

Problem 1. (30 points) Consider a particle of mass m in a 1-D box defined by the following potential energy: $V(x) = 0$ for $0 \leq x \leq a$, and $V(x) = \infty$ for $x < 0$ and $x > a$. The particle is in a state described by the following (unnormalized) wave function: $\Psi(x) = \sqrt{\frac{2}{a}} \left[4 \sin\left(\frac{3\pi}{a}x\right) - 3 \sin\left(\frac{5\pi}{a}x\right) \right]$. Answer the following questions.

A. List all values of the energy of the particle that one can obtain in a single measurement in this state and the corresponding probabilities to measure these values.

From inspecting the individual terms in $\Psi(x)$ it is clear that they are solutions for the particle-in-a-box problem, i.e., $\Psi_{n=3} = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right)$, and $\Psi_{n=5} = \sqrt{\frac{2}{a}} \sin\left(\frac{5\pi x}{a}\right)$, which (by definition) are eigenfunctions of the energy operator, corresponding to n values of $n=3$, and $n=5$, respectively. The (unnormalized) projection coefficients are $b_{n=3} = 4$ and $b_{n=5} = -3$, respectively. Therefore, the energy values that can be obtained in a single measurement are

Energy:

Probability:

$$E_{n=3} = \frac{h^2}{8ma^2} 3^2 = \frac{9h^2}{8ma^2} \text{ with the probability } P_{n=3} = 4^2 / (4^2 + 3^2) = 16/25 = 0.64$$

$$E_{n=5} = \frac{h^2}{8ma^2} 5^2 = \frac{25h^2}{8ma^2} \text{ with the probability } P_{n=5} = (-3)^2 / (4^2 + 3^2) = 9/25 = 0.36$$

Since all these individual wave functions have the same normalization coefficient, to determine the probabilities we just need to square the coefficients “ b ” and normalize them such that the sum of all probabilities equals 1.

B. Calculate the average value of the energy of the particle that will be measured as a result of multiple measurements in this state.

Using statistical approach, as we discussed many times in class,

$$\langle E \rangle = E_{n=3} P_{n=3} + E_{n=5} P_{n=5} = \frac{9h^2}{8ma^2} \frac{16}{25} + \frac{25h^2}{8ma^2} \frac{9}{25} = \frac{369}{25} \frac{h^2}{8ma^2} = \frac{369}{200} \frac{h^2}{ma^2} = 1.84 \frac{h^2}{ma^2}$$

The same result can be obtained by plugging Ψ into the equation for the 4th postulate and directly

evaluating the integrals, taking into account that the wave functions $\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ are

orthonormal, such that only those terms containing the square of the same wave function give nonzero integrals:

$$\begin{aligned} \langle E \rangle &= \frac{\int_0^a \Psi(x)^* \hat{H} \Psi(x) dx}{\int_0^a \Psi(x)^* \Psi(x) dx} = \frac{\int_0^a [4\Psi_{n=3}(x) - 3\Psi_{n=5}(x)] [4E_{n=3}\Psi_{n=3}(x) - 3E_{n=5}\Psi_{n=5}(x)] dx}{\int_0^a [4\Psi_{n=3}(x) - 3\Psi_{n=5}(x)] [4\Psi_{n=3}(x) - 3\Psi_{n=5}(x)] dx} = \\ &= \frac{4^2 E_{n=3} \int_0^a \Psi_{n=3}(x) \Psi_{n=3}(x) dx + 3^2 E_{n=5} \int_0^a \Psi_{n=5}(x) \Psi_{n=5}(x) dx}{4^2 \int_0^a \Psi_{n=3}(x) \Psi_{n=3}(x) dx + 3^2 \int_0^a \Psi_{n=5}(x) \Psi_{n=5}(x) dx} = \frac{16E_{n=3} + 9E_{n=5}}{16 + 9} = \frac{369}{25} \frac{h^2}{8ma^2} = \frac{369}{200} \frac{h^2}{ma^2} \end{aligned}$$

C. List all values of the momentum of the particle that one can obtain in a single measurement in this state and the average value of the momentum that will be measured as a result of multiple measurements.

