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CHM 3411, Dr. Chatfield, February 2, 2009

Exam 1

Each problem is worth 20 points. You may a calculator, your text and notes but not a laptop. If you need extra room, you may use scratch paper, but ***put all final answers on the exam itself***. ***Read all problems carefully***. Set up problems methodically, show your work, and be neat. Partial credit will be given when it is possible for me to follow your work. If you are having trouble with a problem, go on to the next and come back. GOOD LUCK!

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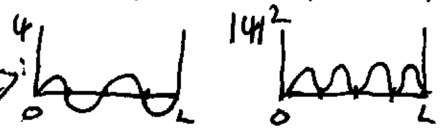
1. Consider the n=4 state of a one-dimensional particle in a box of length L situated along the x axis between 0 and L.

(a) What are the positions (x values) of maximum probability and of minimum probability for finding the particle?

By symmetry:



minima: $0, \frac{L}{4}, \frac{L}{2}, \frac{3L}{4}, L = x$

maxima: $\frac{L}{8}, \frac{3L}{8}, \frac{5L}{8}, \frac{7L}{8} = x$

[If you want to show mathematically, set $\frac{d}{dx}\psi^*\psi = 0$ with $\psi = \sqrt{\frac{2}{L}} \sin\frac{4\pi x}{L}$ and solve for x, test for min. or max.]

(b) Determine the probability of finding the particle between x=0.125L and x=0.5L

$$P = \int_{0.125L}^{0.5L} \psi^*\psi \, dx \qquad \psi = \sqrt{\tfrac{2}{L}} \sin\frac{4\pi x}{L}$$

$$= \frac{2}{L}\int_{0.125L}^{0.5L} \sin^2\frac{4\pi x}{L}\,dx = \frac{2}{L}\left[\frac{x}{2} - \frac{\sin\left[2\left(\frac{4\pi x}{L}\right)\right]}{4(4\pi/L)}\right]_{0.125L}^{0.5L}$$

$$= \frac{2}{L}\left[\frac{L}{4} - \underbrace{\frac{\sin 4\pi}{16\pi/L}}_{0} - \underbrace{\frac{0.125L}{2}}_{\frac{L}{16}} + \underbrace{\frac{\sin\pi}{16\pi/L}}_{0}\right] = \frac{6}{16} = \boxed{\frac{3}{8} = P}$$

(c) If the particle is excited from the n=4 to the n=5 state by absorbing a photon, what is the wavelength of the photon? Take the mass of the particle to equal the mass of an electron, and the length of the box to be L=0.2 nm.

$$\Delta E = E_5 - E_4 = \frac{5^2h^2}{8mL^2} - \frac{4^2h^2}{8mL^2} = (25-16)\frac{h^2}{8mL^2}$$

$h = 6.626\times10^{-34}$ J s $m = 9.109\times10^{-31}$ kg $L = 0.2\times10^{-9}$ m

$$= 1.34\times10^{-17}\ \text{J}$$

$$h\nu = \Delta E \Rightarrow \nu = \frac{\Delta E}{h} = 2.024\times10^{16}\ \text{s}^{-1}$$

$$\lambda = \frac{c}{\nu} = 1.48\times10^{-8}\ \text{m} = \boxed{14.8\ \text{nm} = \lambda}$$

2. Consider the following wavefunction for a one dimensional Schrödinger equation (not an eigenfunction of the particle in a box):

$\psi(x) = N(L^2 - x^2)$ $-L < x < L$

$\psi(x) = 0$ otherwise

(a) Determine the value of N that normalizes the above function.

$$1 = \int_{-\infty}^{\infty} \psi^* \psi \, dx = N^2 \int_{-L}^{L} (L^2 - x^2)^2 \, dx = N^2 \int_{-L}^{L} (L^4 - 2L^2x^2 + x^4)\, dx$$

$$\frac{1}{N^2} = L^4 x - \frac{2L^2}{3} x^3 + \frac{1}{5} x^5 \Big|_{-L}^{L} = L^5 - \frac{2}{3}L^5 + \frac{1}{5}L^5 + L^5 - \frac{2}{3}L^5 + \frac{1}{5}L^5$$

$$= \frac{16}{15}L^5 \qquad \boxed{N = \left(\frac{15}{16L^5}\right)^{1/2}}$$

(b) Determine <p>, the expectation value for the momentum.

