e^{i\phi} \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right) e^{-4i\omega t} \right] \\ &= \frac{1}{\sqrt{a}} e^{-i\omega t} \left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right) e^{i\phi} e^{-3i\omega t} \right]. \end{aligned}$$

$$\begin{aligned} |\Psi(x, t)|^2 &= \frac{1}{a} \left[\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right) + \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi x}{a}\right) (e^{i\phi} e^{-3i\omega t} + e^{-i\phi} e^{3i\omega t}) \right] \\ &= \frac{1}{a} \left[\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right) + 2 \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi x}{a}\right) \cos(3\omega t - \phi) \right]. \end{aligned}$$

$$\text{Then } \langle x \rangle = \frac{a}{2} \left[1 - \frac{32}{9\pi^2} \cos(3\omega t - \phi) \right].$$

$$\text{When } \phi = \pi/2, \langle x \rangle = \frac{a}{2} \left[1 + \frac{32}{9\pi^2} \sin(3\omega t) \right],$$

$$\text{When } \phi = \pi, \langle x \rangle = \frac{a}{2} \left[1 + \frac{32}{9\pi^2} \cos(3\omega t) \right].$$

□

Problem 7 Score: _____. A particle in the infinite square well has the initial wave function

$$\Psi(x, 0) = \begin{cases} Ax, & 0 \leq x \leq a/2, \\ A(a - x), & a/2 \leq x \leq a. \end{cases}$$

- (a) Sketch $\Psi(x, 0)$, and determine the constant A .
- (b) Find $\Psi(x, t)$.
- (c) What is the probability that a measurement of the energy would yield the value E_1 ?
- (d) Find the expectation value of the energy, using Equation 2.21.

Solution: (a)

$$\begin{aligned}
 1 &= \int_0^a |\Psi(x, 0)|^2 dx \\
 &= A^2 \left[\int_0^{a/2} x^2 dx + \int_{a/2}^a (a-x)^2 dx \right] \\
 &= A^2 \left[\frac{x^3}{3} \Big|_0^{a/2} - \frac{(a-x)^3}{3} \Big|_{a/2}^a \right] \\
 &= A^2 \left[\frac{a^3}{24} + \frac{a^3}{24} \right] \\
 &= \frac{A^2 a^3}{12},
 \end{aligned}$$

so $A = \frac{2\sqrt{3}}{a\sqrt{a}}$.

(b)

$$\begin{aligned}
 c_n &= \int_0^a \Psi(x, 0) \psi_n^*(x) dx \\
 &= A \sqrt{\frac{2}{a}} \left[\int_0^{a/2} x \sin\left(\frac{n\pi x}{a}\right) dx + \int_{a/2}^a (a-x) \sin\left(\frac{n\pi x}{a}\right) dx \right] \\
 &= A \sqrt{\frac{2}{a}} \frac{a}{n\pi} \left[-x \cos \frac{n\pi x}{a} \Big|_0^{a/2} + \int_0^{a/2} \cos \frac{n\pi x}{a} dx - (a-x) \cos \frac{n\pi x}{a} \Big|_{a/2}^a - \int_{a/2}^a \cos \frac{n\pi x}{a} dx \right] \\
 &= A \sqrt{\frac{2}{a}} \frac{a}{n\pi} \left[\frac{a}{n\pi} \sin \frac{n\pi x}{a} \Big|_0^{a/2} - \frac{a}{n\pi} \sin \frac{n\pi x}{a} \Big|_{a/2}^a \right] \\
 &= A \sqrt{\frac{2}{a}} \frac{a}{n\pi} \left[\frac{a}{n\pi} \sin \frac{n\pi}{2} + \frac{a}{n\pi} \sin \frac{n\pi}{2} \right] \\
 &= \frac{4\sqrt{6}}{n^2 \pi^2} \sin \frac{n\pi}{2} \\
 &= \begin{cases} \frac{4\sqrt{6}}{n^2 \pi^2} (-1)^{(n-1)/2}, & n = 1, 3, 5, \dots, \\ 0, & n = 2, 4, 6, \dots \end{cases}
 \end{aligned}$$

