Exam 1 Solutions

1. (12 points) Let’s start with some questions about a particle of mass \( m \) that moves along the \( x \) axis only.

(a) Suppose the potential energy is constant (at a value we will take to be zero) over the region from \(-\infty\) to \( x = 0 \). Consider a particle moving with kinetic energy \( T \) over this region. Write an expression for the magnitude of such a particle’s wavevector.

Since the potential energy is zero, the kinetic energy equals the total energy: \( T = E \), and we can relate the kinetic energy to the momentum \( p \):

\[
T = \frac{p^2}{2m} \quad \text{so that} \quad p = \sqrt{2mT} \quad \text{yielding} \quad k_I = \frac{p}{\hbar} = \frac{\sqrt{2mT}}{\hbar}.
\]

(b) Now suppose the potential energy is also constant over the region \( x = 0 \) to \(+\infty\), but constant at a non-zero value \( V_0 \). What is the wavevector in this region (call it \( k_{II} \) for “region II”)? Is there more than one possibility to consider here?

We don’t know (nor do we care at this point) if \( V_0 \) is greater than zero or less than zero, but we do know that \( V_0 \) plus the kinetic energy in region II (call it \( T_{II} \)) equals the total energy \( E \), which is the same as in region I (the total energy is set for all time and space if the system is isolated from any other system or external forces—that’s thermodynamics, not quantum mechanics!). So in general, we can write

\[
p_{II} = \sqrt{2mT_{II}} = \sqrt{2m(E - V_0)} = \sqrt{2m(T - V_0)} \quad \text{yielding} \quad k_{II} = \frac{p_{II}}{\hbar} = \frac{\sqrt{2m(T - V_0)}}{\hbar}.
\]

The only concern here is if \( E < V_0 \), which makes \( k_{II} \) purely imaginary. This would be the case that leads to tunneling in region II.

(c) Finally, suppose a graph of the real part of the particle’s wavefunction shows oscillations in both regions I and II, but with a greater wavelength to the oscillations in region II. What would such a picture tell you about the relationships among the energies: kinetic, \( T \), potential, \( V_0 \), and total, \( E \)?

The big clue here is that the wavefunction is oscillating in both regions. That means the kinetic energy is positive (\( E > V_0 \)) in region II. The second clue is that the oscillations have a greater wavelength in region II. That means the momentum is smaller in region II (the de Broglie wavelength is inversely proportional to \( p \)), which means the kinetic energy is smaller in II, which means \( V_0 > 0 \); the potential in region II is a step up in energy, but a step that is not as great as the particle’s total energy.

2. (18 points) A particle is in a state of definite total angular momentum, but one that allows us to measure only its \( z \) component of angular momentum readily. Repeated measurements of this component always give either of two values: \(+\hbar\) or \(+2\hbar\), but the \(+2\hbar\) value is found twice as often as the \(+\hbar\) value.

(a) What should we report as the expectation value for this component, i.e., for the quantity \( \langle \hat{L}_z \rangle \)?

The probabilities show us that two out of three measurements yield \( 2\hbar \), while one out of three yields \( \hbar \). The expectation value (the average) must be

\[
\langle \hat{L}_z \rangle = \frac{2(2\hbar) + 1(\hbar)}{3} = \frac{5}{3} \hbar.
\]

(b) What, if anything, do these measurements tell us about the total angular momentum quantum number, \( l \), for this particle?
Since this system has a component as large as $2 \hat{m}$, (so that the $m$ quantum number is at least as large as 2 for this system), and since the $l$ quantum number has to be at least as large as the largest $m$, we must have $l \geq 2$.

(c) Now write the $\phi$-dependent part of the wavefunction for this particle, using only the information about the $z$ component values and probabilities.

The $\phi$ part of the eigenfunctions for angular momenta is the part that depends on the $m$ quantum number, and since this state exhibits two $m$ values, 1 and 2, its total wavefunction must be a linear combination of two eigenfunctions. The coefficients of these two eigenfunctions, when squared, give the probabilities for observing the eigenvalue of the eigenfunction they multiply. The coefficients themselves must be the square roots of the probabilities (which are $1/3$ and $2/3$ here):

$$\Phi(\phi) = c_1 \frac{e^{i\phi}}{\sqrt{2\pi}} + c_2 \frac{e^{2i\phi}}{\sqrt{2\pi}} = \sqrt{\frac{1}{3}} \frac{e^{i\phi}}{\sqrt{2\pi}} + \sqrt{\frac{2}{3}} \frac{e^{2i\phi}}{\sqrt{2\pi}}.$$

3. (12 points) Something called the Virial Theorem for the harmonic oscillator says that for any state, the average value of the kinetic energy always equals the average value of the potential energy, or in terms of operators,

$$\langle T \rangle = \langle V \rangle.$$

(a) For the ground state ($v = 0$), write an expression that relates $\langle T \rangle$, $\langle V \rangle$, and the total energy $E$ in terms of the parameters of the oscillator. Define any other symbols you introduce.

