

Name: \_\_\_\_\_

Student Number: \_\_\_\_\_

**CHM 2311**  
**Final Exam**  
**April 29 2009**  
**Professor Darrin Richeson**

There are 15 pages in this exam (including supporting materials and tables). Please count the pages to make sure none are missing.

**You may *carefully remove* the last three pages of the exam and use them for scratch work.**

***Please write legibly and show your work to receive credit for your answers.***  
Partial marks *may in some cases* be awarded for partially correct work.

Question	Mark	Question	Mark
<b>1</b>	<b>/5</b>	<b>8</b>	<b>/4</b>
<b>2</b>	<b>/9</b>	<b>9</b>	<b>/13</b>
<b>3</b>	<b>/7</b>	<b>10</b>	<b>/16</b>
<b>4</b>	<b>/16</b>	<b>11</b>	<b>/5</b>
<b>5</b>	<b>/10</b>	<b>12</b>	<b>/12</b>
<b>6</b>	<b>/9</b>		
<b>7</b>	<b>/4</b>		
		<b>Total</b>	<b>/110</b>

Good luck and have a great summer!

1. (5 points) A hydrogen orbital has the following *complete* wave function (both angular and radial portions of the wave function are included and the angular part is written in Cartesian coordinate form):

$$\psi(r, \theta, \varphi) = R(r)\{Y(\theta, \varphi)\} = \frac{1}{81\sqrt{15}} \left(\frac{2Z}{a_0}\right)^{3/2} (\rho)^2 e^{-\rho/3} \left\{ \frac{1}{4} \sqrt{\frac{15}{\pi}} \frac{x^2 - y^2}{r^2} \right\}$$

where  $\rho = \frac{Zr}{a_0}$  and  $Z = 1$  for a hydrogen atom

$$a_0 = 52.9 \text{ pm}$$

- a. For this orbital, determine the distance from the nucleus in picometers at which **all radial** nodes occur.
- b. Determine the quantum numbers  $n$  and  $l$  for this orbital. **Clearly** show the process by which you determined these values. Identify the orbital (1s, 2s, 2p<sub>x</sub>, etc...).

2. (9 points) a. Calculate  $Z_{\text{eff}}$  for a 2p electron on each of the following species.  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ .

b. Match the ion with the radii in the following table.

Crystal (Ionic) Radius	Ion
119pm	
86pm	
116pm	
126pm	

c. Calculate the  $Z_{\text{eff}}$  for a 4d electron of antimony (symbol Sb)

3. (7 points) There are potentially three isomers for the anion  $\text{NSO}^-$ . The two known species are  $\text{NSO}^-$  and  $\text{SNO}^-$ . The isomer  $\text{SON}^-$  is unknown. Suggest reasonable resonance structures for each of these three isomers.

4. (16 points) Draw the most stable Lewis structure and all *significant* resonance contributors for each of the molecules below. In your final answer, show all bonded pairs of electrons as lines between the bonded atoms and show all non-bonded electrons as dots. Indicate any *non-zero formal charges* on every element where they occur.

a.  $\text{SSO}_3^{2-}$  (thiosulfate)

**Final Answer:**

Geometry: _____
Shape: _____
Hybridization of central S: _____

b.  $\text{XeO}_3$

**Final Answer:**

Geometry: _____
Shape: _____
Hybridization of Xe: _____

c.  $\text{ICl}_4^-$

**Final Answer:**

Geometry: _____
Shape: _____
Hybridization of I: _____

5. (10 points) The series of halate anions  $\text{IO}_3^-$ ,  $\text{BrO}_3^-$ , and  $\text{ClO}_3^-$  is known.

Predict a trend in bond angles for these species. Explain.

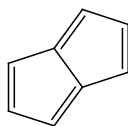
\_\_\_\_\_ < \_\_\_\_\_ < \_\_\_\_\_

Predict a trend in bond lengths for these species. Explain.

\_\_\_\_\_ < \_\_\_\_\_ < \_\_\_\_\_

6. (9 points) Determine the point group for each of the following molecules.