So

$$\begin{aligned}
 \Psi(x, t) &= \sum_{n=1,3,5,\dots} c_n \psi_n(x) e^{-iE_n t/\hbar} \\
 &= \sum_{n=1,3,5,\dots} \frac{4\sqrt{6}}{n^2 \pi^2} (-1)^{(n-1)/2} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) e^{-iE_n t/\hbar}
 \end{aligned}$$

$$= \frac{4\sqrt{6}}{\pi^2} \sqrt{\frac{2}{a}} \sum_{n=1,3,5,\dots} \frac{(-1)^{(n-1)/2}}{n^2} \sin\left(\frac{n\pi x}{a}\right) e^{-iE_n t/\hbar},$$

where $E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$.

(c) The probability that a measurement of the energy would yield the value E_1 is

$$\begin{aligned} P(E_1) &= |c_1|^2 \\ &= \left(\frac{4\sqrt{6}}{\pi^2}\right)^2 \\ &= \frac{96}{\pi^4} \approx 0.9855 \end{aligned}$$

(d) The expectation value of the energy is

$$\begin{aligned} \langle H \rangle &= \sum_{n=1,3,5,\dots} |c_n|^2 E_n \\ &= \sum_{n=1,3,5,\dots} \left(\frac{4\sqrt{6}}{n^2 \pi^2}\right)^2 \frac{n^2 \pi^2 \hbar^2}{2ma^2} \\ &= \sum_{n=1,3,5,\dots} \frac{48\hbar^2}{n^2 \pi^2 ma^2} \\ &= \frac{48\hbar^2}{\pi^2 ma^2} \sum_{n=1,3,5,\dots} \frac{1}{n^2} \\ &= \frac{48\hbar^2}{\pi^2 ma^2} \frac{\pi^2}{8} \\ &= \frac{6\hbar^2}{ma^2}. \end{aligned}$$

□

Problem 8 Score: _____. A particle of mass m in the infinite square well (of width a) starts out in the state

$$\Psi(x, 0) = \begin{cases} A, & 0 \leq x \leq a/2, \\ 0, & a/2 < x \leq a, \end{cases}$$

for some constant A , so it is (at $t = 0$) equally likely to be found at any point in the left half of the well. What is the probability that a measurement of the energy (at some later time t) would yield the value $\pi^2 \hbar^2 / 2ma^2$?

Solution:

$$\begin{aligned} 1 &= \int_0^a |\Psi(x, 0)|^2 dx \\ &= A^2 \left[\int_0^{a/2} dx \right] \\ &= \frac{A^2 a}{2}, \end{aligned}$$

so $A = \sqrt{\frac{2}{a}}$.

$$\begin{aligned}
 c_1 &= \int_0^a \Psi(x, 0) \psi_1^*(x) \, dx \\
 &= A \sqrt{\frac{2}{a}} \int_0^{a/2} \sin\left(\frac{\pi x}{a}\right) \, dx \\
 &= A \sqrt{\frac{2}{a}} \frac{a}{\pi} \left[-\cos\left(\frac{\pi x}{a}\right) \right]_0^{a/2} \\
 &= \frac{2}{\pi}.
 \end{aligned}$$

The probability that a measurement of the energy would yield the value $\pi^2 \hbar^2 / 2ma^2 = E_1$ is

$$\begin{aligned}
 P(E_1) &= |c_1|^2 \\
 &= \left(\frac{2}{\pi}\right)^2 \\
 &= \frac{4}{\pi^2} \approx 0.4053.
 \end{aligned}$$

□

Problem 9 Score: _____. For the wave function in Example 2.2, find the expectation value of H , at time $t = 0$, the “old fashioned” way:

$$\langle H \rangle = \int \Psi(x, 0)^* \hat{H} \Psi(x, 0) \, dx.$$

Compare the result we got in Example 2.3. Note: Because $\langle H \rangle$ is independent of time, there is no loss of generality in using $t = 0$.

