**Chem 6854: Physical Chemistry**

**Homework Assignment #5**

Show all work !

Due Friday 14 March

38 points total +2 pts for just being good folks=40

**Chapter 5 serves two purposes. First, it presents the quantum solutions to the harmonic oscillator and rigid rotor. Second, it gets us prepared for some of the mathematics to come that is used to describe the quantum solution to the H atom.**

**The spherical coordinate system is often used to treat spherically symmetric systems like the H atom, whose quantum eigenvalue problem is taken up in chapter 6. Getting you comfortable with this coordinate system in digestible bits and pieces underlies the problems below.**

5.1 In your own words briefly explain why spherical coordinates seems a better way to describe an electron orbiting

the H nucleus than the traditional (x,y,z) Cartesian system. 3 pts

5.2a In spherical coordinates the differential volume element has the dimensions dV=(r sin θ dφ)\*(rdθ)\*(dr)

Using your knowledge of geometry and trigonometric relationships, re-explain how these terms come about. (See Figure D.2 page 148 to help think through the geometry.) 3 pts

5.2b The spherical coordinate system’s volume element dV (=r sin θ dφ)\*(rdθ)\*(dr) is often written as dA\*dr,

where dA is the area of the outer skin of the volume element. Use this to show how A of a sphere =

4πr2. 2 pts

5.2c When integrating to find the volume of a sphere,V, on page 149, dφ is integrated from 0🡪2π,

but sin θdθ is only integrated from 0🡪π. Provide a brief, qualitative answer for why. 3 pts

5.3. Using Maple and the formulas at the back flap of McQuarrie, evaluate ∫ e-r r3 dr ∫sin3θ dθ ∫cos2 φdφ

For the limits r= 0🡪∞, θ=0🡪π, φ=0🡪2π. *Note that rearranged, the integration has the form:*

*∫f(r,θ,φ) dV where dV =r2sin θ dφ dθ dr and f(r,θ,φ) = re-r sin2 θ cos2 φ* 2 pts

**We will be using the results of the quantum harmonic oscillator solution without attempting to directly solve the problem, since the resulting differential equation no longer contains constant coefficients. The problems below let you gain some experience manipulating the results to obtain physically significant quantities.**

5.4a. The `O-H’ stretch in the infrared region occurs near 3500 cm-1.  Assuming this is the result of a Δn =1

transition for the diatomic molecule O-H, determine the force constant, k, for the diatomic O-H.

(see example 5.3 p. 168) 3 pts

5.4.b If we replace H with D in the above, and assume k is unchanged, at what frequency in cm-1 will O-D

show a Δn=1 absorption ? 3 pts

5.4 c. ? Does the frequency shift make sense physically ? Explain your answer. 2 pts

5.5 Problem 5.14 of text, p. 182 3 pts

**As with the harmonic oscillator, the quantum rigid rotor solution (see pp 175-178) is given without proof since again, the mathematics is too involved. The problems below let you gain some experience with quantities and units associated with rotational energies, moments of inertia, and bond lengths.**

5.6a Problem 5.34 of text, page 186 3 pts

5.6b If we change to D79Br, what is the expected line separation of the rotational transitions ? (Note: The

bond lengths don’t change from normal H-Br to D-Br) Does the change make sense physically? 2 pts

5.7 Problem 5.35 of text, page 186 3 pts

^

**McQuarrie chose to introduce the angular momentum operator L2 =Lop2 as part of his exposition on rigid rotors (see eq. 5.52, page 175). This is a big piece of the H-atom problem to come in chapter 6 and it is important to get used to operating on functions with it correctly.**

5.8. Compute **Lop2**(sin θ)2 3 pts

5.9 Compute **Lop2**(cos θ\*sin φ) 3 pts