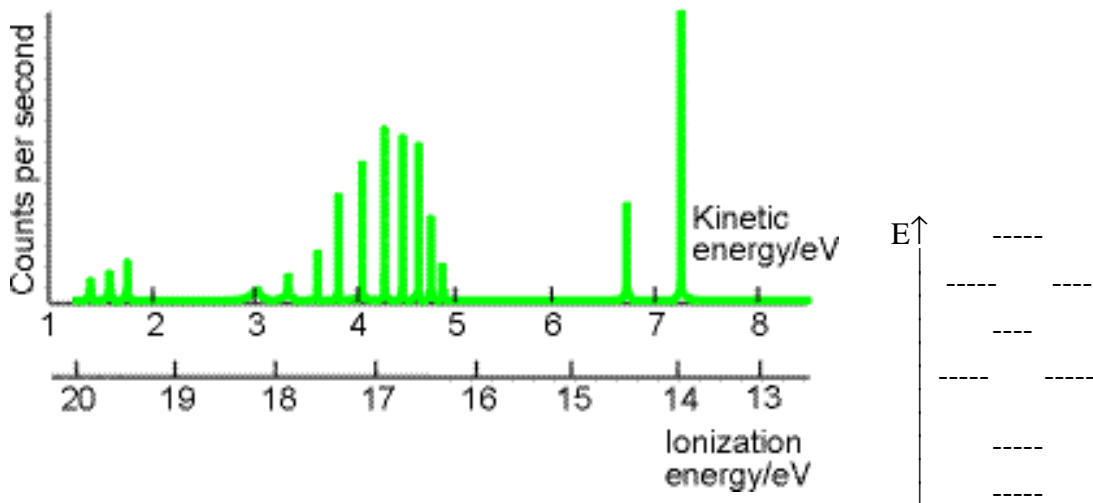


Constants:  $h=6.626 \times 10^{-34}$  J s     $\hbar = 1.054 \times 10^{-34}$  J s     $1 \text{ \AA} = 1 \times 10^{-8} \text{ cm} = 1 \times 10^{-10} \text{ m}$   
 $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$      $R = 8.314 \text{ J/mol K}$      $1 \text{ eV} = 96.485 \text{ kJ/mol}$

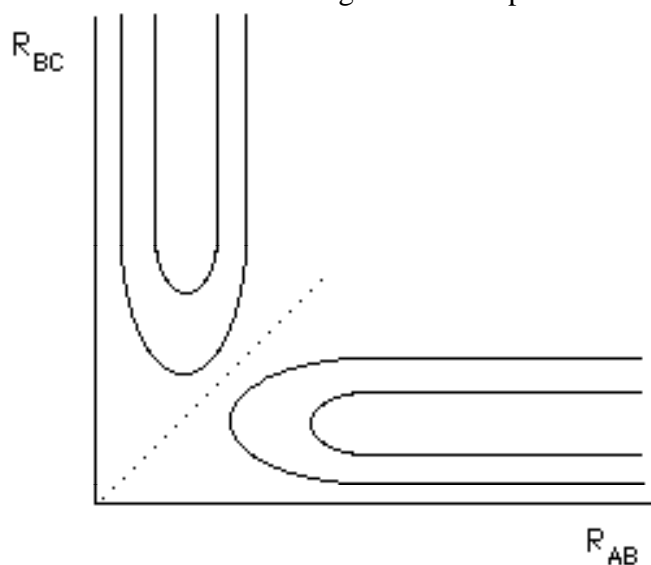
**Part 1.** Answer 7 of the following 8 questions. If you answer more than 7 cross out the one you wish not to be graded. 12 points each.

1. The photoelectron spectrum for CO is shown below and the corresponding energy level diagram is shown at right. Draw circles around all the vibrational transitions that share a common electronic transition. Label the three electronic transitions a, b, and c. Then draw arrows on the energy level diagram showing the ionization process that gives rise to these electronic transitions, and label with the proper letter, a, b, or c.