Solution:

$$\begin{aligned}
 \hat{H} \Psi(x, 0) &= \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \Psi(x, 0) \\
 &= \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} [Ax(a-x)] \\
 &= \frac{-\hbar^2}{2m} (-2A) \\
 &= \frac{\hbar^2 A}{m}.
 \end{aligned}$$

$$\begin{aligned}
 \langle H \rangle &= \int \Psi(x, 0)^* \hat{H} \Psi(x, 0) \, dx \\
 &= \frac{\hbar^2 A^2}{m} \int_0^a x(a-x) \, dx \\
 &= \frac{\hbar^2 A^2}{m} \left[\frac{ax^2}{2} - \frac{x^3}{3} \right]_0^a \\
 &= \frac{\hbar^2 A^2 a^3}{6m}
 \end{aligned}$$

$$= \frac{5\hbar^2}{ma^2}.$$

□

Problem 10 Score: _____. (a) Construct $\psi_2(x)$.

(b) Sketch ψ_0 , ψ_1 , and ψ_2 .

(c) Check the orthogonality of ψ_0 , ψ_1 , and ψ_2 , by explicit integration. *Hint: If you exploit the even-ness and odd-ness of the functions, there is really only one integral left to do.*

Solution: (a)

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2},$$

$$\begin{aligned}\hat{a}_+\psi_0 &= \frac{1}{\sqrt{2\hbar m\omega}} (-i\hat{p} + m\omega\hat{x}) \psi_0 \\ &= \frac{1}{\sqrt{2\hbar m\omega}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left(-\hbar \frac{d}{dx} + m\omega x\right) e^{-\frac{m\omega}{2\hbar}x^2} \\ &= \frac{1}{\sqrt{2\hbar m\omega}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left[-\hbar \left(-\frac{m\omega}{\hbar}x\right) + m\omega x\right] e^{-\frac{m\omega}{2\hbar}x^2} \\ &= \frac{1}{\sqrt{2\hbar m\omega}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} 2m\omega x e^{-\frac{m\omega}{2\hbar}x^2}.\end{aligned}$$

$$\begin{aligned}(\hat{a}_+)^2\psi_0 &= \frac{1}{\sqrt{2\hbar m\omega}} (-i\hat{p} + m\omega\hat{x}) (\hat{a}_+\psi_0) \\ &= \frac{1}{2\hbar m\omega} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} 2m\omega \left(-\hbar \frac{d}{dx} + m\omega x\right) x e^{-\frac{m\omega}{2\hbar}x^2} \\ &= \frac{1}{2\hbar m\omega} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} 2m\omega \left[-\hbar \left(1 - \frac{m\omega}{\hbar}x^2\right) + m\omega x^2\right] e^{-\frac{m\omega}{2\hbar}x^2} \\ &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left[\frac{2m\omega}{\hbar}x^2 - 1\right] e^{-\frac{m\omega}{2\hbar}x^2}.\end{aligned}$$

Therefore,

$$\begin{aligned}\psi_2 &= \frac{1}{\sqrt{2}} (\hat{a}_+)^2 \psi_0 \\ &= \frac{1}{\sqrt{2}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left[\frac{2m\omega}{\hbar}x^2 - 1\right] e^{-\frac{m\omega}{2\hbar}x^2}.\end{aligned}$$

(b)

