PHYS 23410 (Quantum Mechanics I) Problem Sets

Steven Labalme

February 22, 2024

Contents

1 Formalism of Quantum Mechanics

1/12: **1.** The Schrödinger equation is given by

$$\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r},t)\right)\psi(\vec{r},t) = i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}$$

a) Use this equation, and its complex conjugate, to demonstrate the **continuity equation**

$$\frac{\partial|\psi(\vec{r},t)|^2}{\partial t} + \vec{\nabla}\left(\frac{i\hbar}{2m}\right)\left(\psi\vec{\nabla}\psi^* - \psi^*\vec{\nabla}\psi\right) = 0$$

where the first term, with $|\psi|^2 = \psi^*\psi$, is the partial derivative of the probability density, while the second term is the divergence of the probability current density.

Answer. Multiply both sides of the Schrödinger equation by $-i/\hbar$:

$$\frac{\partial\psi}{\partial t} = \left(\frac{i\hbar}{2m}\vec{\nabla}^2 - \frac{i}{\hbar}V\right)\psi$$

We may then obtain the complex conjugate of the above equation by replacing all instances of i with its complex conjugate $-i$ and ψ with its complex conjugate ψ^*. In a nutshell, this works because we have a case of multiplying some complex number $a + bi = \psi(\vec{r})$ on the left by i, which gives $i(a + bi) = -b + ai$, and the complex conjugate of this number is $-b - ai = -i(a - bi) = -i(a + bi)^*$.

$$\frac{\partial\psi^*}{\partial t} = \left(-\frac{i\hbar}{2m}\vec{\nabla}^2 + \frac{i}{\hbar}V\right)\psi^*$$

We will use the above two equations to substitute into the following algebraic derivation, which yields the desired result.

$$\begin{aligned}
\frac{\partial|\psi|^2}{\partial t} &= \frac{\partial}{\partial t}(\psi^*\psi) \\
&= \psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t} \\
&= \psi^*\left(\frac{i\hbar}{2m}\vec{\nabla}^2 - \frac{i}{\hbar}V\right)\psi + \psi\left(-\frac{i\hbar}{2m}\vec{\nabla}^2 + \frac{i}{\hbar}V\right)\psi^* \\
&= \frac{i\hbar}{2m}\left(\psi^*\vec{\nabla}^2\psi - \psi\vec{\nabla}^2\psi^*\right) \\
&= \frac{i\hbar}{2m}\left[\left(\vec{\nabla}\psi^*\vec{\nabla}\psi + \psi^*\vec{\nabla}^2\psi\right) - \left(\vec{\nabla}\psi\vec{\nabla}\psi^* + \psi\vec{\nabla}^2\psi^*\right)\right] \\
&= \frac{i\hbar}{2m}\vec{\nabla}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right) \\
&= -\vec{\nabla}\left(\frac{i\hbar}{2m}\right)\left(\psi\vec{\nabla}\psi^* - \psi^*\vec{\nabla}\psi\right)
\end{aligned}$$

□

b) Discuss the physical interpretation of this equation. What happens if you integrate the first and second terms over a region of space, defined by a finite volume V and separated by the rest of space by a boundary area S?

Hint: Use the analogy with the case of electromagnetic charge. If you integrate over the whole volume of space, the continuity equation leads to charge conservation. The probability current density, just as the charge current density, is assumed to vanish sufficiently fast at infinity, so that there is no flow of probability (charge) at infinity.

Answer. This equation implies that probability density is *locally* conserved. In its current differential form, it states that the change in probability density (first term) is exactly offset by the divergence or the probability current density (second term). This interpretation is clarified upon integrating over a volume V contained within a boundary surface S. In the integral form, the first term becomes the change in probability density within V, i.e., the rate at which the particle becomes more or less likely to exist within V. Moreover, this is equal to the opposite of the second term, which when integrated gives the flux of the probability density through S. Essentially, if the particle is going to become less likely to exist within V, then a corresponding amount of probability density must flow out of V through S (and vice versa if the particle is going to become more likely to exist within V).

Additionally, note that if you take the limit as $V \to \mathbb{C}^3$, both terms go to zero (because probability density is conserved within the entire space). Since the sum of two terms equal to zero is zero, this is another way of verifying the equality in the continuity equation. □

2. Consider the expectation value of the operator $\hat{\vec{p}}^2 = -\hbar^2 \vec{\nabla}^2$, namely

$$\int \mathrm{d}^3\vec{r}\ \psi(\vec{r},t)^* \left(-\hbar^2 \vec{\nabla}^2 \psi(\vec{r},t)\right)$$

a) Using integration by parts, demonstrate that this can be rewritten as the integral of the modulus square of the gradient of $\hbar\psi(\vec{r},t)$ and that it is therefore a positive quantity. As before, assume that the wave functions go sufficiently fast to zero at infinity.

Answer. To begin, we need to derive a three-dimensional analogy to the standard one-dimensional integration by parts formula. Let $u, v : \mathbb{C}^3 \to \mathbb{C}^3$ be functions with smoothness constraints analogous to ψ. As in the one-dimensional case, we'll start with the product rule and integrate.

$$\begin{aligned}
\vec{\nabla} \cdot (u\vec{\nabla}v) &= (\vec{\nabla}u)(\vec{\nabla}v) + u\vec{\nabla}^2 v \\
\int_\Omega \vec{\nabla} \cdot (u\vec{\nabla}v) &= \int_\Omega (\vec{\nabla}u)(\vec{\nabla}v) + \int_\Omega u\vec{\nabla}^2 v \\
\int_\Omega \vec{\nabla} \cdot (u\vec{\nabla}v) - \int_\Omega (\vec{\nabla}u)(\vec{\nabla}v) &= \int_\Omega u\vec{\nabla}^2 v
\end{aligned}$$

We can then apply this result and simplify to yield the final result.

$$\begin{aligned}
\int \mathrm{d}^3\vec{r}\ \psi^* \left(-\hbar^2 \vec{\nabla}^2 \psi\right) &= -\int \mathrm{d}^3\vec{r}\ \underbrace{\hbar\psi^*}_{u}\underbrace{\vec{\nabla}^2(\hbar\psi)}_{\vec{\nabla}^2 v} \\
&= -\underbrace{\int \vec{\nabla} \cdot \left[(\hbar\psi^*)\vec{\nabla}(\hbar\psi)\right]}_{0} + \int \mathrm{d}^3\vec{r}\ \vec{\nabla}(\hbar\psi^*)\vec{\nabla}(\hbar\psi) \\
&= \int \mathrm{d}^3\vec{r}\ |\vec{\nabla}(\hbar\psi)|^2
\end{aligned}$$

To clarify, we know that the first term given by integration by parts goes to zero because of the divergence theorem. In particular, let Ω be a finite region of space encapsulated by $\mathrm{d}\Omega$; we will take the limit as $\Omega \to \mathbb{C}^3$ and $\mathrm{d}\Omega$ approaches the boundary of $\mathbb{C}^3$. Then

$$\int_\Omega \vec{\nabla} \cdot [\hbar\psi^* \vec{\nabla}(\hbar\psi)] = \int_{\mathrm{d}\Omega} [\hbar\psi^* \vec{\nabla}(\hbar\psi)] \cdot \hat{n}\, \mathrm{d}S$$

Essentially, this means that the original integral is equal to an integral of an integrand containing ψ^* (which goes to zero at the "boundary" of $\mathbb{C}^3$) at a surface approaching the boundary through the aforementioned limit. This means that the second integral — under the limit that $\mathrm{d}\Omega$ approaches the "boundary" of $\mathbb{C}^3$ — is zero, justifying the original substitution. □

b) Now consider the expectation value of the Hamiltonian $\hat{\vec{p}}^2/2m + V(\vec{r},t)$ and assume that the function $\psi(\vec{r},t)$ is an eigenfunction of the Hamiltonian. In such a case,

$$\hat{H}\psi(\vec{r},t) = E\psi$$

and the particle therefore has a well-defined energy, equal to E. Demonstrate, based on the result of part (a), that E must be larger than the minimum value of $V(\vec{r},t)$.

Hint: Use $(\hat{\vec{p}}^2/2m)\psi = (E-V)\psi$, and the fact that the mean value of V should be larger than its minimum value.

The lesson is that the particle can enter regions of space where its energy is lower than the potential, but this is not possible everywhere in space. The fact that the particle can go through regions of space where its energy is lower than the potential (the wave function does not vanish in those regions of space) leads to the famous phenomenon of tunneling, namely a particle can go through a *finite region of space where the potential is higher than its energy* and has a probability of being transmitted to the other side.

Answer. Taking the hint, we have that

$$\begin{aligned}
E - \langle V\rangle &= E\cdot 1 - \langle V\rangle \\
&= E\cdot\int \mathrm{d}^3\vec{r}\ \psi^*\psi - \int \mathrm{d}^3\vec{r}\ \psi^* V\psi \\
&= \int \mathrm{d}^3\vec{r}\ \psi^*(E-V)\psi \\
&= \int \mathrm{d}^3\vec{r}\ \psi^*\left(\frac{\hat{\vec{p}}^2}{2m}\right)\psi \\
&= \frac{1}{2m}\int \mathrm{d}^3\vec{r}\ \psi^*(-\hbar^2\vec{\nabla}^2)\psi \\
&= \frac{1}{2m}\int \mathrm{d}^3\vec{r}\ |\vec{\nabla}(\hbar\psi)|^2 && \text{Part (a)} \\
&> 0
\end{aligned}$$

Taking the hint again, we have that

$$\langle V\rangle > V_{\min}$$

Therefore, by transitivity, we have that

$$\begin{aligned}
E - \langle V\rangle &> 0 \\
E > \langle V\rangle &> V_{\min}
\end{aligned}$$

as desired. □

3. We shall define **Hermitian operators** as those ones $\hat{O}$ satisfying the property

$$\int \mathrm{d}^3\vec{r}\ \psi_m^*(\vec{r},t)\hat{O}\psi_n(\vec{r},t) = \left(\int \mathrm{d}^3\vec{r}\ \psi_n^*(\vec{r},t)\hat{O}\psi_m(\vec{r},t)\right)^* \tag{1.1}$$

where ψ_m is a particular solution of the Schrödinger equation. Observe that when you identify $\psi_n = \psi_m$, you obtain that the mean value of a Hermitian operator is real and thus can be associated with an observable.

Observe also that, in general, this could be written as

$$\int \mathrm{d}^3\vec{r}\ \psi_m^*(\vec{r},t)\hat{O}\psi_n(\vec{r},t) = \int \mathrm{d}^3\vec{r}\ [\hat{O}\psi_m(\vec{r},t)]^*\psi_n(\vec{r},t)$$

Therefore, in the case of a Hermitian operator, I can "transfer" the application of the operator from the right to the left.

a) Use this property to demonstrate that if you take two different Hermitian operators and you transfer them in the proper order, then

$$\langle\psi_m|\hat{O}_1\hat{O}_2|\psi_n\rangle = \Big(\langle\psi_n|\hat{O}_2\hat{O}_1|\psi_m\rangle\Big)^*$$

where I used the Dirac notation. Observe that if I take $\hat{O}_2$ to be a real constant, this equation reduces to Equation 1.1.

Answer. We have that

$$\begin{aligned}
\langle\psi_m|\hat{O}_1\hat{O}_2|\psi_n\rangle &= \int \mathrm{d}^3\vec{r}\ \psi_m^*\hat{O}_1\hat{O}_2\psi_n \\
&= \int \mathrm{d}^3\vec{r}\ (\hat{O}_1\psi_m)^*\hat{O}_2\psi_n \\
&= \int \mathrm{d}^3\vec{r}\ [\hat{O}_2(\hat{O}_1\psi_m)]^*\psi_n \\
&= \left(\int \mathrm{d}^3\vec{r}\ \psi_n^*[\hat{O}_2(\hat{O}_1\psi_m)]\right)^* \\
&= \left(\int \mathrm{d}^3\vec{r}\ \psi_n^*\hat{O}_2\hat{O}_1\psi_m\right)^* \\
&= \Big(\langle\psi_n|\hat{O}_2\hat{O}_1|\psi_m\rangle\Big)^*
\end{aligned}$$

as desired. □

b) Use this relation to demonstrate that the mean value of the **commutator** of two Hermitian operators, which is given by

$$[\hat{O}_1,\hat{O}_2] = \hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1$$

is a pure imaginary number, and hence (unless it is multiplied by an imaginary factor), cannot be associated with a physical observable. In the particular example of momentum and position, for instance, $[\hat{p}_i,\hat{r}_j] = -i\hbar\delta_{ij}$, where δ_{ij} is the **Kronecker delta**. Do it for the mean value of the commutator in a particular state with wave function ψ_n.

Answer. We have that

$$\begin{aligned}
\langle\psi|[\hat{O}_1,\hat{O}_2]|\psi\rangle &= \langle\psi|\hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1|\psi\rangle \\
&= \langle\psi|\hat{O}_1\hat{O}_2|\psi\rangle - \langle\psi|\hat{O}_2\hat{O}_1|\psi\rangle \\
&= \underbrace{\langle\psi|\hat{O}_1\hat{O}_2|\psi\rangle}_{a+bi} - (\underbrace{\langle\psi|\hat{O}_1\hat{O}_2|\psi\rangle}_{a-bi})^*
\end{aligned}$$

Since taking the difference of a complex number $a+bi$ and its complex conjugate $a-bi$ yields the purely imaginary number $2bi$, we have the desired result.
Now consider the explicit case where $\hat{O}_1 = \hat{p}_i$, $\hat{O}_2 = \hat{r}_j$, and $\psi = \psi_n$. Then we have that

$$\begin{aligned}
\langle\psi_n|[\hat{p}_i,\hat{r}_j]|\psi_n\rangle &= \langle\psi_n|-i\hbar\delta_{ij}|\psi_n\rangle \\
&= -i\hbar\delta_{ij}\int \mathrm{d}^3\vec{r}\ \psi_n^*\psi_n \\
&= -i\hbar\delta_{ij}\int \mathrm{d}^3\vec{r}\ |\psi_n|^2
\end{aligned}$$

Therefore, the mean value is equal to an imaginary number times an integral that will be real, so the final answer is, indeed, purely imaginary. □

c) Demonstrate that the above relation remains true if you compute the mean value of the commutator for an arbitrary wave function
$$\Psi = \sum_n c_n \psi_n$$
Hint: Organize the total sum that you obtain in pairs that share the same values of m and n, and demonstrate that when you add up the two terms with the same values of m and n, you obtain a purely imaginary number. The terms in the total sum for which $m = n$ don't have pairs, but you can use the result of part (b) to show that they are indeed imaginary.

Answer. We are interested in computing
$$\langle \Psi | [\hat{O}_1, \hat{O}_2] | \Psi \rangle$$
Taking the hint, we break it into two sums as follows.
$$\begin{aligned}
\langle \Psi | [\hat{O}_1, \hat{O}_2] | \Psi \rangle &= \left\langle \sum_n c_n \psi_n \middle| [\hat{O}_1, \hat{O}_2] \middle| \sum_n c_n \psi_n \right\rangle \\
&= \sum_{n,m} \langle c_n \psi_n | [\hat{O}_1, \hat{O}_2] | c_m \psi_m \rangle \\
&= \sum_m \sum_{\substack{n \\ n=m}} c_n^* c_n \langle \psi_n | [\hat{O}_1, \hat{O}_2] | \psi_n \rangle + \sum_m \sum_{\substack{n \\ n \neq m}} c_m^* c_n \langle \psi_m | [\hat{O}_1, \hat{O}_2] | \psi_n \rangle \\
&= \sum_n c_n^* c_n \langle \psi_n | [\hat{O}_1, \hat{O}_2] | \psi_n \rangle \\
&\quad + \sum_{m<n} (c_m^* c_n \langle \psi_m | [\hat{O}_1, \hat{O}_2] | \psi_n \rangle + c_n^* c_m \langle \psi_n | [\hat{O}_1, \hat{O}_2] | \psi_m \rangle) \\
&= \sum_n c_n^* c_n \langle \psi_n | [\hat{O}_1, \hat{O}_2] | \psi_n \rangle \\
&\quad + \sum_{m<n} [c_m^* c_n \langle \psi_m | [\hat{O}_1, \hat{O}_2] | \psi_n \rangle - c_n^* c_m (\langle \psi_m | [\hat{O}_1, \hat{O}_2] | \psi_n \rangle)^*] \\
&= \sum_n c_n^* c_n \langle \psi_n | [\hat{O}_1, \hat{O}_2] | \psi_n \rangle \\
&\quad + \sum_{m<n} [c_m^* c_n \langle \psi_m | [\hat{O}_1, \hat{O}_2] | \psi_n \rangle - (c_m^* c_n \langle \psi_m | [\hat{O}_1, \hat{O}_2] | \psi_n \rangle)^*]
\end{aligned}$$
From part (b), the first sum is a sum of purely imaginary numbers. Additionally, by the same logic as in part (b), the second sum is a sum of purely imaginary numbers. Thus, the overall term is a sum of purely imaginary numbers, and is thus a purely imaginary number, as desired[1]. □

[1]Note that in the above derivation, I derive that terms across the diagonal from each other are complex conjugates of each other. However, I don't even need to do this because the commutator is Hermitian, so we have this by definition!

2 Infinite Well Motion and Quantum Tunneling

1/19: **1.** In class, we demonstrated that given a certain time-independent potential, one can find solutions to the Schrödinger equation such that

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi_n(\vec{r}) + V(\vec{r})\psi_n(\vec{r}) = E_n\psi_n(\vec{r}) \tag{2.1}$$

Assume now that we are in one dimension, with the potential being a square well:

$$\begin{aligned} V(x) &\to \infty \quad \text{for } x \leq 0 \text{ and } x \geq a \\ V(x) &\to 0 \quad \text{for } 0 < x < a \end{aligned} \tag{2.2}$$

Show that in such a case, the solutions are given by

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \tag{2.3}$$

due to the fact that in order to get a finite mean energy value, the wave function must vanish at $x = 0, a$. The energy eigenstates are given by

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{2.4}$$

The factor $\sqrt{2/a}$ comes from the requirement of a good normalized solution, i.e., one with $\langle\psi_n|\psi_n\rangle = 1$. Now, imagine that at $t = 0$, the particle is in the state

$$\psi(x,0) = \frac{A}{\sqrt{a}}\sin\left(\frac{\pi x}{a}\right) + \sqrt{\frac{3}{5a}}\sin\left(\frac{3\pi x}{a}\right) + \frac{1}{\sqrt{5a}}\sin\left(\frac{5\pi x}{a}\right) \tag{2.5}$$

where A is a real constant.

a) Find the value of A such that $\psi(x,0)$ is normalized. (Hint: Use $\langle\psi_n|\psi_m\rangle = \delta_{nm}$.)

Answer. For $\psi(x,0)$ to be normalized, it must satisfy

$$\langle\psi(x,0)|\psi(x,0)\rangle = 1$$

Now recognize that $\psi(x,0)$ is of the form

$$\psi = c_1\psi_1 + c_3\psi_3 + c_5\psi_5$$

Thus, we have that

$$\begin{aligned}
1 &= \langle\psi|\psi\rangle \\
&= \langle c_1\psi_1 + c_3\psi_3 + c_5\psi_5|c_1\psi_1 + c_3\psi_3 + c_5\psi_5\rangle \\
&= \langle c_1\psi_1|c_1\psi_1\rangle + \langle c_3\psi_3|c_3\psi_3\rangle + \langle c_5\psi_5|c_5\psi_5\rangle + 2\underbrace{\langle c_1\psi_1|c_3\psi_3\rangle}_{0} + 2\underbrace{\langle c_1\psi_1|c_5\psi_5\rangle}_{0} + 2\underbrace{\langle c_3\psi_3|c_5\psi_5\rangle}_{0} \\
&= \langle c_1\psi_1|c_1\psi_1\rangle + \langle c_3\psi_3|c_3\psi_3\rangle + \langle c_5\psi_5|c_5\psi_5\rangle \\
&= \int_0^a \frac{A^2}{a}\sin^2\left(\frac{\pi x}{a}\right)\mathrm{d}x + \int_0^a \frac{3}{5a}\sin^2\left(\frac{3\pi x}{a}\right)\mathrm{d}x + \int_0^a \frac{1}{5a}\sin^2\left(\frac{5\pi x}{a}\right)\mathrm{d}x \\
&= \frac{A^2}{2} + \frac{3}{10} + \frac{1}{10} \\
&= \frac{5A^2+4}{10}
\end{aligned}$$

$$\boxed{A = \pm\sqrt{\frac{6}{5}}}$$

□

b) If measurements of the energy are carried out, what are the values that will be found and what are the probabilities of measuring such energies? Calculate the average energy.

