ANSWERS to CHEMISTRY BC 3253x Exam 1 **Monday, October 15, 2007**

This exam has 4 questions, for a total of 100 points. Please show all work clearly. Continue on the back of the pages, as needed. Available: tables of constants and QM facts, basic math facts, periodic tables.

Question 1 (20) ____________ **Question 3 (30) ____________**

Question 2 (20) ____________ **Question 4 (30) ____________**

TOTAL (100) ____________

1) **(20 points)** Physical chemists often study reactions which form hydrogen atoms. One way to detect the presence of these atoms by measuring the absorbance of a laser tuned to the Lyman-α transition. [Reminder: the Lyman series originates from the n = 1 level, and the α transition is the lowest energy member of a series.] What is the wavelength of this laser in nm? Give the answer to six significant figures. (You may make the approximation that the H nucleus is infinitely massive.) In what region of the electromagnetic spectrum does this transition lie?

The Bohr formula for the energy levels of H are $E = -hcR/n^2$, where R is the Rydberg constant in cm^{-1}. If we treat the nucleus as infinitely massive, $R = R_\infty$.

Lyman-α is n=1 to n=2, so $\Delta E = -(hcR)(1/4 - 1/1) = 3(hcR)/4$

$\Delta E = h\nu = hc/\lambda$, so $\lambda = hc/\Delta E$

Therefore $\lambda = 1/[(0.75)R] = 1/(0.75 \times 109737.31\ cm^{-1}) = 1.215022 \times 10^{-5}$ cm

$= 1.215022 \times 10^{-7}$ m = <u>121.502 nm</u>. <u>This is UV</u> (visible starts at about 400 nm.)

Hint: it is very time consuming to calculate two energies and subtract: do algebra first!
I didn't ask for ΔE, so you can calculate λ in one step, avoiding use of constants like h, m....

 Name ________________________

2. (20 points)

a) (5) What is the commutator of the operators $\hat{A}$ = d/dx and $\hat{B}$ = 1/x?

The commutator is defined [d/dx, 1/x] ≡ (d/dx)(1/x) –(1/x)(d/dr)

First term: (d/dx)(f/x) = $-f/x^2$ +(1/x)(df/dx)

Second term: (1/x)(df/dx)

thus [d/dx, 1/x] = = $-1/x^2$

b) (15) Verify that the function F(r) = A e^{-r} is an eigenfunction of the operator $\hat{C}$ below. What is the corresponding eigenvalue?

$$\hat{C} = \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \frac{2}{r}$$

We will need dF/dr = $-Ae^{-r} = -F$ and $d^2F/dr^2 = +Ae^{-r} = F$

Setting up the eigenvalue equation: $\hat{C}$ F = c F where c is the eigenvalue.

The right hand side is $\hat{C}$F = F + (2/r)(–F) + (2/r) F = F

So F = c F. Therefore 1 = c

The <u>eigenvalue is 1</u>

An eigenvalue must be a constant. If you didn't get a constant times F, you did not get an Eigenvalue. (If you told me that it should have been a constant, I gave you some credit!)

3) (20 points) There is great interest today about materials related to “buckyballs”: spheres of pure carbon. Among these are carbon nanotubes: long thin tubes whose walls are sheets of carbon. Under certain circumstances, other atoms can be placed inside these closed tubes. Suppose a single Ne atom is trapped inside a nanotube 0.40 nm in length. **Treat this atom as a particle in a 1D box**.

a) (12 points) What are the frequency and the wavelength of the light which would be required to excite this atom from the ground state to the first excited state?

The P.I.B. energies are $E = n^2h^2/8mL^2$. The lowest allowed value of n is 1.