(c) As ψ_0 and ψ_2 are even and ψ_1 is odd, the only integral left to do is

$$\begin{aligned}\int_{-\infty}^{\infty} \psi_0^* \psi_2 \, dx &= \int_{-\infty}^{\infty} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} \frac{1}{\sqrt{2}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left[\frac{2m\omega}{\hbar}x^2 - 1\right] e^{-\frac{m\omega}{2\hbar}x^2} \, dx \\ &= \frac{1}{\sqrt{2}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_{-\infty}^{\infty} \left[\frac{2m\omega}{\hbar}x^2 - 1\right] e^{-\frac{m\omega}{\hbar}x^2} \, dx\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{\sqrt{2}} \left(\frac{m\omega}{\pi\hbar} \right)^{1/2} \left[\frac{2m\omega}{\hbar} \int_{-\infty}^{\infty} x^2 e^{-\frac{m\omega}{\hbar} x^2} dx - \int_{-\infty}^{\infty} e^{-\frac{m\omega}{\hbar} x^2} dx \right] \\
&= \frac{1}{\sqrt{2}} \left(\frac{m\omega}{\pi\hbar} \right)^{1/2} \left[\frac{2m\omega}{\hbar} \frac{\hbar}{2m\omega} \sqrt{\frac{\pi\hbar}{m\omega}} - \sqrt{\frac{\pi\hbar}{m\omega}} \right] \\
&= 0.
\end{aligned}$$

□

Problem 11 Score: _____. (a) Compute $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$, and $\langle p^2 \rangle$, for the states ψ_0 (Equation 2.60) and ψ_1 (Equation 2.63), by explicit integration.

(b) Check the uncertainty principle for these states.

(c) Compute $\langle T \rangle$ and $\langle V \rangle$ for these states. (*No new integration allowed!*) Is their sum what you would expect?

Problem 12 Score: _____. Find $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$, $\langle p^2 \rangle$, and $\langle T \rangle$, for the n th stationary state of the harmonic oscillator, using the method of Example 2.5. Check that the uncertainty principle is satisfied.

Solution: The expectation value of x is

$$\begin{aligned}
\langle x \rangle &= \sqrt{\frac{\hbar}{2m\omega}} \int_{-\infty}^{\infty} \psi_n^* (\hat{a}_+ + \hat{a}_-) \psi_n dx \\
&= \sqrt{\frac{\hbar}{2m\omega}} \left[\sqrt{n+1} \int_{-\infty}^{\infty} \psi_n^* \psi_{n+1} + \sqrt{n} \int_{-\infty}^{\infty} \psi_n^* \psi_{n-1} dx \right] \\
&= 0.
\end{aligned}$$

Thus the expectation value of p is

$$\begin{aligned}
\langle p \rangle &= \frac{d}{dt} \langle x \rangle \\
&= 0.
\end{aligned}$$

The expectation value of x^2 is

$$\begin{aligned}
\langle x^2 \rangle &= \frac{\hbar}{2m\omega} \int_{-\infty}^{\infty} \psi_n^* (\hat{a}_+ + \hat{a}_-)^2 \psi_n dx \\
&= \frac{\hbar}{2m\omega} \int_{-\infty}^{\infty} \psi_n^* (\hat{a}_+^2 + \hat{a}_-^2 + \hat{a}_+ \hat{a}_- + \hat{a}_- \hat{a}_+) \psi_n dx \\
&= \frac{\hbar}{2m\omega} \left[\sqrt{n+1} \int_{-\infty}^{\infty} \psi_n^* \hat{a}_+ \psi_{n+1} + \sqrt{n} \int_{-\infty}^{\infty} \psi_n^* \hat{a}_- \psi_{n-1} dx + (n+n+1) \int_{-\infty}^{\infty} \psi_n^* \psi_n dx \right] \\
&= \frac{\hbar}{2m\omega} \left[\sqrt{n+1} \sqrt{n+2} \int_{-\infty}^{\infty} \psi_n^* \psi_{n+2} + n \sqrt{n-1} \int_{-\infty}^{\infty} \psi_n^* \psi_{n-2} dx + 2n+1 \right] \\
&= \left(n + \frac{1}{2} \right) \frac{\hbar}{m\omega}.
\end{aligned}$$