Answer. As mentioned above, $\psi(x,0)$ is of the form

$$\psi(x,0) = c_1\psi_1(x) + c_3\psi_3(x) + c_5\psi_5(x)$$

Thus, the energies that will be found are

$$\boxed{E_1 = \frac{\hbar^2\pi^2}{2ma^2} \qquad E_3 = \frac{3^2\hbar^2\pi^2}{2ma^2} \qquad E_5 = \frac{5^2\hbar^2\pi^2}{2ma^2}}$$

Moreover, the probabilities of measuring such energies are given by the integrals calculated in part (a). In other words, the probabilities P_i of measuring energy E_i are

$$\boxed{P_1 = \frac{3}{5} \qquad P_3 = \frac{3}{10} \qquad P_5 = \frac{1}{10}}$$

The average energy could be calculated by evaluating $\langle\psi|\hat{H}|\psi\rangle$, or by calculating

$$\langle E\rangle = E_1P_1 + E_3P_3 + E_5P_5$$

$$\boxed{\langle E\rangle = \frac{29\hbar^2\pi^2}{10ma^2}}$$

□

c) Find the expression of the wave function at a later time t. (Hint: What is $\psi_n(x,t)$?)

Answer. Taking the hint, we know that

$$\psi_n(x,t) = \psi_n(x)\mathrm{e}^{-iE_nt/\hbar} = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)\mathrm{e}^{-iE_nt/\hbar}$$

We can rewrite $\psi(x,0)$ in a form relatable to the above as follows.

$$\begin{aligned}\psi(x,0) &= \pm\sqrt{\frac{6}{5a}}\sin\left(\frac{\pi x}{a}\right) + \sqrt{\frac{3}{5a}}\sin\left(\frac{3\pi x}{a}\right) + \frac{1}{\sqrt{5a}}\sin\left(\frac{5\pi x}{a}\right)\\ &= \pm\sqrt{\frac{3}{5}}\sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right) + \sqrt{\frac{3}{10}}\sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right) + \frac{1}{\sqrt{10}}\sqrt{\frac{2}{a}}\sin\left(\frac{5\pi x}{a}\right)\\ &= \pm\sqrt{\frac{3}{5}}\psi_1(x,0) + \sqrt{\frac{3}{10}}\psi_3(x,0) + \frac{1}{\sqrt{10}}\psi_5(x,0)\end{aligned}$$

Therefore,

$$\begin{aligned}\psi(x,t) &= \pm\sqrt{\frac{3}{5}}\psi_1(x,t) + \sqrt{\frac{3}{10}}\psi_3(x,t) + \frac{1}{\sqrt{10}}\psi_5(x,t)\\ &= \pm\sqrt{\frac{3}{5}}\sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)\mathrm{e}^{-iE_1t/\hbar} + \sqrt{\frac{3}{10}}\sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right)\mathrm{e}^{-iE_3t/\hbar}\\ &\quad + \frac{1}{\sqrt{10}}\sqrt{\frac{2}{a}}\sin\left(\frac{5\pi x}{a}\right)\mathrm{e}^{-iE_5t/\hbar}\end{aligned}$$

$$\boxed{\psi(x,t) = \pm\sqrt{\frac{6}{5a}}\sin\left(\frac{\pi x}{a}\right)\mathrm{e}^{-iE_1t/\hbar} + \sqrt{\frac{3}{5a}}\sin\left(\frac{3\pi x}{a}\right)\mathrm{e}^{-iE_3t/\hbar} + \frac{1}{\sqrt{5a}}\sin\left(\frac{5\pi x}{a}\right)\mathrm{e}^{-iE_5t/\hbar}}$$

□

d) Is the mean value of the position operator independent of time? What about the mean value of the momentum? (Hint: Use symmetry properties with respect to the central point of the well.)

Answer. To determine whether or not the position operator is independent of time, it will suffice to evaluate

$$\frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi(x,t)|\hat{x}|\psi(x,t)\rangle)$$

If the above expression is equal to zero, then the position operator is independent of time, and if it is not equal to zero, then the position operator is not independent of time. Let's begin.

Taking the hint, we may observe that $\psi(x,t)$ is the sum of wave functions which all have odd n, meaning that they are each even about the center point $x = a/2$ of the well. Thus, the entire wave function is even about $a/2$. Since the product of an odd and an even function is an odd function, we consequently have that

$$\begin{aligned}\langle\psi(x,t)|\hat{x}|\psi(x,t)\rangle &= \int_0^a x|\psi(x,t)|^2\,\mathrm{d}x \\ &= \underbrace{\int_0^a \left(x-\frac{a}{2}\right)|\psi(x,t)|^2\,\mathrm{d}x}_{0} + \frac{a}{2}\underbrace{\int_0^a |\psi(x,t)|^2\,\mathrm{d}x}_{1} \\ &= \frac{a}{2}\end{aligned}$$

Just to clarify, $x - a/2$ is odd with respect to the center of the well and $|\psi(x,t)|^2$ is even, so their product is odd. The integral of an odd function over all space is always zero. For the right term, the normalization requirement evaluates it to 1.

The above constant clearly has zero derivative with respect to time. It therefore follows by what we said at the beginning that $\boxed{\text{the mean value of the position operator is independent of time.}}$

As to the second part of the question, we have that

$$\langle\psi(x,t)|\hat{p}|\psi(x,t)\rangle = m\underbrace{\frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi(x,t)|\hat{x}|\psi(x,t)\rangle)}_{0} = 0$$

Therefore, $\boxed{\text{the mean value of the momentum operator is independent of time.}}$ □

e) Would the result of part (d) be different if we replaced ψ_3 by ψ_2 in Eq. 2.5?

Answer. If we replace ψ_3 by ψ_2, then $\psi(x,t)$ will have no definite parity (will be neither even nor odd). Thus, the left integral in part (d) will no longer vanish generically; instead, it will be some function of time. This will also affect the momentum result since it follows from the position result. So overall, $\boxed{\text{yes}}$ the result will be different. □

2. a) Consider now the wave function $\Psi(x,t)$ of a particle moving in one dimension in a potential $V(x)$ such that

$$\begin{aligned} &V(x) \to \infty && \text{for } |x| \geq a/2 \\ &V(x) = 0 && \text{for } -a/2 < x < 0 \\ &V(x) = V_0 && \text{for } 0 \leq x < a/2 \end{aligned} \tag{2.6}$$

Considering that the wave function and its derivative are continuous at $x = 0$, and that the wave function vanishes at $x = \pm a/2$, try to find the equation that gives the possible energy states assuming $E_n > V_0$.

Hint: There are different combinations of sine and cosine functions for positive and negative values of x.

Answer. Taking the hint, split the total wave function $\psi(x)$ into the sum of two parts, $\psi_1(x)$ and $\psi_2(x)$, where $\psi_1(x) = 0$ for $x \geq 0$ and $\psi_2(x) = 0$ for $x \leq 0$. In general, we have

$$\psi_1(x) = S_1 \sin(k_1 x) + C_1 \cos(k_1 x) \qquad \psi_2(x) = S_2 \sin(k_2 x) + C_2 \cos(k_2 x)$$

If $\psi = \psi_1 + \psi_2$ is to be continuous at $x = 0$, then we must have

$$\begin{aligned} \psi_1(0) &= \psi_2(0) \\ C_1 &= C_2 \end{aligned}$$

If $\psi = \psi_1 + \psi_2$ is to have a continuous first derivative at $x = 0$, then we must have

$$\begin{aligned} \psi_1'(0) &= \psi_2'(0) \\ k_1 S_1 &= k_2 S_2 \end{aligned}$$

If we are to have $\psi(-a/2) = \psi_1(-a/2) = 0$ at the left boundary, then we must have

$$\begin{aligned} S_1 \sin\left(-\frac{k_1 a}{2}\right) + C_1 \cos\left(-\frac{k_1 a}{2}\right) &= 0 \\ -S_1 \sin\left(\frac{k_1 a}{2}\right) + C_1 \cos\left(\frac{k_1 a}{2}\right) &= 0 \end{aligned}$$

If we are to have $\psi(a/2) = \psi_2(a/2) = 0$ at the right boundary, then we must have

$$S_2 \sin\left(\frac{k_2 a}{2}\right) + C_2 \cos\left(\frac{k_2 a}{2}\right) = 0$$

Now combining all four boundary condition equations above (and favoring C_1, S_1 over C_2, S_2), we obtain the following two equations.

$$S_1 \sin\left(\frac{k_1 a}{2}\right) = C_1 \cos\left(\frac{k_1 a}{2}\right) \qquad \frac{k_1 S_1}{k_2} \sin\left(\frac{k_2 a}{2}\right) = -C_1 \cos\left(\frac{k_2 a}{2}\right)$$

Now divide the right equation above by the left one.

$$\begin{aligned} \frac{\frac{k_1 S_1}{k_2} \sin\left(\frac{k_2 a}{2}\right)}{S_1 \sin\left(\frac{k_1 a}{2}\right)} &= -\frac{C_1 \cos\left(\frac{k_2 a}{2}\right)}{C_1 \cos\left(\frac{k_1 a}{2}\right)} \\ \frac{k_1}{k_2} &= -\frac{\sin\left(\frac{k_1 a}{2}\right) \cos\left(\frac{k_2 a}{2}\right)}{\cos\left(\frac{k_1 a}{2}\right) \sin\left(\frac{k_2 a}{2}\right)} \\ &\boxed{\frac{k_1}{k_2} = -\tan\left(\frac{k_1 a}{2}\right) \cot\left(\frac{k_2 a}{2}\right)} \end{aligned}$$

Since

$$k_1 = \frac{\sqrt{2mE_n}}{\hbar} \qquad\qquad k_2 = \frac{\sqrt{2m(E_n - V_0)}}{\hbar}$$

the above equation gives one constraint on the possible energy states. An additional one can be obtained directly from these equations and is

$$\boxed{k_2^2 - k_1^2 = -\frac{2mV_0}{\hbar^2}}$$

Together, these two equations can (theoretically) be solved for the two variables k_1, k_2 and, thus, for the energy states E_n. ☐

b) Consider now an energy $E_n < V_0$. What is the form of the solution at positive values of x?
Hint: The solutions at $x > 0$ are no longer given in terms of sine and cosine functions. They can now be written in terms of exponential functions. You can obtain the new solutions by using the same solutions as for $E_n > V_0$, and the known relations between trigonometric and hyperbolic sine and cosine functions, namely $\sin(ix) = i\sinh(x)$ and $\cos(ix) = \cosh(x)$.
In classical mechanics, a particle cannot enter a region where the potential energy is larger than the energy of the particle, since it would imply that the kinetic energy is negative. Is this still true in quantum mechanics? In other words, does the probability of finding the particle at positive values of x vanish?

Answer. We first define the Schrödinger equation at positive values of x in this case.

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_2}{\mathrm{d}x^2} + V_0\psi_2 &= E_n\psi_2 \\ \frac{\mathrm{d}^2\psi_2}{\mathrm{d}x^2} &= \underbrace{\frac{2m(V_0 - E_n)}{\hbar^2}}_{\kappa_2^2}\psi_2 \end{aligned}$$

Taking the hint, the general solution to this equation is

$$\begin{aligned} \psi_2(x) &= A\mathrm{e}^{\kappa_2 x} + B\mathrm{e}^{-\kappa_2 x} \\ &= \frac{\tilde{S}_2 + \tilde{C}_2}{2}\mathrm{e}^{\kappa_2 x} + \frac{\tilde{C}_2 - \tilde{S}_2}{2}\mathrm{e}^{-\kappa_2 x} \\ &= \tilde{S}_2 \cdot \frac{\mathrm{e}^{\kappa_2 x} - \mathrm{e}^{-\kappa_2 x}}{2} + \tilde{C}_2 \cdot \frac{\mathrm{e}^{\kappa_2 x} + \mathrm{e}^{-\kappa_2 x}}{2} \\ &= \tilde{S}_2\sinh(\kappa_2 x) + \tilde{C}_2\cosh(\kappa_2 x) \\ &= -i\tilde{S}_2\sin(i\kappa_2 x) + \tilde{C}_2\cos(i\kappa_2 x) \end{aligned}$$

Now observe that

$$i\kappa_2 = \frac{\sqrt{2m(E_n - V_0)}}{\hbar} = k_2$$

Additionally, define

$$S_2 := -i\tilde{S}_2 \qquad\qquad C_2 := \tilde{C}_2$$

Thus,

$$\boxed{\psi_2(x) = S_2\sin(k_2 x) + C_2\cos(k_2 x)}$$

Additionally, we still have that

$$\psi_1(x) = S_1\sin(k_1 x) + C_1\cos(k_1 x)$$

so the boundary conditions at $x = 0$ imply by transitivity that

$$C_1 = C_2 = \tilde{C}_2 \qquad\qquad k_1 S_1 = k_2 S_2 = (i\kappa_2)(-i\tilde{S}_2) = \kappa_2 \tilde{S}_2$$

Since ψ_2 will vanish if and only if $\tilde{S}_2 = \tilde{C}_2 = 0$, the above two equations imply that in this case, $S_1 = C_1 = 0$, too. Therefore, in general, it is $\boxed{\text{not}}$ still true in quantum mechanics that a particle cannot enter a region where the potential energy is larger than the energy of the particle. In other words, the probability of finding the particle at positive values of x $\boxed{\text{does not}}$ vanish. ☐

c) What happens when $V_0 \to \infty$? In principle, one obtains in this limit an infinite square well of length $a/2$. Hence, the energy eigenstates should change such that

$$\sin\left(\frac{k_n a}{2}\right) = 0 \tag{2.7}$$

with

$$\frac{\hbar^2 k_n^2}{2m} = E_n \tag{2.8}$$

Is this true? What happens to the wave function at positive values of x?

Answer. Here, it will be convenient to write

$$\psi_2(x) = A\mathrm{e}^{\kappa_2 x} + B\mathrm{e}^{-\kappa_2 x}$$

Now since $\kappa_2 \propto V_0^{1/2}$, as $V_0 \to \infty$, $\kappa_2 \to \infty$. Thus, to keep ψ_2 from blowing up at positive x, we must set $A = 0$. Additionally, we will have $\mathrm{e}^{-\kappa_2 x} \to 0$ so that at $V_0 = \infty$,

$$\boxed{\psi_2(x) = 0}$$

Additionally, the boundary conditions at zero (and the fact that $A = 0$) imply that

$$\begin{aligned} \psi_1(0) &= \psi_2(0) & \qquad\qquad \psi_1'(0) &= \psi_2'(0) \\ C_1 &= B & k_1 S_1 &= -\kappa_2 B \end{aligned}$$

Therefore, our last boundary condition gives us that

$$\begin{aligned} 0 &= \psi_1\left(-\frac{a}{2}\right) \\ &= S_1 \sin\left(-\frac{k_1 a}{2}\right) + C_1 \cos\left(-\frac{k_1 a}{2}\right) \\ &= -S_1 \sin\left(\frac{k_1 a}{2}\right) + C_1 \cos\left(\frac{k_1 a}{2}\right) \\ &= \frac{\kappa_2 B}{k_1} \sin\left(\frac{k_1 a}{2}\right) + B\cos\left(\frac{k_1 a}{2}\right) \\ &= \sin\left(\frac{k_1 a}{2}\right) + \frac{k_1}{\kappa_2}\cos\left(\frac{k_1 a}{2}\right) \\ &= \sin\left(\frac{k_1 a}{2}\right) + \frac{k_1}{\infty}\cos\left(\frac{k_1 a}{2}\right) \\ &= \sin\left(\frac{k_1 a}{2}\right) \\ \frac{k_1 a}{2} &= \pi n \\ \frac{\sqrt{2mE_n}}{\hbar} &= \frac{2\pi n}{a} \\ E_n &= \frac{\hbar^2 \pi^2 n^2}{2m(a/2)^2} \end{aligned}$$

as desired. So $\boxed{\text{yes, it is true.}}$ ☐

3. Although planar waves are not well normalized, one can use them to demonstrate the tunneling phenomenon. Note that a well-normalized solution would be a wave packet of these planar waves, namely

$$\psi(x,0) = \frac{1}{\sqrt{2\pi}} \int \mathrm{d}k\, \Phi(k) \mathrm{e}^{ikx} \tag{2.9}$$

Consider a stationary solution of a free particle with finite energy E and forget for the time being the question of normalization. The momentum of the particle will be given by $|\hbar k| = \sqrt{E/2m}$ and

$$\psi(x,t) = A\mathrm{e}^{i(kx-\omega t)} + B\mathrm{e}^{i(-kx-\omega t)} \tag{2.10}$$

with $\hbar\omega = E$.

Observe that there are two solutions, one with positive (incoming wave) and the other with negative (reflected wave) values of the momentum in the x-direction. In the previous problems, they combined to give sine and cosine functions due to the boundary conditions. Now, imagine that we consider that this particle goes through a potential

$$\begin{aligned} V(x) &= 0 \quad \text{for } |x| > a/2 \\ V(x) &= V_0 \quad \text{for } |x| \leq a/2 \end{aligned} \tag{2.11}$$

Since we want to consider the transmission of the particle at the right of the potential barrier, consider the case in which at the right of this finite potential barrier, the wave function is described by a particle moving freely in the positive direction of x via

$$\psi(x,t) = C\mathrm{e}^{i(kx-\omega t)} \tag{2.12}$$

for $x > a/2$ while for $x < -a/2$, we have the function given in Eq. 2.10. The ratio $|B/A|^2$ may be considered as the reflection probability, while $|C/A|^2$ is the transmission probability.

The solutions for $-a/2 \leq x \leq a/2$, instead, are given by

$$\psi(x,t) = F\mathrm{e}^{i(k_2x-\omega t)} + G\mathrm{e}^{i(-k_2x-\omega t)} \tag{2.13}$$

with $k_2 = \sqrt{2m(E-V_0)}/\hbar$. Observe that ω is unchanged.

Using continuity of the wave function and its derivatives at $x = \pm a/2$, calculate the reflection and transmission probabilities. Consider both the case of $E > V_0$ and $E < V_0$, and try to interpret the results. What happens when $V_0 \to \infty$?

Answer. The total spatial wave function is

$$\psi(x) = \begin{cases} A\mathrm{e}^{ikx} + B\mathrm{e}^{-ikx} & x < -\frac{a}{2} \\ F\mathrm{e}^{ik_2x} + G\mathrm{e}^{-ik_2x} & -\frac{a}{2} \leq x \leq \frac{a}{2} \\ C\mathrm{e}^{ikx} & \frac{a}{2} < x \end{cases}$$

For now, we will remain agnostic about whether $E > V_0$ or $E < V_0$, since in the latter case, k_2 will just become imaginary so that the solutions in the middle region are real exponentials.

