**Chem 6854: Physical Chemistry**

**Homework Assignment #1**

**Quantum Beginnings and `Review’ of Complex #**

(36 points/ 3 points per problem)

Show all work !

* 1. ) DeBroglie proposed the notion of a `matter wave’ wherein a mass m’s wavelength λ obeys p = mv= h/λ. Qualitatively explain the source and reasoning underlying this assertion and how you interpret the meaning of the `wavelength’ of matter, λ, conceptually.

*DeBroglie took his cue from the 4th paper of Einstein’s `Annus Mirabilis’* ***Annalen der Physik 18 (13): 639–641***

*wherein: E2 =* (moc2)2 + (pc)2

*Einstein specialized this for the case of light whose rest mass mo= 0 and then grafted Planck’s seminal equation,*

*Elight = hf which led to the chain of relationships below*

*Elight =plight c =hf*

*=> plight = momentum of light = hf/c = h/λ (since c= fλ)*

*DeBroglie hypothesized that if light can have momentum connected to its wavelength, so could matter and posited the notion of a wavelength for matter that followed the same mathematical form as that for light, e.g*

*mv= Pmatter = h/λmatter*

*The interpretation of λmatter is not that it means matter `oscillates’ physically, but that there is a property connected to matter which makes it act wave-like. The λmatter for a substance can also be viewed as a property of its energy state just as density is a property of matter’s `intensity’ of material.*

1.2) DeBroglie’s matter wavelength, λ , was the critical `big idea’ underlying Bohr’s derivation of the H

atom energy and electronic radius. Central to Bohr’s thinking was that if r is the stable

radius of the electron’s orbit in H, then the electron’s radius must obey the equation :

2πr = nλ (see equation 1.15, pg 19)

where λ is specifically the `matter wave’ for the electron and n is a positive integer (1,2,3…)

1. Why can’t n be non-integer ?

*Because then the wave doesn’t terminate neatly as the wave propagates around the circular path and so destructively interferes with itself.*

1. Why can’t n be 0 ?

*If n= 0 then the electron has an orbital radius of 0, which is contradictory…the electron is present always outside the nucleus and exists. If n=0, then one effectively states that the electron doesn’t exist.*

1.3a) Derive Bohr’s prediction for the electron velocity v in an H atom as function of n and physical

constants K, e, h and m given:

Fcentripetal = mv2/r= Fcoulombic = Ke2/r2

p=mv= h/λ

2πr= nλ

E= 1/2mv2 – Ke2/r

*Overall strategy:*

*If we can find an expression for λ in terms of K,e,m and h, we can use DeBroglie’s expression to solve for v since p=mv=h/λ =>*

***0***  *v=h/mλ*

*Fcentripetal expression=> mv2= Ke2/r*

*But since p2/2m = ½ mv2,*

*p2/m = mv2 = Ke2/r*

*Rearranging we get: r= Ke2m/p2*

*Using DeBroglie’s hypothesis that: p=h/λ => λ/h = 1/p*

***1*** *r= Ke2m/p2 =Ke2mλ2/h2*

*However, Since 2πr= nλ =>*

**2**  r=nλ/2π.

Equating **1** and **2** we can isolate a solution for λ as function of *K,e,m and h*

*Ke2mλ2/h2 = nλ/2π =>*

***3*** *λ = nh2/(2πKe2m) or 1/λ = (2πKe2m) /nh2*

Substituting into 0 we get

*v=h/m* \* (*2πKe2m) /nh2* **=*2πKe2/nh = Ke2/n*** *ħ*

1.3b) Given: K=8.992\*109  e= 1.602\*10-19 coulombs ħ=1.055\*10\_34 Joule sec m = 9.1\*10-31 kg

Compute v of an H atom’s electron in the ground (n=1) state using your derived form in 1.3a (units should come out in m/sec).

***v= Ke2/*** *ħ* ***=9\*109\*(1.602\*10-19)2/1.055\*10\_34 =2.1\*106 m/s Note: by way of reference, the speed of light is 3\*108m/s so the electron around H whirls at roughly 1/100th the speed of light.***

1.4. Problem 1-12 of text. (Black Body calculation)

*Using the empiric Wien Law: λmax (m)~ 2.9\*10-3/T(K) = 2.9\*10-3/288 K =* ***1.007\*10-5m = 10070 nm*** *which is in the infrared portion of the spectrum*

1.5. Problem 1-18 of text. (Photoelectric effect calculation)

*We must use equation 1.8 of page 8 to solve this problem:*

*KE= hf-φ =hf-hfo where φ is the work function of the silver and hfo = φ, where fo = threshold frequency for silver.*

*The main difficulty in this problem is that several energy units are used. It is convenient to convert everything to Joules = J*