The expectation value of p^2 is

$$\langle p^2 \rangle = -\frac{\hbar m\omega}{2} \int_{-\infty}^{\infty} \psi_n^* (\hat{a}_+ - \hat{a}_-)^2 \psi_n dx$$

$$\begin{aligned}
&= -\frac{\hbar m \omega}{2} \int_{-\infty}^{\infty} \psi_n^* (\hat{a}_+^2 + \hat{a}_-^2 - \hat{a}_+ \hat{a}_- - \hat{a}_- \hat{a}_+) \psi_n \, dx \\
&= -\frac{\hbar m \omega}{2} \left[\sqrt{n+1} \int_{-\infty}^{\infty} \psi_n^* \hat{a}_+ \psi_{n+1} + \sqrt{n} \int_{-\infty}^{\infty} \psi_n^* \hat{a}_- \psi_{n-1} \, dx - (n+n+1) \int_{-\infty}^{\infty} \psi_n^* \psi_n \, dx \right] \\
&= -\frac{\hbar m \omega}{2} \left[\sqrt{n+1} \sqrt{n+2} \int_{-\infty}^{\infty} \psi_n^* \psi_{n+2} + n \sqrt{n-1} \int_{-\infty}^{\infty} \psi_n^* \psi_{n-2} \, dx - (2n+1) \int_{-\infty}^{\infty} \psi_n^* \psi_n \, dx \right] \\
&= \left(n + \frac{1}{2} \right) \hbar m \omega.
\end{aligned}$$

The expectation value of T is

$$\begin{aligned}
\langle T \rangle &= \frac{1}{2m} \langle p^2 \rangle \\
&= \frac{1}{2} \left(n + \frac{1}{2} \right) \hbar \omega.
\end{aligned}$$

The standard deviation of x is

$$\begin{aligned}
\sigma_x &= \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \\
&= \sqrt{\left(n + \frac{1}{2} \right) \frac{\hbar}{m \omega}}.
\end{aligned}$$

The standard deviation of p is

$$\begin{aligned}
\sigma_p &= \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \\
&= \sqrt{\left(n + \frac{1}{2} \right) \hbar m \omega}.
\end{aligned}$$

The uncertainty principle is

$$\begin{aligned}
\sigma_x \sigma_p &= \sqrt{\left(n + \frac{1}{2} \right) \frac{\hbar}{m \omega}} \sqrt{\left(n + \frac{1}{2} \right) \hbar m \omega} \\
&= \left(n + \frac{1}{2} \right) \hbar \geq \frac{\hbar}{2}.
\end{aligned}$$

□

Problem 13 Score: _____. A particle in the harmonic oscillator potential starts out in the state

$$\Psi(x, 0) = A [3\psi_0(x) + 4\psi_1(x)].$$

- Find A .
- Construct $\Psi(x, t)$ and $|\Psi(x, t)|^2$. Don't get too excited if $|\Psi(x, t)|^2$ oscillates at exactly the classical frequency; what would it have been had I specified $\psi_2(x)$, instead of $\psi_1(x)$?
- Find $\langle x \rangle$ and $\langle p \rangle$. Check that Ehrenfest's theorem (Equation 1.38) holds, for this wave function.
- If you measured the energy of this particle, what values might you get, and with what probabilities?

Solution: (a)

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} |\Psi(x, 0)|^2 dx \\ &= |A|^2(9 + 16), \end{aligned}$$

so $A = \frac{1}{5}$.