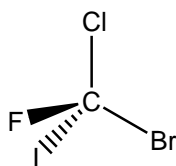
A.



(planar)

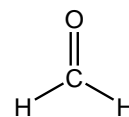
Point Group: A. \_\_\_\_\_

B.



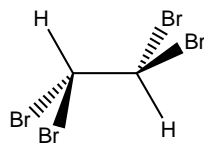
B. \_\_\_\_\_

C.



C. \_\_\_\_\_

D.



Point Group: D. \_\_\_\_\_

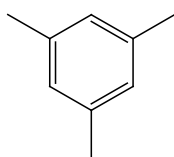
E.  $\text{SbF}_5$

E. \_\_\_\_\_

F.  $d_{xz}$  orbital

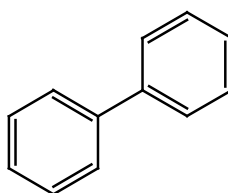
F. \_\_\_\_\_

G.



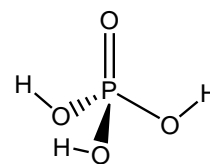
Point Group: G. \_\_\_\_\_

H.



H. \_\_\_\_\_

I.



I. \_\_\_\_\_

7. (4 points; ½ point per blank) In the questions below you will determine the irreducible representations for specific orbitals on a central atom of a molecule in a given point group. You may use the back of one of the exam pages for your scratch work. It is *not necessary to determine the symmetry labels*.

a. A  $d_{xy}$  orbital on the central atom of a molecule in the  $D_3$  point group

$D_3$	E	$2C_3$	$3C_2$		
					$d_z^2$

b. A  $p_z$  orbital on the central atom of a molecule in the  $D_{3h}$  point group

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
					-1		$p_z$

8. (4points; ½ point per blank) Given the symmetry labels for the following irreducible representations, fill in the missing characters:

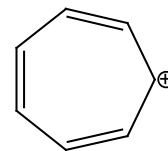
$C_{3v}$	E	$2C_3$	$3\sigma_v$
$A_2$			

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$	
$B_2$	<i>I</i>			<i>I</i>	$d_{yz}$

$D_{3d}$	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$
$A_{2g}$	1				1	-1

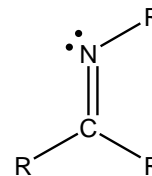
9. **(13 points)** We discussed the bonding in a planar  $\text{AH}_4$  species. In this problem we will extend these ideas to include d orbitals on the central A atom.
- (i) What are the group orbitals for planar  $\text{AH}_4$ ? (provide simple drawings)
  - (ii) Consider all of the d orbitals on the central atom. Clearly indicate the group orbitals that have appropriate symmetry to interact with the d orbitals on A?
  - (iii) What is the maximum number of bonds that could be made for this hypothetical  $\text{AH}_4$  molecule?

10. a. **(15 points)** In the space below, draw a  $\pi$ -MO diagram for the cycloheptatrienyl cation. Your diagram should include the following:
- Sketches of all of the bonding and antibonding  $\pi$ -orbitals
  - Relative energy levels of all orbitals indicated by appropriate placement of orbitals on the vertical energy axis.
  - Electrons in the appropriate molecular orbitals

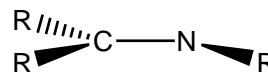
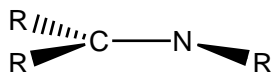


- b. **(2 points)** Does the Hückel rule predict that the cycloheptatrienyl cation will be aromatic or antiaromatic? Is your MO diagram consistent with this prediction? Explain.

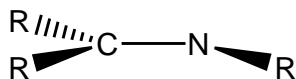
11. The molecule shown to the right belongs to a class called “imines”. (R represents a substituent group whose identity is not important for this problem.) All of the atoms of the imine are in the same plane. Even though you might not know anything about imines, you should be able to apply the orbital concepts to explain some reactivity.