As recommended, we begin with the equations given by the continuity of ψ and its derivatives at the $\pm a/2$ boundaries. For continuity, we have

$$\begin{aligned} \psi_1(-a/2) &= \psi_2(-a/2) \\ A\mathrm{e}^{-ika/2} + B\mathrm{e}^{ika/2} &= F\mathrm{e}^{-ik_2a/2} + G\mathrm{e}^{ik_2a/2} \end{aligned} \qquad \begin{aligned} \psi_2(a/2) &= \psi_3(a/2) \\ F\mathrm{e}^{ik_2a/2} + G\mathrm{e}^{-ik_2a/2} &= C\mathrm{e}^{ika/2} \end{aligned}$$

For continuity of the first derivative, we have

$$\begin{aligned} \psi_1'(-a/2) &= \psi_2'(-a/2) \\ k(A\mathrm{e}^{-ika/2} - B\mathrm{e}^{ika/2}) &= k_2(F\mathrm{e}^{-ik_2a/2} - G\mathrm{e}^{ik_2a/2}) \end{aligned} \qquad \begin{aligned} \psi_2'(a/2) &= \psi_3'(a/2) \\ k_2(F\mathrm{e}^{ik_2a/2} - G\mathrm{e}^{-ik_2a/2}) &= kC\mathrm{e}^{ika/2} \end{aligned}$$

We now algebraically manipulate the above four equations until we arrive at the final answer. To begin, adding the left two boundary conditions gives

$$A\left(1+\frac{k}{k_2}\right)\mathrm{e}^{-ika/2}+B\left(1-\frac{k}{k_2}\right)\mathrm{e}^{ika/2}=2F\mathrm{e}^{-ik_2a/2}$$

while subtracting them gives

$$A\left(1-\frac{k}{k_2}\right)\mathrm{e}^{-ika/2}+B\left(1+\frac{k}{k_2}\right)\mathrm{e}^{ika/2}=2G\mathrm{e}^{ik_2a/2}$$

Additionally, adding the right two boundary conditions gives

$$C\left(1+\frac{k}{k_2}\right)\mathrm{e}^{ika/2}=2F\mathrm{e}^{ik_2a/2}$$

while subtracting them gives

$$C\left(1-\frac{k}{k_2}\right)\mathrm{e}^{ika/2}=2G\mathrm{e}^{-ik_2a/2}$$

It follows by consecutive applications of the transitivity property that

$$A\left(1+\frac{k}{k_2}\right)\mathrm{e}^{-ika/2}+B\left(1-\frac{k}{k_2}\right)\mathrm{e}^{ika/2}=C\left(1+\frac{k}{k_2}\right)\mathrm{e}^{ika/2}\mathrm{e}^{-ik_2a}$$

and

$$A\left(1-\frac{k}{k_2}\right)\mathrm{e}^{-ika/2}+B\left(1+\frac{k}{k_2}\right)\mathrm{e}^{ika/2}=C\left(1-\frac{k}{k_2}\right)\mathrm{e}^{ika/2}\mathrm{e}^{ik_2a}$$

Now divide through both of the above equations by the first term to yield

$$\begin{aligned}1+\underbrace{\left(\frac{B}{A}\right)}_{r}\underbrace{\left(\frac{1-k/k_2}{1+k/k_2}\right)}_{\alpha}\mathrm{e}^{ika}&=\underbrace{\left(\frac{C}{A}\right)}_{t}\mathrm{e}^{i(k-k_2)a}\\ 1+\underbrace{\left(\frac{B}{A}\right)}_{r}\underbrace{\left(\frac{1+k/k_2}{1-k/k_2}\right)}_{\alpha^{-1}}\mathrm{e}^{ika}&=\underbrace{\left(\frac{C}{A}\right)}_{t}\mathrm{e}^{i(k+k_2)a}\end{aligned}$$

Making the suggested substitutions for convenience, we obtain

$$1+r\alpha\mathrm{e}^{ika}=t\mathrm{e}^{i(k-k_2)a}\qquad\qquad 1+r\alpha^{-1}\mathrm{e}^{ika}=t\mathrm{e}^{i(k+k_2)a}$$

This system of two equations is linear in r and t and hence can easily be solved for these variables by formula. In particular, it is a fact of algebra that the solution to $1+xA=yB$ and $1+xC=yD$ is $x=(D-B)/(BC-AD)$ and $y=(C-A)/(BC-AD)$.[2] Thus,

$$\begin{aligned}r&=\frac{\mathrm{e}^{i(k+k_2)a}-\mathrm{e}^{i(k-k_2)a}}{[\mathrm{e}^{i(k-k_2)a}][\alpha^{-1}\mathrm{e}^{ika}]-[\alpha\mathrm{e}^{ika}][\mathrm{e}^{i(k+k_2)a}]}\\&=\frac{\mathrm{e}^{ika}\mathrm{e}^{ik_2a}-\mathrm{e}^{ika}\mathrm{e}^{-ik_2a}}{\alpha^{-1}\mathrm{e}^{ika}\mathrm{e}^{-ik_2a}\mathrm{e}^{ika}-\alpha\mathrm{e}^{ika}\mathrm{e}^{ika}\mathrm{e}^{ik_2a}}\\&=\frac{\mathrm{e}^{ik_2a}-\mathrm{e}^{-ik_2a}}{(\alpha^{-1}\mathrm{e}^{-ik_2a}-\alpha\mathrm{e}^{ik_2a})\mathrm{e}^{ika}}\\&=\frac{2i\sin(k_2a)}{(\alpha^{-1}\mathrm{e}^{-ik_2a}-\alpha\mathrm{e}^{ik_2a})\mathrm{e}^{ika}}\end{aligned}\qquad\begin{aligned}t&=\frac{\alpha^{-1}\mathrm{e}^{ika}-\alpha\mathrm{e}^{ika}}{[\mathrm{e}^{i(k-k_2)a}][\alpha^{-1}\mathrm{e}^{ika}]-[\alpha\mathrm{e}^{ika}][\mathrm{e}^{i(k+k_2)a}]}\\&=\frac{\alpha^{-1}\mathrm{e}^{ika}-\alpha\mathrm{e}^{ika}}{\alpha^{-1}\mathrm{e}^{ika}\mathrm{e}^{-ik_2a}\mathrm{e}^{ika}-\alpha\mathrm{e}^{ika}\mathrm{e}^{ika}\mathrm{e}^{ik_2a}}\\&=\frac{\alpha^{-1}-\alpha}{(\alpha^{-1}\mathrm{e}^{-ik_2a}-\alpha\mathrm{e}^{ik_2a})\mathrm{e}^{ika}}\\&=\frac{1-\alpha^2}{(\mathrm{e}^{-ik_2a}-\alpha^2\mathrm{e}^{ik_2a})\mathrm{e}^{ika}}\end{aligned}$$

[2]This fact can be readily verified by direct substitution. It can be derived via elimination of the original equations.

Thus, we may finally obtain the reflection and transmission coefficients[3] via

$$\begin{aligned}
|r|^2 &= r^* \cdot r \\
&= \frac{-2i\sin(k_2a)}{(\alpha^{-1}e^{ik_2a} - \alpha e^{-ik_2a})e^{-ika}} \cdot \frac{2i\sin(k_2a)}{(\alpha^{-1}e^{-ik_2a} - \alpha e^{ik_2a})e^{ika}} \\
&= \frac{4\sin^2(k_2a)}{(\alpha^{-1}e^{ik_2a} - \alpha e^{-ik_2a}) \cdot (\alpha^{-1}e^{-ik_2a} - \alpha e^{ik_2a})} \\
&= \frac{4\sin^2(k_2a)}{\alpha^{-2} - e^{2ik_2a} - e^{-2ik_2a} + \alpha^2} \\
&= \frac{4\alpha^2\sin^2(k_2a)}{1 + \alpha^4 - \alpha^2(e^{2ik_2a} + e^{-2ik_2a})} \\
\Aboxed{|B/A|^2 &= \frac{4\alpha^2\sin^2(k_2a)}{1 + \alpha^4 - 2\alpha^2\cos(2k_2a)}}
\end{aligned}$$

and

$$\begin{aligned}
|t|^2 &= t^* \cdot t \\
&= \frac{1-\alpha^2}{(e^{ik_2a} - \alpha^2 e^{-ik_2a})e^{-ika}} \cdot \frac{1-\alpha^2}{(e^{-ik_2a} - \alpha^2 e^{ik_2a})e^{ika}} \\
&= \frac{(1-\alpha^2)^2}{(e^{ik_2a} - \alpha^2 e^{-ik_2a}) \cdot (e^{-ik_2a} - \alpha^2 e^{ik_2a})} \\
&= \frac{(1-\alpha^2)^2}{1 - \alpha^2 e^{2ik_2a} - \alpha^2 e^{-2ik_2a} + \alpha^4} \\
&= \frac{(1-\alpha^2)^2}{1 + \alpha^4 - \alpha^2(e^{2ik_2a} + e^{-2ik_2a})} \\
\Aboxed{|C/A|^2 &= \frac{(1-\alpha^2)^2}{1 + \alpha^4 - 2\alpha^2\cos(2k_2a)}}
\end{aligned}$$

At this point, we will cease our agnosticism regarding the parity of $E - V_0$. The answers above correspond to the case that $E > V_0$. In the case that $E < V_0$, we fortunately need only make minor adjustments to the above. In particular, we define the real value $\kappa := \sqrt{2m(V_0 - E)}/\hbar$ so that we may write $k_2 = i\kappa$ and use the imaginary hyperbolic sine and cosine functions from Q2b to yield

$$\begin{aligned}
|B/A|^2 &= \frac{4\alpha^2[\sin(i\kappa a)]^2}{1 + \alpha^4 - 2\alpha^2\cos(i2\kappa a)} \\
&= \frac{4\alpha^2[i\sinh(\kappa a)]^2}{1 + \alpha^4 - 2\alpha^2\cosh(2\kappa a)} \\
\Aboxed{|B/A|^2 &= \frac{-4\alpha^2\sinh^2(\kappa a)}{1 + \alpha^4 - 2\alpha^2\cosh(2\kappa a)}}
\end{aligned}$$

$$\begin{aligned}
|C/A|^2 &= \frac{(1-\alpha^2)^2}{1 + \alpha^4 - 2\alpha^2\cos(i2\kappa a)} \\
\Aboxed{|C/A|^2 &= \frac{(1-\alpha^2)^2}{1 + \alpha^4 - 2\alpha^2\cosh(2\kappa a)}}
\end{aligned}$$

Lastly, we consider the case where $V_0 \to \infty$. In this case, V_0 will eventually exceed any value of E, so we will work with the second pair of equations defining the reflection and transmission coefficients. To begin, observe that by definition, $\kappa \propto V_0^{1/2}$. Thus, as $V_0 \to \infty$, $\kappa \to \infty$ and, in particular,

$$\alpha = \frac{1 - k/i\kappa}{1 + k/i\kappa} = \frac{i - k/\kappa}{i + k/\kappa} \to \frac{i - k/\infty}{i + k/\infty} = \frac{i}{i} = i \cdot (-i) = 1$$

Thus, by the form of the numerator of $|C/A|^2$, $\boxed{|C/A|^2 \to 0.}$ But this must imply that $\boxed{|B/A|^2 \to 1.}$ That is, there is no tunneling and the particle is completely reflected. □

[3] Note that a good sanity check for the following answers is that they sum to 1.

3 The Harmonic Oscillator

1/26: **1.** Harmonic oscillator in Earth's gravity.

In class, we solved the Harmonic Oscillator Problem, which has the potential

$$V(x) = \frac{m\omega^2 x^2}{2} \tag{3.1}$$

with $\omega = \sqrt{k/m}$ being the classical frequency. Now assume that x is a vertical direction and that we place the harmonic oscillator close to the Earth's surface. Now, if x grows upwards, the potential will be

$$V(x) = \frac{m\omega^2 x^2}{2} + mgx + C \tag{3.2}$$

with $g = 9.8\,\mathrm{m/s^2}$ and C an arbitrary (and irrelevant) constant.

a) First, think about the classical problem. The equilibrium point is no longer at $x = 0$, but a displaced point where the tension and gravity forces are equilibrated. Find that point and rewrite the potential in terms of a new variable representing departures from the equilibrium point. What would be the motion of a classical particle under the potential given in Eq. 3.2?

Answer. The equilibrium point x_{eq} will correspond to a minimum of V. Thus, we may solve

$$V'(x_{\text{eq}}) = 0$$

for x_{eq}. Doing this, we obtain

$$\begin{aligned}
0 &= \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{m\omega^2 x^2}{2} + mgx + C\right)\bigg|_{x_{\text{eq}}} \\
&= m\omega^2 x_{\text{eq}} + mg \\
&\boxed{x_{\text{eq}} = -\frac{g}{\omega^2}}
\end{aligned}$$

Let

$$u := x - x_{\text{eq}}$$

Then $x = u + x_{\text{eq}}$, so

$$\begin{aligned}
V(u) &= \frac{m\omega^2 (u + x_{\text{eq}})^2}{2} + mg(u + x_{\text{eq}}) + C \\
&= \frac{m\omega^2 u^2}{2} + m\omega^2 x_{\text{eq}} u + mgu + \frac{m\omega^2 x_{\text{eq}}^2}{2} + mgx_{\text{eq}} + C \\
V(u) &= \frac{m\omega^2 u^2}{2} + m\omega^2\left(-\frac{g}{\omega^2}\right) u + mgu + C \\
&\boxed{V(u) = \frac{m\omega^2 u^2}{2} + C}
\end{aligned}$$

Note that we combine all constants from the second to the third line above, which we may do because only relative — not absolute — values of the potential matter.

This result reveals that the motion of a classical particle under the potential given in Eq. 3.2 is $\boxed{\text{simple harmonic motion about } x_{\text{eq}}.}$ □

b) Now think about the quantum problem. Without gravity, the energy eigenvalues are given by $E_n^{\text{HO}} = \hbar\omega(n+1/2)$ and the corresponding wave functions ψ_n^{HO} can be written in terms of odd and even Hermite polynomials and a Gaussian function of x. (Here, HO means "harmonic oscillator.") Using these results, derive the new energy eigenvalues E_n and eigenfunctions ψ_n in the presence of gravity, Eq. 3.2. *Hint*: Can you make a similar redefinition of the coordinates as you did in the classical case?

Answer. To derive E_n, ψ_n, we must solve the following ODE.

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi_n(x) + \left[\frac{m\omega^2x^2}{2} + mgx + C\right]\psi_n(x) = E_n\psi_n(x)$$

Define u as in part (a). Fold C into the energy to get rid of it, and substitute $\psi_n(u)$ and $x = u + x_{\text{eq}}$ into the above equation.

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{\mathrm{d}}{\mathrm{d}x}\psi_n(u)\right] + \frac{m\omega^2u^2}{2}\psi_n(u) &= E_n\psi_n(u)\\
-\frac{\hbar^2}{2m}\frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{\mathrm{d}}{\mathrm{d}u}\psi_n(u)\cdot\underbrace{\frac{\mathrm{d}u}{\mathrm{d}x}}_{1}\right] + \frac{m\omega^2u^2}{2}\psi_n(u) &= E_n\psi_n(u)\\
-\frac{\hbar^2}{2m}\frac{\mathrm{d}}{\mathrm{d}u}\left[\frac{\mathrm{d}}{\mathrm{d}u}\psi_n(u)\right]\cdot\underbrace{\frac{\mathrm{d}u}{\mathrm{d}x}}_{1} + \frac{m\omega^2u^2}{2}\psi_n(u) &= E_n\psi_n(u)\\
-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}u^2}\psi_n(u) + \frac{m\omega^2u^2}{2}\psi_n(u) &= E_n\psi_n(u)
\end{aligned}$$

We worked out the solutions to this equation already in class. They are

$$\psi_n(u) = \psi_n^{\text{HO}}(u) \qquad\qquad E_n - C = E_n^{\text{HO}}$$

It follows by returning the substitution that

$$\boxed{\psi_n(x) = \psi_n^{\text{HO}}(x - x_{\text{eq}})} \qquad\qquad \boxed{E_n = E_n^{\text{HO}} + C}$$

□

c) What would be the mean value of x and p in this system (for a given energy eigenstate, not a generic state)? What would be the mean value of x^2 and p^2 in the ground state of the system? *Hint*: Use properties of the wave functions under displacements from the equilibrium point, and write $x = x_{\text{eq}} + (x - x_{\text{eq}})$, where x_{eq} is the equilibrium point.

Answer. Piggybacking off of the results from class, we will have

$$\boxed{\langle\psi_n|\hat{x}|\psi_n\rangle = x_{\text{eq}}} \qquad\qquad \boxed{\langle\psi_n|\hat{p}|\psi_n\rangle = 0}$$

In the ground state of the system, we have (taking the hint) that

$$\begin{aligned}
\langle\psi_0|\hat{x}^2|\psi_0\rangle &= \int \psi_0^*(x)x^2\psi_0(x)\,\mathrm{d}x\\
&= \int [\psi_0^{\text{HO}}]^*(u)(x_{\text{eq}} + u)^2\psi_0^{\text{HO}}(u)\,\mathrm{d}u\\
&= x_{\text{eq}}^2\int [\psi_0^{\text{HO}}]^*(u)\psi_0^{\text{HO}}(u)\,\mathrm{d}u + 2x_{\text{eq}}\int [\psi_0^{\text{HO}}]^*(u)u\psi_0^{\text{HO}}(u)\,\mathrm{d}u\\
&\quad + \int [\psi_0^{\text{HO}}]^*(u)u^2\psi_0^{\text{HO}}(u)\,\mathrm{d}u
\end{aligned}$$

The leftmost integral above evaluates to 1. The middle integral above evaluates to zero because its integrand is an odd function (the product of an odd and even function). The right integral expands to

$$\int_{-\infty}^{\infty} u^2 \left(\frac{m\omega}{\hbar\pi}\right)^{1/2} \mathrm{e}^{-m\omega u^2/\hbar}\,\mathrm{d}u = \frac{\hbar}{2m\omega}$$

upon plugging in the harmonic oscillator's ground state wave function, and may be evaluated using computational software. Thus, altogether,

$$\boxed{\langle\psi_0|\hat{x}^2|\psi_0\rangle = x_{\mathrm{eq}}^2 + \frac{\hbar}{2m\omega}}$$

Similar explicit computations for the mean value of p^2 yield

$$\boxed{\langle\psi_0|\hat{p}^2|\psi_0\rangle = \frac{\hbar m\omega}{2}}$$

□

d) Think about the uncertainty principle. What is the value of $\sigma_x\sigma_p$ in the ground state of this system? Does it differ from the value we obtained in the absence of gravity?

Answer. We have that

$$\sigma_x^2 = \langle\psi_0|\hat{x}^2|\psi_0\rangle - (\langle\psi_0|\hat{x}|\psi_0\rangle)^2 = x_{\mathrm{eq}}^2 + \frac{\hbar}{2m\omega} - x_{\mathrm{eq}}^2 = \frac{\hbar}{2m\omega}$$

and

$$\sigma_p^2 = \langle\psi_0|\hat{p}^2|\psi_0\rangle - (\langle\psi_0|\hat{p}|\psi_0\rangle)^2 = \frac{\hbar m\omega}{2}$$

Therefore, the value of $\sigma_x\sigma_p$ in the ground state of this system is

$$\begin{aligned}\sigma_x^2\cdot\sigma_p^2 &= \frac{\hbar}{2m\omega}\cdot\frac{\hbar m\omega}{2}\\ &= \frac{\hbar^2}{4}\\ \boxed{\sigma_x\sigma_p = \frac{\hbar}{2}}\end{aligned}$$

This $\boxed{\text{does not differ}}$ from the value we obtained in the absence of gravity in class on 1/22. □

2. Bouncing harmonic oscillator.

Assume now that we add an infinite potential floor just at the equilibrium point, so that the particle can no longer go below it. Under this modification, the new potential is

$$V(x) = \begin{cases} \frac{m\omega^2x^2}{2} + mgx + C & x > x_{\mathrm{eq}} \\ \infty & x \leq x_{\mathrm{eq}} \end{cases} \tag{3.3}$$

where x_{eq} is the equilibrium point. Classically, every time the particle hits the floor, it will bounce back with the same modulus of the momentum, but in the upwards direction.

a) What is the mathematical description of $x(t)$ of the classical motion? *Hint*: Think about the oscillator without a floor and the symmetry regarding displacements in the positive and negative directions from the equilibrium point.