(b)

$$\begin{aligned} \Psi(x, t) &= \frac{1}{5} [3\psi_0(x)e^{-iE_0t/\hbar} + 4\psi_1(x)e^{-iE_1t/\hbar}] \\ &= \frac{1}{5} [3\psi_0(x)e^{-\frac{1}{2}i\omega t} + 4\psi_1(x)e^{-\frac{3}{2}i\omega t}]. \end{aligned}$$

$$\begin{aligned} |\Psi(x, t)|^2 &= \frac{1}{25} [9|\psi_0(x)|^2 + 16|\psi_1(x)|^2 + 12\psi_0(x)\psi_1(x)(e^{i\omega t} + e^{-i\omega t})] \\ &= \frac{1}{25} [9|\psi_0(x)|^2 + 16|\psi_1(x)|^2 + 24\psi_0(x)\psi_1(x)\cos(\omega t)]. \end{aligned}$$

(c)

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} \Psi(x, 0)^* x \Psi(x, 0) dx \\ &= \frac{1}{25} \left[9 \int_{-\infty}^{\infty} \psi_0 x \psi_0 dx + 16 \int_{-\infty}^{\infty} \psi_1 x \psi_1 dx + 24 \cos(\omega t) \int_{-\infty}^{\infty} \psi_0 x \psi_1 dx \right] \\ &= \frac{24}{25} \cos(\omega t) \int_{-\infty}^{\infty} \psi_0 x \psi_1 dx \\ &= \frac{24}{25} \cos(\omega t) \sqrt{\frac{m\omega}{\pi\hbar}} \sqrt{\frac{2m\omega}{\hbar}} \int_{-\infty}^{\infty} x e^{-\frac{m\omega}{2\hbar}x^2} x e^{-\frac{m\omega}{2\hbar}x^2} dx \\ &= \frac{24}{25} \cos(\omega t) \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{m\omega}{\hbar}x^2} dx \\ &= \frac{24}{25} \sqrt{\frac{\hbar}{2m\omega}} \cos(\omega t). \end{aligned}$$

Then,

$$\begin{aligned} \langle p \rangle &= m \frac{d}{dt} \langle x \rangle \\ &= -\frac{24}{25} \sqrt{\frac{\hbar m \omega}{2}} \sin(\omega t). \end{aligned}$$

We have

$$\frac{d\langle p \rangle}{dt} = -\frac{24}{25} \sqrt{\frac{\hbar m \omega}{2}} \omega \cos(\omega t),$$

and

$$\frac{dV}{dx} = m\omega^2 x.$$

Therefore,

$$\begin{aligned} -\left\langle \frac{dV}{dx} \right\rangle &= -m\omega^2 \langle x \rangle \\ &= -\frac{24}{25} \sqrt{\frac{\hbar m \omega}{2}} \omega \cos(\omega t) \\ &= \frac{d\langle p \rangle}{dt}, \end{aligned}$$

so Ehrenfest's theorem holds.

- (d) We can get the energy $E_0 = \frac{\hbar\omega}{2}$ with probability $\frac{9}{25}$ and the energy $E_1 = \frac{3\hbar\omega}{2}$ with probability $\frac{16}{25}$. \square

Problem 14 Score: _____. In the ground state of the harmonic oscillator, what is the probability (correct to three significant digits) of finding the particle outside the classically allowed region?

Hint: Classically, the energy of an oscillator is $E = (1/2)m\omega^2 a^2$, where a is the amplitude. So the "classically allowed region" for an oscillator of energy E extends from $-\sqrt{2E/m\omega^2}$ to $+\sqrt{2E/m\omega^2}$. Look in a math table under "Normal Distribution" or "Error Function" for the numerical value of the integral, or evaluate it by computer.

Solution: Classically,

$$E_0 = \frac{1}{2}m\omega^2 x^2 = \frac{\hbar\omega}{2},$$

which gives us the amplitude of oscillation as

$$x_0 = \sqrt{\frac{\hbar}{m\omega}},$$

i.e., $\xi_0 = 1$. Then for the ground state of the harmonic oscillator,

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\xi^2/2},$$

the probability of finding the particle outside the classically allowed region is

$$\begin{aligned} P &= 2 \int_{x_0}^{\infty} \psi_0^2 dx \\ &= 2 \sqrt{\frac{m\omega}{\pi\hbar}} \sqrt{\frac{\hbar}{m\omega}} \int_1^{\infty} e^{-\xi^2} d\xi \\ &\approx 0.157 \end{aligned}$$

\square

Problem 15 Score: _____. Use the recursion formula (Equation 2.85) to work out $H_5(\xi)$ and $H_6(\xi)$. Invoke the convention that the coefficient of the highest power of ξ is 2^n to fix the overall constant.

