

Physical Chemistry  
Spring 2017, Prof. Shattuck

Test 2

Name \_\_\_\_\_

**Part I.** Answer 6 of the following 9 questions. 12 points each. Answer more for extra credit.

1. What is the magnitude of the orbital angular momentum of a 3d electron? Give the numbers of angular and radial nodes for a 3d orbital.

2. In the perturbation theory treatment of the helium atom, (a) what term in the Hamiltonian is used as the perturbation? (the answer in words is fine, no equation necessary).

(b). Describe in words the first-order perturbation correction to the energy of the helium atom (how is the first-order correction calculated)?

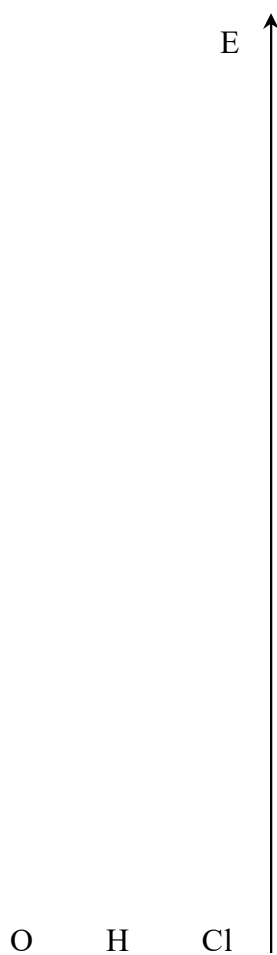
3. Why is the first ionization potential of Al less than Mg? Discuss the effective nuclear charge for the highest energy valence electrons in each atom.

4. (a.) What is the advantage of a split valence shell when using a Gaussian orbital such as 3-21G in a molecular orbital calculation?

(b). What does configuration interaction mean?

(c). What type of orbitals for carbon are added when going from 3-21G to 3-21G\*?

5. The reaction between OH and  $\text{Cl}^-$  gives the radical ion  $\text{OHCl}^-$ . The ion is linear. Construct the molecular orbital diagram using only p orbitals on the O and Cl along with the 1s orbital on H. Fill with electrons. What is the qualitative bond order of each of the individual bonds?



6. Describe the spin-orbit interaction for an atom. In particular:

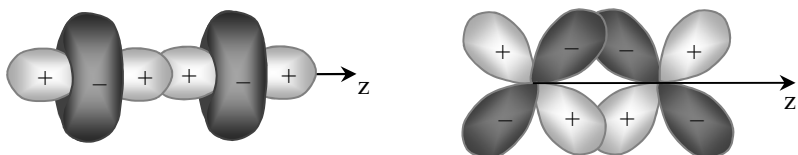
(a) What causes the spin-orbit interaction?

(b) What spin and what orbit quantum numbers are required?

(c) How does the magnitude of the spin-orbit interaction vary with the position of the element in the periodic table?

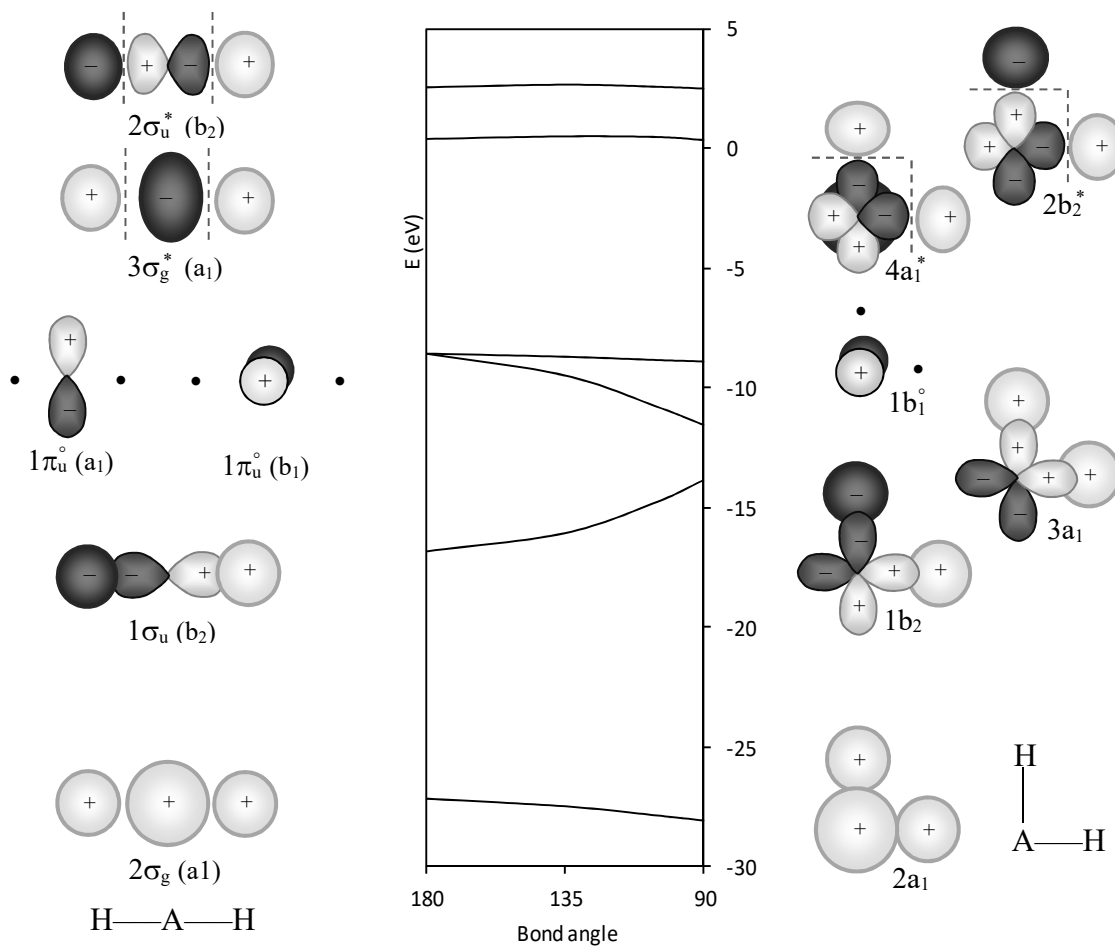
(d) What degeneracy does the spin-orbit interaction break?

