**Physical Chemistry 6854 Exam 2: Take-home portion (66 pts total)**

Due Monday 7 April 2014 (use answer sheet and append work)

1)Compute the average position of θ, the average (angular) momentum, and average energy

E = <ψ\*| ψ> for a hypothetical quantum system over the range 0🡪2π whose energy Hamiltonian is

*=*

-iħ =

where I and A are constants and for which the pertinent wave function is ψ= cos2 θ. **(6 pts)**

2a) Using just the H35Cl and H37Cl data found on the last page determine the spectroscopic constants

below **(1pt each/4 pts)**

1. υe
2. Be
3. De
4. αe

2b) Determine the bond length re(pm) of H35Cl predicted by the data **(2 pts)**

2c) Compute and tabulate the % error for the data’s predictions for υe, Be, De, αe and re vs those found

for HCl on page 499, Table 13.2 of McQuarrie. **(2 pts)**

3a. What is the overlap integral <ψ300|ψ100> for the H atom assuming the units Z=ao = π=1. You may

use Table 6.6, page 218 and Maple if necessary. **(3 pts)**

3b. Explain why, by inspection, we expect <ψ300| |ψ100> = <ψ300|ψ100>, where is the H atom

Hamiltonian, (eq. 6.2 of text ,pg. 191.) **(4 pts)**

3c. Using the assumed unit system Z=ao = π=1, what is the value of the integral <ψ300|ψ300> ? **(3 pts)**

4. What is the ratio of the second to the first Bohr **s** orbital radius ? Put mathematically, what is:

Use Table 6.6, page 218 and Maple to help define the functions. Here, you must use ao, me, Z=1 and

with their actual values. **(5 pts)**

rn=2 = <ψ200|r|ψ200>

rn=1 <ψ100|r|ψ100>

5. In problem 6.36 page 223, McQuarrie indicates that the ground state energy of regular H is only

0.99928 that of deuterium, an H atom with an extra neutron. Since the neutron has no electric field

and only serves to increase the mass of the nucleus explain how this small, but measurable

difference in ground state energies arises. (Hint: what approximation is made when McQuarrie uses

me = mass of electron in eq. 6.2 page 191 ?) **(4 pts)**

6. A rotational (microwave) spectrum of 12C16O in the gas phase reveals a series of equally spaced lines

separated by 3.8626 cm-1.

1. What is Be in cm-1 ? **2 pts**
2. What is re in pm ? **3 pts**

7. A trial wave function of the form: φ(x) = ax4 -2x2 -bx is used to estimate the true wave function for a particle on a string in the unit system where π=m= ħ=1. In this system,

The exact energy at n= 1 in this system = ½

1. Given the boundary conditions φ(0) = φ(1) = 0, what must be the value of b if a ≠ 0 ? **1 pt**
2. What is the detailed mathematical expression for:  **9 pts**

Eφ = <φ(x)|**|φ(x)>**

<φ|φ>

(you can physically `cut and paste’ your answer from Maple in)

1. For what value(s) of **a** is **Eφ** minimized (to 5 places) ?  **2 pts**
2. What are the minimum Eφ for the assumed trial function φ at your determined **a**? **3 pts**
3. What is the % error of this energy vs the exact value ? (it will suck…) 1 pt

8. For the sake of simplicity, let’s set k=μ=1 so that α=1 and let’s assume a unit system where .

For the simple harmonic oscillator, this means the quantum hamiltonian reduces to:

The exact energy of the system under these conditions reduces to:E= n+ ½, n=0,1,2….The ground state exact energy for this system is then, Eo = ½.

Suppose we define a trial wave function φ for the above system with the linear combination below:

**φ = c1φ1 +c2φ2 = c1 e- x + c2x e-2x**

a)Find the lowest value for Eφ by solving the secular equation. (See Supplement 8). 9 pts

b) Based on your answer, have we found an `exception’ to the Variational principle, or did we `conveniently’ ignore a basic assumption that must apply to any choice of trial wave function. If so, explain our oversight.

3 pts

Data for Problem 2 ((cm-1))

|  |  |  |
| --- | --- | --- |
| m | ( H35Cl) | (H37Cl) |
| 11 | 3072.88 | 3070.63 |
| 10 | 3059.36 | 3056.99 |
| 9 | 3045.05 | 3042.77 |
| 8 | 3030.12 | 3027.77 |
| 7 | 3014.41 | 3012.13 |
| 6 | 2998.04 | 2995.8 |
| 5 | 2981.01 | 2978.77 |
| 4 | 2963.28 | 2961.1 |
| 3 | 2944.91 | 2942.74 |
| 2 | 2925.89 | 2923.74 |
| 1 | 2906.24 | 2904.12 |
| -1 | 2865.11 | 2863.06 |
| -2 | 2843.63 | 2841.61 |
| -3 | 2821.57 | 2819.58 |
| -4 | 2798.95 | 2796.99 |
| -5 | 2775.76 | 2773.85 |
| -6 | 2752.04 | 2750.14 |
| -7 | 2727.78 | 2725.96 |
| -8 | 2702.99 | 2701.22 |