Transition is from n=1 to n=2 so $\Delta E = 3h^2/8mL^2$

$\Delta E = h\nu$, so $\nu = \Delta E/h = 3h/8mL^2$

$$\nu = \frac{3(6.626\times10^{-34}\,\text{kg}-\text{m}^2/\text{s})(6.022\times10^{23}/\text{mole})}{8(20.179\times10^{-3}\,\text{kg}/\text{mole})(0.40\times10^{-9}\,\text{m})^2} = 4.63\times10^{10}\,\text{s}^{-1}$$

$\lambda = c/\nu = (2.9979 \times 10^8$ m/s$)/(4.63 \times 10^{10}$ s$^{-1}) =$ <u>6.46×10^{-4} m</u> = 0.646 mm (radiofrequency)

Are these numbers quite different from what we have been seeing? Yes: a Ne atom is much heavier than an electron, so this is a much lower energy transition.

b) (18 points) What is the probability that the Ne in the ground state will be found in the middle half of the nanotube (i.e. between L/4 and 3L/4, or from 0.10 nm to 0.30 nm from either end)? Do the integral and find the numerical result. Compare with the classical result.

$\Psi_0 = (2/L)^{1/2} \sin(n\pi x/L)$

$$P = \int_{L/4}^{3L/4} \Psi_0^*\Psi_0 dx = \frac{2}{L}\int_{L/4}^{3L/4} \sin^2\left(\frac{\pi x}{L}\right)dx = \frac{2}{L}\left[\frac{x}{2} - \frac{L}{4\pi}\sin\left(\frac{2\pi x}{L}\right)\right]_{L/4}^{3L/4}$$

Integral #1, with $a = \pi/L$

$$= \frac{2}{L}\left[\frac{3L}{8} - \frac{L}{8} - \frac{L}{4\pi}\left\{\sin\left(\frac{2\pi 3L}{4L}\right) - \sin\left(\frac{2\pi L}{4L}\right)\right\}\right] = \frac{2}{L}\left[\frac{L}{4} - \frac{L}{4\pi}\left\{\sin\left(\frac{3\pi}{2}\right) - \sin\left(\frac{\pi}{2}\right)\right\}\right]$$

$$= \left[\frac{1}{2} - \frac{1}{2\pi}\{(-1)-(1)\}\right] = \frac{1}{2} + \frac{1}{\pi} = 0.818$$

Classically, the answer would be ½ = 0.5. As we saw earlier, in the ground state, the QM particle is much more likely to be in the middle of the box, away from the walls.

4) (30 points) The wavefunctions for particular system are

$$\Psi_n(x) = A_n\, e^{-x/2}\, L_n(x)$$

where $L_n(x)$ is a Laguerre Polynomial. The coordinate x extends from 0 to +∞. The first three Laguerre polynomials are

n	$L_n(x)$
0	1
1	$1 - x$
2	$1 - 2x + x^2/2$

a) (10) Show that Ψ_0 and Ψ_1 are orthogonal.

We can ignore the A's, since they are constants. We need to examine the integral

$$\int_0^\infty e^{-x/2}(1)\, e^{-x/2}(1-x)\, dx = \int_0^\infty e^{-x}(1-x)dx = \int_0^\infty e^{-x}dx - \int_0^\infty xe^{-x}dx = 1 - 1 = 0$$

(I have used the definite integral tables, #1 with a=1 twice: n=0 and n=1)

b) (10) Find the normalization constant A_0 for the ground state Ψ_0.

$$A_0^2\int_0^\infty e^{-x/2}(1)\, e^{-x/2}(1)\, dx = A_0^2\int_0^\infty e^{-x}dx = A_0^2(1) = 1$$

so $\underline{A_0 = 1}$ (the function is already normalized!

c) (10) The normalization constant A_1 is equal to one: $A_1 = 1$. What is $\langle x \rangle$ for a system in the state Ψ_1?

The operator corresponding to position x is x.

$$\langle x \rangle = A_1^2\int_0^\infty e^{-x/2}(1-x)\, x\, e^{-x/2}(1-x)\, dx = \int_0^\infty e^{-x}x(1-x)^2 dx$$

$$= \int_0^\infty x\, e^{-x}dx - 2\int_0^\infty x^2\, e^{-x}dx + \int_0^\infty x^3\, e^{-x}dx \quad \text{<< definite integral #1 with a =1}$$

$= 1(1!) - 2(2!) + 3! = 1 - 4 + 6 = \underline{3 = \langle x \rangle}$