Chemistry 410A   Final Exam   Fall 2011

NAME:

Instructions:

1. **Keep this exam closed until instructed to begin.**

2. **Please write your name on this page but not on any other page.**

3. Please silence any noisy electronic devices you have. Calculators are the only electronics permitted for the exam.

4. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam.

5. To receive full credit for your work, please

   (a) show all your work, using only the exam papers, including the back of this sheet if necessary;

   (b) specify the correct units, if any, for your final answers;

   (c) use an appropriate number of significant digits for final numerical answers;

   (d) **stop writing and close your exam immediately when time is called.**

Other notes:

- **Part I of the exam (Problem 1) is worth 120 points.** Partial credit for these problems is not necessarily available.

- **Part I of the exam (Problems 2–9) is worth 180 points.** Your 6 best scores of these 9 problems (30 points each) will count towards the rest. Partial credit is available for these problems, so try each problem and do not erase any of your work.

Part 1: 120 points.

1. (a) What is the difference in energy (in J) between a red photon at $650\,\text{nm}$ and a blue photon at $480\,\text{nm}$?

   (b) What is the transition energy ΔE **in kJ/mol** of the $n = 5 \rightarrow 4$ emission in Li^{2+}?

   (c) Write the expression for the *complex conjugate* of the $3p_{m_l=1}$ orbital wavefunction in B^{4+}.

   (d) Pretend you want to solve the vector model for ground state protactinium, with electron configuration $[\text{Rn}]7s^2 6d^1 5f^2$. Draw any **two** valid microstates (the diagrams with the little arrows) for this configuration, and write the M_L and M_S values.

(e) If we count *all* of the spatial coordinates that describe one H_2O molecule,

    i. How many of these are translational coordinates?

    ii. How many of these are rotational coordinates?

    iii. How many of these are vibrational coordinates?

    iv. How many of these are electronic coordinates?

(f) Hexamethylene triperoxide diamine (HMTD) was one of the explosive compounds identified at a property in Escondido in November 2010, which led to the house being intentionally burned to the ground by authorities. Each atom is equivalent to the other atoms of same atomic number (so all six carbons are equivalent, both nitrogens, and so on). Assign HMTD to its point group, and identify the representation of the vibrational motion where the two nitrogens twist in opposite directions.
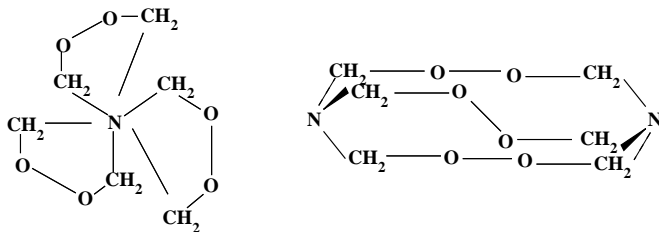
(g) Write the MO configuration and term symbol for the ground state of O_2^{2+}.

(h) Estimate the $v = 1 \rightarrow 2$ transition energy of $^2D^{19}F$.

(i) What homonuclear diatomic molecule has a bond length of $2.56\,\text{Å}$ and an equilibrium rotational constant (for its most abundant isotope) of $0.0396\,\text{cm}^{-1}$?

(j) Using two point charges for a dipole, and four point charges for a quadrupole, draw an orientation in the xz plane of a dipole and a quadrupole such that there is no net attraction or repulsion.

(k) Calculate the *change* in energy when two tetrahedral Ar_4 clusters combine to form a cubic Ar_8 cluster, assuming that each nearest-neighbor interaction is $-\epsilon$.

(l) The following equation is proposed as a model pair correlation function:

$$\mathcal{G}(R) \approx [1 - \cos(\pi R/R_0)]\, e^{-R/R_0}.$$

In what limit of R and in what way does this function have the wrong behavior?

Part 2: 180 points.