7. Consider the end-to-end and side-to-side overlap of two d orbitals in a diatomic molecule. (See also the orbitals at the front of the room.) Are these molecular orbitals sigma, pi, or delta? Are they bonding or anti-bonding? Are they g or u?



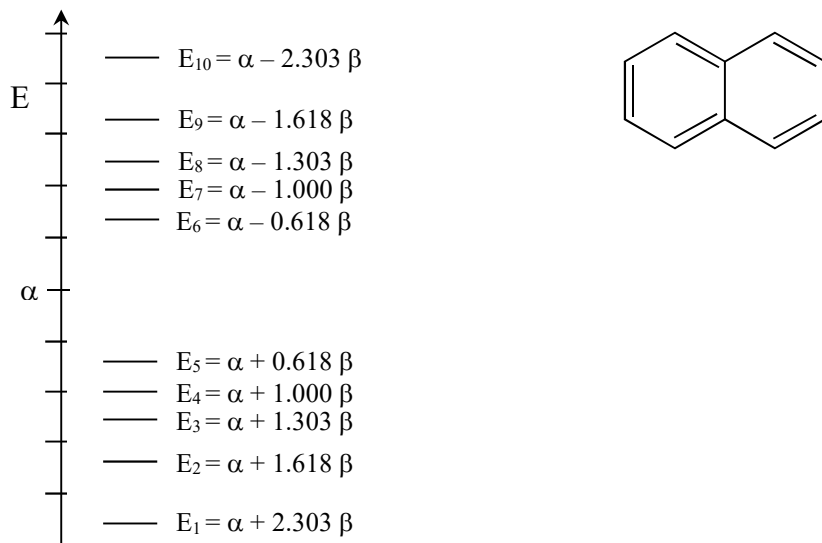
8. Give the term symbol for the ground state of F. Include the letter, spin multiplicity, and the possible total angular momentum J values.

9. Use the following Walsh diagram to estimate the bond angle in the radical,  $\text{NH}_2\cdot$ . Give the filling of the orbitals. Use the orbital filling to estimate the bond angle, choosing from bent or linear. Make sure to explain your reasoning. (For example, you can compare  $\text{NH}_2\cdot$  to  $\text{CH}_2$ .)



**Part III.** Answer three of the following four questions. If you answer more than 3 cross out the problem you don't wish to have graded. 10 points each.

10. A Hückel calculation for naphthalene,  $C_{10}H_8$ , gives the molecular-orbital energy levels shown below. Calculate the  $\pi$  delocalization energy for naphthalene.



11. The molecular orbitals for  $N_2$  are given below from an AM1 calculation.

**$N_2$  Molecular Orbitals** ( literature bond length, AM1 level )

ROOT NO.	1	2	3	4	5	6	7	8	
	-41.748	-21.382	-16.361	-16.361	-14.282	1.105	1.105	6.081	
S N	1	-.6203	.6478	.0000	.0000	-.3393	.0000	.0000	.2833
PX N	1	-.3393	-.2833	.0000	.0000	.6203	.0000	.0000	.6478
PY N	1	.0000	.0000	.0523	-.7051	.0000	-.2095	.6753	.0000
PZ N	1	.0000	.0000	.7051	.0523	.0000	.6753	.2095	.0000
S N	2	-.6203	-.6478	.0000	.0000	-.3393	.0000	.0000	-.2833
PX N	2	.3393	-.2833	.0000	.0000	-.6203	.0000	.0000	.6478
PY N	2	.0000	.0000	.0523	-.7051	.0000	.2095	-.6753	.0000
PZ N	2	.0000	.0000	.7051	.0523	.0000	-.6753	-.2095	.0000

a) Calculate the % s character in the  $\sigma^*(2p_x)$  orbital.

b) Draw the  $\sigma^*(2p_x)$  orbital. Include both s and p character in your drawing. Is the s interaction bonding or anti-bonding?