Because $\sin \alpha = (e^{i\alpha} - e^{-i\alpha}) / 2i$, the wave function can be rewritten as

$$\Psi(x) = \frac{1}{2i} \sqrt{\frac{2}{a}} \left[4 \left(e^{\frac{3\pi x}{a}} - e^{-\frac{3\pi x}{a}} \right) - 3 \left(e^{\frac{5\pi x}{a}} - e^{-\frac{5\pi x}{a}} \right) \right].$$
 Each of the exponentials is an eigenfunction of the

momentum operator, so this expression presents the wave function Ψ as a superposition of four eigenfunctions of the momentum operator. The values of the momentum that will be measured are the corresponding eigenvalues: $3\pi\hbar/a$, $-3\pi\hbar/a$, $5\pi\hbar/a$, and $-5\pi\hbar/a$, or after simplification by cancelling π : $1.5\hbar/a$, $-1.5\hbar/a$, $2.5\hbar/a$, and $-2.5\hbar/a$. It is also clear from the above expression that the values of the momentum with the “+” and “-” sign are equally probable, therefore the average measured value is expected to be zero.

Problem 2. (15 points) Is it possible to know with arbitrary precision both the angular coordinate ϕ and the angular momentum l_z of a particle moving on a ring? Support your answer by evaluating the corresponding commutator. Based on your results, formulate a mathematical equation representing the uncertainty principle for these two observables.

Evaluate the commutator of the corresponding QM operators:

$$[\hat{\phi}, \hat{l}_z] \Psi = \left[\hat{\phi}, -i\hbar \frac{d}{d\phi} \right] \Psi = -i\hbar \left(\phi \frac{d}{d\phi} \Psi - \frac{d}{d\phi} \phi \Psi \right) = -i\hbar \left(\phi \frac{d}{d\phi} \Psi - \Psi - \phi \frac{d}{d\phi} \Psi \right) = i\hbar \Psi. \text{ Thus}$$

$[\hat{\phi}, \hat{l}_z] = i\hbar$. Because the commutator is not zero, we conclude that the corresponding two physical observables (the angular momentum l_z and the angular coordinate ϕ of the particle) cannot be known simultaneously with arbitrary precision.

By full analogy of this commutator with the commutator for \hat{x} and \hat{p} , and the analogy between x and ϕ and between p and l_z , we can formulate the uncertainty principle for ϕ and l_z as $\Delta\phi \times \Delta l_z \geq \frac{\hbar}{2}$. The same

result can be obtained rigorously by plugging in $[\hat{\phi}, \hat{l}_z] = i\hbar$ into the equation that relates the uncertainties of observables A and B to the commutator of the corresponding operators:

$$\Delta A \times \Delta B \geq \frac{1}{2} \left| \langle [\hat{A}, \hat{B}] \rangle \right| \rightarrow \Delta\phi \times \Delta l_z \geq \frac{1}{2} |i\hbar| = \frac{\hbar}{2}.$$

Problem 3. (25 points) A quantum mechanical harmonic oscillator with mass μ and force (spring) constant k is in a state characterized by the quantum number $n = 2$.

A. Write the expression for the probability density to find the oscillator at a given value of coordinate x .

$$P(x) = |\Psi_{n=2}(x)|^2 = (\Psi_{n=2}(x))^2 = \frac{1}{2} \left(\frac{\alpha}{\pi} \right)^{1/2} (2\alpha x^2 - 1)^2 e^{-\alpha x^2}$$

Notes after grading: no points were given when the probability density was written as an integral; in this case 2 pnts were given for correct expression for $\Psi_{n=2}(x)$.

B. Determine the nodes, i.e. the values of coordinate x at which there is zero probability to find the oscillator.

The probability density = 0 when $2\alpha x^2 - 1 = 0 \rightarrow x = \pm \sqrt{\frac{1}{2\alpha}} = \pm \sqrt{\frac{\hbar}{2\sqrt{k\mu}}}$

C. Where are you more likely to find the quantum mechanical oscillator: at the very bottom of the potential well (i.e. at $x = 0$) or at the turning points of the classical oscillator (where its total energy equals its potential energy, i.e., $E_n = \frac{kx^2}{2}$)? Support your answer by calculating the corresponding probability densities.

The probability density to find the quantum harmonic oscillator at the bottom of the potential well is

$$P(x=0) = |\Psi_{n=2}(0)|^2 = \frac{1}{2} \left(\frac{\alpha}{\pi} \right)^{1/2}.$$

The turning points (I'll designate them here as x_{\max}) for the classical harmonic oscillator with energy E

obey the equation $E = \frac{kx_{\max}^2}{2} \rightarrow x_{\max}^2 = \frac{2E}{k}$ (or $x_{\max} = \pm \sqrt{\frac{2E}{k}}$). For a quantum harmonic oscillator in the

state with $n=2$, $E_{n=2} = \frac{5}{2} \hbar \nu = \frac{5}{2} \hbar \sqrt{\frac{k}{\mu}}$, and $x_{\max}^2 = \frac{5}{k} \hbar \sqrt{\frac{k}{\mu}} = \frac{5\hbar}{\sqrt{k\mu}}$. Since the expression for $P(x)$ contains

x^2 only as a product with α (see the answer to Q.A), it is helpful to first calculate $\alpha x_{\max}^2 = \frac{5\hbar}{\sqrt{k\mu}} \frac{\sqrt{k\mu}}{\hbar} = 5$.