2. An electron has a normalized wavefunction

$$\psi(x) = \sqrt{\frac{30}{a^5}} \left[(a/2)^2 - x^2 \right] \qquad\qquad -a/2 < x \leq a/2$$
$$\psi(x) = 0 \qquad\qquad x \leq -a/2, \ x > a/2$$

which is not an eigenfunction of the kinetic energy operator. Find the expectation value of the kinetic energy in terms of the constant a.

3. Write the explicit integral necessary to find the electron-electron repulsion energy in the triplet $1s2s$ excited state of atomic helium to first order in perturbation theory.

4. The table below lists orbital energies in E_h from a Hartree-Fock calculation on the N_2 molecule. The total Hartree-Fock energy of the molecule is $-108.983\,E_\mathrm{h}$.

   (a) Assign each energy to the correct molecular orbital in the MO configuration.

-15.682
-15.678
-1.470
-0.777
-0.632
-0.612
-0.612

   (b) Calculate the total electron-electron *repulsion* energy in E_h.

   (c) To estimate the strength of the electron-nuclear interaction, calculate the effective atomic number of an electron in the highest energy orbital.

5. Construct a set of sp^3 hybrid orbitals from s, p_x, p_y, and p_z atomic orbitals such that one orbital has exactly 40% s character and the other three orbitals are all equivalent.

6. The cyclopentadienyl radical has the structure drawn below. All the carbons are equivalent and all the hydrogens are equivalent.
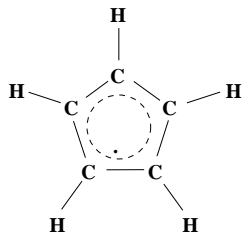
(a) Find the point group for this molecule.

(b) Show that the HOMO→LUMO transition (highest occupied to lowest unoccupied MO) in the π-bonding system of cyclopentadienyl must be allowed by electric dipole selection rules. (You do not need the character table for this point group to answer the question.)

7. For the $^7\Sigma_u^+$ state of N_2 in Fig. 6.7:

(a) What is the spin S of this state?

(b) What is the minimum number of unpaired electrons in this electronic state?

(c) What are the term symbols for the N atoms in the large-R limit?

(d) What is the MO configuration for this state?

8. The expectation value of x^2 in the harmonic oscillator is given by

$$\langle x^2 \rangle = \frac{\omega_e}{k} \left(v + \tfrac{1}{2} \right).$$

Use this to find an expression for $\langle p^2 \rangle$ in terms of μ, ω_e, and v.

9. Based on the parameters below, estimate **in kJ/mol** the total intermolecular potential energy for attraction between freely rotating HI and CO at a separation of $4.0\,\text{Å}$ and a temperature of $298\,\text{K}$:

	ΔE (eV)	μ (D)	α (Å^3)
HI	7.72	0.45	5.44
CO	8.07	0.11	1.95

10. Benzene crystallizes at $1\,\text{atm.}$ and $278.5\,\text{K}$ to an orthorhombic lattice with lattice constants $a = 7.49\,\text{Å}$, $b = 9.71\,\text{Å}$, and $c = 7.07\,\text{Å}$. The density of the unit cell is $0.606\,\text{amu}/\text{Å}^3$. If we put one molecule at each lattice point, where in the unit cell will we find the molecules?

$$\text{entropy} \quad S_{\text{Boltzmann}} = k_B \ln \Omega \qquad S_{\text{Gibbs}} = -N k_B \sum_i \mathcal{P}(i) \ln \mathcal{P}(i)$$

$$\text{vibrations} \quad E_{\text{vib}} = \omega_e v$$

$$\text{rotations} \quad E_{\text{rot}} = B_v J(J+1) \qquad g_{\text{rot}} = 2J + 1$$

$$\text{equipartition} \quad E = \frac{1}{2} N_{\text{ep}} N k_B T = \frac{1}{2} N_{\text{ep}} n R T$$

$$\text{virial/van der Waals} \quad P = RT \left[V_m + B_2(T) V_m^2 \right] \qquad RT = \left(P + \frac{a}{V_m^2} \right) (V_m - b)$$

$$dE = TdS - PdV + \mu_1 dn_1 + \dots \qquad dH = TdS + VdP + \mu_1 dn_1 + \dots$$

$$dF = -SdT - PdV + \mu_1 dn_1 + \dots \qquad dG = -SdT + VdP + \mu_1 dn_1 + \dots$$