Answer. The motion will be identical for $x \geq x_{\text{eq}}$, but instead of continuing past x_{eq}, the particle will elastically reflect back. Mathematically, if motion in Q1a was described by

$$x(t) = A\sin(\omega t) + B\cos(\omega t) + x_{\text{eq}}$$

then motion now is described by

$$\boxed{x(t) = |A\sin(\omega t) + B\cos(\omega t)| + x_{\text{eq}}}$$

□

b) Now go back to the quantum mechanical problem. Similarly to the infinite square well that we solved last week, what should happen to the wave functions at $x = x_{\text{eq}}$ and why?

Answer. At and below $x = x_{\text{eq}}$, the potential goes to infinity, so just like in the infinite square well, the particle no longer has a probability of existing there so the wave function $\boxed{\text{must go to zero.}}$ □

c) Now look at the Schrödinger equation for positive values of the displacement with respect to the equilibrium point. Does it change from the one we had without the floor? Find the energy eigenvalues and the corresponding functions ψ_n to this problem. *Hint*: Observe that the boundary condition at $x = x_{\text{eq}}$ eliminates some solutions.

Answer. The Schrödinger equation for positive values of the displacement with respect to the equilibrium point $\boxed{\text{does not}}$ change from the one we had without the floor because the potential in that region has not changed.

Since the Schrödinger equation does not change, we can solve it as in Q1b. However, taking the hint, only the odd solutions will be allowed by the boundary condition. Additionally, allowable space has halved from $(-\infty, \infty)$ to $[x_{\text{eq}}, \infty)$, so we must renormalize the odd eigenstates. Fortunately, this is fairly straightforward since $|\psi_n|^2$ is even, so

$$\begin{aligned}
1 &= \int_{x_{\text{eq}}}^{\infty} |\psi_n(x - x_{\text{eq}})|^2 \,\mathrm{d}x \\
&= \frac{1}{2}\int_{-\infty}^{\infty} |\psi_n(x - x_{\text{eq}})|^2 \,\mathrm{d}x \\
&= \frac{1}{2}\int_{-\infty}^{\infty} |A\psi_n^{\text{HO}}(x - x_{\text{eq}})|^2 \,\mathrm{d}x \\
2 &= A^2 \\
A &= \sqrt{2}
\end{aligned}$$

Thus, the energy eigenvalues and corresponding functions are

$$\boxed{\psi_n(x) = \sqrt{2}\psi_n^{\text{HO}}(x - x_{\text{eq}}) \qquad E_n = E_n^{\text{HO}} + C \qquad n = 1, 3, 5, \dots}$$

□

d) What is the minimal energy solution once we add the floor to the system? Is it the same as the system without the floor? What is the corresponding eigenfunction of this solution?

Answer. The minimal energy is now that which corresponds to the new smallest eigenstate, i.e.,

$$\boxed{E_1 = \frac{3\hbar\omega}{2} + C}$$

This is $\boxed{\text{not}}$ the same as the system without the floor, which had minimal energy $\hbar\omega/2 + C$. The corresponding eigenfunction is $\boxed{\psi_1(x).}$ □

e) Find σ_x and σ_p for the minimum energy solution. Is $\sigma_x\sigma_p$ the same as in the system without the wall?

Answer. Per part (d), the minimum energy solution is the wave function

$$\begin{aligned}
\psi_1(x) &= \sqrt{2}\psi_1^{\text{HO}}(x - x_{\text{eq}}) \\
&= \sqrt{2}\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \frac{H_1(\xi)}{\sqrt{2^1 1!}} \mathrm{e}^{-\xi^2/2} \\
&= \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \left[(-1)^1 \mathrm{e}^{\xi^2} \cdot \frac{\mathrm{d}}{\mathrm{d}\xi}\left(\mathrm{e}^{-\xi^2}\right)\right] \mathrm{e}^{-\xi^2/2} \\
&= \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \left[-\mathrm{e}^{\xi^2} \cdot -2\xi \mathrm{e}^{-\xi^2}\right] \mathrm{e}^{-\xi^2/2} \\
&= 2\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \xi \mathrm{e}^{-\xi^2/2} \\
&= 2\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} u \left(\frac{m\omega}{\hbar}\right)^{1/2} \mathrm{e}^{-m\omega u^2/2\hbar} \\
&= \frac{2}{\pi^{1/4}}\left(\frac{m\omega}{\hbar}\right)^{3/4} (x - x_{\text{eq}}) \mathrm{e}^{-m\omega(x - x_{\text{eq}})^2/2\hbar}
\end{aligned}$$

From here, we can use computational software to learn that

$$\begin{aligned}
\langle\psi_1|\hat{x}|\psi_1\rangle &= \int_{x_{\text{eq}}}^{\infty} x\psi_1^2(x)\,\mathrm{d}x = \int_0^{\infty} (u + x_{\text{eq}})\psi_1^2(u + x_{\text{eq}})\,\mathrm{d}u = 2\sqrt{\frac{\hbar}{m\omega\pi}} + x_{\text{eq}} \\
\langle\psi_1|\hat{x}^2|\psi_1\rangle &= x_{\text{eq}}^2 + \frac{3\hbar}{2m\omega} + 4x_{\text{eq}}\sqrt{\frac{\hbar}{m\omega\pi}} \\
\langle\psi_1|\hat{p}|\psi_1\rangle &= 0 \\
\langle\psi_1|\hat{p}^2|\psi_1\rangle &= \frac{3\hbar m\omega}{2}
\end{aligned}$$

Thus,

$$\sigma_x^2 = \left(x_{\text{eq}}^2 + \frac{3\hbar}{2m\omega} + 4x_{\text{eq}}\sqrt{\frac{\hbar}{m\omega\pi}}\right) - \left(2\sqrt{\frac{\hbar}{m\omega\pi}} + x_{\text{eq}}\right)^2 = \frac{3\hbar}{2m\omega} - \frac{4\hbar}{m\omega\pi}$$

and

$$\sigma_p^2 = \frac{3\hbar m\omega}{2}$$

so

$$\sigma_x\sigma_p = \sqrt{\left(\frac{3\hbar}{2m\omega} - \frac{4\hbar}{m\omega\pi}\right)\left(\frac{3\hbar m\omega}{2}\right)} = \hbar\sqrt{\frac{9}{4} - \frac{6}{\pi}} \approx 0.58\hbar$$

Since $0.58\hbar \neq \hbar/2$ (the answer to Q1d), $\boxed{\text{no,}}$ $\sigma_x\sigma_p$ is not the same as in the system without the wall. □

3. For the harmonic oscillator, consider the ladder operators $a_\pm = (\mp ip + m\omega x)/\sqrt{2\hbar m\omega}$. Recall that $[a_-, a_+] = 1$, the Hamiltonian may be written as $\hat{H} = \hbar\omega(a_+a_- + 1/2)$, and the eigenfunctions describing the eigenstates of energy $E_n = \hbar\omega(n + 1/2)$ are related by $a_+\psi_n = \sqrt{n+1}\psi_{n+1}$ and $a_-\psi_n = \sqrt{n}\psi_{n-1}$.

a) Compute the mean value of x and p in the energy eigenstates described by ψ_n.

Answer. We have that

$$\begin{aligned}\langle\psi_n|\hat{\vec{x}}|\psi_n\rangle &= \sqrt{\frac{\hbar}{2m\omega}}\,[\,\langle\psi_n|a_+|\psi_n\rangle + \langle\psi_n|a_-|\psi_n\rangle]\\ &= \sqrt{\frac{\hbar}{2m\omega}}\Big[\sqrt{n+1}\,\underbrace{\langle\psi_n|\psi_{n+1}\rangle}_{0} + \sqrt{n}\,\underbrace{\langle\psi_n|\psi_{n-1}\rangle}_{0}\Big]\end{aligned}$$

$$\boxed{\langle\psi_n|\hat{\vec{x}}|\psi_n\rangle = 0}$$

and

$$\begin{aligned}\langle\psi_n|\hat{\vec{p}}|\psi_n\rangle &= i\sqrt{\frac{\hbar m\omega}{2}}\,[\,\langle\psi_n|a_+|\psi_n\rangle - \langle\psi_n|a_-|\psi_n\rangle]\\ &= i\sqrt{\frac{\hbar m\omega}{2}}\Big[\sqrt{n+1}\,\underbrace{\langle\psi_n|\psi_{n+1}\rangle}_{0} - \sqrt{n}\,\underbrace{\langle\psi_n|\psi_{n-1}\rangle}_{0}\Big]\end{aligned}$$

$$\boxed{\langle\psi_n|\hat{\vec{p}}|\psi_n\rangle = 0}$$

□

b) Compute the mean value of x^2 and p^2 in these states.

Answer. As derived in class,[4] we have that

$$\left\langle\psi_n\left|\frac{k\hat{x}^2}{2}\right|\psi_n\right\rangle = \frac{E_n}{2} \qquad\qquad \left\langle\psi_n\left|\frac{\hat{p}^2}{2m}\right|\psi_n\right\rangle = \frac{E_n}{2}$$

Therefore,

$$\langle\psi_n|\hat{x}^2|\psi_n\rangle = \frac{2}{k}\cdot\frac{E_n}{2} \qquad\qquad \langle\psi_n|\hat{p}^2|\psi_n\rangle = 2m\cdot\frac{E_n}{2}$$

$$\boxed{\langle\psi_n|\hat{x}^2|\psi_n\rangle = \frac{\hbar\omega}{k}\left(n+\frac{1}{2}\right)} \qquad\qquad \boxed{\langle\psi_n|\hat{p}^2|\psi_n\rangle = \hbar\omega m\left(n+\frac{1}{2}\right)}$$

□

c) What would the uncertainty principle tell me about $\sigma_x\sigma_p$?

Answer. Since[5]

$$\sigma_x^2 = \langle\psi_n|\hat{\vec{x}}^{\,2}|\psi_n\rangle - (\,\langle\psi_n|\hat{\vec{x}}|\psi_n\rangle)^2 \qquad\qquad \sigma_p^2 = \langle\psi_n|\hat{\vec{p}}^{\,2}|\psi_n\rangle - (\,\langle\psi_n|\hat{\vec{p}}|\psi_n\rangle)^2$$

we have that

$$\sigma_x^2\cdot\sigma_p^2 = \hbar^2\left(n+\frac{1}{2}\right)^2$$

$$\boxed{\sigma_x\sigma_p = \frac{\hbar}{2}(2n+1)}$$

□

d) Verify that the uncertainty principle is fulfilled for the energy eigenstates.

[4] For future reference, they would have liked me to show this derivation and I did lose points for just stating this result.

[5] There is an entirely different derivation of these facts in the solutions key; one that works directly from the formal commutator definition of the uncertainty principle. Pretty cool!

Answer. Per part (c), we have that

$$\sigma_x\sigma_p = \frac{\hbar}{2}(2n+1) \geq \frac{\hbar}{2}$$

for all $n \geq 0$, as desired. ☐

e) Write a formal expression for the mean value of the position and the momentum for the general solution $\psi(x,t)$. Work it out as much as you can, using the orthonormality of the wave functions ψ_n.

Hint: For instance, the mean value of the operators x^q and p^q can be obtained by computing

$$\langle x^q \rangle = \left(\frac{\hbar}{2m\omega}\right)^{q/2} \int \psi(x)^*(a_+ + a_-)^q \psi(x)\,\mathrm{d}x \tag{3.4}$$

and

$$\langle p^q \rangle = i^q \left(\frac{\hbar}{2m\omega}\right)^{q/2} \int \psi(x)^*(a_+ - a_-)^q \psi(x)\,\mathrm{d}x \tag{3.5}$$

Observe that due to orthonormality of the real functions ψ_n and the fact that $a_\pm$ are ladder operators, the only nonvanishing contributions are

$$\begin{aligned}
\int \psi_m(x) a_+^q \psi_n(x)\,\mathrm{d}x &\qquad \text{Non-vanishing for } m = n+q \\
\int \psi_m(x) a_-^q \psi_n(x)\,\mathrm{d}x &\qquad \text{Non-vanishing for } m = n-q \\
\int \psi_m(x) a_-^q a_+^r \psi_n(x)\,\mathrm{d}x &\qquad \text{Non-vanishing for } m = n+r-q \\
\int \psi_m(x) a_+^q a_-^r \psi_n(x)\,\mathrm{d}x &\qquad \text{Non-vanishing for } m = n-r+q
\end{aligned} \tag{3.6}$$

Two useful cases, as follows from the above, are $\langle \psi_n | a_+ a_- | \psi_n \rangle = n$ and $\langle \psi_n | a_- a_+ | \psi_n \rangle = n+1$.

Answer. See Lecture 4.2. ☐

4 Observables and Operators

2/3: **1.** Imagine a one-dimensional free particle ($V(x) = 0$) of mass m whose mean value of the position and momentum at time $t = 0$ are given by x_0 and p_0.

a) Demonstrate that the mean value of the momentum and its powers is time-independent, that is

$$\frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi|\hat{p}^n|\psi\rangle) = 0 \tag{4.1}$$

Hint: Use the fact that for time-independent operators, $\mathrm{d}\langle\psi|\hat{O}|\psi\rangle \Big/ \mathrm{d}t = (i/\hbar)\langle\psi|[\hat{H},\hat{O}]|\psi\rangle$.

Answer. To prove that the mean value of the momentum is time-independent, it will suffice to show that

$$[\hat{H},\hat{p}^n] = 0$$

for all $n \in \mathbb{N}$. To do so, we induct on n. For the base case $n = 1$, we have that

$$[\hat{H},\hat{p}] = \left[\frac{\hat{p}^2}{2m},\hat{p}\right] = \frac{1}{2m}(\hat{p}^3 - \hat{p}^3) = 0$$

Now suppose inductively that we have prove the claim for n, that is, we know that $[\hat{H},\hat{p}^n] = 0$; we now seek to prove the claim for $n+1$. Here, we have that

$$[\hat{H},\hat{p}^{n+1}] = \hat{p}\underbrace{[\hat{H},\hat{p}^n]}_{0} + \underbrace{[\hat{H},\hat{p}^n]}_{0}\hat{p} = 0$$

This closes the induction. □

b) Compute $\mathrm{d}\langle\psi|\hat{x}|\psi\rangle/\mathrm{d}t$, and show that

$$\langle\psi|\hat{x}|\psi\rangle(t) = \frac{p_0 t}{m} + x_0 \tag{4.2}$$

Answer. We have from Lecture 1.2 that

$$\frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi|\hat{x}|\psi\rangle) = \frac{\langle\psi|\hat{p}|\psi\rangle}{m}$$

Now part (a) tells us that $\langle\psi|\hat{p}|\psi\rangle$ is time-independent, which means that if $\langle\psi|\hat{p}|\psi\rangle = p_0$ at $t = 0$, then $\langle\psi|\hat{p}|\psi\rangle = p_0$ for all time t. Thus,

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi|\hat{x}|\psi\rangle) = \frac{p_0}{m}}$$

It follows by integrating that

$$\begin{aligned}
\int_0^t \frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi|\hat{x}|\psi\rangle)\,\mathrm{d}t &= \int_0^t \frac{p_0}{m}\,\mathrm{d}t' \\
\langle\psi|\hat{x}|\psi\rangle(t) - \langle\psi|\hat{x}|\psi\rangle(0) &= \frac{p_0}{m}t - \frac{p_0}{m}0 \\
\langle\psi|\hat{x}|\psi\rangle(t) - x_0 &= \frac{p_0 t}{m} \\
\langle\psi|\hat{x}|\psi\rangle(t) &= \frac{p_0 t}{m} + x_0
\end{aligned}$$

as desired. □

c) Show also that

$$\frac{\mathrm{d}}{\mathrm{d}t}\big(\langle\psi|\hat{x}^2|\psi\rangle\big) = \frac{2}{m}\langle\psi|\hat{p}\hat{x}|\psi\rangle + \frac{i\hbar}{m} \tag{4.3}$$

Hint: Use the fact that $[\hat{A}\hat{B},\hat{C}] = \hat{A}[\hat{B},\hat{C}] + [\hat{A},\hat{C}]\hat{B}$ and $[\hat{A},\hat{B}\hat{C}] = \hat{B}[\hat{A},\hat{C}] + [\hat{A},\hat{B}]\hat{C}$.

Answer. We have that

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\big(\langle\psi|\hat{x}^2|\psi\rangle\big) &= \frac{i}{\hbar}\langle\psi|[\hat{H},\hat{x}^2]|\psi\rangle \\
&= \frac{i}{2m\hbar}\langle\psi|[\hat{p}^2,\hat{x}^2]|\psi\rangle \\
&= \frac{i}{2m\hbar}\langle\psi|\hat{p}[\hat{p},\hat{x}^2] + [\hat{p},\hat{x}^2]\hat{p}|\psi\rangle \\
&= \frac{i}{2m\hbar}\langle\psi|\hat{p}(\hat{x}[\hat{p},\hat{x}] + [\hat{p},\hat{x}]\hat{x}) + (\hat{x}[\hat{p},\hat{x}] + [\hat{p},\hat{x}]\hat{x})\hat{p}|\psi\rangle \\
&= \frac{i}{2m\hbar}\big(\langle\psi|\hat{p}\hat{x}[\hat{p},\hat{x}]|\psi\rangle + \langle\psi|\hat{p}[\hat{p},\hat{x}]\hat{x}|\psi\rangle + \langle\psi|\hat{x}[\hat{p},\hat{x}]\hat{p}|\psi\rangle + \langle\psi|[\hat{p},\hat{x}]\hat{x}\hat{p}|\psi\rangle\big) \\
&= \frac{i}{2m\hbar}\big(\langle\psi|\hat{p}\hat{x}(-i\hbar)|\psi\rangle + \langle\psi|\hat{p}(-i\hbar)\hat{x}|\psi\rangle + \langle\psi|\hat{x}(-i\hbar)\hat{p}|\psi\rangle + \langle\psi|(-i\hbar)\hat{x}\hat{p}|\psi\rangle\big) \\
&= \frac{1}{2m}\big(\langle\psi|\hat{p}\hat{x}|\psi\rangle + \langle\psi|\hat{p}\hat{x}|\psi\rangle + \langle\psi|\hat{x}\hat{p}|\psi\rangle + \langle\psi|\hat{x}\hat{p}|\psi\rangle\big) \\
&= \frac{1}{2m}(2\langle\psi|\hat{p}\hat{x}|\psi\rangle + 2\langle\psi|\hat{p}\hat{x} + i\hbar|\psi\rangle) \\
&= \frac{1}{2m}(4\langle\psi|\hat{p}\hat{x}|\psi\rangle + 2i\hbar\langle\psi|\psi\rangle) \\
&= \frac{2}{m}\langle\psi|\hat{p}\hat{x}|\psi\rangle + \frac{i\hbar}{m}
\end{aligned}$$

as desired. $\square$

d) Compute, in terms of $\langle\psi|\hat{p}^2|\psi\rangle$ and $\langle\psi|\hat{p}|\psi\rangle$, the values of

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\big(\langle\psi|\hat{x}^2|\psi\rangle\big) \qquad \frac{\mathrm{d}^2}{\mathrm{d}t^2}\big[(\langle\psi|\hat{x}|\psi\rangle)^2\big] \tag{4.4}$$

Hint: Use the commutation of $\hat{p}\hat{x}$ with $\hat{H} = \hat{p}^2/2m$.