- a. (2 points) A nucleophile is a chemical reagent that reacts with a site of positive charge on another molecule. Such a reaction can be viewed as the nucleophile donating a pair of electrons. To evaluate attack of the imine  $\pi$ -system by a nucleophile, we need to identify the HOMO and LUMO orbitals of the imine. On the skeletons below, sketch these “frontier orbitals” and label them as HOMO and LUMO respectively.



- b. (1 point) Circle the orbital above whose interaction with the nucleophile is most important to the success of this reaction.
- c. (2 points) Will the nucleophile be more likely to attack at the C or the N atom? Use an arrow to show the preferred *angle of approach* of the nucleophile on the skeleton below and explain the rationale behind your prediction.



12. (12 points) In this problem you will prepare a molecular orbital diagram for the  $\pi$  **system only** for the molecule ozone ( $O_3$ ). Explain clearly the steps that you use to reach your final answer. You should clearly indicate the nature of all of the  $\pi$  interactions in your MO energy level diagram, indicate the number of electrons involved in the  $\pi$  system and provide the **overall** bond order for ozone?

Element	Orbital Potential Energy (eV)						
	1s	2s	2p	3s	3p	4s	4p
H	-13.6						
He	-24.5						
Li		-5.5					
Be		-9.3					
B		-14.0	-8.3				
C		-19.5	-10.7				
N		-25.5	-13.1				
O		-32.4	-15.9				
F		-46.4	-18.7				
Ne		-48.5	-21.6				
Na				-5.2			
Mg				-7.7			
Al				-11.3	-6		
Si				-15.0	-7.8		
P				-18.7	-10.0		
S				-20.7	-12.0		
Cl				-25.3	-13.7		
Ar				-29.3	-15.9		
K						-4.3	
Ca						-6.1	
Zn						-9.4	
Ga						-12.6	-6
Ge						-15.6	-7.6
As						-17.6	-9.1
Se						-20.8	-11.0
Br						-24.1	-12.5
Kr						-27.5	-14.3

D <sub>2h</sub>	E	C <sub>2</sub> (z)	C <sub>2</sub> (y)	C <sub>2</sub> (x)	<i>i</i>	σ(xy)	σ(xz)	σ(yz)	
A <sub>g</sub>	1	1	1	1	1	1	1	1	x <sup>2</sup> , y <sup>2</sup> , z <sup>2</sup>
B <sub>1g</sub>	1	1	-1	-1	1	1	-1	-1	R <sub>z</sub> , xy
B <sub>2g</sub>	1	-1	1	-1	1	-1	1	-1	R <sub>y</sub> , xz
B <sub>3g</sub>	1	-1	-1	1	1	-1	-1	1	R <sub>x</sub> , yz
A <sub>u</sub>	1	1	1	1	-1	-1	-1	-1	
B <sub>1u</sub>	1	1	-1	-1	-1	-1	1	1	z
B <sub>2u</sub>	1	-1	1	-1	-1	1	-1	1	y
B <sub>3u</sub>	1	-1	-1	1	-1	1	1	-1	x

$C_{4v}$	E	$2C_4$	$C_2$	$2\sigma_v$	$2\sigma_d$	
$A_1$	1	1	1	1	1	$z, x^2+y^2, z^2$
$A_2$	1	1	1	-1	-1	$R_z$
$B_1$	1	-1	1	1	-1	$x^2-y^2$
$B_2$	1	-1	1	-1	1	$xy$
E	2	0	-2	0	0	$(x,y) (R_x, R_y) (xz, yz)$

