**Chem 6854: Physical Chemistry**

**Homework Assignment #6**

Show work/include Maple outputs

Due Wednesday 13 April

**35 pts total (1 point for your name)**

The properties of the H atom solution should be explored to verify the basic properties asserted for them, e.g. normalization and orthogonality. The latter property insures that once centrosymmetry of the potential is lifted as we add electrons, that individual

N,L, m states will be unique in energy. This is where the seeds of the Periodic Table lie within Schrodinger’s H atom solution.

**6.1. Problem 6.16 of text, page 221**. Use Maple and Table 6.5 page 208 to verify that:

1. <1s|2s>=0 **2 pts**
2. <2s|2p>=0 for 2p with L=1, m=0 **2 pts**

You are advised to write out the relevant integrals for the above long hand here before using Maple to check their values. In case it pops up, remember that limr🡪∞ for e-kr🡪 0.

Notes: σ in the table is r/ao, the convenient variable for electronic distance from the nucleus. Also Z=1, and ao= constant. Remember that the integration must be taken over the differential volume: r2 sinθ dr dθdφ.

**6.2. Using Maple or the table of integrals on the back flap and Table 6.5 page 208, verify that :**

<3s|3s> =1 **3 pts**

You are advised to write out the relevant integrals for the above long hand here before using Maple to check their values. (See example 6.9 page 209-210). FYI- Maple supplies an unnecessarily complex answer to many integrals of the class used here, so the McQuarrie equations on the back flap are actually easier to deal with.

If you insist on using Maple, remember that limr🡪∞ e-kr🡪 0.

Problem 6.3 gets your hands dirty working with the associated spherical coordinate differential equation, 6.4, page 192 of your text for the simplest case of the 1s ( n=1,L=0, m=0) wave function. You also should gain insight into the source of the assertion that: Bohr’s radius ao =h2εo/mπe2.

**6.3 Problem 6.17 of text**. This problem is probably best done by hand rather than via Maple so that you can `experience’ using the H atom spherical coordinate quantum Hamiltonian in the basic eigenvalue problem form used to solve for the wave functions originally). To simplify the clerical task, note that the leading constant term for ψ100 =(π-1/2\* (1/ao)3/2 cancels out on both sides of the equation so that the reduced wave function becomes just: e-r/ao, where ao is the Bohr radius. Also, note that in order for the solution to work, a solution for ao falls out as a side benefit. Somewhere during your proof, you should reach the crucial equation below:

*e= electron charge, m=electron mass, a= ao = the Bohr radius and K= 1/4πεo*

The equation is true only if : so that E = -

You should also be able to manipulate :

and reproduce Bohr’s radius equation ao =h2εo/mπe2. **6 pts**

Problems 6.4 and 6.5 applies quantum postulate 4 to the H atom and again gives you some practice working the basic spherical integration over r2 sin θ dθ dφ dr. Note that one of the e-mailed Maple examples I sent solves a problem like 6.5

**6.4 Problem 6.20 of text page 221** .Can be done via Maple where the `approximate’ function allows

computation of the numeric answer. Note that if you do the integral correctly with unspecified ao ,

the Bohr radius, ao ,disappears from the final answer. **3 pts**

**6.5 Problem 6.28 of text page 222.** Either McQuarrie’s expressions or Maple can be used here. If the latter is

used, remember that limit x🡪∞ for any function P(r) e-ar🡪 0 if P(r) is a polynomial in r. **5 pts**

Make sure to answer the question about the `surprise.’ Can you rationalize your results physically? **3 pts**

Problems 7.10 and 7.11 provide relevant review of determinant methods, which are useful when we examine the `variational’ method of approximation in chapter 7 which we take up this week.

**6.6 Problems E-1, E2,E-3 pp 238-239 of text**. **6 pts**

**6.7 Problems E-4, E-5 p 239 of text except:**

**Row 2 of problem E-4 should be changed from [1 x 0 0] to: [1 x2 1 0]**

**Row 2 of problem E-5 should be changed from [1 x 1 1] to: [1 x2 1 0]**

**If you Use Maple, I need to see the hard copy of the outputs** **4 pts**