**Take home exam 1:**

**Chemistry 6854**

**Physical Chemistry**

**Alfred State College**

**Spring 2016**

**Due Friday 4 March**

**100 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 5 weeks and should be within your reach.**

**Problem 1: Old School Physics and Dilemmas (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 according to Wiens empiric rule? (3 pts)

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)

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)

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

Using the Bohr model :

1. Derive a general expression for the momentum of an electron in the Bohr atom (12 pts)
2. compute the apparent momentum p=mv (m2/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. (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) = -ZKe2/r K=1/4πεo , 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.

You can re-write the above in the form: d2x/dt2 + γ/m dx/dt + (k/m)x =0

The correct solution of this non-ideal case yields a decaying oscillation reflective of the `damping’ force has the general form:

x(t)= e-at (C1cos bt +C2sin bt )

Find the **specific** form to the solution where you have substituted the definitions: 1/T = γ/m and ωo2=k/m in your final solution. I expect you to show your work….which means use Maple only to check your pencil and paper efforts.

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