

**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:  $\Psi(x) = \sqrt{\frac{2}{a}} \left[ 5 \sin\left(\frac{3\pi}{a}x\right) - 3 \sin\left(\frac{5\pi}{a}x\right) \right]$ . 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  $b_{n=3} = 5$  and  $b_{n=5} = -3$ , respectively. Therefore, the energy values that can be obtained in a single measurement are

Energy:

Probability:

$$E_{n=3} = \frac{h^2}{8ma^2} 3^2 = \frac{9h^2}{8ma^2} \text{ with the probability } P_{n=3} = \frac{5^2}{(5^2+3^2)} = \frac{25}{34} = 0.7353$$

$$E_{n=5} = \frac{h^2}{8ma^2} 5^2 = \frac{25h^2}{8ma^2} \text{ with the probability } P_{n=5} = \frac{(-3)^2}{(5^2+3^2)} = \frac{9}{34} = 0.2646$$

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,

$$\langle E \rangle = E_{n=3} P_{n=3} + E_{n=5} P_{n=5} = \frac{9h^2}{8ma^2} \frac{25}{34} + \frac{25h^2}{8ma^2} \frac{9}{34} = \frac{450}{34} \frac{h^2}{8ma^2} = \frac{225}{136} \frac{h^2}{ma^2} = 1.6544 \frac{h^2}{ma^2}$$

The same result can be obtained by plugging  $\Psi$  into the equation for the 4<sup>th</sup> 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:

$$\begin{aligned} \langle E \rangle &= \frac{\int_0^a \Psi(x)^* \hat{H} \Psi(x) dx}{\int_0^a \Psi(x)^* \Psi(x) dx} = \frac{\int_0^a [5\Psi_{n=3}(x) - 3\Psi_{n=5}(x)] [5E_{n=3}\Psi_{n=3}(x) - 3E_{n=5}\Psi_{n=5}(x)] dx}{\int_0^a [5\Psi_{n=3}(x) - 3\Psi_{n=5}(x)] [5\Psi_{n=3}(x) - 3\Psi_{n=5}(x)] dx} = \\ &= \frac{5^2 E_{n=3} \int_0^a \Psi_{n=3}(x) \Psi_{n=3}(x) dx + 3^2 E_{n=5} \int_0^a \Psi_{n=5}(x) \Psi_{n=5}(x) dx}{5^2 \int_0^a \Psi_{n=3}(x) \Psi_{n=3}(x) dx + 3^2 \int_0^a \Psi_{n=5}(x) \Psi_{n=5}(x) dx} = \frac{25E_{n=3} + 9E_{n=5}}{25 + 9} = \frac{450}{34} \frac{h^2}{8ma^2} = \frac{225}{136} \frac{h^2}{ma^2} \end{aligned}$$

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

Neither  $\Psi_{n=3}$  nor  $\Psi_{n=5}$  is an eigenfunction of the momentum operator. However, because

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

$$\Psi(x) = \frac{1}{2i} \sqrt{\frac{2}{a}} \left[ 5 \left( e^{i\frac{3\pi x}{a}} - e^{-i\frac{3\pi x}{a}} \right) - 3 \left( e^{i\frac{5\pi x}{a}} - e^{-i\frac{5\pi x}{a}} \right) \right].$$

Each of the exponentials here is an eigenfunction of the momentum operator, so this expression presents the wave function  $\Psi$  as a superposition of four eigenfunctions of the momentum operator. The values of the momentum that will be measured in single measurements 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  $\pi$ :  $1.5h/a$ ,  $-1.5h/a$ ,  $2.5h/a$ , and  $-2.5h/a$ . It is also clear from the above expression that the values of the momentum with the “+” and “-” sign are equally probable, therefore the average value of the momentum obtained in multiple measurements is expected to be zero:  $\langle p \rangle = 0$ .

You can come to the same conclusion by using the expectation value equation.

