**Physical Chemistry 6854 Exam 2:Take-home portion (67 pts total)**

**Due Friday 12 April 2013**

**Your name: \_\_\_\_\_\_\_\_\_\_\_answers\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

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

= <ψ\*| ψ> = \_\_\_\_\_\_\_3/4\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ 2 pts

= <ψ\*| ψ> = \_\_\_\_\_\_\_\_*- i*ħ/π\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ 2 pts

E = <ψ\*| ψ> = \_\_\_\_\_\_\_ E = ¾ A/π + ½ Iħ2/π + 2 pts

where I and A are constants and for which the pertinent wave function is ψ= cos2 θ.

2a)

|  |  |  |  |
| --- | --- | --- | --- |
| **Spectroscopic term** | **Experiment (cm-1)** | **Accepted(cm-1) 1** | **% error2** |
| e | ***3009.80*** | **2990.946** | ***+0.63*** |
| **Be** | ***10.5900*** | **10.5934** | ***-0.032*** |
| **αe** | ***0.3036*** | **0.3072** | ***-1.33*** |
| **D­e** | ***5.341\*10‑4*** | **5.319\*10‑4** | ***+1.17*** |
| **(2b) r(pm)** | ***127.46*** | **127.46** | ***~0*** |

3a. <ψ300|ψ100> = \_\_\_\_\_0\_\_\_ 3 pts

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

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

|ψ100> = E100 a constant so <ψ300| |ψ100> = E100<ψ300|ψ100> = E100\*0 from results in 3a above

∴<ψ300| |ψ100> = <ψ300|ψ100> = 0 (orthogonal !)

3c. <ψ300|ψ300> = \_\_\_\_\_1\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Z=ao = π=1 3 pts

<ψ300|ψ300> = 4 =1

4.

4

rn=2 = <ψ200|r|ψ200> = 6 pts

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**

*The chief approximation is that the reduced mass μ between the nucleus and the electron is approximated as me in the H atom solutions presented by McQuarrie.*

*Using the mp and me supplied by McQuarrie*

*μH = mp\*me/(me+mp) = 1.672\*10-27\*9.109\*10-31/(1.672\*10-27+9.109\*10-31)=9.104\*10-31 kg*

*vs 9.109\*10-31kg for me*

*If we don’t correct for this in deuterium, there is no correction for a doubling in the nuclear mass. However, if we do, then the reduced mass increases to:*

*μD = 2mp\*me/(me+2mp) = 2\*1.672\*10-27\*9.109\*10-31/(2\*1.672\*10-27+9.109\*10-31)=9.1065\*10-31*

*Since E ~ μ this means that energy EH/ED  = μH/ μD = 9.104/9.1065 = 0.99973 , close to the value in McQuarrie. The difference is in the assumed value for the neutron. (I assumed it equal to the proton which isn’t quite exact.)*

6. Be = \_\_\_\_**1.9313** \_\_\_ cm-1 **2 pts**

re = \_\_\_\_**112.83 pm** \_\_\_\_\_pm **3 pts**

7a) b= \_\_\_\_\_\_ **b=a-2** \_\_\_\_\_\_ 1 pt

b)Eφ =  **9 pts**



(you can physically `cut and paste’ your answer from Maple in) 7 pts

1. Possible **a** minimizing Eφ  **2 pts**

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1. Minimum Eφ = \_\_\_\_\_5\_\_\_\_\_\_\_\_\_\_\_\_\_\_ **3 pts**
2. % error vs the exact value \_\_\_\_\_\_\_100\*(5-0.5)/0.5%=900% yuck 1 pt

8. Final form of the secular determinant, x= E=eigen values for assumed φ1=e-x and φ2 =xe-2x



a) Minimum Eφ = \_\_\_\_\_\_\_-0.0147 \_\_or -6.80\_\_\_\_\_\_\_(less than exact result) 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.

*The actual harmonic oscillator solution requires finite solution (e.g. a boundary condition) across the entire range from -∞ 🡪 +∞. The selected functions blow up at -∞ since e-x increases without bound as x🡪 -∞*

3 pts