(You can easily obtain a more general relationship: $\alpha x_{\max}^2 = 2n+1$ for a state with the quantum number n .) Substituting this result into the expression for $P(x)$ we obtain the probability density to find the oscillator at one of the two turning point to be

$$P(x_{\max}) = \frac{1}{2} \left(\frac{\alpha}{\pi} \right)^{1/2} (2\alpha x_{\max}^2 - 1)^2 e^{-\alpha x_{\max}^2} = \frac{1}{2} \left(\frac{\alpha}{\pi} \right)^{1/2} (2 \cdot 5 - 1)^2 e^{-5} = \frac{1}{2} \left(\frac{\alpha}{\pi} \right)^{1/2} 81 \times e^{-5} = 0.5458 \cdot P(x=0).$$

Thus, the quantum harmonic oscillator is more likely to be found at the bottom of the potential than *at one of the turning points*. However, if we sum up the probabilities for each of the two turning point, then the total probability to find the oscillator *at the turning points* is slightly higher than to find it at the bottom of the potential well: $P = 2 \cdot P(x_m) = 1.0916 \cdot P(x=0) > P(x=0)$.

Problem 4. (30 points) Consider a chlorine molecule (Cl_2) in gas phase. Assume that there is no coupling between the translational, vibrational, and rotational states, i.e. these motions are independent from each other. You studied this molecule and obtained the following results: the quantum of energy absorbed upon transition from the ground state to the first excited rotational state is 9.6864×10^{-24} J; the quantum of energy required for a transition from the ground state to the first vibrational state is 1.112×10^{-20} J. Answer the following questions. The atomic mass of Cl is 35 a.m.u.

A. From these data, determine the equilibrium bond length in the molecule. Explain your assumptions. Assume that rotational motion of the molecule can be described by the particle-on-a-sphere (or 3D rigid rotor) model.

Using the energy conservation law, the quantum of energy absorbed upon a transition between rotational

states is $\Delta E^{\text{rot}} = E_{l=1}^{\text{rot}} - E_{l=0}^{\text{rot}} = \frac{\hbar^2}{2\mu r^2} 2 = \frac{\hbar^2}{\mu r^2}$, where r is the equilibrium bond length. From here we

determine the bond length: $r = \sqrt{\frac{\hbar^2}{\mu \Delta E^{\text{rot}}}} = \hbar \sqrt{\frac{1}{\mu \Delta E^{\text{rot}}}} = 1.988 \times 10^{-10} \text{ m} = 1.988 \text{ \AA}$. (The reduced mass of

Cl_2 is $\mu = 35/2 \text{ amu} = 2.905 \times 10^{-26} \text{ kg}$)

B. Determine the force (spring) constant for the Cl-Cl bond. Explain your assumptions.

Assume that bond vibrations in Cl_2 can be described by the harmonic oscillator model. Using the energy

conservation law: $\Delta E^{\text{vibr}} = E_{n+1}^{\text{vibr}} - E_n^{\text{vibr}} = h\nu = \hbar \sqrt{\frac{k}{\mu}}$. From here, we determine the force constant to be

$$k = \mu \left(\frac{\Delta E^{\text{vibr}}}{\hbar} \right)^2 = 323 \text{ N/m}.$$

C. Assume the chlorine molecule is placed in a 3-D box/cube of size 10 \AA ($1 \text{ \AA} = 10^{-10} \text{ m}$). Calculate the energy of the ground state of translational motion of the molecule in that box.

Using solutions for a particle in a 3D box, the ground state corresponds to each of the three quantum

numbers equal 1. It's energy equals $E_{1,1,1} = \frac{h^2}{8ma^2} (1^2 + 1^2 + 1^2) = \frac{h^2 3}{8ma^2} = 1.4169 \times 10^{-24} \text{ J}$. Here $m = 70 \text{ amu} = 1.162 \times 10^{-25} \text{ kg}$ is the total mass of Cl_2 molecule.