Answers to take-home exam 1

**Problem 1: Black Body Model (10 pts)**

1a) A typical `old-school’ tungsten light bulb –which is a good approximation of a black body radiator- produces a maximum in intensity at about 500 nm (yellow light). What ~ temperature is the tungsten operating at to reach this temperature in K ? (3 pts)

*Use Wien Law λmax(m) T(K) = 2.90\*10-3 m\*K*

 *λmax = 500 nm = 500\*10-9m =5\*10-7*

*T(K) = 2.9\*10-3/5\*10-7 = 5800 K*

1b) In qualitative terms describe what the problem is with the classical Rayleigh-Jeans prediction

of the energy density emitted by a black body. Be sure to include why this problem is often called “the ultraviolet catastrophe.” (3 pts)

*The catastrophe is that the classic prediction is that the density of energy rises to infinity as f heads towards higher values into the uv (hence the `uv catastrophe’ language) and there is no `maximum’ in temperature vs f for a black body radiator, whereas clear maxima are observed as per Figure 1.1. page 3.*

1c) In qualitative terms, describe why the photoelectric effect experiment caused such

 enormous problems for the classical theory that light is a wave. (3 pts)

*The classical theory of light fundamentally connects energy of the wave to wave amplitude*

*whereas the Photoelectric Effect shows that the electrons from a given metal are ejected only when a specific threshold frequency is reached. The amount (amplitude) of light is completely irrelevant.*

**Problem 2: Bohr’s Model (part 1) (15 pts)**

Using the Bohr model :

1. Derive a general expression for the velocity of an electron in the Bohr atom (12 pts)

*Applying Bohr’s `DeBroglie-like’ assertion: mevr=n ħ =>*

***1*** *v= n ħ/mer*

*From Bohr’s model r= 4πεo ħ2n2*

 *mee2*

*Substituting Bohr’s r into* ***1:***

***v= (n ħ/me)\* mee2/4πεo ħ2n2 = e2/4πεo ħn = Ke2/nħ =e2/2εohn***

b)compute the apparent velocity v (m/s) , of an electron around the H atom at n= 1. Use the physical constant values provided by McQuarrie on the inside front cover of the text to do your calculations. What % of the speed of light is the electron moving at n=1 ? (3 pts)

*v= = e2*

 *2εohn*

*e=1.602\*10-19 C εo = 8.85\*10-12 h =6.626\*10-34 n = 1 c =3\*108*

*v= (1.602\*10-19 )2  =* ***2.2\*106 m/s => 2.2\*106/c \* 100 = 0.7% the speed of light***

 *2\*8.85\*10-12 \*6.626\*10-34 \*1*

**Problem 3: Bohr’s Model (part 2) (15 pts)**

While it is rare to find terrestrial conditions that can cause elements to lose all but a single electron, the temperatures common to stars can often breed seriously `electron poor’ elements. These charged species are effectively H atoms with Z = proton count >1, but only one electron. Given that such 1 electron, Z proton elements have a coulombic potential V(r) with the form:

V(r) = -ZKe2/r K=1/4π εo , Z= # protons in nucleus

1. Re-derive Bohr’s total energy E for the electron for the case of Z>1. ( 10 pts)

*Following the derivation as per homework 1.3, except substituting Ze2/Kr for V(r) we get:*

