**Take home exam 1:**

**Chemistry 6854**

**Physical Chemistry**

**Alfred State College**

**Spring 2014**

**Due Monday 3 March**

**90 pts**

**Rules:**

* **You can work together but must turn in work separately.**
* **Use the answer sheets provided and include extra pages if necessary**

**Note: The problems are all based on previous homework and/or lecture material presented in the last 4 weeks and should be within your reach.**

**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 (K) is the tungsten operating at to reach this color? (3 pts)

1b) As described in lecture, the classical Rayleigh-Jeans model for black body radiators assumed you

could distribute the absorbed energy of the box as `energy waves’ with various frequencies f. Like our particle-on-a-wire analysis, it was assumed that the allowed waves had 0 amplitude at x=0 and x=L , where L = the box length. This assumption is why the classical energy density ρ ends up ∝ f2.

Given a black body box which is 0.5 meter on a side, make a semi-quantitative argument for how this f2 relationship arises by deducing the count of waves whose wavelengths allow at least one full wave to exist in box so that it’s end points are zero a x= 0 and L in the box for the ranges 1-10 m, 0.1-1 m, 0.01-0.1 m, 0.001-0.01 m etc. (hint: remember that we showed the allowed λ=2L/n , n=1,2,3….) (5 pts)

1c) Why is the classical result that ρ ~f2 called the `ultraviolet catastrophe’ ? (2 pts)

**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)
2. 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)

**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) = -Ze2/Kr 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)
2. 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)

**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)

**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 ωot, 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

1. Given that vo = 1, T=0.25, ωo =√101 what is the exact form of the solution to x(t) ? 6 pts
2. Plot your exact solution above for the case of T=0.25, ωo =√101 for t= 0🡪π/2 using Maple. 4 pts

**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

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.) 5 pts

**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