2. Use "garden variety" values for the partition functions to estimate the equilibrium constant for the reaction:  $\text{O}_2 + \text{F} \rightarrow \text{OF} + \text{O}$  at 298K, which is a possible reaction in the ozone depletion in the stratosphere. Remember the approximations  $q_t/N_A = 1 \times 10^7$ ,  $q_r = 100$ , and  $q_v = 1$ . The bond dissociation energies are:  $D_o(\text{O}_2) = 5.12 \text{ eV} = 494. \text{ kJ/mol}$ ,  $D_o(\text{OF}) = 2.2 \text{ eV} = 212 \text{ kJ/mol}$ . Ignore the effect of the electronic ground state degeneracy of each species.

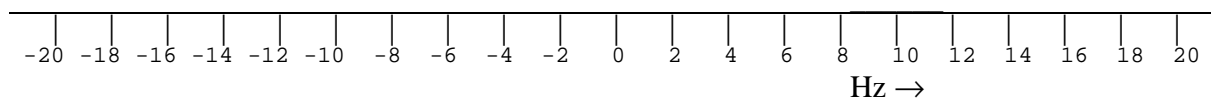
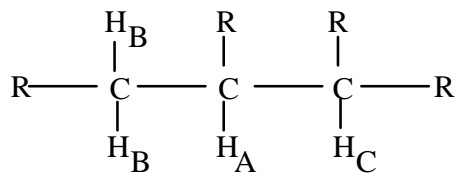
3. Sketch the trajectory of a collision with a long lived transition state that reacts to give products. Label the reactant side of the diagram and the product side of the diagram.



4. What are the  $l$  and  $m_l$  quantum numbers for the orbital in the front of the room? What is the magnitude of the total orbital angular momentum for this orbital?

5. For  $^{127}\text{I}^{35}\text{Cl}$ ,  $\tilde{\nu}_e = 384.3 \text{ cm}^{-1}$  and  $\chi_e \tilde{\nu}_e = 1.5 \text{ cm}^{-1}$ . Calculate the wavenumber of the  $v=0$  to  $v=1$  vibrational transition.

6. Show the spin-spin splitting pattern for nucleus A in the following molecular fragment.  $J_{AB} = 10$  Hz and  $J_{AC} = 15$  Hz. Indicate the relative intensities.



7. The  $[\text{F-H-F}]^-$  is a very stable linear ion. Draw the molecular orbitals and molecular orbital diagram for this ion. Use only p orbitals on F. Fill the diagram with the proper number of electrons.

8. The rotational constant of  $^{127}\text{I}^{35}\text{Cl}$  is  $0.1142\text{ cm}^{-1}$ . Calculate the bond length of the molecule. The mass of  $^{127}\text{I}$  is  $126.9045\text{ g mol}^{-1}$  and  $^{35}\text{Cl}$  is  $34.9688\text{ g mol}^{-1}$ .

**Part 2**. Answer 7 of the following 8 questions. If you answer more than 7 cross out the one you wish not to be graded. If you did the Take Home question do 6 of the following 8. 17 points each.

9. Calculate the rotational contribution to the Gibbs Free Energy of one mole of  $\text{O}_2$ . The  $\tilde{B}_e$  for  $\text{O}_2$  is  $1.446\text{ cm}^{-1}$ . The temperature is  $298.2\text{ K}$ .

10. The MOPAC semi-empirical MO coefficients for HF and HCl are given below. Every General Chemistry student knows that HF has a stronger bond than HCl. However, which has the more ionic character in the gas phase? To answer this question, calculate the % ionic character for MO's 1 and 2 for each molecule:

for HF MO1: \_\_\_\_\_%, MO2: \_\_\_\_\_%, and for HCl MO1: \_\_\_\_\_%, MO2: \_\_\_\_\_%.

		HF EIGENVECTORS				
Root No.		1	2	3	4	5
		-23.542	-17.094	-16.145	-16.145	3.608
S	F 1	.7088	.5632	.0000	.0000	-.4246
Px	F 1	.3460	-.8022	.0000	.0000	-.4865
Py	F 1	.0000	.0000	-.3830	-.9238	.0000
Pz	F 1	.0000	.0000	.9238	-.3830	.0000
S	H 2	.6147	-.1979	.0000	.0000	.7635

		HCl EIGENVECTORS				
Root No.		1	2	3	4	5
		-55.560	-14.950	-11.060	-11.060	1.543
S	Cl 1	.9765	.1730	.0000	.0000	.1282
Px	Cl 1	.0463	-.7502	.0000	.0000	.6596
Py	Cl 1	.0000	.0000	.0000	1.0000	.0000
Pz	Cl 1	.0000	.0000	1.0000	.0000	.0000
S	H 2	.2103	-.6382	.0000	.0000	-.7406

11. Of 1000 molecules, how many would be found in the  $v=1$  vibrational state of a harmonic oscillator with fundamental vibration frequency of  $200\text{ cm}^{-1}$  at room temperature.