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \kappa_X \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_X$$

$$C_P = C_V + V\alpha \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right]$$

$$\text{isothermal exp:} \quad w_{\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1} \right) \qquad w_{\text{irr}} = -P_{\text{ex}} \Delta V$$

$$\text{rev. adiabatic exp:} \quad w_{\text{rev}} = C_V \Delta T \qquad V_2 = V_1 \left(\frac{P_2}{P_1} \right)^{-C_V/(C_V + nR)}$$

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) \quad \Delta S = nC_{Pm} \ln \left(\frac{T_f}{T_i} \right)$$

$$\text{Joule-Thompson:} \quad \left(\frac{\partial T}{\partial P} \right)_H = \frac{\frac{2a}{RT} - b}{C_{Pm}}$$

$$\Delta S_{\text{mix}} = -R(n_A \ln X_A + n_B \ln X_B)$$

$$\Delta G_{\text{mix}} = RT(n_A \ln X_A + n_B \ln X_B)$$

$$\text{Gibbs-Duhem} \quad \sum_i n_i \mu_i = 0$$

$$\text{Clapeyron/Claus.-Clap.} \quad \frac{dP}{dT} = \frac{\Delta_\phi H}{T \Delta_\phi V} \qquad \ln P(\text{bar}) = \frac{\Delta_{\text{vap}} H_m^\ominus}{R} \left(\frac{1}{T_b^\ominus} - \frac{1}{T} \right)$$

$$\Delta T_f = -\frac{RT_f^{\bullet 2} X_B}{\Delta_{\text{fus}} H}$$

$$\Pi = \frac{RT X_B}{V_m} = RT[B]$$

$$T_{\text{ad}} = T_1 - \frac{\Delta H_{,\text{rxn}}(T_1)}{C_P(\text{products})}$$

$$\Delta_{\text{rxn}} G = \Delta_{\text{rxn}} G^\ominus + RT \ln \Xi$$

$$\ln K_{\text{eq}}(T_2) = \ln K_{\text{eq}}(T_1) + \frac{1}{R} \int_{T_1}^{T_2} \frac{\Delta_{\text{rxn}} H^\ominus}{T^2} dT$$

$$\text{rate constants} \quad k_{\text{SCT}} = p\sigma_{AB} \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} e^{-E_a/(RT)} N_A \qquad k_{\text{TST}} = \frac{k_B T}{Ch} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/(RT)}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

Fundamental Constants

Avogadro's number	$\mathcal{N}_A$	$6.0221367 \cdot 10^{23}$ mol^{-1}
Bohr radius	$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	$5.29177249 \cdot 10^{-11}$ m
Boltzmann constant	k_B	$1.380658 \cdot 10^{-23}$ J K^{-1}
electron rest mass	m_e	$9.1093897 \cdot 10^{-31}$ kg
fundamental charge	e	$1.6021773 \cdot 10^{-19}$ C
permittivity factor	$4\pi\epsilon_0$	$1.113 \cdot 10^{-10}$ C^2 J^{-1} m^{-1}
gas constant	R	8.314510 J K^{-1} mol^{-1}
	R	0.08314510 L bar K^{-1} mol^{-1}
	R	0.08206 L atm K^{-1} mol^{-1}
hartree	$E_{\text{h}} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ J
Planck's constant	h	$6.6260755 \cdot 10^{-34}$ J s
	$\hbar$	$1.05457266 \cdot 10^{-34}$ J s
proton rest mass	m_p	$1.6726231 \cdot 10^{-27}$ kg
neutron rest mass	m_n	$1.6749286 \cdot 10^{-27}$ kg
speed of light	c	$2.99792458 \cdot 10^8$ m s^{-1}