$D_{4h}$	E	$2C_4$	$C_2$	$2C_2'$	$2C_2''$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$	
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	$x^2+y^2, z^2$
$A_{2g}$	1	1	1	-1	-1	1	1	1	-1	-1	$R_z$
$B_{1g}$	1	-1	1	1	-1	1	-1	1	1	-1	$x^2-y^2$
$B_{2g}$	1	-1	1	-1	1	1	-1	1	-1	1	$xy$
$E_g$	2	0	-2	0	0	2	0	-2	0	0	$(xz, yz)$
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1	
$A_{2u}$	1	1	1	-1	-1	-1	-1	-1	1	1	$z$
$B_{1u}$	1	-1	1	1	-1	-1	1	-1	-1	1	
$B_{2u}$	1	-1	1	-1	1	-1	1	-1	1	-1	
$E_u$	2	0	-2	0	0	-2	0	2	0	0	$(x, y)$

1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18	
IA		IIA		IIIB		IIB		VIIB		VIB		VIB		VIB		VIII		VIII		IB		IIB		IIIA		IVA		VA		VIA		VIIA		VIIIA	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Electronegativity	Symbol	Atomic number	Relative atomic mass	Most frequent oxidation number	Name	Electronegativity	Symbol	Atomic number	Relative atomic mass	Most frequent oxidation number	Name	Electronegativity	Symbol	Atomic number	Relative atomic mass	Most frequent oxidation number	Name	Electronegativity	Symbol	Atomic number	Relative atomic mass	Most frequent oxidation number	Name	Electronegativity	Symbol	Atomic number	Relative atomic mass	Most frequent oxidation number	Name	Electronegativity	Symbol	Atomic number	Relative atomic mass	Most frequent oxidation number	Name
2.1	H 1	1.00794	1.00794	1+	Hydrogen	2.1	H 1	1.00794	1+	Hydrogen	2.1	H 1	1.00794	1+	Hydrogen	2.1	H 1	1.00794	1+	Hydrogen	2.1	H 1	1.00794	1+	Hydrogen	2.1	H 1	1.00794	1+	Hydrogen	2.1	H 1	1.00794	1+	Hydrogen
1.0	Li 3	6.941	9.012182	1+	Lithium	1.5	Be 4	9.012182	2+	Beryllium	1.5	Be 4	9.012182	2+	Beryllium	1.5	Be 4	9.012182	2+	Beryllium	1.5	Be 4	9.012182	2+	Beryllium	1.5	Be 4	9.012182	2+	Beryllium	1.5	Be 4	9.012182	2+	Beryllium
0.8	Na 11	22.989768	24.3050	1+	Sodium	1.3	Mg 12	24.3050	2+	Magnesium	1.3	Mg 12	24.3050	2+	Magnesium	1.3	Mg 12	24.3050	2+	Magnesium	1.3	Mg 12	24.3050	2+	Magnesium	1.3	Mg 12	24.3050	2+	Magnesium	1.3	Mg 12	24.3050	2+	Magnesium
0.8	K 19	39.0983	40.078	1+	Potassium	1.3	Ca 20	40.078	2+	Calcium	1.3	Ca 20	40.078	2+	Calcium	1.3	Ca 20	40.078	2+	Calcium	1.3	Ca 20	40.078	2+	Calcium	1.3	Ca 20	40.078	2+	Calcium	1.3	Ca 20	40.078	2+	Calcium
0.8	Rb 37	85.4678	87.62	1+	Rubidium	1.3	Sr 38	87.62	2+	Strontium	1.3	Sr 38	87.62	2+	Strontium	1.3	Sr 38	87.62	2+	Strontium	1.3	Sr 38	87.62	2+	Strontium	1.3	Sr 38	87.62	2+	Strontium	1.3	Sr 38	87.62	2+	Strontium
0.8	Cs 55	132.90543	137.327	1+	Cesium	1.3	Ba 56	137.327	2+	Barium	1.3	Ba 56	137.327	2+	Barium	1.3	Ba 56	137.327	2+	Barium	1.3	Ba 56	137.327	2+	Barium	1.3	Ba 56	137.327	2+	Barium	1.3	Ba 56	137.327	2+	Barium