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p} \psi \, dx = \frac{\hbar}{i}\left(\frac{15}{16L^5}\right) \int_{-L}^{L} (L^2 - x^2) \underbrace{\frac{d}{dx}(L^2 - x^2)}_{-2x} \, dx$$

$$\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$$

$$= \frac{\hbar}{i}\left(\frac{15}{16L^5}\right) \underbrace{\int_{-L}^{L} (-2)(L^2 x - x^3)\, dx}_{= -2\left[\frac{L^2}{2}x^2 - \frac{1}{4}x^4\right]_{-L}^{L} = 0}$$

$$\boxed{\langle p \rangle = 0}$$

(c) Determine <p^2>, the expectation value for the square of the momentum.

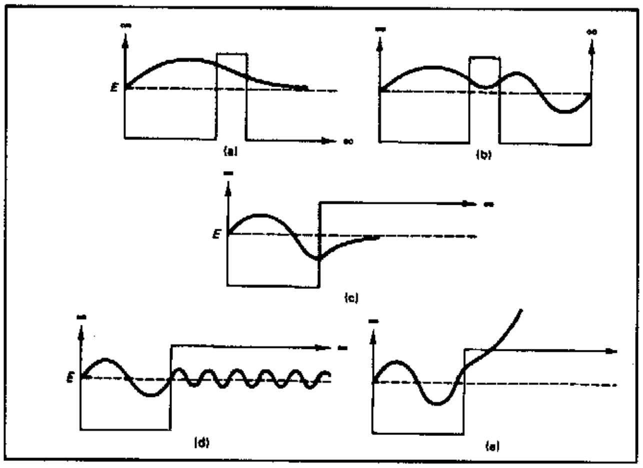
$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p}^2 \psi \, dx = N^2(-\hbar^2) \underbrace{\int_{-L}^{L} (L^2 - x^2) \underbrace{\frac{d^2}{dx^2}(L^2 - x^2)}_{-2} \, dx}$$

$$-2\int_{-L}^{L} (L^2 - x^2)\, dx = -2\left[L^2 x - \frac{1}{3}x^3\right]_{-L}^{L}$$

$$= -2\left(L^3 - \frac{1}{3}L^3 + L^3 - \frac{1}{3}L^3\right) = -\frac{8}{3}L^3$$

$$\langle p^2 \rangle = \frac{8}{3}\left(\frac{15}{16L^5}\right)\hbar^2 = \boxed{\frac{5}{2L^2}\hbar^2 = \langle p^2 \rangle}$$

3. In a few words, indicate what is wrong with the wavefunctions sketched in the potentials shown below. If the solution appears to be acceptable, indicate this fact. Give your explanations at the bottom of the page. (The wavefunctions may be complex, but only the real parts are shown.)



(a) Wrong. Should oscillate, not decay, on right of barrier where E>V.

(b) Wrong. By symmetry, wavelength should be same on both sides of barrier (kinetic energy same).

(c) Wrong. Should not have cusp at edge of barrier (ψ must be smooth). [Also accepted "correct" because cusp hard to see.]

(d) Wrong. Should decay, not oscillate, within barrier where E<V.

(e) Wrong. Should not increase without bound as $x \to \infty$.

4. A particle of mass m is confined to a one-dimensional box of length L. Suppose that the state of the particle is given by the normalized wavefunction:

$$\psi = \frac{1}{3}\psi_1 + \frac{1}{3}\psi_2 + \left(\frac{7}{9}\right)^{1/2}\psi_3$$

where $\psi_n(x)$ is a normalized particle-in-a-box wavefunction corresponding to quantum number n. Such a sum is called a "superposition of states" because the state of the system, ψ, is not itself an eigenfunction of the Hamiltonian, but it can be written as a sum of such eigenfunctions.

(a) What are the possible outcomes when an individual measurement of the energy of the particle is made (i.e. what are the possible measured values of the energy)? Give you answer in terms of h, m, and L.