Unit Conversions

	K	cm^{-1}	kJ mol^{-1}	kcal mol^{-1}	J	kJ
kHz =	$4.799 \cdot 10^{-8}$	$3.336 \cdot 10^{-8}$	$3.990 \cdot 10^{-10}$	$9.537 \cdot 10^{-11}$	$6.626 \cdot 10^{-31}$	$6.626 \cdot 10^{-34}$
MHz =	$4.799 \cdot 10^{-5}$	$3.336 \cdot 10^{-5}$	$3.990 \cdot 10^{-7}$	$9.537 \cdot 10^{-8}$	$6.626 \cdot 10^{-28}$	$6.626 \cdot 10^{-31}$
GHz =	$4.799 \cdot 10^{-2}$	$3.336 \cdot 10^{-2}$	$3.990 \cdot 10^{-4}$	$9.537 \cdot 10^{-5}$	$6.626 \cdot 10^{-25}$	$6.626 \cdot 10^{-28}$
K =	1	0.6950	$8.314 \cdot 10^{-3}$	$1.987 \cdot 10^{-3}$	$1.381 \cdot 10^{-23}$	$1.381 \cdot 10^{-26}$
cm^{-1} =	1.4388	1	$1.196 \cdot 10^{-2}$	$2.859 \cdot 10^{-3}$	$1.986 \cdot 10^{-23}$	$1.986 \cdot 10^{-26}$
kJ mol^{-1} =	$1.203 \cdot 10^2$	83.59	1	0.2390	$1.661 \cdot 10^{-21}$	$1.661 \cdot 10^{-24}$
kcal mol^{-1} =	$5.032 \cdot 10^2$	$3.498 \cdot 10^2$	4.184	1	$6.948 \cdot 10^{-21}$	$6.948 \cdot 10^{-24}$
eV =	$1.160 \cdot 10^4$	$8.066 \cdot 10^3$	96.49	23.06	$1.602 \cdot 10^{-19}$	$1.602 \cdot 10^{-22}$
hartree =	$3.158 \cdot 10^5$	$2.195 \cdot 10^5$	$2.625 \cdot 10^3$	$6.275 \cdot 10^2$	$4.360 \cdot 10^{-18}$	$4.360 \cdot 10^{-21}$
erg =	$7.243 \cdot 10^{15}$	$5.034 \cdot 10^{15}$	$6.022 \cdot 10^{13}$	$1.439 \cdot 10^{13}$	10^{-7}	10^{-10}
J =	$7.243 \cdot 10^{22}$	$5.034 \cdot 10^{22}$	$6.022 \cdot 10^{20}$	$1.439 \cdot 10^{20}$	1	10^{-3}
bar L =	$7.243 \cdot 10^{24}$	$5.034 \cdot 10^{24}$	$6.022 \cdot 10^{22}$	$1.439 \cdot 10^{22}$	100.0	0.1000
kJ =	$7.243 \cdot 10^{25}$	$5.034 \cdot 10^{25}$	$6.022 \cdot 10^{23}$	$1.439 \cdot 10^{23}$	10^3	1

distance	1 Å =	10^{-10} m	
mass	1 amu =	$1.66054 \cdot 10^{-27}$ kg	
energy	1 J =	1 kg m^2 s^{-2}	$= 10^7$ erg
force	1 N =	1 kg m s^{-2}	$= 10^5$ dyn
electrostatic charge	1 C =	1 A s	$= 2.9979 \cdot 10^9$ esu
	1 D =	$3.3357 \cdot 10^{-30}$ C m	$= 1 \cdot 10^{-18}$ esu cm
magnetic field strength	1 T =	1 kg s^{-2} A^{-1}	$= 10^4$ gauss
pressure	1 Pa =	1 N m^{-2}	$= 1$ kg m^{-1} s^{-2}
	1 bar =	10^5 Pa	$= 0.98692$ atm