*mv2= KZe2/r*

*p2/m = KZe2/r*

*r= KZe2m/p2 = mKZe2/[(h/λ)2] = mKZe2λ2/h2=>*

***1*** *1/r= h2/ mKZe2λ2*

*Applying the DeBroglie condition as before with the modified r above:*

*2πr = 2π mKZe2λ2/h2= nλ*

***2*** *λ= nh2/2πmKZe2 = 2πn ħ2/mKZe2*

 *1/λ = 2πmKZe2/nh2 = mKZe2/2πn ħ2 =>*

***3*** *1/λ2 = m2K2 Z2 e4/4π2 n2 ħ4*

*Using 2, we find r*

 *r=nλ/2π = n/2π (2πn ħ2/mKZe2) =>*

***4a***  *r= n2 ħ2/mKZe2*

***4b*** *1/r = mKZe2/ n2 ħ2*

*To find EZ we use old physics expression for energy:*

*EZ =p2/2m - KZe2/r = (h/λ)2/2m -KZe2/r*

*Substituting in* ***3*** *and* ***4b***

*EZ = h2 \*(m2K2 Z2 e4) - KZe2\*( mKZe2)*

 *2m 4π2 n2 ħ4 n2 ħ2*

*EZ = ħ2\*(m2K2 Z2 e4) - KZe2\*( mKZe2)*

 *2m n2 ħ4 n2 ħ2*

*EZ = (mK2 Z2 e4) - mKZ2e4)*

 *2n2 ħ2 n2 ħ2*

***5*** *EZ = -(mK2 Z2 e4) = Z2EH(n), where EH(n) is the Hydrogen atom energy*

 *2n2 ħ2*

*= -mZ2e4 =- mZ2e4*

 *2n2(4πεo)2h2/4π2 8n2εo2h2*

*In cm-1, EH = -R∞n2= 109,677.6n2 cm-1 so*

1. **EZ = -109,677n-2Z2 (cm-1)**

b)An observatory reports a `Lyman’ series for emissions from Cygnus 4, a star in a galaxy far-far- away. The n=4 🡪 n=1 emission occurs at 10.8061 nm. What is the element ? (5 pts)

*10.8061 nm =10.8061\*10-9 m\*102 cm/m = 1.0806\*10-6 cm => 1/λ(cm) = 9.254\*105 cm-1*

*ΔEZ = 109,677Z2 [1-1/ni2] (cm-1) = 109,677Z2 [1-1/42]= 1.02822\*105Z2 = 9.254\*105*

*Z2= 9.254\*105/1.02822\*105 = 9=>* ***Z= 3, element is Lithium***

 **Problem 4: Uncertainty and Measurement (5 pts)**

A 2nd year physics grad student triumphantly reports measuring an emission line to within ± 1\*10-11 Hz- a world record- using his lab’s new `atto second’ resolution spectrometer, an instrument with measurement speeds having pulse uncertainties of ± 10‑18 seconds. Should the research director jump for joy and buy the student a big pitcher of Heineken’s, or kick him/her in the shorts? Provide a rationale for your answer.(hint: see problem 1-37 of homework #1) (5 pts)

*ΔE\*Δt > h =6.63\*10-34 J\*s*

*The uncertainty in the measurement is ~ 10-18 s so the minimum uncertainty in ΔE*

 *= 6.63\*10-34/10-18~6.6\*10-16J*

*Converting the student’s line width to an equivalent uncertainty in energy:*

*ΔE = 6.63\*10-34 \*1\*10‑11 = 6.63\*10-45 J< than minimum Heisenberg uncertainty prediction of 6.6\*10-16*

*…****Butt kick is in order….***

**Problem 5: Old School Physics and the Homogenous, 2nd order Differential Method (25 pts)**

For an ideal spring, Fideal =md2x/dt2 =-kx leads to the homogeneous differential equation discussed in problem 2-7 ,pp 56-57 of your text:

 m d2x/dt2 + kx =0 (ξ in your text is replaced with x here)

The solution to this is of the form: A sin ωt, a continuous and undiminished oscillation in time. Often, however, springs tend to `damp’ because of friction and metal fatigue. These factors add an additional drag force which varies with dx/dt. The force Fnon-ideal for such springs is expressed as below, where γ is called the `damping’ coefficient.

 Fnon-ideal = Fideal + drag = md2x/dt2= -kx - γdx/dt.

The correct solution of this non-ideal case yields a decaying oscillation reflective of the `damping’ force.