12. Given that in a linear molecule an atom takes on nearly  $sp$  hybridization with:

$$\psi_1 = 0.80s + 0.60p \quad \text{and} \quad \psi_2 = 0.60s - 0.80p, \text{ show that the two hybrids are orthogonal.}$$

13. a. (7pts) What are polarization functions?

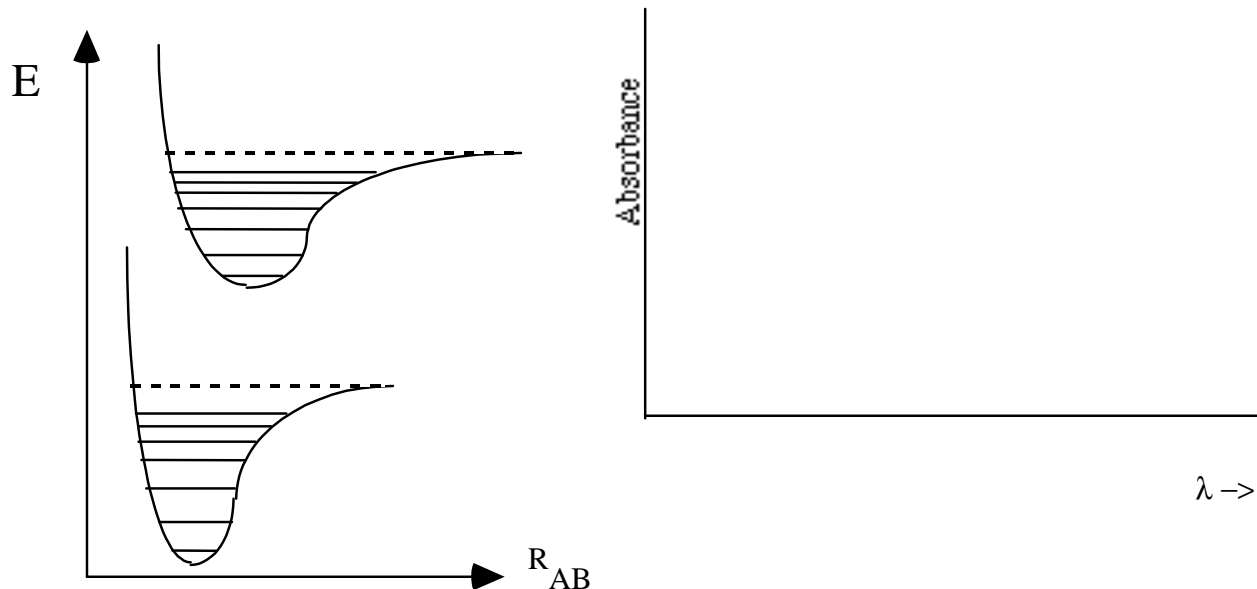
b. (4pts) What do Density Functional calculations take into account that pure Hartree Fock calculations do not?

c. (6pts) Order the following with respect to the expected agreement with experimental values: HF/6-31G\*, HF/6-311G\*, AM1, B3LYP/6-311G\*, MP2/6-311G\*.

Best: \_\_\_\_\_, \_\_\_\_\_, \_\_\_\_\_, \_\_\_\_\_, \_\_\_\_\_:Worst

14. Calculate the expectation value of the momentum of a harmonic oscillator in its lowest vibrational state. Just make all necessary substitutions, don't do the integral. (The answer is zero by the way).

15. Use the Franck Condon principle to predict the intensity of the different vibrational transitions in the fluorescence spectrum of the following system. Label each peak with the vibrational quantum numbers for the transition (e.g.  $4 \leftarrow 0$ ).



16. Sketch a  $3d_{xy}$  orbital. Give the angular portion of the orbital in terms of  $\theta$  and  $\phi$ .

