

Unless specified otherwise, you don't need to show all your calculations – simple answers written in the allocated spaces will be sufficient, unless you want me to follow your math. For problems 1-2, if your answers contain h or \hbar or other constants, keep them as letters, no need to substitute them with their numeric values.

Problem 1 (10 points).

A quantum mechanical particle of mass m is in a state described by the following wave function:

$$\Psi = \left(7e^{-i6x} + 6ie^{i3x} - 5ie^{i6x} \right) / \sqrt{2L}$$

Assume it's a free particle defined in the interval $(-L, L)$, where $L \rightarrow \infty$. Using the postulates of QM, answer the following questions:

(A) List all values of the kinetic energy of the particle that can be obtained in a single measurement.

According to the 3rd postulate, the only value(s) you can measure in a single measurement is one

of the eigenvalues of the kinetic energy operator $\hat{K} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$. Because Ψ is not an

eigenfunction of \hat{K} (you can easily check this!), to answer this question you need to present/express Ψ as a linear combination of such eigenfunctions. Luckily, the above expression for Ψ already is a linear combination of three exponentials, and each exponential term in this expression is an eigenfunction of the kinetic energy operator. As we discussed in class, e^{ikx} is an

eigenfunction of \hat{K} , and the corresponding eigenvalue is $\frac{\hbar^2 k^2}{2m}$. Thus, the values of kinetic

energy that will be measured in this state are

$$\frac{\hbar^2 6^2}{2m} = 18 \frac{\hbar^2}{m} \quad (\text{from both the first and third exponential terms}) \quad \text{and} \quad \frac{\hbar^2 3^2}{2m} = 9 \frac{\hbar^2}{2m}; \quad (\text{from the second term}).$$

(B) List all values of the linear momentum p that can be obtained in a single measurement and their probabilities.

The same consideration as above applies here because, generally, e^{ikx} is an eigenfunction of the linear momentum operator, and the corresponding eigenvalue is $\hbar k$. Because each of the exponential terms is already normalized (the $\sqrt{2L}$ in the denominator does this job), the corresponding probability can be calculated as square-modulus of the coefficient in front of the exponential term in the numerator divided by the sum of the square-moduli of all such coefficients in the equation for Ψ . The answers are

$$\text{value} = -6\hbar; \text{probability} = 7^2/(7^2+6^2+5^2) = 49/110$$

$$\text{value} = 3\hbar; \text{probability} = 6^2/(7^2+6^2+5^2) = 36/110$$

$$\text{value} = 6\hbar; \text{probability} = 5^2/(7^2+6^2+5^2) = 25/110$$

(C) Calculate the average value of the linear momentum p that you expect to obtain as a result of a very large number of measurements.

You can calculate the average value of the momentum using statistical consideration, as sum of all different measured values multiplied by their probabilities:

$$\langle p \rangle = \sum_i p_i \times \text{Probability}(p_i) = -6\hbar \frac{49}{110} + 3\hbar \frac{36}{110} + 6\hbar \frac{25}{110} = -\frac{36\hbar}{110} \approx -0.327\hbar$$

Alternatively, you can use the expectation value equation (4th postulate, remember?) and calculate the corresponding integrals in both numerator and denominator (you need to calculate

the denominator because Ψ as defined in this problem is not normalized). I include this calculation below so that you can follow it

$$\begin{aligned} \langle p \rangle &= \frac{\int \Psi^* \hat{p} \Psi dx}{\int \Psi^* \Psi dx} = \frac{-\frac{i\hbar}{2L} \int_{-L}^L (7e^{i6x} - 6ie^{-i3x} + 5ie^{-i6x}) \frac{d}{dx} (7e^{-i6x} + 6ie^{i3x} - 5ie^{i6x}) dx}{\frac{1}{2L} \int_{-L}^L (7e^{i6x} - 6ie^{-i3x} + 5ie^{-i6x})(7e^{-i6x} + 6ie^{i3x} - 5ie^{i6x}) dx} = \\ &= -i\hbar \frac{\frac{1}{2L} \int_{-L}^L (7e^{i6x} - 6ie^{-i3x} + 5ie^{-i6x})(-42ie^{-i6x} - 18e^{-i3x} + 30e^{i6x}) dx}{\frac{1}{2L} \int_{-L}^L (7e^{i6x} - 6ie^{-i3x} + 5ie^{-i6x})(7e^{-i6x} + 6ie^{i3x} - 5ie^{i6x}) dx} = \\ &= -i\hbar \frac{\frac{1}{2L} \int_{-L}^L (-36i + \text{terms containing } e^{iax}) dx}{\frac{1}{2L} \int_{-L}^L (110 + \text{terms containing } e^{iax}) dx} = \xrightarrow{L \rightarrow \infty} -\frac{36}{110} \hbar \end{aligned}$$