1. Re-derive the specific solution to this differential equation in the form:

x(t)= C1 e-atcos bt +C2e-atsin bt

where you have substituted the definitions: 1/T = γ/m and ωo2=k/m in your final solution.

Assume the boundary conditions:

dx/dt=vo at t=0

x(t)= 0 at t=0

and that: (γ/m)2- 4(k/m) < 0

(hint: remember that c1eiθ + c2e-iθ = C1cos θ + C2 sin θ and apply boundary conditions)15 pts

*Applying the usual analysis,*

*md2x/dt2= -kx - γdx/dt🡪 d2x/dt2 +(γ/m)dx/dt +(k/m)x = 0*

*Substituting in 1/T = γ/m and ωo2=k/m*

*d2x/dt2 +(1/T) dx/dt +(ωo2 )x = 0*

*Assuming the usual form x= c1er1\*t +cer2\*t*

*(r1 ,r2) = -1/T ±(1/T2 -4ωo2)1/2*

 *2*

*Since 1/T2 -4ωo2 < 0 => (4ωo2-1/T2) > 0 and we write the radical term so:*

*(r1 ,r2) = -1/T ±[(-1)(4ωo2-1/T2)] 1/2*

 *2*

*(r1 ,r2) = -1/T ±i[(4ωo2-1/T2)] 1/2*

 *2*

*x(t) = c1 e-t/2Texp(i\* ½ [(4ωo2-1/T2)] 1/2 t + c2 e-1/2Texp(-i\* ½ [(4ωo2-1/T2)] 1/2 t*

*= e-t/2T[c1 exp(i\*[(ωo2-1/4T2)] 1/2t + c2 exp(-i\*[(ωo2-1/4T2)] 1/2 t*

*=e-t/2T [C1 cos(ωo2-1/4T2) 1/2t + C2 sin(ωo2-1/4T2) 1/2t ]*

*Applying boundary condition x(0)=0*

*x(0) = e0/2T(C1 cos 0 + C2 sin 0)=0 iffi C1 = 0*

**∴x(t) = C2 e-t/2T sin ½ (ωo2-1/4T2) 1/2t**

1. Given that vo = 1, T=0.25, ωo =√101 what is the exact form of the solution to x(t) ? 6 pts

*dx/dt= C2(-1/2T e-t/2T sin(ωo2-1/4T2) 1/2t +C2e-t/2T ((ωo2-1/4T2) 1/2cos (ωo2-1/4T2) 1/2t )*

*at t= 0, the sin term 🡪0 leaving dx(0)/dt= C2e-0/2T ((ωo2-1/4T2) 1/2cos (ωo2-1/4T2) ½\*0 )*

*vo= dx/dt= C2(ωo2-1/4T2) ½=1*

*C2 = 1/(ωo2-1/4T2) ½*

***x(t) =*** *1/(ωo2-1/4T2) ½****e-t/2T sin(ωo2-1/4T2) 1/2t ]***

*Plugging in given values:*

***X(t) = 1/(101-1)1/2 e-t/0.25 sin(101-1)1/2t= 1/10 e-2t sin 10t***

1. Plot your exact solution above for the case of T=0.25, ωo =√101 for t= 0🡪 ½ π



**Problem 6: The particle in a less-than-perfectly symmetric 2D Box (10 pts)**

The solution for a particle in a 2D box described in **Supplement 2: The 2-D particle in-a-box applied to a real molecule,** assumes the porphyrin described is a square with equal box sides of length L. Suppose this is not the case, but instead Lx = ½ Ly, e.g. the 2D box is now a rectangle.

a) Express the final energy for the system with Lx = ½ Ly 5 pts

*Starting with the derived form in Supplement 2:*

***7a*** ***Ex*** *=* ***(nx π ħ)2  nx =1,2,3…***

 ***2mLx2***

***7b Ey = (nyπ ħ)2  ny =1,2,3…***

 ***2mLy2***

*We simply note that the two axes no longer have a common side so we simply replace Ly in 7b with Ly =2Lx*

