Chemistry 422
Spring 2014
Practice Exam 1 Solutions

Name: __________________________

Instructions:
Check the exam to make sure that it contains exactly 6 different pages, including this one and a periodic table at the end.

Some useful constants and equations:

\[ R_H = 109,737 \text{ cm}^{-1} \quad N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \]

\[ m_e = 9.11 \times 10^{-31} \text{ kg} \quad h = 6.63 \times 10^{-34} \text{ J s} \quad \hbar = h/2\pi \]

\[ c = 3.00 \times 10^8 \text{ m s}^{-1} \quad k_B = 1.38 \times 10^{-23} \text{ J K}^{-1} \quad 1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg} \]

\[ \lambda = h/p \quad \Delta E = h \ c \ R_H(1/n_i^2 - 1/n_f^2) \]

\[ E_n = n^2 h^2/8m_e a^2, \quad n = 1, 2, 3, \ldots \quad \psi_n(x) = \sqrt{2/a} \sin(n\pi x / a) \]

\[ \Delta E = (N+1)h^2/8m_e a^2 \quad \lambda = 8m_e a^2 c/(N+1)h \]

\[ \lambda \nu = c \quad \tilde{\nu} = 1/\lambda \quad E = h \nu \quad \Delta x \Delta p \geq \hbar /2 \]

3N-6 (nonlinear molecule) or 3N-5 (linear molecule) vibrational modes

\[ E_{\text{vib}} = (n + \frac{1}{2})h\nu, \quad n = 0, 1, 2, \ldots \quad \nu = (k/\mu)^{1/2}2\pi \quad \text{(vibrational frequency)} \]

\[ \mu = m_A m_B/(m_A+m_B) \quad \text{(reduced mass)} \]

\[ E_{\text{rot}} = J(J+1)h^2/8\pi^2 I, \quad J = 0, 1, 2, \ldots \quad (2J+1)-degenerate \quad I = \mu r_0^2 \]

\[ n_2/n_1 = (g_2/g_1)\exp[-(E_2-E_1)/k_B T] \]

\[ \psi_n(x) = A \exp\left(-x\sqrt{2m(V_0 - E)/\hbar^2}\right) \quad (A = \text{constant; particle in barrier}) \]
Part 1. Write the letter of the answer which best satisfies each statement or question in the blank at the left. Please check your answers. Credit will only be given for the letter written in the blank (3 points each).

A

1. The minimum energy needed to remove an electron (ionize) from the ground state of the hydrogen atom is equal to which of the following?
   (A) $h c R_H$  (B) $4h c R_H$ (C) $(h c R_H)/4$  (D) $(N+1)\hbar^2/8m_e a^2$

B

2. If the velocity of a particle increases, the wavelength associated with the particle
   (A) increases  (B) decreases  (C) remains the same

C

3. Which of the following functions is an acceptable wave function over the interval $0 < x < \infty$?
   (A) $x^2 e^{-2\pi i x}$  (B) $x^2 e^{-2\pi i x}$  (C) exp$(-x^2/2)$  (D) exp$(x^2/2)$

A

4. The wave function for the particle in the box is 0 everywhere outside the box. This means that
   (A) the particle cannot be found outside the box.
   (B) the particle is as likely to be found outside the box as inside the box
   (C) the particle is most likely in the middle of the box.
   (D) the particle is neither inside nor outside the box.

C

5. Which of the following molecules is not infrared active?
   (A) H$_2$O  (B) CO$_2$ (C) N$_2$ (D) HCl

B

6. By increasing the length of a linear polyene from 4 to 6 carbons, the frequency of light needed to excite the molecule from the ground to first excited state
   (A) increases  (B) decreases  (C) remains the same

A

7. For a particle in a 1D box of length $a$, the expectation value of its position $\langle x \rangle$
   (A) is always $a/2$  (B) is largest at the boundaries of the box
   (C) is equal to $\langle x^2 \rangle^{1/2}$  (D) depends on the value of the quantum number $n$.

C

8. The number of vibrational modes of H$_2$O is
   (A) 1  (B) 2  (C) 3  (D) 4

B

9. The probability for a particle to tunnel through a barrier increases if which of the following increases?
   (A) mass of particle  (B) energy of particle  (C) energy of barrier  (D) width of barrier

A

10. Which of the following operators does not commute with $\hat{P}_x = -i\hbar \frac{\partial}{\partial x}$?
    (A) $\hat{x}$  (B) $\hat{y}$  (C) $\hat{p}_y$  (D) $\hat{p}_x$
Part II. Short answer: Answer the following in the space provided. (12 points each)

1. A \pi electron is somewhere along a linear polyene of length 16.2 Å, but within this length we are uncertain where. What is the minimum uncertainty in its velocity? (1Å = 1 \times 10^{-10} m.)

The uncertainty in momentum is

\[ \Delta p = \frac{h}{4\pi \Delta x} = 6.63 \times 10^{-34} \text{ J s}/4\pi(16.2 \times 10^{-10} \text{ m}) = 3.26 \times 10^{-26} \text{ kg m s}^{-1} \]

The uncertainty in velocity is just the uncertainty of the electron’s momentum over its mass,

\[ \Delta v = \frac{\Delta p}{m} = \frac{3.26 \times 10^{-26} \text{ kg m s}^{-1}}{9.11 \times 10^{-31} \text{ kg}} = 3.57 \times 10^{4} \text{ m s}^{-1} \]

2. It takes 334 J to melt 1 g of ice at 0 °C. How many photons at 660 nm must be absorbed to melt 5.0 \times 10^{2} g of ice? (1nm = 10^{-9} m).