(remember that $e^{-ia} \times e^{ia} = 1$, so after opening the brackets in the integrands you will have terms that are just numbers and terms that contain exponential functions e^{iax}). Integrals of those numbers will give $number * 2L / (2L) = number$. The e^{iax} -containing terms will need to be dealt differently, as I mentioned in class. Recall that for a free particle, in order to get Ψ normalized we assumed that the particle is moving in the interval from $-L$ to L , where L is large and eventually set to infinity ($L \rightarrow \infty$). Therefore the integrals of the e^{-iax} -containing terms (where $a \neq 0$) in the numerator and the denominator become negligible when $L \rightarrow \infty$:

$$\frac{1}{2L} \int_{-L}^L e^{iax} dx = \frac{1}{2L} \frac{e^{iaL} - e^{-iaL}}{ia} = \frac{\sin(aL)}{aL} \rightarrow 0 \text{ when } L \rightarrow \infty, \text{ because } \sin(aL) \text{ is bounded}$$

($|\sin(aL)| \leq 1$), and the only non-zero terms come from $\frac{1}{2L} \int_{-L}^L dx = \frac{2L}{2L} = 1$. This gives

$$\langle p \rangle = -i\hbar \frac{-36i}{110} = -\frac{36}{110} \hbar, \text{ the same result as obtained above using the statistics-based approach.}$$

(D) Is the particle more likely to be found moving in the positive or negative direction of the x axis? *Explain your reasoning.*

To answer this question you need to count the total probabilities to find the particle moving in each direction. For this we need to know the sign of the individual p values to be measured in a single measurement in this state and their probabilities. From the answers to Q.B, you know that the second and third terms in Ψ correspond to particle moving in the positive direction of the x -axis while the first term corresponds to particle moving in the negative direction. The combined probability corresponding to the 2nd and 3rd terms is $61/110$, while the probability corresponding to the second term is $49/110$. This means that, for example, in 61 out of 110 measurements you will find the particle moving to the right (positive direction) and in 49 out of 110 it will be found moving to the left. Therefore the particle is more likely to be found moving in the *positive* direction, or from left to right.

Note that this question is about the probability not about the average value of p , which in this case is negative.

Problem 2 (6 points). A particle of mass m in the 1D box ($0 \leq x \leq a$) is in the state corresponding to the quantum number $n=6$. Answer the following questions:

(A) Write the complete expression for the wave function $\Psi(x,t)$ describing the particle. Make sure the wave function is normalized and *explicitly* includes the time dependence.

$$\Psi(x,t) = \Psi_{n=6}(x) \times e^{-i\frac{E_{n=6}t}{\hbar}} = \sqrt{\frac{2}{a}} \sin\left(\frac{6\pi}{a}x\right) \times e^{-i\frac{36\pi\hbar}{4ma^2}t}$$

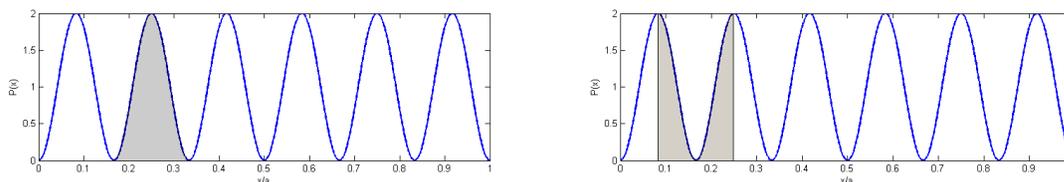
(B) In which points inside the box you are unlikely to find the particle? List their coordinates.

These are nodes, i.e. points where $\Psi(x) = 0$ inside the box, hence $\sin(6\pi x/a) = 0$: $x = a/6, 2a/6, 3a/6, 4a/6,$ and $5a/6$. The particle also cannot be found at the edges of the box: $x = 0$ and $x = a$.

(C) Consider the following two intervals inside the box: (1) $a/6 \leq x \leq a/3$ and (2) $a/12 \leq x \leq a/4$. Calculate and compare the probabilities to find the particle within each interval: which one is more likely? *Explain your reasoning.*

If you plot $P(x)$ (see below) you will find out that, based on the symmetry of $P(x)$, this is one-seventh of the total area under $P(x)$, hence the probability is $1/6$.