12. Show that the following two-electron determinantal wave function factors into a spatial part and a spin part.

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$$

13. On the last two pages is the MOPAC printout for geometry optimized H<sub>2</sub>O and H<sub>2</sub>S. Use of only p orbitals on the central atom gives 90° bond angles. Using only p-orbitals, the hybridization is described as p<sup>2</sup> or p<sup>3</sup>. Remember semi empirical uses valence electrons only.

a.) Note that the minimized bond angle for H<sub>2</sub>O is 108° and for H<sub>2</sub>S is 93°. Based on these angles alone, decide if the qualitative idealized hybridization of each molecule is closer to p<sup>3</sup> or to sp<sup>3</sup> hybridization.

H<sub>2</sub>O hybridization: \_\_\_\_\_

H<sub>2</sub>S hybridization: \_\_\_\_\_

b.) Use the sigma-pi bond-order matrix to determine the actual quantitative hybridization on O and S. Do these results agree with your answers to part a? (Give your reasoning for credit)

H<sub>2</sub>O hybridization: \_\_\_\_\_

H<sub>2</sub>S hybridization: \_\_\_\_\_

c.) Do both H<sub>2</sub>O and H<sub>2</sub>S have the same type of HOMO? Describe this orbital in each case (sigma or pi; bonding, nonbonding, or antibonding; delocalized or atomic on a single atom).

**H<sub>2</sub>S (OPTIMIZED PM3)**

ATOM NUMBER	CHEMICAL SYMBOL	BOND LENGTH (ANGSTROMS)	BOND ANGLE (DEGREES)	TWIST ANGLE (DEGREES)
1	S			
2	H	1.29072 *		1
3	H	1.29058 *	93.36387 *	1 2

## EIGENVECTORS

ROOT NO.	1	2	3	4	5	6
	-27.5984	-15.5724	-12.3141	-9.6289	.5550	1.3227
S S 1	.8176	-.0001	.5191	.0000	-.2489	-.0001
PX S 1	.1640	-.5141	-.4799	.0000	-.4620	.5147
PY S 1	.1739	.4848	-.5089	.0000	-.4899	-.4854
PZ S 1	.0000	.0000	.0000	1.0000	.0000	.0000
S H 2	.3703	-.5003	-.3472	.0000	.4922	-.4996
S H 3	.3703	.5003	-.3472	.0000	.4921	.4997

## SIGMA-PI BOND-ORDER MATRIX

	S-SIGMA	P-SIGMA	P-PI	S-SIGMA	S-SIGMA
	S 1	S 1	S 1	H 2	H 3
S-SIGMA S 1	.120110				
P-SIGMA S 1	.000000	1.878910			
P-PI S 1	.000000	.000000	.000016		
S-SIGMA H 2	.060050	.939461	.000008	.999740	
S-SIGMA H 3	.060060	.939449	.000008	.000221	.999738

**H<sub>2</sub>O (OPTIMIZED PM3)**

ATOM NUMBER	CHEMICAL SYMBOL	BOND LENGTH (ANGSTROMS)	BOND ANGLE (DEGREES)	TWIST ANGLE (DEGREES)
1	O			
2	H	.95124 *		1
3	H	.95114 *	107.77271 *	1 2

## EIGENVECTORS

ROOT NO.	1	2	3	4	5	6
	-36.8201	-17.5820	-14.5191	-12.3157	4.0560	5.3328
S O 1	.8780	-.0000	.3328	.0000	-.3439	-.0001
PX O 1	.0617	-.6203	-.4920	.0000	-.3187	.5173
PY O 1	.0846	.4526	-.6744	.0000	-.4364	-.3776
PZ O 1	.0000	.0000	.0000	1.0000	.0000	.0000
S H 2	.3302	-.4529	-.3100	.0000	.5431	-.5428
S H 3	.3302	.4528	-.3100	.0000	.5427	.5432

## SIGMA-PI BOND-ORDER MATRIX

	S-SIGMA	P-SIGMA	P-PI	S-SIGMA	S-SIGMA
	O 1	O 1	O 1	H 2	H 3
S-SIGMA O 1	.279038				
P-SIGMA O 1	.000000	1.648385			
P-PI O 1	.000000	.000000	.008221		
S-SIGMA H 2	.139503	.824208	.004111	.967822	
S-SIGMA H 3	.139535	.824177	.004110	.000000	.967822