Answer. By part (c), we have that

$$\begin{aligned}
\frac{\mathrm{d}^2}{\mathrm{d}t^2}\big(\langle\psi|\hat{x}^2|\psi\rangle\big) &= \frac{2}{m}\frac{\mathrm{d}}{\mathrm{d}t}\big(\langle\psi|\hat{p}\hat{x}|\psi\rangle\big) \\
&= \frac{2i}{m\hbar}\langle\psi|[\hat{H},\hat{p}\hat{x}]|\psi\rangle \\
&= \frac{i}{m^2\hbar}\Big(\langle\psi|\hat{p}^2\underbrace{[\hat{p},\hat{x}]}_{-i\hbar}|\psi\rangle + \langle\psi|\hat{p}\underbrace{[\hat{p},\hat{p}]}_{0}\hat{x}|\psi\rangle + \langle\psi|\hat{p}\underbrace{[\hat{p},\hat{x}]}_{-i\hbar}\hat{p}|\psi\rangle + \langle\psi|\underbrace{[\hat{p},\hat{p}]}_{0}\hat{x}\hat{p}|\psi\rangle\Big)
\end{aligned}$$

$$\boxed{\frac{\mathrm{d}^2}{\mathrm{d}t^2}\big(\langle\psi|\hat{x}^2|\psi\rangle\big) = \frac{2}{m^2}\langle\psi|\hat{p}^2|\psi\rangle}$$

By part (b), we have that

$$\begin{aligned}
\frac{\mathrm{d}^2}{\mathrm{d}t^2}\left[(\langle\psi|\hat{x}|\psi\rangle)^2\right] &= \frac{\mathrm{d}}{\mathrm{d}t}[2\langle\psi|\hat{x}|\psi\rangle\cdot\frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi|\hat{x}|\psi\rangle)] \\
&= 2\frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi|\hat{x}|\psi\rangle)\cdot\frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi|\hat{x}|\psi\rangle) + 2\langle\psi|\hat{x}|\psi\rangle\cdot\frac{\mathrm{d}^2}{\mathrm{d}t^2}(\langle\psi|\hat{x}|\psi\rangle) \\
&= \frac{2p_0^2}{m^2} + 2x_0\cdot\underbrace{\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{p_0}{m}\right)}_{0}
\end{aligned}$$

$$\boxed{\frac{\mathrm{d}^2}{\mathrm{d}t^2}\left[(\langle\psi|\hat{x}|\psi\rangle)^2\right] = \frac{2}{m^2}(\langle\psi|\hat{p}|\psi\rangle)^2}$$

□

e) Show that the position and momentum fluctuations are related by

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\left(\sigma_x^2\right) = \frac{2\sigma_p^2}{m^2} \tag{4.5}$$

where $\sigma_{\hat{O}}^2 = \langle\psi|\hat{O}^2|\psi\rangle - (\langle\psi|\hat{O}|\psi\rangle)^2$, and that the solution to this equation at sufficiently large values of t is given by

$$\sigma_x \approx \frac{\sigma_p t}{m} \tag{4.6}$$

where σ_p is independent of time. Discuss the implications of this result. Can you understand this result intuitively in terms of the fact that the momentum is not well-defined, meaning that there is a probability of finding the particle at different momentum values at a given time?

Answer. By part (d), we have that

$$\begin{aligned}
\frac{\mathrm{d}^2}{\mathrm{d}t^2}\left(\sigma_x^2\right) &= \frac{\mathrm{d}^2}{\mathrm{d}t^2}\left(\langle\psi|\hat{x}^2|\psi\rangle\right) - \frac{\mathrm{d}^2}{\mathrm{d}t^2}\left[(\langle\psi|\hat{x}|\psi\rangle)^2\right] \\
&= \frac{2}{m^2}\left[\langle\psi|\hat{p}^2|\psi\rangle - (\langle\psi|\hat{p}|\psi\rangle)^2\right] \\
&= \frac{2\sigma_p^2}{m^2}
\end{aligned}$$

Since σ_p is constant with respect to time — as we may extrapolate from part (a) — the solution to this ODE may be found via integration to be

$$\begin{aligned}
\frac{\mathrm{d}^2}{\mathrm{d}t^2}\left(\sigma_x^2\right) &= \frac{2\sigma_p^2}{m^2} \\
\frac{\mathrm{d}}{\mathrm{d}t}\left(\sigma_x^2\right) &= \frac{2\sigma_p^2}{m^2}t + c \\
\sigma_x^2 &= \frac{\sigma_p^2}{m^2}t^2 + ct + d
\end{aligned}$$

where c, d are constants of integration. Moreover, when we make t sufficiently large, the $ct + d$ terms are negligible and

$$\begin{aligned}
\sigma_x^2 &\approx \frac{\sigma_p^2}{m^2}t^2 \\
\sigma_x &\approx \frac{\sigma_p}{m}t
\end{aligned}$$

as desired. Additionally, note that by requiring t be "sufficiently large," we are eliminating consideration of the case $t = 0$, in which we would have $\sigma_x = 0$ which cannot happen by the Heisenberg uncertainty principle.

We now discuss the implications of this result. In part (a), we proved that the $\langle\psi|\hat{p}^n|\psi\rangle$ are fixed for all time, which means in particular that

$$\sigma_p^2 = \langle\psi|\hat{p}^2|\psi\rangle - (\,\langle\psi|\hat{p}|\psi\rangle)^2$$

is fixed. Thus, Eq. 4.6 essentially implies that for sufficiently large time t, the uncertainty in the position of the free particle increases approximately linearly with time. We may visualize this as the particle "spreading out" as time passes, much like a wave function might expand after it collapses.

The fact that the momentum is not well-defined is the *reason* that the particle spreads out over time. Essentially, different "parts" of the particle will move with different momenta, so as the free particle "moves," some parts of it will move faster and some will move slower, causing it to spread out! This further justifies the linear relation, which in these terms essentially says that the greater the uncertainty in momenta, the greater the difference in speed of different parts of the particle, and the greater the spread in x as time goes on. □

2. The power of completeness. Imagine that I have a complete set $\{\psi_n\}$ of energy eigenstate functions and that any given wave function ψ can be expressed as a linear combination of these functions via

$$\psi(x) = \sum_{n=0}^{\infty} c_n\psi_n(x) \tag{4.7}$$

a) Demonstrate, using the fact that $\int \psi_m^*(x)\psi_n(x)\,\mathrm{d}x = \delta_{mn}$, that these functions fulfill a completeness relation, in the sense that

$$\delta(x_1 - x_2) = \sum_m \psi_m(x_1)\psi_m^*(x_2) \tag{4.8}$$

Hint: Demonstrate that if you integrate this sum multiplied by an arbitrary function $\psi(x_2)$, you obtain the same function at the point $\psi(x_1)$.

Answer. Let $\psi : \mathbb{R} \to \mathbb{C}$ be an arbitrary, smooth function in the variable x_2. To prove the equality in Eq. 4.8, it will suffice to show that

$$\int \delta(x_1 - x_2)\psi(x_2)\,\mathrm{d}x_2 = \int \sum_m \psi_m(x_1)\psi_m^*(x_2)\psi(x_2)\,\mathrm{d}x_2$$

Note that this integral and all following integrals are over all space, that is, $(-\infty, \infty)$. By the properties of the Dirac delta function, the left side of the above equality evaluates to

$$\int \delta(x_1 - x_2)\psi(x_2)\,\mathrm{d}x_2 = \psi(x_1)$$

The right side is a bit more complicated since it involves the expansion of ψ that we are allowed to do by Eq. 4.7. However, it evaluates directly all the same, as follows.

$$\begin{aligned}
\int \sum_m \psi_m(x_1)\psi_m^*(x_2)\psi(x_2)\,\mathrm{d}x_2 &= \int \sum_m \psi_m(x_1)\psi_m^*(x_2)\left(\sum_{n=0}^{\infty} c_n\psi_n(x_2)\right)\mathrm{d}x_2 \\
&= \sum_m \sum_{n=0}^{\infty} c_n\psi_m(x_1)\int \psi_m^*(x_2)\psi_n(x_2)\,\mathrm{d}x_2 \\
&= \sum_{n=0}^{\infty} c_n\psi_n(x_1) \\
&= \psi(x_1)
\end{aligned}$$

Therefore, by transitivity, we have the desired equality. □

b) Imagine that you want to calculate the mean value of some real function $h(x)$ of the operator $\hat{x} = x$ that can be expressed as a product of two real functions, i.e., $h(x) = f(x)g(x)$. For instance, $x^4 = x^2x^2$. Then to compute the mean value of $h(x)$ in a particular energy eigenstate described by ψ_n, one needs to compute

$$\langle\psi_n|h(x)|\psi_n\rangle = \int \psi_n^*(x)f(x)g(x)\psi_n(x)\,\mathrm{d}x = \iint \psi_n^*(x_1)f(x_1)\delta(x_1-x_2)g(x_2)\psi_n(x_2)\,\mathrm{d}x_1\,\mathrm{d}x_2 \tag{4.9}$$

Verify that this is true by performing the integral over one of two variables, x_1 or x_2.

Answer. Working backward from the RHS of Eq. 4.9, we have that

$$\begin{aligned}
\text{RHS} &= \iint \psi_n^*(x_1)f(x_1)\delta(x_1-x_2)g(x_2)\psi_n(x_2)\,\mathrm{d}x_1\,\mathrm{d}x_2 \\
&= \int \left[\int \psi_n^*(x_1)f(x_1)\delta(x_1-x_2)\,\mathrm{d}x_1\right] g(x_2)\psi_n(x_2)\,\mathrm{d}x_2 \\
&= \int \left[\psi_n^*(x_2)f(x_2)\right] g(x_2)\psi_n(x_2)\,\mathrm{d}x_2 \\
&= \int \psi_n^*(x)f(x)g(x)\psi_n(x)\,\mathrm{d}x \\
&= \int \psi_n^*(x)h(x)\psi_n(x)\,\mathrm{d}x \\
&= \langle\psi_n|h(x)|\psi_n\rangle
\end{aligned}$$

$\square$

c) Use this expression to obtain the mean value of $h(x)$ as a function of a sum of the products of the matrix elements $f_{mn}(x)$ and $g_{mn}(x)$, defined as

$$f_{mn} = \int \psi_m^*(x)f(x)\psi_n(x)\,\mathrm{d}x \qquad\qquad g_{mn} = \int \psi_m^*(x)g(x)\psi_n(x)\,\mathrm{d}x \tag{4.10}$$

Answer. By part (a) and Eq. 4.8, we have that

$$\begin{aligned}
\langle\psi_n|h(x)|\psi_n\rangle &= \iint \psi_n^*(x_1)f(x_1)\delta(x_1-x_2)g(x_2)\psi_n(x_2)\,\mathrm{d}x_1\,\mathrm{d}x_2 \\
&= \iint \psi_n^*(x_1)f(x_1)\left[\sum_m \psi_m(x_1)\psi_m^*(x_2)\right] g(x_2)\psi_n(x_2)\,\mathrm{d}x_1\,\mathrm{d}x_2 \\
&= \sum_m \iint \psi_n^*(x_1)f(x_1)\psi_m(x_1)\psi_m^*(x_2)g(x_2)\psi_n(x_2)\,\mathrm{d}x_1\,\mathrm{d}x_2 \\
&= \sum_m \int \left[\int \psi_n^*(x_1)f(x_1)\psi_m(x_1)\,\mathrm{d}x_1\right] \psi_m^*(x_2)g(x_2)\psi_n(x_2)\,\mathrm{d}x_2 \\
&= \sum_m \int f_{nm}\psi_m^*(x_2)g(x_2)\psi_n(x_2)\,\mathrm{d}x_2 \\
&= \sum_m f_{nm}\int \psi_m^*(x_2)g(x_2)\psi_n(x_2)\,\mathrm{d}x_2
\end{aligned}$$

$$\boxed{\langle\psi_n|h(x)|\psi_n\rangle = \sum_m f_{nm}g_{mn}}$$

$\square$

d) Apply the above to compute the mean value of $x^4 = x^2x^2$ for the harmonic oscillator in its energy eigenstate. *Hint*: Use the ladder operators.

Answer. By part (c), we have that

$$\langle\psi_n|x^4|\psi_n\rangle = \sum_m \langle n|x^2|m\rangle \; \langle m|x^2|n\rangle$$

The left term expands as follows.

$$\begin{aligned}
\langle n|x^2|m\rangle &= \frac{\hbar}{2m\omega}\langle n|(a_+ + a_-)^2|m\rangle \\
&= \frac{\hbar}{2m\omega}\left[\langle n|a_+^2|m\rangle + \langle n|a_-^2|m\rangle + 2\langle n|a_+a_-|m\rangle + \langle n|1|m\rangle\right] \\
&= \frac{\hbar}{2m\omega}\left[\sqrt{(m+1)(m+2)}\,\langle n|m+2\rangle + \sqrt{m(m-1)}\,\langle n|m-2\rangle + (2m+1)\langle n|m\rangle\right] \\
&= \frac{\hbar}{2m\omega}\left[\sqrt{(m+1)(m+2)}\delta_{n,m+2} + \sqrt{m(m-1)}\delta_{n,m-2} + (2m+1)\delta_{n,m}\right]
\end{aligned}$$

Analogously, the right term expands to

$$\langle m|x^2|n\rangle = \frac{\hbar}{2m\omega}\left[\sqrt{(n+1)(n+2)}\delta_{m,n+2} + \sqrt{n(n-1)}\delta_{m,n-2} + (2n+1)\delta_{m,n}\right]$$

Now since

$$(\delta_{n,m+2} + \delta_{n,m-2} + \delta_{n,m})(\delta_{m,n+2} + \delta_{m,n-2} + \delta_{m,n}) = \delta_{n,m+2}\delta_{m,n-2} + \delta_{n,m}\delta_{m,n} + \delta_{n,m-2}\delta_{m,n+2}$$

we have that

$$\begin{aligned}
\langle\psi_n|x^4|\psi_n\rangle &= \frac{\hbar^2}{4m^2\omega^2}\sum_m \left[\sqrt{(m+1)(m+2)}\delta_{n,m+2} + \sqrt{m(m-1)}\delta_{n,m-2} + (2m+1)\delta_{n,m}\right] \\
&\quad\cdot\left[\sqrt{(n+1)(n+2)}\delta_{m,n+2} + \sqrt{n(n-1)}\delta_{m,n-2} + (2n+1)\delta_{m,n}\right] \\
&= \frac{\hbar^2}{4m^2\omega^2}\sum_m \Big[\sqrt{(m+1)(m+2)}\sqrt{n(n-1)}\delta_{n,m+2}\delta_{m,n-2} \\
&\quad + (2m+1)(2n+1)\delta_{n,m}\delta_{m,n} + \sqrt{m(m-1)}\sqrt{(n+1)(n+2)}\delta_{n,m-2}\delta_{m,n+2}\Big]
\end{aligned}$$

When $m = n-2$, the first term will be nonzero. When $m = n$, the second term will be nonzero. And when $m = n+2$, the third term will be nonzero. Taken together, this means that

$$\begin{aligned}
\langle\psi_n|x^4|\psi_n\rangle &= \frac{\hbar^2}{4m^2\omega^2}\Big[\sqrt{(n-1)n}\sqrt{n(n-1)} \\
&\quad + (2n+1)(2n+1) + \sqrt{(n+2)(n+1)}\sqrt{(n+1)(n+2)}\Big] \\
&= \frac{\hbar^2}{4m^2\omega^2}\left[n(n-1) + (2n+1)^2 + (n+1)(n+2)\right]
\end{aligned}$$

$$\boxed{\langle\psi_n|x^4|\psi_n\rangle = \frac{\hbar^2}{4m^2\omega^2}(6n^2+6n+3)}$$

□

Comment: In Dirac notation, the above procedure is equivalent to adding an identity operator, in the sense that

$$\sum_m |m\rangle\langle m| = I \tag{4.11}$$

and

$$\langle n|\hat{O}_1\hat{O}_2|n\rangle = \langle n|\hat{O}_1 I\hat{O}_2|n\rangle = \sum_m \langle n|\hat{O}_1|m\rangle\;\langle m|\hat{O}_2|n\rangle = \sum_m O_{1,nm}O_{2,mn} \tag{4.12}$$

3. In class, and in PSet 3, we computed the time dependence of the mean value of $\hat{x}$ in a harmonic oscillator and showed that it had some resemblance with the classical case. Use your preferred computational code language and the form of the energy eigenstate solutions in terms of Hermite polynomials and Gaussian factors to compute the variation of the mean value of the position as a function of time for different coefficients c_n with

$$\Psi(x,t) = \sum_n c_n \psi_n(x) \mathrm{e}^{-iE_n t/\hbar} \tag{4.13}$$

Additionally, demonstrate numerically that — as expected — it always moves with a classical frequency ω such that $E_n = \hbar\omega(n + 1/2)$. Compute also the value of $|\psi(x,t)|^2$ and draw it for different times to show that its shape does not vary over a period of time and is also recovered after half a period but for the opposite values of x, i.e.,

$$|\psi(x, t + T/2)|^2 = |\psi(-x, t)|^2 \tag{4.14}$$

Hint: This is shown analytically in Wagner's notes.

Do this also for a coherent state where $c_{n+1}/c_n = 1/\sqrt{n+1}$. In order to perform this computation, define $\hbar = 1 = m = \omega$ and don't worry about the overall normalization. You may use for guidance the Mathematica code that is posted on Canvas and which does some of this.

5 Three Dimensional Mathematical Tools

2/17: **1.** Consider a three-dimensional box, such that the potential is given by

$$V(x,y,z) = V_1\theta(|x|-a) + V_2\theta(|y|-b) + V_3\theta(|z|-c) \tag{5.1}$$

where the function θ is such that

$$\theta(u) = \begin{cases} 1 & u \geq 0 \\ 0 & u < 0 \end{cases} \tag{5.2}$$

This means that the potential is zero inside the box that extends from $x=-a$ to $x=a$ in the x-direction, $y=-b$ to $y=b$ in the y-direction, and $z=-c$ to $z=c$ in the z-direction and increases in steps otherwise.

a) Analyze first the case wherein all of $V_1, V_2, V_3 \to \infty$. This is the infinite square well in three dimensions. What is the general solution for $\psi(x,y,z)$? *Hint*: Use the method of separation of variables and write $\psi(x,y,z) = X(x)Y(y)Z(z)$.

Answer. The Schrödinger equation for this case is

$$\begin{aligned} -\frac{\hbar^2}{2m}\vec{\nabla}^2\psi &= E\psi \\ -\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) &= E\psi \end{aligned}$$

along with the boundary conditions

$$\psi(\pm a,y,z) = 0 \qquad \psi(x,\pm b,z) = 0 \qquad \psi(x,y,\pm c) = 0$$

Taking the hint and writing $\psi = XYZ$, we can rearrange the above equation into the form

$$\frac{1}{X}\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}\right] + \frac{1}{Y}\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}\right] + \frac{1}{Z}\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2}\right] = E$$

Note that we switch from partial to total derivatives here because now each function is only a function of one variable (e.g., $X(x)$ depends only on x).

Moving on, since the sum of these three independent terms is constant, each term must be equal to a constant, too. Thus, we can split the above equation into the following three.

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = E_{n_1}X \qquad -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} = E_{n_1}Y \qquad -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} = E_{n_1}Z$$

As to the boundary conditions, the rewrite in the hint gives us, for example,

$$0 = \psi(\pm a,y,z) = X(\pm a)Y(y)Z(z)$$

Since Y,Z may both be nonzero for some y,z, the zero product property tells us that we must have

$$X(\pm a) = 0$$

Doing the same for the other two boundary conditions, we obtain the following three new boundary conditions.

$$X(\pm a) = 0 \qquad Y(\pm b) = 0 \qquad Z(\pm c) = 0$$

We will now solve the three independent boundary-value problems. Since they are all directly analogous, we will concentrate on the X-case and know that the other solutions may be observed from there via a change of variables.