Solution: $n = 5$:

$$a_3 = \frac{-2 \times 4}{2 \times 3} a_1 = -\frac{4}{3} a_1$$

$$a_5 = \frac{-2 \times 2}{4 \times 5} a_3 = -\frac{1}{5} a_3 = \frac{4}{15} a_1,$$

then,

$$\begin{aligned} H_5(\xi) &= a_1 \xi + a_3 \xi^3 + a_5 \xi^5 \\ &= a_1 \left(\xi - \frac{4}{3} \xi^3 + \frac{4}{15} \xi^5 \right), \end{aligned}$$

setting $a_1 = \frac{15}{4} 2^5 = 120$, we have

$$\begin{aligned} H_5(\xi) &= 120 \left(\xi - \frac{4}{3} \xi^3 + \frac{4}{15} \xi^5 \right) \\ &= 32\xi^5 - 160\xi^3 + 120\xi. \end{aligned}$$

$n = 6$:

$$\begin{aligned} a_2 &= \frac{-2 \times 6}{1 \times 2} a_0 = -6a_0, \\ a_4 &= \frac{-2 \times 4}{3 \times 4} a_2 = -\frac{2}{3} a_2 = 4a_0, \\ a_6 &= \frac{-2 \times 2}{5 \times 6} a_4 = -\frac{2}{15} a_4 = -\frac{8}{15} a_0, \end{aligned}$$

then,

$$\begin{aligned} H_6(\xi) &= a_0 + a_2 \xi^2 + a_4 \xi^4 + a_6 \xi^6 \\ &= a_0 \left(1 - 6\xi^2 + 4\xi^4 - \frac{8}{15} \xi^6 \right). \end{aligned}$$

Setting $a_0 = -\frac{15}{8} 2^6 = -120$, we have

$$\begin{aligned} H_6(\xi) &= -120 \left(1 - 6\xi^2 + 4\xi^4 - \frac{8}{15} \xi^6 \right) \\ &= 64\xi^6 - 480\xi^4 + 720\xi^2 - 120. \end{aligned}$$

□

Problem 16 Score: _____. In this problem we explore some of the more useful theorems (stated without proof) involving Hermite polynomials.

(a) The Rodrigues formula says that

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}.$$

Use it to derive H_3 and H_4 .

(b) The following recursion relation gives you $H_{n+1}(\xi)$ in terms of the two preceding Hermite polynomials:

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2n H_{n-1}(\xi).$$

Use it, together with your answer in (a), to obtain H_5 and H_6 .

- (c) If you differentiate an n th-order polynomial, you get a polynomial of order $(n - 1)$. For the Hermite polynomials, in fact,

$$\frac{dH_n}{d\xi} = 2nH_{n-1}(\xi).$$

Check this, by differentiating H_5 and H_6 .

- (d) $H_n(\xi)$ is the n th z -derivative, at $z = 0$, of the generating function

$$e^{-z^2+2z\xi} = \sum_{n=0}^{\infty} \frac{z^n}{n!} H_n(\xi).$$

Use this to obtain H_1 , H_2 , and H_3 .