**Problem 2.** (30 points) A quantum mechanical harmonic oscillator with mass  $\mu$  and force (spring) constant  $k$  is in a stationary 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  $x$ .

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

B. Determine the nodes, i.e. the values of coordinate  $x$  where 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 corresponding 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  $n = 2$ ,  $E_{n=2} = \frac{5}{2} h\nu = \frac{5}{2} \hbar \sqrt{\frac{k}{\mu}}$ , 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  $\alpha$  (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 take into account that there are two turning points, and sum up the probabilities for each of the two turning points, 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 3.** (30 points) Consider a fluorine molecule ( $F_2$ ) absorbed on a flat surface. Assume that there is no coupling between the translational, vibrational, and rotational states, i.e. these motions are independent of 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  $1.768 \times 10^{-23}$  J; the quantum of energy required for a transition from the ground state to the first vibrational state is  $1.821 \times 10^{-20}$  J. Answer the following three questions (Note: question C is on the next page).

**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-ring (or 2D rigid rotor) model. Using the energy conservation law, the quantum of energy absorbed upon a transition

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

here we determine the bond length:  $r = \sqrt{\frac{\hbar^2}{2\mu \Delta E^{rot}}} = \frac{\hbar}{\sqrt{2\mu \Delta E^{rot}}} = 1.412 \times 10^{-10} \text{ m} = 1.412 \text{ \AA}$ .

(The reduced mass of  $F_2$  is  $\mu = 19/2 \text{ amu} = 1.577 \times 10^{-26} \text{ kg}$ )

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

Assume that bond vibrations in  $F_2$  can be described by the harmonic oscillator model. Using the energy

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

$$k = \mu \left( \frac{\Delta E^{vibr}}{\hbar} \right)^2 = 470 \text{ N/m}.$$

**C.** Assume the fluorine molecule's translational motion is restricted to a square 2-D box with the side length of  $10 \text{ \AA}$  ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ). Calculate the energy of the ground state of translational motion of the molecule in that box.

Using solutions for a particle in a 2-D box, the ground state corresponds to each of the two quantum

numbers equal 1. Its energy equals  $E_{1,1} = \frac{h^2}{8ma^2} (1^2 + 1^2) = \frac{h^2 2}{8ma^2} = \frac{h^2}{4ma^2} = 1.74 \times 10^{-24} \text{ J}$ . Here  $m = 38 \text{ amu} = 6.3 \times 10^{-26} \text{ kg}$  is the total mass of  $F_2$  molecule.

**Problem 4.** (10 points) Consider a quantum mechanical particle on a ring (2D rigid rotor) in a state described by the following wave function:  $\Psi(\phi) = \frac{1}{\sqrt{2\pi}} [2ie^{i3\phi} + 5e^{-i3\phi}]$ . Is this a stationary state?

Explain your reasoning and support your answer by calculations.

A stationary state is the state where the probability density is time independent. Therefore, to answer this question you need to consider/calculate the probability density using time-dependent form of the wave function in question. This means that for the individual wave functions you need to use solutions for the time-dependent Schrödinger equation. The individual wave functions in this expression are eigenfunctions of the Hamiltonian corresponding to the states of a particle on a ring with the quantum numbers  $m_l = 3$

and  $m_l = -3$ . These states have the same value of energy (degeneracy):  $E_{m_l=3} = E_{m_l=-3} = \frac{9\hbar^2}{2I}$ , therefore, we

can write:  $\Psi(\phi, t) = \frac{1}{\sqrt{2\pi}} [2ie^{i3\phi} e^{-iE_{m_l=3}t/\hbar} + 5e^{-i3\phi} e^{-iE_{m_l=-3}t/\hbar}] = \frac{1}{\sqrt{2\pi}} [2ie^{i3\phi} + 5e^{-i3\phi}] e^{-iE_{m_l=3}t/\hbar}$ , and the

corresponding probability density  $P(\phi, t) = |\Psi(\phi, t)|^2 = \frac{1}{2\pi} [2ie^{i3\phi} + 5e^{-i3\phi}]^2$  is time-independent.

