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

Due Monday 7 April (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

*=*

*-i*ħ =

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

= <ψ\*| ψ> = = 3/4

= <ψ\*| ψ> =*-i*ħ dθ =- *i*ħ (2 sin2(θ) -2 cos2(θ)) dθ

*= i*ħ/π

E = <ψ\*| ψ> =

= +

= + (2 sin2(θ) -2 cos2(θ))dθ

E = ¾ A/π + ½ Iħ2/π

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

**From fit of H35Cl gas phase IR data on last page:**

(cm-1) = -2.002647E-03x3 - 3.035657E-01x2 + 2.057289E+01x + 2.885973E+03 r² = 9.999999912E-01  
**From fit of H37Cl gas phase IR data on last page:**

(cm-1) = -1.960449E-03x3 - 3.027672E-01x2 + 2.053903E+01x + 2.883882E+03 r2 = 9.999999510E-01  
**From equation 10 of lab text (Shoemaker & Garland 8th edition):**

(cm-1) = o +(2Be -2αe)m –αem2 - 4Dem3  where o = e -2exe

Matching terms:

**Theory** **experimental fit (cm-1)**

**αe** (35)= 0.303566 **αe (35)** = **0.303566**

**2Be(35)-2αe** (35)=2Be-2\*(0.303566) =20.5757289=>

**Be(35)** = ½ (20.5757289+2\*(0.303566))

= **10.5912**

**4De (35)=**2.002647E-03 => **De(35)** = ¼(2.002647E-03)

**= 0.00050066**

To find e (35) we use equation 17 found on page 84 of the lab manual, and the experimentally fit value for o(37)= 2.883882E+03 listed above for H37Cl: **e (35)**

={0.9795925\*2885.973/0.9810773} -2883.882 **=3009.80 cm‑1**

0.9795925/0.9810773 –(0.9795925/0.9810773)1/2

Summarizing :

**νe(cm-1) αe(cm-1) Be(cm-1) De(cm-1)**

HCl35 **3009.80**  0.303566 10.5900 5.0066\*10-4

2b) Use your experimental data to determine the bond length re(pm) of HCl **(2 pts)**

I = μr2 = h/8π2 Bec

μ= \*(0.9795925)\*1.66054\*10-27kg=1.62665\*10-27kg

r2 = h/8π2 μBec = 6.626\*10-34/(8\*π2\*1.62665\*10-27kg \*1059.34 \*2.9979\*108) =1.62448\*10-20 m2

**r= 1.27455\*10-10m =127.46 pm**

2c) Compute and tabulate the % error for your 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)**

**The experimental results compare well vs the accepted values**

|  |  |  |  |
| --- | --- | --- | --- |
| **Spectroscopic term** | **Experiment (cm-1)** | **Accepted(cm-1) 1** | **% error2** |
| e | ***3009.80*** | **2990.946** | ***+0.63*** |
| **xe**e | ***n/a*** | **52.819** | ***-*** |
| **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*** |
| **r(pm)** | ***127.46*** | **127.46** | ***~0*** |

**1McQuarrie table 13.2: pg 499 2100\* (obs-accepted)/accepted**

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

use Table 6.5, page 208 and Maple if necessary. **(3 pts)**

If you recall, all H wavefunctions are orthogonal so **<ψ300|ψ100> = 0**

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)**

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

∴<ψ300| |ψ100> = <ψ300|ψ100> = 0

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

In our reduced unit system: ψ300 =

<ψ300|ψ300> = 4 =1

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. **(6 pts)**

rn=2 = <ψ200|r|ψ200>

rn=1 <ψ100|r|ψ100>

r200 =

r100 =

r200 =

r100

=

R200 = (1/8a3)\*48a4 =6a =4

R100  (4/a3) \* 3a4/8 1.5a

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. 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 f=2Be so Be = ½ \*3.8626=1.9313 cm-1 =193.13 m-1**
2. What is re in pm ? **3 pts**
3. I = μr2 = h/8π2 Bec
4. μ= \*(12\*16/28)\*1.66054\*10-27kg=1.138\*10-26kg
5. r2 = h/8π2 μBec = 6.626\*10-34/(8\*π2\*1.138\*10-26\*193.13 \*3\*108) =1.272\*10-20 m2
6. **r= 1.128\*10-10m =112.8 pm (see McQuarrie Table…re(CO) =112.83 pm**

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**

**At L=1, a-2-b=0 => b=a-2 =>** ax4 -2x2 –(a-2)x

1. 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)

Eφ = <φ(x)|**|φ(x)> =**

<φ|φ>



1. For what value(s) of **a** is **Eφ** minimized (to 5 places) ?  **2 pts**

There are two solutions for **a**:

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****

1. What are the minimum Eφ for the assumed trial function φ at your determined **a**? **3 pts**

1.1228 = a=> E=42.4 (yeccch !) 0.0573 = a=> E= 9.99 (also yecch)

1. What is the % error of this energy vs the exact value ? (it will suck…) 1 pt

838 % and 190% …definitely sucky and proof that quadratics won’t be a good choice for trial function.

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

det H11 – ES11 H12-ES12 =0 **the secular determinant**

H21- ES21 H22-ES22

Using Maple we can plug in directly to find S11, S12  and S22 where **φ1 =** **e- x φ2 = x e-2x**

S11 = S12 = S22 =

H|φ1 =

H|φ2 =

To compute H11, H12, H21 and H22 I worked out by hand the individual expressions:

φ1|H|φ1 = e-x ( =

φ1|H|φ2 = ()= =

φ2|H|φ1 = xe-2x(=

φ2|H|φ2 = xe-2x( =x

I then integrated from 0🡪∞ using Maple:

H11 = <φ1|H|φ1 > = -1/8

H12 = <φ1|H|φ2 > =14/27

H21 = <φ2|H|φ1> = -1/54

H22 =<φ2|H|φ2> = 19/256

det -1/8 – ½ x 14/27- x/9=0 **the secular determinant** , x=E

-1/54- x/9 19/256-x/32



Positive x solutions = -0.0145 or -6.8015 vs ½=0.50 `best’

-6.8015 vs 0.50 best

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. 3 pts

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🡪 -∞

|  |  |  |
| --- | --- | --- |
| 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 |