**Chem 6854: Physical Chemistry**

**Homework Assignment #4**

40 points total

Show all work !

Due Friday 26 February

Problems 4.1 and 4.2 are designed to illustrate how the simple 1D particle-in-a-box model mirrors behavior in systems like the 1 electron H spectrum, and, how it presages the sharp differences in electronic vs nuclear energies.

4.1 Given melectron =9.1\*10-31 kg, h= 6.636\*10-34 J\*s, c= speed of light=2.998\*108 m/s and a box length L= 2\*10-10 m (typical molecular bond

length), use the particle-in-the box energy to :

a)compute the wavelengths(in nm) of emission for the six transitions 4 pts

n=2🡪1 n=3🡪1 n = 4🡪1 (`Lyman’ series for particle-in-a box)

n=3🡪2 n=4🡪2 n =5🡪2 (‘Balmer’ series for particle-in-a-box)

b) plot the `spectral’ lines above on a graph as `lines’ vs nm (see for example, figure 1.5 page 11)

Verbalize the trend in the line spectrum as value increases 1 pt

Is it consistent with the observations for an H atom in Figure 1.5 page 11? Why ? 1 pt

4.2a. Repeat the exercise above but change the mass m to that of a proton=1.67\*10-27 kg and assume a box length L=2\*10-15m (about the diameter of the atomic nucleus). 4 pts

4.2b. Does the difference in wavelengths of emission between the proton and electron domains make

sense? Why or why not. 1 pt

Problem 4.3 is designed to illustrate how the quantum world evolves to become the classical world as the quantum number n approaches large values…an expression of the `correspondence’ principle.

4.3a. Use Maple to help you plot the particle-in-a-box probability density:

(2/L) sin2(nπx/L) vs x

where L=1 over the range from x=0🡪1 for three cases:

n=2,20 and 200. Provide separate plots of each case 3 pts

4.3b. The trend in your 3 plots is an example of the `correspondence’ principle. (see page 86).

Explain what you think the correspondence principle means and how the three plots support the principle. 2 pts

The next three problems provide mathematical exercise and (hopefully) insight into some common properties of integrals often encountered in quantum calculations. The hoped-for `lessons’ are in parentheses below)

(4 pts each/12 pts total)

* 1. Problem 3.14 page 98 (odd-even trig functions integrate to zero over symmetric ranges)
  2. Problem 3.15 page 98 (∫ψ dx = 0…so ψ can’t be by itself a measure of probability density)
  3. Problem 3.17 page 98 (eigen functions of different quantum states cannot overlap to form a new state)

Hint: Use Integral tables or Maple for 4.6 to simplify your proof.

The last problem extends the particle-in-a box solution to a circular rather than linear particle-in-a box

* 1. Problem 3.28 page 100

Direct substitution proof assuming ψ(θ) = A einθ showing how/why n=(2IE)1/2 /ħ (ħ=h/2π) 3 pts

Qualitative (common sense) argument for why boundary condition is ψ(θ) = ψ(θ+2π) 1 pt

Showing E= n2 ħ2/2I 3 pts

Showing why A= (1/2π)1/2 3 pts