Naturally, you can do this by integrating the probability density $P(x)$ from $a/6$ to $2a/6$ or from $a/12$ to $3a/12$ (see below) but it might be simpler to inspect the plot of $P(x)$ – see the figure below where the corresponding areas of interest are shaded



For example, a direct integration of the probability density over the first interval gives:

$$P\left(\frac{a}{6} \leq x \leq \frac{2a}{6}\right) = \int_{a/6}^{2a/6} [\Psi_6(x)]^2 dx = \frac{2}{a} \int_{a/6}^{2a/6} \sin^2\left(\frac{6\pi}{a}x\right) dx = \frac{1}{a} \int_{a/6}^{2a/6} \left[1 - \cos\left(\frac{12\pi}{a}x\right)\right] dx =$$

$$= \frac{a}{6a} - \frac{1}{a} \frac{a}{12\pi} [\sin(4\pi) - \sin(2\pi)] = \frac{1}{6}$$

Problem 3 (3 points). A particle in a 1D box ($0 \leq x \leq a$) is in a state described by the wave function $\Psi = A(ax - x^2)$. This is an acceptable wave function for a particle in a 1D box, see, for example, Problem 4.16 in the textbook. Is the particle in a stationary state? *Explain your reasoning and support it with calculations.*

It's easy to see that Ψ is not an eigenfunction of the Hamiltonian by acting directly on Ψ :

$$\hat{H}\Psi = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \left\{ A(ax - x^2) \right\} = A \frac{\hbar^2}{m} \neq C\Psi, \text{ and therefore we can qualitatively conclude that it}$$

does not correspond to a stationary state. But we can do more, namely substitute this results into the right-hand-side of the time-dependent Schrödinger equation and then solve it for Ψ as a function of time:

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H}\Psi = A \frac{\hbar^2}{m} \rightarrow \Psi(t) = -iA \frac{\hbar}{m} t + \Psi(0)$$

This function gives the probability density that is time dependent:

$$P \propto |\Psi(t)|^2 = \left[iA \frac{\hbar}{m} t + \Psi^*(0) \right] \left[-iA \frac{\hbar}{m} t + \Psi(0) \right] = A^2 \frac{\hbar^2}{m^2} t^2 + iA \frac{\hbar}{m} t [\Psi(0) - \Psi^*(0)] + |\Psi(0)|^2,$$

which means that the state described by this wave function is not a stationary state.

Problem 4 (6 points). As a simplified model of the hydrogen atom, consider an electron in a 1D box with the size of 1 Å (=10⁻¹⁰ m) (approximately the diameter of the lowest orbit in Bohr's model).

(A) Calculate the energy difference, ΔE , between the ground state and the first excited state of the electron. *Show your calculation.*

The ground state of a particle (in this case electron) in a 1D box corresponds to the quantum number n equal 1. The first excited state corresponds to n equal 2.

$$\Delta E = E_{n=2} - E_{n=1} = \frac{h^2}{8ma^2} (2^2 - 1) = \frac{3h^2}{8ma^2}. \text{ Substituting } m=m_e=9.1 \times 10^{-31} \text{ kg; } a=10^{-10} \text{ m, we get}$$

$$\Delta E_{\text{electron}} = 1.8 \cdot 10^{-17} \text{ J.}$$

(B) Now consider the same box as a model for the nucleus of the hydrogen atom. Perform the same calculation as in question A, now for the proton.

$$\text{Substituting } m = m_p = 1.67 \times 10^{-27} \text{ kg in the equation in Q.A we get } \Delta E_{\text{proton}} = 9.86 \times 10^{-21} \text{ J.}$$

(C) Compare your results in A and B with the average kinetic energy ($\frac{1}{2} k_B T$ per degree of freedom) at room temperature (assume $T = 300$ K) to answer the question whether classical or quantum mechanics should be used to describe each of these particles in this model.

$$\langle E_{\text{thermal}} \rangle = \frac{1}{2} k_B T = 2.07 \times 10^{-21} \text{ J at } T=300 \text{ K (it's a 1-D motion, hence one degree of freedom).}$$

For electron $\Delta E_{\text{electron}} \approx 8740 \times \langle E_{\text{thermal}} \rangle$, therefore, QM must be used in this case.

For the proton, $\Delta E_{\text{proton}} \approx 4.8 \times \langle E_{\text{thermal}} \rangle$, so QM is the preferred treatment in this case too.