To begin, it will be useful to define

$$u(x) := x + a \qquad\qquad L := 2a$$

Observe that under this definition, $\mathrm{d}u/\mathrm{d}x = 1$. Changing variables in the ODE, we get

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{\mathrm{d}}{\mathrm{d}x}[X(u(x))]\right] &= E_{n_1}X(u(x)) \\
-\frac{\hbar^2}{2m}\frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{\mathrm{d}}{\mathrm{d}u}[X(u)]\cdot\frac{\mathrm{d}u}{\mathrm{d}x}\right] &= E_{n_1}X(u) \\
-\frac{\hbar^2}{2m}\frac{\mathrm{d}}{\mathrm{d}u}\left[\frac{\mathrm{d}}{\mathrm{d}u}[X(u)]\cdot 1\right]\cdot\frac{\mathrm{d}u}{\mathrm{d}x} &= E_{n_1}X(u) \\
-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}u^2}[X(u)] &= E_{n_1}X(u)
\end{aligned}$$

Additionally, since $u(-a) = 0$ and $u(a) = 2a = L$, the relevant boundary condition with respect to u is

$$X(u = 0) = X(u = L) = 0$$

Altogether, the first ODE and boundary condition in terms of u become

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}u^2} = E_{n_1}X \qquad\qquad X(0) = X(L) = 0$$

which is entirely analogous to the infinite square well ODE we solved in class on 1/17. Thus, the solutions are

$$X_{n_1}(u) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi n_1 u}{L}\right)$$

Returning the u-substitution to obtain the solutions in terms of x, we get

$$X_{n_1}(x) = \sqrt{\frac{1}{a}}\sin\left[\frac{\pi n_1(x+a)}{2a}\right]$$

As mentioned above, we can do something analogous in the other two directions. Therefore, the general solution is

$$\boxed{\psi_{n_1n_2n_3}(x,y,z) = \sqrt{\frac{1}{abc}}\sin\left[\frac{\pi n_1(x+a)}{2a}\right]\sin\left[\frac{\pi n_2(y+b)}{2b}\right]\sin\left[\frac{\pi n_3(z+c)}{2c}\right]}$$

□

b) Give an expression for the total energy of the system in terms of the energies associated with the propagation in the three space directions.

Answer. Return to the step in part (a) at which we had finally obtained an ODE fully analogous to the one solved in class on 1/17. We did not state it in part (a) because it was not relevant, but just as we obtained $X_{n_1}(u)$, our work in class on 1/17 gives us the corresponding energy expression

$$E_{n_1} = \frac{\hbar^2\pi^2n_1^2}{2mL^2} = \frac{\hbar^2\pi^2n_1^2}{8ma^2}$$

Analogous results exist in the other two directions. Additionally, as in class on 2/12, setting all of our ODEs equal to constants in the separation of variables step *also* gives us the equation

$$E = E_{n_1} + E_{n_2} + E_{n_3}$$

Thus, the expression for the total energy of the system in terms of the energies associated with the propagation in the three space directions is

$$\boxed{E_{n_1n_2n_3} = \frac{\hbar^2\pi^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)}$$

□

c) What happens when one of the three V_i's becomes finite, and we are in a bounded state such that $E < V_i$? What would be the possible energies in such a case?

Answer. Suppose WLOG that V_1 becomes finite. The Schrödinger equation for this case is

$$
\begin{aligned}
-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi + V(x,y,z)\psi &= E\psi \\
-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V_1\theta(|x|-a)\psi &= E\psi
\end{aligned}
$$

along with the boundary conditions

$$
\psi(x,\pm b,c) = 0 \qquad\qquad \psi(x,y,\pm c) = 0
$$

Writing $\psi = XYZ$, we can rearrange the above equation into the form

$$
\frac{1}{X}\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} + V_1\theta(|x|-a)X\right] + \frac{1}{Y}\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}\right] + \frac{1}{Z}\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2}\right] = E
$$

Separating variables, we obtain two ODEs familiar from part (a) and one new one. We will focus on the new one from here on out. If we let Region I span $(-\infty,-a)$, Region II span $[-a,a]$, and Region III span (a,∞), then this new ODE can be written as

$$
\begin{aligned}
-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X_{\mathrm{I}}}{\mathrm{d}x^2} + V_1X_{\mathrm{I}} &= E_{n_1}X_{\mathrm{I}} \\
-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X_{\mathrm{II}}}{\mathrm{d}x^2} &= E_{n_1}X_{\mathrm{II}} \\
-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X_{\mathrm{III}}}{\mathrm{d}x^2} + V_1X_{\mathrm{I}} &= E_{n_1}X_{\mathrm{III}}
\end{aligned}
$$

along with the four boundary conditions

$$
\begin{aligned}
X_{\mathrm{I}}(-a) &= X_{\mathrm{II}}(-a) & \qquad X_{\mathrm{II}}(a) &= X_{\mathrm{III}}(a) \\
X_{\mathrm{I}}'(-a) &= X_{\mathrm{II}}'(-a) & \qquad X_{\mathrm{II}}'(a) &= X_{\mathrm{III}}'(a)
\end{aligned}
$$

Define

$$
k_{\mathrm{I}} = \frac{\sqrt{2m(E_{n_1}-V_1)}}{\hbar} \qquad\qquad k_{\mathrm{II}} = \frac{\sqrt{2mE_{n_1}}}{\hbar}
$$

Given that $E_{n_1} < V_1$, then per PSet 2, Q2b, the solutions will be

$$
\begin{aligned}
X_{\mathrm{I}}(x) &= A\mathrm{e}^{\kappa_{\mathrm{I}}x} + B\mathrm{e}^{-\kappa_{\mathrm{I}}x} \\
X_{\mathrm{II}}(x) &= S_{\mathrm{II}}\sin(k_{\mathrm{II}}x) + C_{\mathrm{II}}\cos(k_{\mathrm{II}}x) \\
X_{\mathrm{III}}(x) &= F\mathrm{e}^{\kappa_{\mathrm{I}}x} + G\mathrm{e}^{-\kappa_{\mathrm{I}}x}
\end{aligned}
$$

where $i\kappa_{\mathrm{I}} = k_{\mathrm{I}}$. Now just like in PSet 2, Q2c, some of the exponential terms diverge. In particular, $B\mathrm{e}^{-\kappa_{\mathrm{I}}x}$ diverges as $x \to -\infty$ and $F\mathrm{e}^{\kappa_{\mathrm{I}}x}$ diverges as $x \to \infty$. Thus, to keep the solution from blowing up, we must set

$$
B = F = 0
$$

to get

$$
\begin{aligned}
X_{\mathrm{I}}(x) &= A\mathrm{e}^{\kappa_{\mathrm{I}}x} \\
X_{\mathrm{II}}(x) &= S_{\mathrm{II}}\sin(k_{\mathrm{II}}x) + C_{\mathrm{II}}\cos(k_{\mathrm{II}}x) \\
X_{\mathrm{III}}(x) &= G\mathrm{e}^{-\kappa_{\mathrm{I}}x}
\end{aligned}
$$

Before we apply the boundary conditions, there is one more thing we can do to simplify the above solutions. Let $X_{n_1}(x)$ be a full, piecewise eigenstate of the relevant Schrödinger equation. Then since this potential is symmetric about the origin — that is, $V(x) = V(-x)$ — $X_{n_1}(-x)$ will also be an eigenstate of the relevant Schrödinger equation:

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 X_{\mathrm{I}}(-x)}{\mathrm{d}x^2} + V(x)X_{\mathrm{I}}(-x) &= -\frac{\hbar^2}{2m}(-1)^2\frac{\mathrm{d}^2 X_{\mathrm{I}}(-x)}{\mathrm{d}(-x)^2} + V(-x)X_{\mathrm{I}}(-x) \\
&= -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 X_{\mathrm{I}}(-x)}{\mathrm{d}(-x)^2} + V(-x)X_{\mathrm{I}}(-x) \\
&= E_{n_1}X_{\mathrm{I}}(-x)
\end{aligned}$$

It follows by the linearity of the Schrödinger equation that $X_{n_1}(x) + X_{n_1}(-x)$ and $X_{n_1}(x) - X_{n_1}(-x)$ are also eigenstates of with energy E_{n_1}. Essentially, this means that we can always choose our eigenstates to be even or odd functions of x. Going back to our solutions $X_{\mathrm{I}}, X_{\mathrm{II}}, X_{\mathrm{III}}$, this means that we need not consider X_{II} in full generality but can rather divide the solutions up into those with $S_{\mathrm{II}} = 0$ (even) and those with $C_{\mathrm{II}} = 0$ (odd). For the even solutions, the boundary conditions tell us that

$$\begin{aligned}
A\mathrm{e}^{-\kappa_{\mathrm{I}}a} &= C_{\mathrm{II}}\cos(k_{\mathrm{II}}a) \\
\kappa_{\mathrm{I}}A\mathrm{e}^{-\kappa_{\mathrm{I}}a} &= k_{\mathrm{II}}C_{\mathrm{II}}\sin(k_{\mathrm{II}}a) \\
C_{\mathrm{II}}\cos(k_{\mathrm{II}}a) &= G\mathrm{e}^{-\kappa_{\mathrm{I}}a} \\
-k_{\mathrm{II}}C_{\mathrm{II}}\sin(k_{\mathrm{II}}a) &= -\kappa_{\mathrm{I}}G\mathrm{e}^{-\kappa_{\mathrm{I}}a}
\end{aligned}$$

From here, we may obtain the important result that

$$\kappa_{\mathrm{I}} = k_{\mathrm{II}}\tan(k_{\mathrm{II}}a)$$

$$\boxed{\frac{\sqrt{2m(V_1 - E_{n_1})}}{\hbar} = \frac{\sqrt{2mE_{n_1}}}{\hbar}\tan\left(\frac{\sqrt{2mE_{n_1}}}{\hbar}a\right)}$$

Similarly, for the odd solutions, we may obtain that

$$\boxed{\frac{\sqrt{2m(V_1 - E_{n_1})}}{\hbar} = -\frac{\sqrt{2mE_{n_1}}}{\hbar}\cot\left(\frac{\sqrt{2mE_{n_1}}}{\hbar}a\right)}$$

Energies may be obtained by solving either of these equations. This energy may then be added onto the other two as in part (b). □

d) What happens when the three V_i's become finite?

Answer. We will obtain three energies of the form in part (c), all of which may be added together as in part (b). □

2. In the presence of a central force, the potential depends only on the radial distance and not on the direction, i.e.,

$$V(\vec{r}) = V(\sqrt{x^2 + y^2 + z^2}) \tag{5.3}$$

a) Show that in such a potential, the momentum is not conserved (that is, its mean value is not independent of time), but the angular momentum $\vec{L} = \vec{r} \times \vec{p}$ is conserved. *Hint*: Use commutation relations with $\hat{H}$. Test this for each component of $\vec{L}$ separately.

Answer. Taking the hint, recall from the 1/29 lecture that

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{p}_y\hat{z}$$

Additionally, recall that

$$\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + \hat{V}(r)$$

Thus, we have that

$$\begin{aligned}
[\hat{H}, \hat{L}_x] &= \left[\frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + \hat{V}(r), \hat{y}\hat{p}_z - \hat{z}\hat{p}_y\right] \\
&= \left[\frac{\hat{p}_x^2}{2m}, \hat{y}\hat{p}_z\right] + \left[\frac{\hat{p}_y^2}{2m}, \hat{y}\hat{p}_z\right] + \left[\frac{\hat{p}_z^2}{2m}, \hat{y}\hat{p}_z\right] \\
&\quad + \left[\frac{\hat{p}_x^2}{2m}, -\hat{z}\hat{p}_y\right] + \left[\frac{\hat{p}_y^2}{2m}, -\hat{z}\hat{p}_y\right] + \left[\frac{\hat{p}_z^2}{2m}, -\hat{z}\hat{p}_y\right] \\
&\quad + [\hat{V}(r), \hat{y}\hat{p}_z] + [\hat{V}(r), -\hat{z}\hat{p}_y] \\
&= \left[\frac{\hat{p}_y^2}{2m}, \hat{y}\hat{p}_z\right] + \left[\frac{\hat{p}_z^2}{2m}, -\hat{z}\hat{p}_y\right] + i\hbar\left(\hat{y}\frac{\partial V}{\partial z} - \hat{z}\frac{\partial V}{\partial y}\right) \\
&= -\frac{i\hbar\hat{p}_y\hat{p}_z}{m} + \frac{i\hbar\hat{p}_y\hat{p}_z}{m} + i\hbar\frac{\partial V}{\partial r}\left(y\frac{\partial r}{\partial z} - z\frac{\partial r}{\partial y}\right) \\
&= 0
\end{aligned}$$

Now let's investigate some of the above substitutions a bit more closely. From line 1 to line 2, we split the commutator into $4 \cdot 2 = 8$ terms using its bilinearity. From line 2 to line 3, we eliminated all commutators that go to zero among the first six, and evaluated the last two commutators using a combination of Rule 3 and properties mentioned at the beginning of the lecture.

Notice that the only two of the first six commutators that did *not* go to zero were those for which the variable in the squared momentum operator matched the position operator, i.e., in

$$\left[\frac{\hat{p}_y^2}{2m}, \hat{y}\hat{p}_z\right]$$

we may observe that $\hat{p}_y^2$ and $\hat{y}$ both concern y. Example evaluation:

$$\begin{aligned}
\left[\frac{\hat{p}_x^2}{2m}, \hat{y}\hat{p}_z\right] &= \frac{1}{2m}[\hat{p}_x^2, \hat{y}\hat{p}_z] \\
&= \frac{1}{2m}(\hat{p}_x[\hat{p}_x, \hat{y}\hat{p}_z] + [\hat{p}_x, \hat{y}\hat{p}_z]\hat{p}_x) \\
&= \frac{1}{2m}(\hat{p}_x(\hat{y}\underbrace{[\hat{p}_x, \hat{p}_z]}_{0} + \underbrace{[\hat{p}_x, \hat{y}]}_{0}\hat{p}_z) + (\hat{y}\underbrace{[\hat{p}_x, \hat{p}_z]}_{0} + \underbrace{[\hat{p}_x, \hat{y}]}_{0}\hat{p}_z)\hat{p}_x) \\
&= 0
\end{aligned}$$

Example evaluation:

$$\begin{aligned}
\left[\frac{\hat{p}_y^2}{2m}, \hat{y}\hat{p}_z\right] &= \frac{1}{2m}[\hat{p}_y^2, \hat{y}\hat{p}_z] \\
&= \frac{1}{2m}(\hat{p}_y[\hat{p}_y, \hat{y}\hat{p}_z] + [\hat{p}_y, \hat{y}\hat{p}_z]\hat{p}_y) \\
&= \frac{1}{2m}(\hat{p}_y(\hat{y}\underbrace{[\hat{p}_y, \hat{p}_z]}_{0} + \underbrace{[\hat{p}_y, \hat{y}]}_{-i\hbar}\hat{p}_z) + (\hat{y}\underbrace{[\hat{p}_y, \hat{p}_z]}_{0} + \underbrace{[\hat{p}_y, \hat{y}]}_{-i\hbar}\hat{p}_z)\hat{p}_y) \\
&= \frac{1}{2m}(\hat{p}_y(-i\hbar\hat{p}_z) + (-i\hbar\hat{p}_z)\hat{p}_y)
\end{aligned}$$

$$
\begin{aligned}
&= -\frac{i\hbar}{2m}(\hat{p}_y\hat{p}_z + \hat{p}_z\hat{p}_y) \\
&= -\frac{i\hbar}{2m}(\hat{p}_y\hat{p}_z + \hat{p}_y\hat{p}_z) \\
&= -\frac{i\hbar\hat{p}_y\hat{p}_z}{m}
\end{aligned}
$$

Note that $\hat{p}_z\hat{p}_y = \hat{p}_y\hat{p}_z$ because $[\hat{p}_y, \hat{p}_z] = 0$.
Example evaluation:

$$
\begin{aligned}
[\hat{V}(r), \hat{y}\hat{p}_z] &= \hat{y}\underbrace{[\hat{V}(r), \hat{p}_z]}_{i\hbar\,\partial V/\partial z} + \underbrace{[\hat{V}(r), \hat{y}]}_{0}\hat{p}_z \\
&= i\hbar\hat{y}\frac{\partial V}{\partial z}
\end{aligned}
$$

Returning to the original set of equations, from line 3 to line 4, we evaluated the last two commutators and applied the chain rule. From line 4 to line 5, we algebraically expanded and cancelled everything (using $r = \sqrt{x^2 + y^2 + z^2}$ for the partial derivatives).
Moving on, similar to the above, we obtain that

$$[\hat{H}, \hat{L}_y] = [\hat{H}, \hat{L}_z] = 0$$

Thus, by bilinearity once more,

$$[\hat{H}, \hat{\vec{L}}] = [\hat{H}, \hat{L}_x + \hat{L}_y + \hat{L}_z] = 0$$

$\square$

b) What happens if the system has a translational invariance in the z-direction and

$$V(\vec{r}) = V(\sqrt{x^2 + y^2}) \tag{5.4}$$

for all z? Is any component of the momentum or angular momentum preserved?

Answer. First, observe that

$$\left[\hat{V}(\sqrt{x^2+y^2}), \hat{x}\right] = V(\sqrt{x^2+y^2})x - xV(\sqrt{x^2+y^2}) = V(\sqrt{x^2+y^2})x - V(\sqrt{x^2+y^2})x = 0$$

and

$$\left[\hat{V}(\sqrt{x^2+y^2}), \hat{p}_y\right] f = -i\hbar V(\sqrt{x^2+y^2})\frac{\partial f}{\partial y} + i\hbar\frac{\partial}{\partial y}\left(V(\sqrt{x^2+y^2})f\right) = i\hbar\frac{\partial}{\partial y}[V(\sqrt{x^2+y^2})]f$$

Therefore,

$$
\begin{aligned}
[\hat{H}, \hat{L}_z] &= \left[\frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + \hat{V}(\sqrt{x^2+y^2}), \hat{x}\hat{p}_y - \hat{y}\hat{p}_x\right] \\
&= \left[\frac{\hat{p}_x^2}{2m}, \hat{x}\hat{p}_y\right] + \left[\frac{\hat{p}_y^2}{2m}, -\hat{y}\hat{p}_x\right] + \left[\hat{V}(\sqrt{x^2+y^2}), \hat{x}\hat{p}_y\right] + \left[\hat{V}(\sqrt{x^2+y^2}), -\hat{y}\hat{p}_x\right] \\
&= -\frac{i\hbar\hat{p}_x\hat{p}_y}{m} + \frac{i\hbar\hat{p}_x\hat{p}_y}{m} + i\hbar\frac{\mathrm{d}V(u)}{\mathrm{d}u}\left[x\frac{\partial}{\partial y}\left(\sqrt{x^2+y^2}\right) - y\frac{\partial}{\partial x}\left(\sqrt{x^2+y^2}\right)\right] \\
&= 0
\end{aligned}
$$

so $\boxed{\hat{L}_z \text{ is conserved.}}$ None of the other angular momentum directions are conserved because we need the cross partial derivatives to cancel as they do above, and that doesn't occur anywhere else.

Additionally, observe that

$$\left[\hat{V}(\sqrt{x^2+y^2}),\hat{p}_z\right]f = -i\hbar V(\sqrt{x^2+y^2})\frac{\partial f}{\partial z} + i\hbar\frac{\partial}{\partial z}\Big(V(\sqrt{x^2+y^2})f\Big) = 0$$

Therefore,

$$\begin{aligned}[\hat{H},\hat{p}_z] &= \left[\frac{\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2}{2m}+\hat{V}(\sqrt{x^2+y^2}),\hat{p}_z\right] \\ &= \left[\frac{\hat{p}_z^2}{2m},\hat{p}_z\right] + \left[\hat{V}(\sqrt{x^2+y^2}),\hat{p}_z\right] \\ &= 0\end{aligned}$$

so $\boxed{\hat{p}_z \text{ is conserved.}}$ None of the other momentum directions are conserved either because we need the right commutator in line 2 to cancel as proven above, and it does not in any other case as proven above with the representative example of $\hat{p}_y$. ☐

3. Imagine I have a potential such that I can find simultaneous eigenstates of $\hat{\vec{L}}^2$, $\hat{L}_z$, and $\hat{H}$ with respective eigenvalues $\hbar^2\ell(\ell+1)$, $\hbar m$, and $E_{n\ell}$. Suppose that $[\hat{L}_i,\hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$, $[\hat{\vec{L}}^2,\hat{L}_i] = [\hat{H},\hat{L}_i] = 0$, and $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$.

a) Show that $[\hat{L}_\pm,\hat{L}_z] = \mp\hbar\hat{L}_\pm$.