0.7	Fr 87	223.0197	226.0254	1+	Francium	1.1	Ra 88	226.0254	2+	Radium	1.1	Ra 88	226.0254	2+	Radium	1.1	Ra 88	226.0254	2+	Radium	1.1	Ra 88	226.0254	2+	Radium	1.1	Ra 88	226.0254	2+	Radium	1.1	Ra 88	226.0254	2+	Radium
0.7	Ac 89	227.0278	227.0278	3+	Actinium	1.1	Th 90	232.0381	4+	Thorium	1.1	Th 90	232.0381	4+	Thorium	1.1	Th 90	232.0381	4+	Thorium	1.1	Th 90	232.0381	4+	Thorium	1.1	Th 90	232.0381	4+	Thorium	1.1	Th 90	232.0381	4+	Thorium
0.7	Pa 91	231.03588	231.03588	5+	Protactinium	1.3	U 92	238.0289	6+	Uranium	1.3	U 92	238.0289	6+	Uranium	1.3	U 92	238.0289	6+	Uranium	1.3	U 92	238.0289	6+	Uranium	1.3	U 92	238.0289	6+	Uranium	1.3	U 92	238.0289	6+	Uranium
0.7	Np 93	237.04371	237.04371	5+	Neptunium	1.3	Pu 94	244.0642	4+	Plutonium	1.3	Pu 94	244.0642	4+	Plutonium	1.3	Pu 94	244.0642	4+	Plutonium	1.3	Pu 94	244.0642	4+	Plutonium	1.3	Pu 94	244.0642	4+	Plutonium	1.3	Pu 94	244.0642	4+	Plutonium
0.7	Am 95	243.0614	243.0614	3+	Americium	1.3	Cm 96	247	3+	Curium	1.3	Cm 96	247	3+	Curium	1.3	Cm 96	247	3+	Curium	1.3	Cm 96	247	3+	Curium	1.3	Cm 96	247	3+	Curium	1.3	Cm 96	247	3+	Curium
0.7	Bk 97	247.0703	247.0703	3+	Berkelium	1.3	Cf 98	251.0796	3+	Californium	1.3	Cf 98	251.0796	3+	Californium	1.3	Cf 98	251.0796	3+	Californium	1.3	Cf 98	251.0796	3+	Californium	1.3	Cf 98	251.0796	3+	Californium	1.3	Cf 98	251.0796	3+	Californium
0.7	Es 99	252.083	252.083	3+	Einsteinium	1.3	Fm 100	257.0951	3+	Fermium	1.3	Fm 100	257.0951	3+	Fermium	1.3	Fm 100	257.0951	3+	Fermium	1.3	Fm 100	257.0951	3+	Fermium	1.3	Fm 100	257.0951	3+	Fermium	1.3	Fm 100	257.0951	3+	Fermium
0.7	Md 101	258.1082	258.1082	3+	Mendelevium	1.3	No 102	259.1009	3+	Nobelium	1.3	No 102	259.1009	3+	Nobelium	1.3	No 102	259.1009	3+	Nobelium	1.3	No 102	259.1009	3+	Nobelium	1.3	No 102	259.1009	3+	Nobelium	1.3	No 102	259.1009	3+	Nobelium
0.7	Lr 103	260.1053	260.1053	3+	Lawrencium	1.3	Lr 103	260.1053	3+	Lawrencium	1.3	Lr 103	260.1053	3+	Lawrencium	1.3	Lr 103	260.1053	3+	Lawrencium	1.3	Lr 103	260.1053	3+	Lawrencium	1.3	Lr 103	260.1053	3+	Lawrencium	1.3	Lr 103	260.1053	3+	Lawrencium
0.7	Uu 118	289	289	-	Ununoctium	0.7	Uu 118	289	-	Ununoctium	0.7	Uu 118	289	-	Ununoctium	0.7	Uu 118	289	-	Ununoctium	0.7	Uu 118	289	-	Ununoctium	0.7	Uu 118	289	-	Ununoctium	0.7	Uu 118	289	-	Ununoctium

Under normal conditions, bold symbols correspond to solid state, bold italics correspond to liquid state, italic correspond to gaseous state and normal correspond to synthetic elements.