For the ground state of the harmonic oscillator of force constant $k$ and reduced mass $\mu$, the energy is the constant value

$$E = \frac{\hbar \omega}{2} = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}}$$

which is equal to the sum of the expectation values for the kinetic energy and the potential energy:

$$E = \frac{\hbar \omega}{2} = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}} = \langle T \rangle + \langle V \rangle.$$

(b) Now use the Virial Theorem and the expression you wrote in part (a) along with the definition of $\hat{V}$ for the oscillator to find a value for $\langle \hat{x}^2 \rangle$ for this state.

The potential energy operator is just the potential energy, $kx^2/2$, and if we calculate the expectation value of this operator, the constant factor $k/2$ multiplies the expectation value of the square of the coordinate, $\langle x^2 \rangle$. The Virial Theorem, applied to the expression in part (a), tells us that the total energy equals twice the expectation value of the potential energy:

$$E = \frac{\hbar \omega}{2} = \langle T \rangle + \langle V \rangle = 2 \langle \hat{x}^2 \rangle + 2 \frac{k}{2} \langle \hat{x}^2 \rangle = k \langle \hat{x}^2 \rangle.$$

This gives the final expression (which can be written in several equivalent ways)

$$\langle \hat{x}^2 \rangle = \frac{E}{k} = \frac{\hbar \omega}{2k} = \frac{\hbar}{2\sqrt{k\mu}}.$$

(c) Is $\langle \hat{x}^2 \rangle = \langle x \rangle^2$ for the harmonic oscillator? (Explain your answer in English or prove it mathematically. Either is acceptable here.)

By symmetry (the oscillator motion is equally likely to be at $x \geq 0$ as it is to be at $x \leq 0$), the expectation value for $x$ must be zero: $\langle x \rangle = 0$. On the other hand, $x^2$ must
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always be zero (if \( x = 0 \)) or positive (because squares of positive or negative \( x \) values must be positive). Therefore, \( \langle \hat{x}^2 \rangle \) must be greater than zero. Therefore, \( \langle \hat{x}^2 \rangle \neq \langle \hat{x} \rangle^2 \).

4. (5 + 5 + 2 points) Here are some questions about operators and eigenfunctions:

(a) Prove that \( [\hat{L} \hat{z}, \phi] = \frac{\hbar}{i} \) and explain the physical significance of this result.

To prove anything about any operator expression, we must see how the operator operates on some arbitrary function of the coordinates of the operator. Let \( f(\phi) \) be such a function. We write

\[
[\hat{L} \hat{z}, \phi(f(\phi)) = \hat{L} \hat{z} \phi(f(\phi)) - \phi(f(\phi)) \hat{L} \hat{z} f(\phi)
\]

\[
= \frac{\hbar}{i} \frac{\partial f(\phi)}{\partial \phi} \frac{\partial \phi(f(\phi))}{\partial \phi} - \phi \frac{\hbar}{i} \frac{\partial f(\phi)}{\partial \phi} \frac{\partial \phi}{\partial \phi}
\]

\[
= \frac{\hbar}{i} f(\phi)
\]

This proves the commutator relation. Its physical significance stems from the commutator not being equal to zero. The Heisenberg Uncertainty Principle says that for such a situation, we cannot know the value of the physical quantities represented by the two operators in the commutator simultaneously to arbitrary precision.

(b) We’ve written the 1-D particle-in-a-box wavefunctions as \( \psi(x) = \sqrt{2/L} \sin(n \pi x / L) \) with eigenvalues for the total energy as given on the front page of the exam. Show that you get the same eigenvalues if you write \( \psi(x) = \sqrt{2/L} \cos(n \pi x / L) \). (Hint: If you can’t remember the total energy operator for this system—it’s not on the front page—you should be able to construct it if you remember that the total energy here is just kinetic energy and the classical expression for kinetic energy is \( p^2 / 2m \).

The Hamiltonian is

\[
\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2},
\]

and we have

\[
\hat{H} \psi(x) = -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = -\frac{\hbar^2}{2m} \sqrt{\frac{\pi}{L}} \frac{d^2 \cos(n \pi x / L)}{dx^2}
\]

\[
= -\frac{\hbar^2}{2m} \sqrt{\frac{\pi}{L}} \left[ \cos \left( \frac{n \pi x}{L} \right) \right]^2
\]

\[
= \frac{\hbar^2}{2mL^2} \sqrt{\frac{\pi}{L}} \cos \left( \frac{n \pi x}{L} \right)
\]

\[
= \frac{\hbar^2}{2mL^2} \psi(x),
\]

which has the same eigenvalue as the wavefunction we wrote using sine instead of cosine.
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(c) So, given the result from part (b), why didn’t we write our particle-in-a-box wavefunctions as cosine functions?