Answer. We have by the the commutator relations among the $\hat{L}_i$ that

$$[\hat{L}_\pm,\hat{L}_z] = [\hat{L}_x \pm i\hat{L}_y,\hat{L}_z] = -i\hbar\hat{L}_y \pm i(i\hbar\hat{L}_x) = -i\hbar\hat{L}_y \mp \hbar\hat{L}_x = \mp\hbar(\hat{L}_x \pm i\hat{L}_y) = \mp\hbar\hat{L}_\pm$$

as desired. ☐

b) Show also that this implies that, given an eigenfunction $Y_{\ell m}$ of $\hat{\vec{L}}^2$ and $\hat{L}_z$,

$$\hat{L}_\pm Y_{\ell m} \propto Y_{\ell(m\pm1)} \tag{5.5}$$

Answer. Let $Y_{\ell m}$ be an eigenstate of $\hat{\vec{L}}^2,\hat{L}_z$. Then we have the following by hypothesis.

$$\hat{\vec{L}}^2 Y_{\ell m} = \hbar^2\ell(\ell+1)Y_{\ell m} \qquad \hat{L}_z Y_{\ell m} = \hbar m Y_{\ell m}$$

When we apply $\hat{L}_z$ to $\hat{L}_+Y_{\ell m}$, we get

$$\begin{aligned}\hat{L}_z(\hat{L}_+Y_{\ell m}) &= \left[\hat{L}_+\hat{L}_z - (\hat{L}_+\hat{L}_z - \hat{L}_z\hat{L}_+)\right]Y_{\ell m} \\ &= \hat{L}_+\hbar m Y_{\ell m} + \hbar\hat{L}_+Y_{\ell m} \\ &= \hbar(m+1)(\hat{L}_+Y_{\ell m})\end{aligned}$$

Thus,

$$\hat{L}_+Y_{\ell m} \propto Y_{\ell(m+1)}$$

We can prove in a similar fashion that

$$\hat{L}_-Y_{\ell m} \propto Y_{\ell(m-1)}$$

☐

c) Show that $\hat{\vec{L}}^2 = \hat{L}_-\hat{L}_+ + \hbar\hat{L}_z + \hat{L}_z^2$.

Answer. We have that

$$\begin{aligned}
\hat{L}_-\hat{L}_+ &= (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) \\
&= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 - i[\hat{L}_y, \hat{L}_x] - \hat{L}_z^2 \\
&= \hat{\vec{L}}^{\,2} - \hat{L}_z^2 - \hbar\hat{L}_z \\
\hat{\vec{L}}^{\,2} &= \hat{L}_-\hat{L}_+ + \hbar\hat{L}_z + \hat{L}_z^2
\end{aligned}$$

□

d) With the above information, use the ladder operators $\hat{L}_\pm$ to compute the mean value of $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_x^2$, and $\hat{L}_y^2$ in an eigenstate of $\hat{\vec{L}}^{\,2}$ and $\hat{L}_z$.

Answer. We have that

$$\langle n\ell m|\hat{L}_x|n\ell m\rangle = \langle n\ell m|\frac{1}{2}(\hat{L}_+ + \hat{L}_-)|n\ell m\rangle$$

$$\boxed{\langle n\ell m|\hat{L}_x|n\ell m\rangle = 0}$$

Similarly,

$$\boxed{\langle n\ell m|\hat{L}_y|n\ell m\rangle = 0}$$

Additionally, we have that

$$\langle n\ell m|(\hat{L}_x^2 + \hat{L}_y^2)|n\ell m\rangle = \langle n\ell m|(\hat{\vec{L}}^{\,2} - \hat{L}_z^2)|n\ell m\rangle = \hbar^2[\ell(\ell+1) - m^2]$$

Since the above eigenvalue must be greater than or equal to zero, $|m| \leq \ell$. Recall that $\hat{L}_x, \hat{L}_y$ are incompatible with $\hat{L}_z$. This is why we have an uncertainty associated with the quantity $\hbar^2[\ell(\ell+1) - m^2]$. This is also why we have

$$\langle n\ell m|(\hat{L}_x^2 + \hat{L}_y^2)|n\ell m\rangle = 2\,\langle n\ell m|\hat{L}_x^2|n\ell m\rangle = 2\,\langle n\ell m|\hat{L}_y^2|n\ell m\rangle$$

so

$$\boxed{\langle n\ell m|\hat{L}_x^2|n\ell m\rangle = \langle n\ell m|\hat{L}_y^2|n\ell m\rangle = \frac{\hbar^2}{2}[\ell(\ell+1) - m^2]}$$

□

6 Time-Independent Problems in 3D

2/24: **1. Infinite spherical well.** A particle of mass M moves in the central potential

$$V(r) = \begin{cases} 0 & r < a \\ \infty & r \geq a \end{cases} \tag{6.1}$$

We know that the generic solution is given by

$$\psi_{n\ell m} = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \tag{6.2}$$

where $U_{n\ell}(r) = rR_{n\ell}(r) \to 0$ for $r = 0, a$ is the solution for an effective one-dimensional problem with an effective potential

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2Mr^2} \tag{6.3}$$

a) Write the solutions of the Schrödinger equation for $\ell = 0$. Observe that there are infinite possible solutions $(n = 1, 2, \dots)$ for each value of ℓ.

Answer. If $\ell = 0$, then

$$V_{\text{eff}}(r) = 0 + \frac{\hbar^2 0(0+1)}{2Mr^2} = 0$$

for all $0 \leq r \leq a$. Thus, the relevant effective Schrödinger equation is

$$-\frac{\hbar^2}{2M} \frac{\mathrm{d}^2}{\mathrm{d}r^2} [U_{n\ell}(r)] = E_{n\ell} U_{n\ell}(r)$$

along with the boundary conditions

$$U_{n\ell}(0) = U_{n\ell}(a) = 0$$

This setup is entirely analogous to the infinite square well ODE we solved in class on 1/17. Thus, the solutions for $\ell = 0$ are

$$\boxed{U_{n\ell}(r) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi n r}{a}\right)}$$

As noted in the problem statement, we can indeed see that that there are infinite possible solutions $(n = 1, 2, \dots)$ for the value $\ell = 0$.[6] ☐

b) For $\ell = 0$, what is the probability density of finding the particle for $r \to 0$?

Answer. The probability density of finding the particle for $r \to 0$ is given by

$$\lim_{r \to 0} |U_{n\ell}(r)|^2 = \lim_{r \to 0} \frac{2}{a} \sin^2\left(\frac{\pi n r}{a}\right)$$
$$\boxed{\lim_{r \to 0} |U_{n\ell}(r)|^2 = 0}$$

☐

c) For $\ell \neq 0$, go back to the equation for $R_{n\ell}$ and use your knowledge of the spherical Bessel equation

$$u^2 \frac{\mathrm{d}^2}{\mathrm{d}u^2} [J_\ell(u)] + 2u \frac{\mathrm{d}}{\mathrm{d}u} [J_\ell(u)] + [u^2 - \ell(\ell+1)] J_\ell(u) = 0 \tag{6.4}$$

to show that $R_{n\ell}(r)$ can be solved in terms of $J_\ell(u)$ if one makes the simple redefinition $u = k_{n\ell} r$, where $\hbar^2 k_{n\ell}^2 = 2ME_{n\ell}$ is the square of the particle momentum.

[6] Yunjia said in his 2/20 office hours that $\ell = 0$ is the only value of ℓ we need to discuss in this part of this problem, despite the "for each value of ℓ" wording in the problem statement.

Answer. In class on 2/2, we derived the following equation for $R_{n\ell}$, which will be our starting point herein.

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}[R_{n\ell}(r)]\right)-\frac{2Mr^2}{\hbar^2}[V(r)-E_{n\ell}]R_{n\ell}(r)=\ell(\ell+1)R_{n\ell}(r)$$

As in part (a), we know that $V(r)=0$ for $0\leq r\leq a$. Additionally, recall from the problem statement that $E_{n\ell}=\hbar^2k_{n\ell}^2/2M$. These facts allows us to algebraically rearrange the above equation as follows.

$$\begin{aligned}0&=\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}[R_{n\ell}(r)]\right)-\frac{2Mr^2}{\hbar^2}[0-E_{n\ell}]R_{n\ell}(r)-\ell(\ell+1)R_{n\ell}(r)\\&=r^2\frac{\mathrm{d}^2}{\mathrm{d}r^2}[R_{n\ell}(r)]+2r\frac{\mathrm{d}}{\mathrm{d}r}[R_{n\ell}(r)]+k_{n\ell}^2r^2R_{n\ell}(r)-\ell(\ell+1)R_{n\ell}(r)\end{aligned}$$

Now define $u:=k_{n\ell}r$ as suggested in the problem statement and initiate a change of variables in the above differential equation.

$$\begin{aligned}0=&\left(\frac{u}{k_{n\ell}}\right)^2\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\mathrm{d}}{\mathrm{d}u}[R_{n\ell}(u(r))]\cdot\frac{\mathrm{d}u}{\mathrm{d}r}\right)+\frac{2u}{k_{n\ell}}\frac{\mathrm{d}}{\mathrm{d}u}[R_{n\ell}(u(r))]\cdot\frac{\mathrm{d}u}{\mathrm{d}r}\\&+k_{n\ell}^2\left(\frac{u}{k_{n\ell}}\right)^2R_{n\ell}(u(r))-\ell(\ell+1)R_{n\ell}(u(r))\\=&\frac{u^2}{k_{n\ell}^2}\frac{\mathrm{d}}{\mathrm{d}u}\left(\frac{\mathrm{d}}{\mathrm{d}u}[R_{n\ell}(u)]\cdot k_{n\ell}\right)\cdot\frac{\mathrm{d}u}{\mathrm{d}r}+\frac{2u}{k_{n\ell}}\frac{\mathrm{d}}{\mathrm{d}u}[R_{n\ell}(u)]\cdot k_{n\ell}+u^2R_{n\ell}(u)-\ell(\ell+1)R_{n\ell}(u)\\=&u^2\frac{\mathrm{d}^2}{\mathrm{d}u^2}[R_{n\ell}(u)]+2u\frac{\mathrm{d}}{\mathrm{d}u}[R_{n\ell}(u)]+[u^2-\ell(\ell+1)]R_{n\ell}(u)\end{aligned}$$

This leads us to derive the spherical Bessel equation exactly. Thus, the solutions for $\ell\neq 0$ are

$$R_{n\ell}(u)=J_\ell(u)$$
$$\boxed{R_{n\ell}(r)=J_\ell(k_{n\ell}r)}$$

□

d) The general form of $J_\ell(u)$ is

$$J_\ell(u)=(-u)^\ell\left(\frac{1}{u}\frac{\mathrm{d}}{\mathrm{d}u}\right)^\ell\left(\frac{\sin u}{u}\right)\tag{6.5}$$

Find the first solutions of this equation, for $\ell=0,1$. Just like the regular sinusoidal functions, the spherical Bessel functions have infinite zeros. The energy of the particle is obviously

$$E_{n\ell}=\frac{\hbar^2k_{n\ell}^2}{2M}\tag{6.6}$$

Show that $k_{n\ell}$ may be given in terms of the position of the zeros of the spherical Bessel function

$$J_\ell(k_{n\ell}a)=0\tag{6.7}$$

Answer. For $\ell=0$, we have that

$$\begin{aligned}R_{n0}(r)&=J_0(k_{n0}r)\\&=(-k_{n0}r)^0\left(\frac{1}{k_{n0}r}\frac{\mathrm{d}}{\mathrm{d}(k_{n0}r)}\right)^0\left(\frac{\sin(k_{n0}r)}{k_{n0}r}\right)\end{aligned}$$
$$\boxed{R_{n0}(r)=\frac{\sin(k_{n0}r)}{k_{n0}r}}$$

while for $\ell = 1$, we have that

$$\begin{aligned} R_{n1}(r) &= J_1(k_{n1}r) \\ &= (-k_{n1}r)^1 \frac{1}{k_{n1}r} \frac{\mathrm{d}}{\mathrm{d}(k_{n1}r)} \left(\frac{\sin(k_{n1}r)}{k_{n1}r} \right) \\ &= -\frac{k_{n1}r\cos(k_{n1}r) - \sin(k_{n1}r)}{(k_{n1}r)^2} \end{aligned}$$

$$\boxed{R_{n1}(r) = \frac{\sin(k_{n1}r) - k_{n1}r\cos(k_{n1}r)}{k_{n1}^2 r^2}}$$

Additionally, since this differential equation was solved in concert with the boundary condition

$$R_{n\ell}(a) = 0$$

we must have that

$$J_\ell(k_{n\ell}a) = R_{n\ell}(a) = 0$$

as desired. Since $k_{n\ell}$ is the only unknown in the above equation, this equation can indeed be used to solve for $k_{n\ell}$, i.e., $k_{n\ell}$ may be given in terms of the position of the zeros of the spherical Bessel function. □

e) In the classical case, if the particle has $\vec{L}^2 = 0$, it would move in paths that cross the origin and bounce back and forth against the wall. There are infinite paths depending on the direction of motion, with a common convergence point at $r = 0$. Compare this result with the probability density in the quantum case.

Answer. $\vec{L}^2$ is the eigenvalue of $\hat{\vec{L}}^2$, so if $\vec{L}^2 = 0$, then $\hbar^2\ell(\ell+1) = 0$ and hence $\ell = 0$. Thus, as in part (b), the probability density[7] is given by

$$|U_{n\ell}(r)|^2 = \frac{2}{a}\sin^2\left(\frac{\pi n r}{a}\right)$$

One thing that this equation implies is that the probability density is always spherically symmetric, very similar to how the classical particle can move along any of the infinitely many paths through the origin. One place where the interpretations differ is that in the quantum case, the probability goes to zero near the origin while in the classical case, the probability is greatest at the origin (since every particle passes through it, regardless of which linear path it is on). □

f) In the classical motion at $\hat{\vec{L}}^2 \neq 0$, the particle will never cross the origin, but the motion will be given by trajectories where the particle hits the wall periodically and continues moving until hitting the wall again, conserving the tangential momentum and changing the sign of the normal one. Compare this with the solution of the quantum case for $\ell = 1$.

Answer. Using the result from part (d), we can write that for $\ell = 1$, the probability density is given by

$$|U_{n\ell}(r)|^2 = r^2|R_{n1}(r)|^2 = \frac{[\sin(k_{n1}r) - k_{n1}r\cos(k_{n1}r)]^2}{k_{n1}^4 r^2}$$

Thus, although the distribution is different, the probability density is still radially symmetric in the quantum case, unlike in the classical case. Additionally, note that the probability density does still go to zero at the origin, so just like in the classical case, this quantum particle cannot pass through the origin. □

[7] Both Yunjia and Matt said in office hours that this interpretation of "probability density" — i.e., as *radial* probability density — is the correct way to address this problem. This interpretation is also consistent with how Wagner used the phrase "probability density" in the 2/19 lecture to refer to $|U_{n\ell}|^2$. However, Nick said in office hours that the correct interpretation of "probability density" is as $|\psi|^2$, but to go with what the other two TAs and Wagner said because he's not grading this week.

2. In class, we solved the isotropic harmonic oscillator for a particle of mass M moving in a potential

$$V(x,y,z) = \frac{M\omega^2}{2}(x^2+y^2+z^2) \tag{6.8}$$

in Cartesian coordinates as well as in spherical coordinates. In Cartesian coordinates, it is better to use the method of separation of variables

$$\psi_{n_x n_y n_z}(x,y,z) = X_{n_x}(x)Y_{n_y}(y)Z_{n_z}(z) \tag{6.9}$$

This results in harmonic oscillator equations for the three functions $X_{n_x}, Y_{n_y}, Z_{n_z}$. The total energy is given by

$$E_{n_x n_y n_z} = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right) \tag{6.10}$$

In spherical coordinates, one can take eigenfunctions $Y_{\ell m}(\theta,\phi)$ of $\hat{L}_z, \hat{\vec{L}}^2$ and solve for the radial function $U_{n\ell}(r) = rR_{n\ell}(r)$. Studying the asymptotic behavior at $r \to 0$ and $r \to \infty$ leads to a solution

$$U_{n\ell}(r) = f_{n\ell}(r) r^{\ell+1} \mathrm{e}^{-M\omega r^2/2\hbar} \tag{6.11}$$

where $f_{n\ell}$ can be expressed in terms of a series expansion that must terminate at some order n for the solution to be normalizable. The resulting energy is

$$E_{n\ell} = \hbar\omega\left(n + \ell + \frac{3}{2}\right) \tag{6.12}$$

a) How do you relate the three-fold degeneracy of the energy solutions in the Cartesian case to the two-fold degeneracy in the spherical case? Write the first simple examples that establish this relationship.

Answer. The varying degeneracies are reconciled in the fact that different rules govern the possible values such that the variables always produce an identical number of possible values and mathematically equivalent solutions up to a change in coordinates.

For example, for $\bar{n} = 0$, the only possible Cartesian values are $n_1 = n_2 = n_3 = 0$ and the only possible spherical values are $n = \ell = 0$, so we have one solution in both cases.

For $\bar{n} = 1$, things get slightly more complicated. In Cartesian coordinates, we could have $n_1 = 1$, $n_2 = n_3 = 0$; $n_2 = 1$, $n_1 = n_3 = 0$; or $n_3 = 1$, $n_2 = n_3 = 0$. These are the only possible values because of the constraints that $n_1 + n_2 + n_3 = \bar{n}$ and $n_i \in \mathbb{Z}_{\geq 0}$ $(i = 1,2,3)$. In spherical coordinates, we have $n = 0$; $\ell = 1$; and $m = 1$, $m = 0$, or $m = -1$. Note that no $n = 1$ and $\ell = 0$ case exists because of the constraint that $n \in (2\mathbb{N} - 2)$. Thus, we see once again that we have an equal number of solutions (3) in both cases.

Using the same constraints as above, we have for $\bar{n} = 2$ that

n_1	n_2	n_3
0	0	2
0	2	0
2	0	0
0	1	1
1	0	1
1	1	0

(a) Cartesian coordinates.

n	ℓ	m
0	2	2
0	2	1
0	2	0
0	2	-1
0	2	-2
2	0	0

(b) Spherical coordinates.

Thus, we see one more time that there is an equal number of solutions (6) in both cases. This pattern continues. □

b) Write the solution for $\bar{n} = n_x + n_y + n_z = 1$ in Cartesian coordinates and for $\bar{n} = n + \ell = 1$ in spherical coordinates. Demonstrate that the solutions in the spherical case are linear combinations of the ones found in the Cartesian case.

Answer. As given in class on 2/14, the three Cartesian solutions for $\bar{n} = 1$ are

$$\boxed{x\mathrm{e}^{-M\omega r^2/2\hbar} \qquad y\mathrm{e}^{-M\omega r^2/2\hbar} \qquad z\mathrm{e}^{-M\omega r^2/2\hbar}}$$

and the three corresponding spherical solutions are

$$\boxed{r\mathrm{e}^{-M\omega r^2/2\hbar}\sin\theta\mathrm{e}^{i\phi} \qquad r\mathrm{e}^{-M\omega r^2/2\hbar}\cos\theta \qquad r\mathrm{e}^{-M\omega r^2/2\hbar}\sin\theta\mathrm{e}^{-i\phi}}$$

We may write the three spherical solutions as linear combinations of the Cartesian ones as follows.

$$\begin{aligned}
r\mathrm{e}^{-M\omega r^2/2\hbar}\sin\theta\mathrm{e}^{i\phi} &= [r\sin\theta(\cos\phi + i\sin\phi)]\mathrm{e}^{-M\omega r^2/2\hbar} \\
&= [r\sin\theta\cos\phi + ir\sin\theta\sin\phi]\mathrm{e}^{-M\omega r^2/2\hbar} \\
&= [x + iy]\mathrm{e}^{-M\omega r^2/2\hbar}
\end{aligned}$$

$$\boxed{r\mathrm{e}^{-M\omega r^2/2\hbar}\sin\theta\mathrm{e}^{i\phi} = (x\mathrm{e}^{-M\omega r^2/2\hbar}) + i(y\mathrm{e}^{-M\omega r^2/2\hbar})}$$

$$r\mathrm{e}^{-M\omega r^2/2\hbar}\cos\theta = [r\cos\theta]\mathrm{e}^{-M\omega r^2/2\hbar}$$

$$\boxed{r\mathrm{e}^{-M\omega r^2/2\hbar}\cos\theta = z\mathrm{e}^{-M\omega r^2/2\hbar}}$$

$$\begin{aligned}
r\mathrm{e}^{-M\omega r^2/2\hbar}\sin\theta\mathrm{e}^{-i\phi} &= [r\sin\theta(\cos\phi - i\sin\phi)]\mathrm{e}^{-M\omega r^2/2\hbar} \\
&= [r\sin\theta\cos\phi - ir\sin\theta\sin\phi]\mathrm{e}^{-M\omega r^2/2\hbar} \\
&= [x - iy]\mathrm{e}^{-M\omega r^2/2\hbar}
\end{aligned}$$

$$\boxed{r\mathrm{e}^{-M\omega r^2/2\hbar}\sin\theta\mathrm{e}^{-i\phi} = (x\mathrm{e}^{-M\omega r^2/2\hbar}) - i(y\mathrm{e}^{-M\omega r^2/2\hbar})}$$

□

c) Discuss the behavior of the probability density for the different solutions for $\bar{n} = 0$ and $\bar{n} = 1$. *Hint*: Concentrate on the overall behavior of the density, and not on the normalization factors.

