Physical Chemistry Cumulative Exam October 1, 2015
Professor Trenary

100 points total.

The general form of the time independent Schrödinger equation for a particle of mass *m* for one dimensional systems is

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi(x)=E\psi(x)\ .$$

This equation can be solved exactly when the potential energy is constant in various regions of space. The most general form of the wavefunction for regions of constant potential is:

$$\psi_j(x)=A_j e^{ik_j x}+B_j e^{-ik_j x}$$

where

$$\hbar k_j=\sqrt{2m(E-V_j)}$$

and where V_j is a constant potential in region j. This form applies both to cases where $E > V_j$, in which case k_j is a real number, and for cases where $E < V_j$, in which case k_j is an imaginary number. For each region of constant potential, we would have different values for the constants A_j, B_j, and k_j. Use this form for the wavefunction to solve the following problems.

1. (15 pts). Consider the case where $V = 0$ everywhere.

   a) (5 pts) Are there any boundary conditions that would lead to energy quantization?
   b) (5 pts) Are there any constraints on the values that *A* and *B* can assume?
   c) (5 pts) Can the wavefunction be normalized? Explain your answer.

2. (30 pts). Consider an infinite square well of width *a* defined by

   $V_1 = \infty$, x < 0 (Region 1, (j = 1))
   $V_2 = 0$, $0 \leq x \leq a$ (Region 2, (j = 2))
   $V_3 = \infty$, x > *a* (Region 3, (j = 3))

   a) (5 pts) What are the values of A_j and B_j in regions 1 and 3?
   b) (5 pts) The boundary conditions for this problem require that the wavefunction be continuous at x = 0. What constraints does this place on the general form of the wavefunction?
   c) (10 pts) The wavefunction must also be continuous at x = a. Use this condition to find an expression for the energy.
   d) (10 pts) Derive an expression for the normalization constant for the wavefunction in Region 2.

30. (30 pts) Now consider the semi-infinite square well defined by

$V_1 = \infty$, x < 0 (Region 1, (j = 1))
$V_2 = 0$, $0 \leq x \leq a$ (Region 2, (j = 2))
$V_3 = V_0$ = finite positive constant for x > a (Region 3, (j = 3))

For this problem, assume that $E < V_0$.

a) (5 pts) Sketch this potential.

b) (5 pts) What are the values of A_1, and B_1 in Region 1?

c) (5 pts) What constraints are placed on the form of the wavefunction by requiring continuity at x = 0?

d) (5 pts) Do you expect the energy to be quantized in this case? Explain your answer.

e) (10 pts) By requiring continuity of the wavefunction, and continuity of the first derivative of the wavefunction, at x = a, obtain an expression for the energy. Explain how you would solve the equation, even if you can't do so, to obtain numerical values for the energy for given values of a, m, and V_0.

4. (25 pts). Again consider the semi-infinite square well defined in problem 3, but this time assume $E > V_0$.

a) (5 pts) What are the values of A_1, and B_1 in Region 1?

b) (5 pts) What constraints are placed on the form of the wavefunction by requiring continuity at x = 0?

c) (10 pts) Do you expect the energy to be quantized in this case? Explain your answer.

d) (5 pts) Suppose the particle is incident from the right, i.e, coming from the +x direction towards the -x direction. Without doing any explicit calculations, what can you say about the reflection coefficient? Explain your answer.

Miscellaneous Information

$de^{-x}/dx = -e^{-x}$, $q = \sum_i g_i e^{-\beta\varepsilon_i}$, $\frac{e^{-x}}{1+e^{-x}} = \frac{1}{1+e^{x}}$

$$\sum_{v=0}^{\infty}\exp[-\omega_e(v+\tfrac{1}{2})\beta]=\exp[-\frac{\omega_e\beta}{2}]\sum_{v=0}^{\infty}\{\exp[-\omega_e\beta]\}^v=\frac{\exp[-\frac{\omega_e}{2}\beta]}{1-\exp[-\omega_e\beta]}$$

$$\sin^2\theta=\frac{1-\cos(2\theta)}{2} \qquad \cos^2\theta=\frac{1+\cos(2\theta)}{2}$$

$$\sinh(x)=\frac{e^x-e^{-x}}{2}, \qquad \cosh(x)=\frac{e^x+e^{-x}}{2}$$