An individual measurement of energy must be an eigenfunction of the corresponding operator, i.e. $\hat{H}$. The wavefunction is a sum of eigenfunctions for $n=1,2,3$. Thus ~~three~~ individual measurements are possible:

$$\boxed{E_1 = \frac{h^2}{8mL^2}, \quad E_2 = \frac{4h^2}{8mL^2}, \quad E_3 = \frac{9h^2}{8mL^2}}$$

(b) What is the expectation value of the energy (<E>), i.e. the mean value of many measurements? Give you answer in terms of h, m, and L.

$$\langle E\rangle = \int \psi^* \hat{H}\psi\, dx = \int \left(\tfrac{1}{3}\psi_1 + \tfrac{1}{3}\psi_2 + \sqrt{\tfrac{7}{9}}\psi_3\right)^* \underbrace{\hat{H}\left(\tfrac{1}{3}\psi_1 + \tfrac{1}{3}\psi_2 + \sqrt{\tfrac{7}{9}}\psi_3\right)}_{= \frac{1}{3}E_1\psi_1 + \frac{1}{3}E_2\psi_2 + \sqrt{\frac{7}{9}}E_3\psi_3} dx$$

$$= \frac{1}{9}E_1 \underbrace{\int \psi_1^*\psi_1\, dx}_{1} + \frac{1}{9}E_2 \underbrace{\int \psi_2^*\psi_2\, dx}_{1} + \frac{7}{9}\underbrace{\int \psi_3^*\psi_3\, dx}_{} + \frac{1}{9}E_2 \underbrace{\int \psi_1^*\psi_2\, dx}_{0} + \cdots$$

all others are zero

$$= \frac{1}{9}E_1 + \frac{1}{9}E_2 + \frac{7}{9}E_3 = \frac{68}{72}\cdot\frac{h^2}{mL^2} = \boxed{\frac{17}{18}\frac{h^2}{mL^2} = \langle E\rangle}$$

(c) What is the probability of each of the possible outcomes in part (a)?

$$\boxed{\begin{aligned} P(E_1) &= \tfrac{1}{9} \\ P(E_2) &= \tfrac{1}{9} \\ P(E_3) &= \tfrac{7}{9} \end{aligned}}$$

$$\sum |c_i|^2 = 1$$

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 = \sum_i c_i\psi_i$$

$$1 = \psi^*\psi = \sum_i \underbrace{|c_i|^2}_{P_i} \quad \text{(orthonormality)}$$

5. We saw in class that degenerate eigenfunctions may result from symmetry in the potential energy. What about the case that the potential is not symmetric? Even then, in some cases energy levels may be degenerate. In this situation we speak of "accidental degeneracy."

Consider a two-dimensional box in which the length of one side is an integral multiple of the other, i.e. $L_2=\lambda L_1$ where λ is an integer. The quantum numbers for a particle in a two dimensional box are n_1 and n_2.

(a) Suppose that particular values $n_1=a$ and $n_2=b$ correspond to one of a pair of degenerate eigenstates. Derive expressions for the values of n_1 and n_2 that correspond to the other eigenstate. Your expressions should be in terms of a, b, and λ.

$$E = \frac{h^2}{8m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right) = \frac{h^2}{8mL_1^2}\left(n_1^2 + \left(\frac{n_2}{\lambda}\right)^2\right)$$

$$n_1 = a \quad n_2 = b \Rightarrow E = \frac{h^2}{8mL_1^2}\left(a^2 + \left(\frac{b}{\lambda}\right)^2\right)$$

$$\text{Let } n_1 = \frac{b}{\lambda} \quad n_2 = a\lambda \Rightarrow E = \frac{h^2}{8mL_1^2}\left(\left(\frac{b}{\lambda}\right)^2 + a^2\right) \text{ degenerate } \checkmark$$

$$\Rightarrow \boxed{n_1 = \frac{b}{\lambda} \quad n_2 = a\lambda}$$

(b) Determine the lowest energy level that is degenerate for the case that $\lambda=2$. The value of the energy should be written in terms of h, m, and L_1 (where h is Planck's constant and m is the mass of the particle). (Complete credit will be given only if your reasoning is shown.)

Lowest energy will be smallest a, b for which $a, a\lambda, b, \frac{b}{\lambda}$ are all integer.

$$\text{For } \lambda = 2 \Rightarrow a = 1,\ b = \lambda = 2$$

$$E = \frac{h^2}{8mL_1^2}\left(1^2 + \left(\frac{2}{2}\right)^2\right) = \boxed{\frac{h^2}{4mL_1^2} = E}$$