Answer. For $\bar{n} = 0$, the probability density is

$$|U_{00}(r)|^2 = r^2|R_{00}(r)|^2 = r^2\mathrm{e}^{-M\omega r^2/\hbar}$$

This means that the probability density is spherically symmetric, zero at the origin, increases until it peaks at a distance $r = \sqrt{\hbar/M\omega}$ from the origin, and then tends back toward zero as $r \to \infty$.

For $\bar{n} = 1$, one example of the probability density is

$$|\psi|^2 = x^2\mathrm{e}^{-M\omega r^2/\hbar}$$

This means that the probability density is *not* spherically symmetric. It will still be zero at the origin and peak at $(\pm\sqrt{\hbar/M\omega}, 0, 0)$. But then the probability density will be concentrated at those two maxima and fall off as we move away from them in any direction. This yields the typical p_x-orbital density distribution. Analogously, the other two spherical harmonics will produce p_y- and p_z-orbital type distributions oriented along the other two Cartesian axes. □

3. In class, we solved the hydrogen atom. One can imagine a more generic potential, namely

$$V(r) = \frac{A}{r^2} - \frac{B}{r} \tag{6.13}$$

The effective one-dimensional problem for the function $U_{n\ell}(r) = rR_{n\ell}(r)$ would be given by

$$-\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] + \left[V(r) + \frac{\hbar^2\ell(\ell+1)}{2m_e r^2}\right]U_{n\ell}(r) = E_{n\ell}U_{n\ell}(r) \tag{6.14}$$

where

$$\psi_{n\ell m}(\vec{r}) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi) \tag{6.15}$$

Assume that A, B are real, positive, and carry the proper units to make the potential meaningful.

a) Redefine

$$A + \frac{\hbar^2\ell(\ell+1)}{2m_e} = \frac{\hbar^2 w(w+1)}{2m_e} \tag{6.16}$$

where w is a real number and study the asymptotic behavior of $U_{n\ell}$ for $r\to\infty$ and $r\to 0$.

Answer. In the limiting case that r is large ($r\to\infty$), we can approximate the potential as going to zero and giving us

$$-\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] = E_{n\ell}U_{n\ell}(r)$$

Thus, since the ansatz $\mathrm{e}^{-k_{n\ell}r}$ satisfies the above ODE (where $E_{n\ell} = -\hbar^2k_{n\ell}^2/2m_e$), we have that

$$U_{n\ell} \propto \mathrm{e}^{-k_{n\ell}r}$$

In the limiting case that r is small ($r\to 0$), we can approximate the potential as giving us

$$\begin{aligned} 0 &= -\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] + \left[\frac{\hbar^2 w(w+1)}{2m_e r^2}\right]U_{n\ell}(r) \\ \frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] &= \left[\frac{w(w+1)}{r^2}\right]U_{n\ell}(r) \end{aligned}$$

Thus, since the ansatz r^{w+1} satisfies the above ODE, we also have that

$$U_{n\ell}(r) \propto r^{w+1}$$

Therefore, we have overall that

$$U_{n\ell}(r) \propto r^{w+1}\mathrm{e}^{-k_{n\ell}r}$$

and hence

$$U_{n\ell}(r) = f_{n\ell}(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r}$$

where $f_{n\ell}(r)$ is some function. □

b) Consider only bound states (that is, those where $\hbar^2k_{n\ell}^2/2m_e = |E_{n\ell}|$) and — looking at what was done in the case of the hydrogen atom — obtain an equation for the function $f(z)$ such that

$$U_{n\ell}(r) = f_{n\ell}(z)r^{w+1}\mathrm{e}^{-k_{n\ell}r} \tag{6.17}$$

Hint: You do not need to derive the equation. Just look at what happens in the hydrogen atom and proceed by analogy with that case.

Answer. Taking the hint, we can develop an analogy between this potential and the hydrogen atom potential as follows. Essentially, we want

$$V(r) = \left[\frac{A}{r^2} + \frac{\hbar^2\ell(\ell+1)}{2m_e r^2}\right] - \left[\frac{B}{r}\right] = \left[\frac{\hbar^2 w(w+1)}{2m_e r^2}\right] - \left[\frac{e^2}{4\pi\epsilon_0 r}\right] = V_{^1\mathrm{H}}(r)$$

Thus, we must change

$$\ell \to w \qquad\qquad \frac{e^2}{4\pi\epsilon_0} \to B$$

in the relevant ODE from the 2/16 lecture. In particular,

$$f_{n\ell}''(r) + f_{n\ell}'(r)\left[\frac{2(\ell+1)}{r} - 2k_{n\ell}\right] + f_{n\ell}(r)\left[-\frac{2k_{n\ell}(\ell+1)}{r} + \frac{2m_e}{\hbar^2}\frac{e^2}{4\pi\epsilon_0 r}\right] = 0$$

becomes

$$\boxed{f_{n\ell}''(r) + f_{n\ell}'(r)\left[\frac{2(w+1)}{r} - 2k_{n\ell}\right] + f_{n\ell}(r)\left[-\frac{2k_{n\ell}(w+1)}{r} + \frac{2m_eB}{\hbar^2 r}\right] = 0}$$

Alternatively, here is the full derivation. To obtain an ODE constraining the values of $f_{n\ell}$, substitute the version of $U_{n\ell}$ obtained in part (a) back into the original differential equation and simplify as follows.

$$\begin{aligned}
0 &= -\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] + \left[\frac{A}{r^2} - \frac{B}{r} + \frac{\hbar^2\ell(\ell+1)}{2m_er^2}\right]U_{n\ell}(r) - E_{n\ell}U_{n\ell}(r)\\
&= -\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[f_{n\ell}(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r}] + \left[\frac{A}{r^2} - \frac{B}{r} + \frac{\hbar^2\ell(\ell+1)}{2m_er^2} - E_{n\ell}\right]f_{n\ell}(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r}\\
&= \frac{\mathrm{d}^2}{\mathrm{d}r^2}[f_{n\ell}(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r}] - \frac{2m_e}{\hbar^2}\left[\frac{A}{r^2} - \frac{B}{r} + \frac{\hbar^2\ell(\ell+1)}{2m_er^2} - E_{n\ell}\right]f_{n\ell}(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r}\\
&= \frac{\mathrm{d}}{\mathrm{d}r}[f_{n\ell}'(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r} + (w+1)f_{n\ell}(r)r^{w}\mathrm{e}^{-k_{n\ell}r} - k_{n\ell}f_{n\ell}(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r}]\\
&\quad - \frac{2m_e}{\hbar^2}\left[\frac{A}{r^2} - \frac{B}{r} + \frac{\hbar^2\ell(\ell+1)}{2m_er^2} - E_{n\ell}\right]f_{n\ell}(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r}\\
&= [f_{n\ell}''(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r} + (w+1)f_{n\ell}'(r)r^{w}\mathrm{e}^{-k_{n\ell}r} - k_{n\ell}f_{n\ell}'(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r}\\
&\quad + (w+1)f_{n\ell}'(r)r^{w}\mathrm{e}^{-k_{n\ell}r} + w(w+1)f_{n\ell}(r)r^{w-1}\mathrm{e}^{-k_{n\ell}r} - k_{n\ell}(w+1)f_{n\ell}(r)r^{w}\mathrm{e}^{-k_{n\ell}r}\\
&\quad - k_{n\ell}f_{n\ell}'(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r} - k_{n\ell}(w+1)f_{n\ell}(r)r^{w}\mathrm{e}^{-k_{n\ell}r} + k_{n\ell}^2f_{n\ell}(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r}]\\
&\quad - \frac{2m_e}{\hbar^2}\left[-\frac{B}{r} + \frac{\hbar^2w(w+1)}{2m_er^2} - E_{n\ell}\right]f_{n\ell}(r)r^{w+1}\mathrm{e}^{-k_{n\ell}r}\\
&= [f_{n\ell}''(r)r^{w+1} + (w+1)f_{n\ell}'(r)r^{w} - k_{n\ell}f_{n\ell}'(r)r^{w+1}\\
&\quad + (w+1)f_{n\ell}'(r)r^{w} + w(w+1)f_{n\ell}(r)r^{w-1} - k_{n\ell}(w+1)f_{n\ell}(r)r^{w}\\
&\quad - k_{n\ell}f_{n\ell}'(r)r^{w+1} - k_{n\ell}(w+1)f_{n\ell}(r)r^{w} + k_{n\ell}^2f_{n\ell}(r)r^{w+1}]\\
&\quad - \frac{2m_e}{\hbar^2}\left[-\frac{B}{r} + \frac{\hbar^2w(w+1)}{2m_er^2} - E_{n\ell}\right]f_{n\ell}(r)r^{w+1}\\
&= \Bigg[f_{n\ell}''(r) + \frac{w+1}{r}f_{n\ell}'(r) - k_{n\ell}f_{n\ell}'(r)\\
&\quad + \frac{w+1}{r}f_{n\ell}'(r) + \frac{w(w+1)}{r^2}f_{n\ell}(r) - \frac{k_{n\ell}(w+1)}{r}f_{n\ell}(r)\\
&\quad - k_{n\ell}f_{n\ell}'(r) - \frac{k_{n\ell}(w+1)}{r}f_{n\ell}(r) + k_{n\ell}^2f_{n\ell}(r)\Bigg]\\
&\quad - \frac{2m_e}{\hbar^2}\left[-\frac{B}{r} + \frac{\hbar^2w(w+1)}{2m_er^2} - E_{n\ell}\right]f_{n\ell}(r)\\
&= f_{n\ell}''(r) + \left[\frac{2(w+1)}{r} - 2k_{n\ell}\right]f_{n\ell}'(r) + \left[\frac{w(w+1)}{r^2} - \frac{2k_{n\ell}(w+1)}{r} + k_{n\ell}^2\right]f_{n\ell}(r)\\
&\quad - \frac{2m_e}{\hbar^2}\left[-\frac{B}{r} + \frac{\hbar^2w(w+1)}{2m_er^2} - E_{n\ell}\right]f_{n\ell}(r)
\end{aligned}$$

$$
\begin{aligned}
&= f_{n\ell}''(r) + \left[\frac{2(w+1)}{r} - 2k_{n\ell}\right] f_{n\ell}'(r) + \left[-\frac{2k_{n\ell}(w+1)}{r} + k_{n\ell}^2\right] f_{n\ell}(r) \\
&\quad + \frac{2m_e}{\hbar^2}\left[\frac{B}{r} + E_{n\ell}\right] f_{n\ell}(r) \\
&= f_{n\ell}''(r) + 2\left[\frac{w+1}{r} - k_{n\ell}\right] f_{n\ell}'(r) + \left[\frac{2m_eB}{\hbar^2 r} - \frac{2k_{n\ell}(w+1)}{r} + \frac{2m_eE_{n\ell}}{\hbar^2} + k_{n\ell}^2\right] f_{n\ell}(r) \\
&= f_{n\ell}''(r) + 2\left[\frac{w+1}{r} - k_{n\ell}\right] f_{n\ell}'(r) + 2\left[\frac{m_eB}{\hbar^2 r} - \frac{k_{n\ell}(w+1)}{r}\right] f_{n\ell}(r)
\end{aligned}
$$

□

c) Propose a series expansion for $f_{n\ell}(z)$ and assuming that it should terminate in order to obtain a normalizable solution, derive the value of the energies that one should obtain in this case. For this, call

$$B\sqrt{m_e/2|E_{n\ell}|} = q\hbar \tag{6.18}$$

and demonstrate that $q - w - 1 = n$ must be a positive integer (or zero). Therefore, the energy is given by

$$E_{n\ell} = -\frac{2B^2m_e}{\hbar^2}\left[2n + 1 + \sqrt{(2\ell+1)^2 + 8m_eA/\hbar^2}\right]^{-2} \tag{6.19}$$

Show that this reduces to the hydrogen atom in the appropriate limit. *Hint*: Observe that $4x(x+1)+1 = (2x+1)^2$ and the square root in Eq. 6.19 is nothing but $(2w+1)$.

Answer. Postulate that

$$f_{n\ell}(r) = \sum_j a_j r^j$$

Substituting this power series into the ODE from part (b), we obtain

$$
\begin{aligned}
0 &= f_{n\ell}''(r) + 2\left[\frac{w+1}{r} - k_{n\ell}\right] f_{n\ell}'(r) + 2\left[\frac{m_eB}{\hbar^2 r} - \frac{k_{n\ell}(w+1)}{r}\right] f_{n\ell}(r) \\
&= \sum_j j(j-1)a_j r^{j-2} + 2\left[\frac{w+1}{r} - k_{n\ell}\right]\sum_j j a_j r^{j-1} + 2\left[\frac{m_eB}{\hbar^2 r} - \frac{k_{n\ell}(w+1)}{r}\right]\sum_j a_j r^j
\end{aligned}
$$

Multiply through this expression that's equal to zero by r.

$$= \sum_j j(j-1)a_j r^{j-1} + 2(w+1-k_{n\ell}r)\sum_j j a_j r^{j-1} + 2\left[\frac{m_eB}{\hbar^2} - k_{n\ell}(w+1)\right]\sum_j a_j r^j$$

Rearrange and reindex select terms.

$$
\begin{aligned}
&= \sum_j j(j-1)a_j r^{j-1} + 2(w+1)\sum_j j a_j r^{j-1} \\
&\quad - 2k_{n\ell}\sum_j j a_j r^j + 2\left[\frac{m_eB}{\hbar^2} - k_{n\ell}(w+1)\right]\sum_j a_j r^j \\
&= \sum_{j=0}^{\infty} j(j+1)a_{j+1} r^j + 2(w+1)\sum_{j=0}^{\infty}(j+1)a_{j+1} r^j \\
&\quad - 2k_{n\ell}\sum_{j=0}^{\infty} j a_j r^j + 2\left[\frac{m_eB}{\hbar^2} - k_{n\ell}(w+1)\right]\sum_{j=0}^{\infty} a_j r^j \\
&= \sum_{j=0}^{\infty}\left[j(j+1)a_{j+1} + 2(w+1)(j+1)a_{j+1} - 2k_{n\ell} j a_j + \frac{2m_eBa_j}{\hbar^2} - 2k_{n\ell}(w+1)a_j\right] r^j \\
&= \sum_{j=0}^{\infty}\left[(j+2w+2)(j+1)a_{j+1} + 2\left(\frac{m_eB}{\hbar^2} - k_{n\ell}(j+w+1)\right)a_j\right] r^j
\end{aligned}
$$

Because each term in the above summation is affixed to a different power of r, meaning that no two terms can cancel, not only is the entire sum above equal to zero, but each individual term in it is equal to zero, too. Thus, for all $j \in \mathbb{Z}_{\geq 0}$,

$$\begin{aligned} 0 &= (j + 2w + 2)(j + 1)a_{j+1} + 2\left[\frac{m_e B}{\hbar^2} - k_{n\ell}(j + w + 1)\right] a_j \\ a_{j+1} &= \frac{2[k_{n\ell}(j + w + 1) - m_e B/\hbar^2]}{(j + 2w + 2)(j + 1)} a_j \end{aligned}$$

Per the problem statement, assume that the series expansion should terminate at some $n := j_{\max}$ in order to obtain a normalizable solution. Then if we are to have $a_{n+1} = 0$, the numerator of the above expression must equal zero. This yields

$$\begin{aligned} 0 &= 2\left[k_{n\ell}(n + w + 1) - \frac{m_e B}{\hbar^2}\right] \\ k_{n\ell}(n + w + 1) &= \frac{m_e B}{\hbar^2} \\ k_{n\ell} &= \frac{m_e B}{\hbar^2(n + w + 1)} \end{aligned}$$

Before we plug this into the energy equation, take the hint to learn that

$$\begin{aligned} \frac{\hbar^2 w(w + 1)}{2m_e} &= \frac{\hbar^2 \ell(\ell + 1)}{2m_e} + A \\ w(w + 1) &= \ell(\ell + 1) + \frac{2m_e A}{\hbar^2} \\ 4w(w + 1) + 1 &= 4\ell(\ell + 1) + 1 + \frac{8m_e A}{\hbar^2} \\ (2w + 1)^2 &= (2\ell + 1)^2 + \frac{8m_e A}{\hbar^2} \\ 2w + 1 &= \sqrt{(2\ell + 1)^2 + 8m_e A/\hbar^2} \end{aligned}$$

Therefore, combining the last two results, we have that

$$\begin{aligned} E_{n\ell} &= -\frac{\hbar^2 k_{n\ell}^2}{2m_e} \\ &= -\frac{m_e B^2}{2\hbar^2(n + w + 1)^2} \\ &= -\frac{4m_e B^2}{2\hbar^2(2n + 2w + 2)^2} \\ &= -\frac{2m_e B^2}{\hbar^2}\left[2n + 1 + 2w + 1\right]^{-2} \\ &= -\frac{2m_e B^2}{\hbar^2}\left[2n + 1 + \sqrt{(2\ell + 1)^2 + 8m_e A/\hbar^2}\right]^{-2} \end{aligned}$$

as desired.

Note that line 2 above is of a form directly analogous to Eq. 6.18 if we identify $q := n + w + 1$:

$$\begin{aligned} B\sqrt{m_e/2|E_{n\ell}|} &= q\hbar \\ \frac{B^2 m_e}{2|E_{n\ell}|} &= q^2\hbar^2 \\ |E_{n\ell}| &= \frac{m_e B^2}{2\hbar^2 q^2} \end{aligned}$$

By this identification, we also have the related equality $q - w - 1 = n$, as desired. And by the definition of n as the maximum value $j_{\max}$ of a counter that starts at zero (that is to say, j), we know that n must be a positive integer (or zero), as desired.

As to the second part of the question, the limit that reduces V to the hydrogen atom is $A \to 0$ and $B \to e^2/4\pi\epsilon_0$. Substituting these values into the above energy function, we obtain

$$\begin{aligned}
E_{n\ell} &= -\frac{2m_e}{\hbar^2} \cdot \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \cdot \left[2n + 1 + \sqrt{(2\ell+1)^2 + 8m_e(0)/\hbar^2}\right]^{-2} \\
&= -\frac{2\hbar^2}{m_e} \cdot \left(\frac{m_e e^2}{4\pi\epsilon_0\hbar^2}\right)^2 \cdot [2n + 1 + 2\ell + 1]^{-2} \\
&= -\frac{2\hbar^2}{m_e(2n + 2\ell + 2)^2} \cdot \left(\frac{1}{a_{\mathrm{B}}}\right)^2 \\
&= -\frac{\hbar^2}{2m_e a_{\mathrm{B}}^2 (n + \ell + 1)^2}
\end{aligned}$$

as desired. $\square$