Solution: (a)

$$\begin{aligned} \frac{d}{d\xi} e^{-\xi^2} &= -2\xi e^{-\xi^2}, \\ \frac{d^2}{d\xi^2} e^{-\xi^2} &= \frac{d}{d\xi} (-2\xi e^{-\xi^2}) \\ &= (4\xi^2 - 2)e^{-\xi^2}, \\ \frac{d^3}{d\xi^3} e^{-\xi^2} &= \frac{d}{d\xi} (4\xi^2 - 2)e^{-\xi^2} \\ &= (-8\xi^3 + 12\xi)e^{-\xi^2}, \\ \frac{d^4}{d\xi^4} e^{-\xi^2} &= \frac{d}{d\xi} (-8\xi^3 + 12\xi)e^{-\xi^2} \\ &= (16\xi^4 - 48\xi^2 + 12)e^{-\xi^2}. \end{aligned}$$

Therefore, we have

$$\begin{aligned} H_3(\xi) &= (-1)^3 e^{\xi^2} \frac{d^3}{d\xi^3} e^{-\xi^2} \\ &= -e^{\xi^2} (-8\xi^3 + 12\xi)e^{-\xi^2} \\ &= 8\xi^3 - 12\xi, \\ H_4(\xi) &= (-1)^4 e^{\xi^2} \frac{d^4}{d\xi^4} e^{-\xi^2} \\ &= e^{\xi^2} (16\xi^4 - 48\xi^2 + 12)e^{-\xi^2} \\ &= 16\xi^4 - 48\xi^2 + 12. \end{aligned}$$

(b)

$$\begin{aligned} H_5(\xi) &= 2\xi H_4(\xi) - 2 \times 4H_3(\xi) \\ &= 2\xi(16\xi^4 - 48\xi^2 + 12) - 8(8\xi^3 - 12\xi) \\ &= 32\xi^5 - 160\xi^3 + 120\xi, \\ H_6(\xi) &= 2\xi H_5(\xi) - 2 \times 5H_4(\xi) \\ &= 2\xi(32\xi^5 - 160\xi^3 + 120\xi) - 10(16\xi^4 - 48\xi^2 + 12) \\ &= 64\xi^6 - 480\xi^4 + 720\xi^2 - 120. \end{aligned}$$

(c)

$$\begin{aligned}
\frac{dH_5}{d\xi} &= 160\xi^4 - 480\xi^2 + 120, \\
&= 10(16\xi^4 - 48\xi^2 + 12) \\
&= 2 \times 5H_4(\xi), \\
\frac{dH_6}{d\xi} &= 384\xi^5 - 1920\xi^3 + 1440\xi \\
&= 12(32\xi^5 - 160\xi^3 + 120\xi) \\
&= 2 \times 6H_5(\xi).
\end{aligned}$$

(d)

$$\frac{d}{dz} e^{-z^2+2z\xi} = (-2z + 2\xi) e^{-z^2+2z\xi},$$

setting $z = 0$ gives us $H_1(\xi) = 2\xi$.

$$\begin{aligned}
\frac{d^2}{dz^2} e^{-z^2+2z\xi} &= \frac{d}{dz} (-2z + 2\xi) e^{-z^2+2z\xi} \\
&= -2e^{-z^2+2z\xi} + (-2z + 2\xi)(-2z + 2\xi) e^{-z^2+2z\xi} \\
&= [-2 + (-2z + 2\xi)^2] e^{-z^2+2z\xi},
\end{aligned}$$

setting $z = 0$ gives us $H_2(\xi) = 4\xi^2 - 2$.

$$\begin{aligned}
\frac{d^3}{dz^3} e^{-z^2+2z\xi} &= \frac{d}{dz} [-2 + (-2z + 2\xi)^2] e^{-z^2+2z\xi} \\
&= -2 \times 2(-2z + 2\xi) e^{-z^2+2z\xi} + [-2 + (-2z + 2\xi)^2] (-2z + 2\xi) e^{-z^2+2z\xi} \\
&= [(-2z + 2\xi)^3 - 6(-2z + 2\xi)] e^{-z^2+2z\xi},
\end{aligned}$$

setting $z = 0$ gives us $H_3(\xi) = 8\xi^3 - 12\xi$.

□