Need energy: 334 J/g ice (500 g ice) = 1.67 \times 10^{5} \text{ J}

From 1 photon: \[ E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^{8} \text{ m s}^{-1})}{(6.60 \times 10^{-7} \text{ m})} = 3.01 \times 10^{-19} \text{ J} \]

Number of photons needed = \( \frac{1.67 \times 10^{5} \text{ J}}{3.01 \times 10^{-19} \text{ J}} = 5.55 \times 10^{23} \) (roughly 1 mole)

3. Consider a particle in a 2-dimensional square box. What is the lowest energy of the particle? What is the energy of the first excited state? What is the degeneracy of the first excited state?

Ground state energy: \[ E = \frac{2(h^{2}/8m_{e}a^{2})}{h^{2}/4m_{e}a^{2}} = h^{2}/4m_{e}a^{2} \]

First excited state energy: \[ E = h^{2}/8m_{e}a^{2} + 4h^{2}/8m_{e}a^{2} = 5h^{2}/8m_{e}a^{2}. \]

The first excited state is doubly degenerate.
Part III. Write your answer to the problems below in the space provided. Please show all work. Partial credit will be given based on work shown. (17 points each)

1. (a) The fundamental frequency of vibration for $D^{35}Cl$ is given by $\tilde{\nu} = 2081.0 \text{ cm}^{-1}$. ($D$ is $^2\text{H}$.) Calculate the force constant, $k$, in N m$^{-1}$ for the $D^{35}Cl$ bond. (12 points)

$$\nu = \frac{(k/\mu)^{1/2}}{2\pi}$$

and $\nu = c\tilde{\nu} = (3.00 \times 10^8 \text{ m s}^{-1})(2081.0 \text{ cm}^{-1})(100 \text{ cm/1 m}) = 6.24 \times 10^{13} \text{ s}^{-1}$

$D = ^2\text{H} = \text{deuterium}.$

The reduced mass for $D^{35}Cl$ is

$$\mu = \frac{m_D m_{Cl}}{m_D + m_{Cl}}$$

$$= (1.66 \times 10^{-27} \text{ kg amu}^{-1}) (2.01 \text{ amu})(35.0 \text{ amu})/(2.01 \text{ amu} + 35.0 \text{ amu})$$

$$\mu = 3.16 \times 10^{-27} \text{ kg}.$$ Then using the first equation above,

$$k = 4\pi^2 \mu \nu^2 = 4\pi^2 (3.16 \times 10^{-27} \text{ kg})(6.24 \times 10^{13} \text{ s}^{-1})^2 = 487 \text{ kg s}^{-2} = 487 \text{ N m}^{-1}$$

(b) Calculate the ratio of the population of $D^{35}Cl$ molecules in the first excited vibrational level to the population of $D^{35}Cl$ in the ground vibrational level at 300 K. Are the vibrations of $D^{35}Cl$ a quantum mechanical property? (5 points)

$$n_1/n_0 = \exp\left((-6.63 \times 10^{34} \text{ J s})(6.24 \times 10^{13} \text{ s}^{-1})/(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})\right)$$

$$n_1/n_0 = 4.57 \times 10^{-5}$$

Big change in probability to occupy state in going from ground state to first excited state, which means that $k_BT$ is much smaller than the difference in energy between these states. The vibrations are therefore quantum mechanical.
2. A microwave spectrum for carbon monoxide (CO) shows a series of lines separated by $1.15 \times 10^{11}$ Hz. The first line at $1.15 \times 10^{11}$ Hz corresponds to the $J = 0$ to $J = 1$ transition. Calculate the length (in Å) of the carbon-oxygen bond. (12 points)

\[
\Delta \nu = 1.15 \times 10^{11} \text{ Hz} = \Delta E_{rot}/h = \frac{1(1+1)h}{8\pi^2 I}
\]

\[
I = \frac{h}{4\pi^2(1.15 \times 10^{11} \text{ s}^{-1})} = \frac{(6.63 \times 10^{-34} \text{ Js})}{4\pi^2(1.15 \times 10^{11} \text{ s}^{-1})} = 1.46 \times 10^{-46} \text{ kg m}^2
\]

\[
\mu = (12.01)(16.00)/(28.01) \text{ amu} \times (1.66 \times 10^{-27} \text{ kg/amu}) = 1.14 \times 10^{-26} \text{ kg}
\]

\[
r_0^2 = \frac{I}{\mu} = 1.46 \times 10^{-46} \text{ kg m}^2/1.14 \times 10^{-26} \text{ kg} = 1.28 \times 10^{-20} \text{ m.}
\]

\[
r_0 = 1.13 \times 10^{-10} \text{ m} = 1.13 \text{ Å}
\]

(b) What is the energy of the photon needed to excite CO from the $J = 1$ level to the $J = 2$ level? (5 points)

\[
\Delta E_{rot} = 2(2 + 1) - 1(1+1)h^2/8\pi^2 I = 4 h^2/8\pi^2 I, \text{ which is twice the energy of the photon needed for the } J = 0 \text{ to } J = 1\text{ transition.}
\]

Therefore $\Delta E_{rot} = 2(1.15 \times 10^{11} \text{ s}^{-1})h = 1.52 \times 10^{-22} \text{ J}$