You can arrive at the same answer by verifying that  $\Psi(\phi)$  is an eigenfunction of the Hamiltonian operator for particle on a ring.

$$\begin{aligned} \hat{H}\Psi(\phi) &= -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} \Psi(\phi) = -\frac{\hbar^2}{2I} \frac{1}{\sqrt{2\pi}} \left[ 2i \frac{d^2}{d\phi^2} e^{i3\phi} + 5 \frac{d^2}{d\phi^2} e^{-i3\phi} \right] = \\ &= -\frac{\hbar^2}{2I} \frac{1}{\sqrt{2\pi}} \left[ -9 \times 2ie^{i3\phi} - 9 \times 5 \frac{d^2}{d\phi^2} e^{-i3\phi} \right] = \frac{9\hbar^2}{2I} \frac{1}{\sqrt{2\pi}} \left[ 2ie^{i3\phi} + 5 \frac{d^2}{d\phi^2} e^{-i3\phi} \right] = \frac{9\hbar^2}{2I} \Psi(\phi) \end{aligned}$$

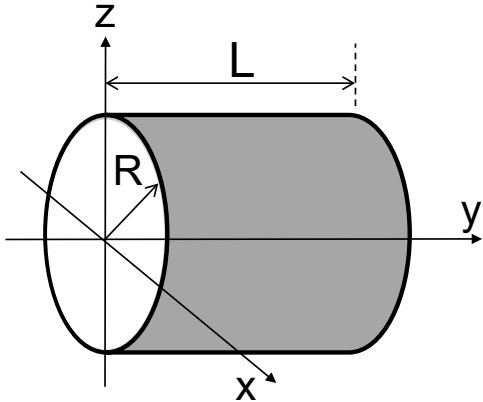
If you are done with the rest of the problems, you might want to solve the following one for an extra credit.

**Bonus question.** (10 points)

Consider a quantum mechanical particle of mass  $m$  moving on the outer surface of a hollow horizontal cylinder (tube) of radius  $R$  and length  $L$ , see the drawing below. Ignore the gravitational force. Write the expressions for the energies and the wave functions that correspond to stationary states of the particle.

*Explain your reasoning.*

*Hint:* you can but don't need to write and solve the Schrödinger equation to answer these questions – just consider what motions the particle is involved in, try to decompose them into simple independent motions and use solutions to the respective problems that we already covered in this course.



Motion of a particle on the surface of the cylinder can be decomposed into two independent motions: (1) 1-D translational motion along the  $y$  axis and (2) 2-D rotational motion on a ring of radius  $R$  that is parallel to the  $x$ - $z$  plane (imagine slicing the cylinder perpendicular to the  $y$  axis like a “salami”). The first motion can be modeled by the free particle in a 1D box with infinite walls model (as the motion along the  $y$  axis is limited to the interval  $(0, L)$  but otherwise no force is applied along the  $y$  axis). The second motion can be modeled by a free particle on a ring of radius  $R$ . We already know now to describe each of this motions in QM, and the respective quantization rules.

$$E^{trans} = E_n = \frac{\hbar^2 n^2}{8mL^2} \text{ where } n = 1, 2, 3, \dots$$

$$E^{2Drot} = E_{m_l} = \frac{\hbar^2}{2mR^2} m_l^2 \text{ where } m_l = 0, \pm 1, \pm 2, \pm 3, \dots$$

Because these motions are independent of each other, their energies add and wave functions multiply:

$$E = E^{trans} + E^{2Drot} = \frac{\hbar^2 n^2}{8mL^2} + \frac{\hbar^2}{2mR^2} m_l^2$$

$$\Psi(y, \phi) = \Psi^{trans}(y) \times \Psi^{2Drot}(\phi) = \Psi_n(y) \times \Psi_{m_l}(\phi) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi n}{L} y\right) \times \frac{1}{\sqrt{2\pi}} e^{im_l \phi}$$