*E(modified) =* ***(nx π ħ)2  + (nyπ ħ)2 nx =1,2,3… ny =1,2,3…***

 *2mLx2 2m(2)2Lx2*

*E(modified)= (****π ħ)2*** *[nx2+ ny2/4]*

 *2mLx2*

b) Compute the expected HOMO->LUMO transition wavelength λ(nm) for the above assuming 18 electrons in the porphryin, assuming: Lx =1 nm = 10-9m . Electron mass m=9.1\*10-31 kg, ħ= 1.054\*10-34J\*s and h= 6.626\*10-34 J\*s, c= 3\*108 m/s. (Be careful about how you construct the energy manifold. A standard bit of chemical wisdom is that losing molecular symmetry means splitting once equivalent energy levels.)

 *E(modified)= (****π ħ)2*** *[nx2+ ny2/4] = (****π ħ)2(4nx2+ ny2)***

 *2mLx2 8mLx2*

*Plugging in the various constants we get:*

*1.5061\*10-20[4nx2+ ny2] J*

*Note that loss of the square shape and its conversion to a rectangle means (nx, ny)= (1,2) is no longer the same in energy as (nx, ny)= (2,1).To fill in 18 electrons means we have to carefully combine (nx, ny) ranked in order of increasing size according to the magnitude of [nx2+ 4 ny2]*

[4nx2+ ny2]=

**(nx,ny**) **E (in ( π ħ)2 /2mLx2 unitstotal electroncount**

**(1,1) 5 2**

 **(1,2) 8 4**

 **(1,3) 13 6**

 **(2,1) 17 8**

 **(1,4) (2,2) 20 12**

 **(2,3) 25 14**

 **(1,5) 29 16**

 **(2,4) 32 18 HOMO**

**(1,3) 37 LUMO**

***ΔE= ( π ħ)2 /2mL2) (37-32) J =****1.506\*10-20\*5=7.53\*10-20J = hc/λ=1.99\*10-25/λ(M)*

**λ= *1.99\*10-25/7.53\*10-20 J=2.643\*1067m ~2643 nm (near IR band)***

**Problem 7: benzene as a particle in a circle**

The ***observed*** HOMO🡪 LUMO uv transition for gas phase benzene occurs at 180 nm *(Takahashi, J. Chem. Phys. 57(6) 1972 pp 2526-2531).* Provide evidence-yea or nay- that the particle-on-a-circle model for benzene is a reasonable one . You can assume that the ~ radius of benzene to be 0.2 nm (2\*10-10m) and that only its π electrons move freely. 10 pts

***Use the circle’s circumference = L =2πr we can simply assume the particle-in-a-box model applies and substitute 2πr for L in the usual solution for the particle-in-a-box so:***

***En = h2n2*** = h2n2 = ***ħ2 n2***

 ***8mL2 8m(2π)2r2 8mr2***

***This circular solution could be used to model a 6 electron system where the HOMO n=3 and the LUMO n=4where the radius of the benzene molecule is= r and m=electron mass.***

***Predicted HOMO🡪LUMO (n=4) absorption should happen atΔE(J)= (16-9)*** *ħ2/8mr2=****7 ħ2/8mr2***

 ***Setting r= 2.0\*10-10 meters, m=9.1\*10-31kg, ħ=1.054\*10‑34 =2.675\*10-19J=>744 nm Obs band for benzene near 180 nm (Takahashi, J. Chem. Phys. 57(6) 1972 pp 2526-2531)…Not great.***

*A more sophisticated approach is to assume the system is a rotator (not covered until test was due)*

*In which case En =* ħ 2 n2/2mr2 which is an answer 4 times that of the simple particle-in-box approximation=>

 ΔE = 4\*2.675\*10‑19 = 1.07\*10‑18 J => λ = hc/ΔE = 185 nm… a much better fit to observed.