*KE= 0.805 eV\* 1.602\*10-19 J /eV =  1.289\*10-19 J*

*230 nm = λ = c/f=> f= c/λ =3\*108 ms-1/230\*10-9 m = 1.30\*1015 s-1*

*hf = 6.626\*10-34 J\*s\*1.30\*1015 s-1 =8.64\*10‑19 J*

*Plugging in the values above now in J:*

*1.289\*10-19 = 8.64\*10\_19 - hfo*

*Workfunction for silver = 8.64\*10-19 -1.289\*10\_19= hfo  = φ = 7.353\*10‑19 J*

*Equivalent threshold frequency fo = φ/h= 7.353\*10‑19 J/6.626\*10-34 = 1.11\*1015Hz*

1.6. Problem 1-21 of text. (H atom line spectrum calculation)

*Lyman series => nf = 1 = final state*

*from eq. 1.25, p. 22: υ(m-1) = 1.09\*107 (1/nf2 -1/ni2) = 1.09\*107 (1 -1/ni2) for Lyman line*

*λobs = 1.03\*10-7m => 1/ λobs = 1/1.03\*10-7= 9.709\*106= υobs*

*9.709\*104 = 109,677(1-1/ni2 )*

*9.709\*106 - 1 = -1/ni2*

*1.09\*107*

*0.8907-1 = -1/ni2*

*0.1093= 1/ni2*

*(9.149)0.5 =ni2 => ni = 3.02 ~3*

1.7. Problem 1-22 of text. (H atom line spectrum calculation)

*Since the H is in the ground state, the 97.2 nm light must initially excite the H atom from ni =1 to some other integer state nf. We use υ(m-1)) =1/97.2\*10-9=1.0288\*107 . Since this absorption must follow the Rydberg equation:*

*1.0288\*107 = 1.097\*107 (1/ni2 -1/nf2) = = 1.097\*107 (1 -1/nf2) n=4*

*1.0288\*107/1.097\*107 =0.9378 =1-1/nf2 486 nm*

*1-0.9378=0.0622=1/nf2 =>nf =4 97 nm n=2*

*Now, during subsequent emission, the emitted photon starts at ni = 4 and has an energy = 1/(486 \*10-9) m-1 =2.058\*106m-1*

*Using the Rydberg equation again”*

*2.058\*106 = 1.097\*107 (1/nf2 -1/ni2)= 1.097\*107 (1/nf2 -1/42). n=1*

*Solving for nf:*

*2.058\*106/1.097\*107 = 0.1876=1/nf2 -0.0625*

*0.1876+0.0625= 0.2501=1/n­f2=>* ***nf =2***

1.8 Problem 1.25a of text. (De Broglie wavelength problem) Note that:

E=100 eV = 1.6\*10-17J and that p2/2m = E

*Using the DeBroglie hypothesis: p=h/λ=> λ = h/p*

*Since p2/2m = E=> p =(2mE)1/2 =(2\*9.1\*10-31kg\*1.6\*10-17)1/2 = 5.396\*10-24*

***λ= h/p= 6.626\*10-34/5.396\*10-24=0.123 nm***

1.9. Problem 1-27 of text. (DeBroglie wavelength🡪 potential problem) Note that:

Ve= p2/2m

e(proton) = 1.602\*10-19 C

m(proton) = 1.66\*10-24 g = 1.66\*10-27 kg

=>V in volt units

***For a charged particle in a electric field***

***Vq= p2/2m***

***q(proton) = 1.602\*10-19*** *C*

*m(proton) = 1.66\*10-24 g = 1.66\*10-27 kg*

*p=h/λ=6.634\*10-34/1\*10-10 =6.634\*10-24*

*V= p2/2mq*

*V= (6.634\*10-24 )2 /(2\*1.66\*10-27\* 1.602\*10-19) volts =* ***0.082 V***

1.10 Problem 1.37 of text (equivalent Heisenberg uncertainty relationships)

*h has units of joule\*s and since ΔE is in Joules and Δt is in seconds,*

*ΔE\*Δt = J\*s has same units as h √*

1.11 Problem 1.38 of text (Heisenberg time uncertainty)

*Δt<h/mc2 = 6.626\*10-34/(2.5\*10-28\*(3\*108)2) = 2.94\*10‑23s*

1.12 Imaginary number expressions: (see page 35 MathChapter A) (1 pt per answer)

Problems A-1 b, A-2b, A-3b

*A-1b)* ***eπi/2  = cos (π/2) + isin (π/2) = i*** *since cos (π/2) =0 and sin (π/2) =1*

*A-2b ) Re{z2} = Re{( x+2iy)(x+2iy)} = Re{x2 + 4ixy –4y2} =* ***Re { x2-4y2 + i4xy)} = x2 -4y2***

*A 3-b) reiθ = rcos θ + i rsin θ = 4 -i√2*

*i r sin θ/cos θ = i tan θ= -i√2/4 => arctan (-√2/4 )= θ=-0.3398 radians*

*cos(0.3398) =0.9428 => r cos θ = 4= r\*0.9428=> r= 4/0.9428=4.24257*

***4 -i√2 = 4.243\*[cos(-0.3398o) –i sin -0.3398)] = 4.243e-0.3398i*** *(note: 3√2 ~4.243)*