Most fundamentally, the particle-in-a-box in 1-D is simply a region of length \( L \) of zero potential energy surrounded on both sides with regions of infinite potential energy. At each end of the box, the wavefunction has to equal zero because the wavefunction is zero outside the box, and wavefunction has to vary continuously throughout all space. In class, we chose to set \( x = 0 \) at one end of the box and thus \( x = L \) at the other. This choice forces the wavefunction to be \( \sin(n\pi x/L) \), which is zero at \( x = 0 \) and \( L \). Had we chosen to place \( x = 0 \) at the middle of the box (with edges at \( x = \pm L/2 \)), then a cosine would have been appropriate; \( \cos(n\pi x/L) = 0 \) for \( x = \pm L/2 \).

5. (15 points) Here is a contour plot of a two-dimensional harmonic oscillator wavefunction in a particular state. Note that a few of the contours are labeled to help you distinguish the positive from the negative regions of the wavefunction. Note as well that the force constants of this oscillator are all equal.

Tell me the oscillator’s quantum numbers, the oscillator’s total energy, and the degeneracy of this state (i.e., the total number of states of this oscillator, including this one, with the same energy as this state).

Harmonic oscillator quantum numbers \( \nu \) range from 0 to \( \infty \) in unit steps, and the quantum number counts the number of nodes in the wavefunction for the coordinate with which the quantum number is associated. Here, we have two quantum numbers, call them \( \nu_x \) and \( \nu_y \), and counting nodes in the contour plot shows that \( \nu_x = 3 \) and \( \nu_y = 2 \). The energy expression is

\[
E = \hbar \sqrt{\frac{k_x}{\mu}} \left( \nu_x + \frac{1}{2} \right) + \hbar \sqrt{\frac{k_y}{\mu}} \left( \nu_y + \frac{1}{2} \right) \\
= \hbar \sqrt{\frac{k}{\mu}} (\nu_x + \nu_x + 1) \\
= \hbar \omega (\nu_x + \nu_x + 1) = 6 \hbar \omega .
\]
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The degeneracy equals the number of ways we can write sets of allowed quantum numbers that all have this energy. There are six such sets in all: (0,5), (1,4), (2,3), (3,2), (4,1), (5,0).

6. (16 points) Here are more wavefunction picture questions, both from the web site.

(a) The picture above is the real part of one of the spherical harmonic functions, $Y_{l,m}$. What is its $l$ value?
There are three nodes (all are planes—no cones here!), and $l = \text{the number of nodes}$:
\[ l = 3 \]

(b) Be as specific as you can: what are the three curves shown below?

heavy solid curve: This is the wavefunction for the $v = 5$ state of a 1-D harmonic oscillator.
dotted curve: This is the square of the wavefunction: the probability distribution function.

dashed curve: This is the classical probability distribution for the oscillator’s position. Note that it is largest at the classical turning points of the motion; at these points, the oscillator pauses instantaneously as it reverses direction of motion.

7. (5 points each) A few quick spectroscopic calculations:
(a) A sodium atom spectrum shows a series of absorptions from the ground state, each appearing as doublets, each doublet centered at 16956 cm\(^{-1}\), 30267 cm\(^{-1}\), 35040 cm\(^{-1}\), 37297 cm\(^{-1}\), 38540 cm\(^{-1}\), and so on, ever more closely spaced. What do the excited states of each of these transitions have in common? Since absorptions start in the ground state, since the ground state is 3S for Na, and since the selection rule for transitions from an S state permit transitions only to P states, the excited states are all \(nP\) states.

(b) The energy needed to excite \(H_2\) from its lowest vibrational state to the next highest is about 4381 cm\(^{-1}\) or \(8.703 \times 10^{-20}\) J. What is the \(H_2\) bond force constant? The excitation energy (considering \(H_2\)’s bond to be a harmonic oscillator) is given by
\[
\Delta E = E_1 - E_0 = \frac{\hbar \omega}{2} \sqrt{\frac{k}{\mu}} = 8.703 \times 10^{-20}\text{ J}
\]
where \(k\) is the force constant and \(\mu\) is the reduced mass. The mass of one H atom is about 1 amu, or \(1.66 \times 10^{-27}\) kg, and the reduced mass is
\[
\mu = \frac{m_1 m_1}{m_1 + m_1} = \frac{m_1}{2} = \frac{1.66 \times 10^{-27}\text{ kg}}{2} = 8.30 \times 10^{-28}\text{ kg}
\]
so that \(k\) is
\[
\frac{\Delta E^2 \mu}{\hbar^2} = 560\text{ N m}^{-1}
\]
(c) If an energy of 2000 cm\(^{-1}\) is needed to excite a particle in a 1-D box from its ground to its first excited state, what energy is needed to excite it from the first to the second excited state? Energy for a particle in a box varies as \(n^2\) with \(n = 1, 2, 3, \ldots\) for the ground, first excited, second excited, \ldots states. The energy between \(n = 1\) and 2 (the 2000 cm\(^{-1}\) value) is thus proportional to \((2^2 - 1^2) = 3\), while the 2 to 3 energy difference is proportional to \((3^2 - 2^2) = 5\). Therefore, the excitation energy increases from 2000 cm\(^{-1}\) to \((5/3)(2000 \text{ cm}^{-1}) = 3333 \text{ cm}^{-1}\).