Name: _____ **Seat Number: _____**

Student Number: _____

CHM 2311
Midterm 2
March 18, 2012

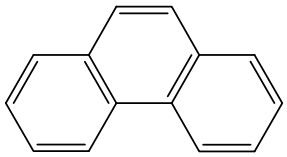
You have 80 minutes to complete this exam.
Please read the questions carefully.
There some useful data and a periodic table on the last 2 pages of the exam.

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.**

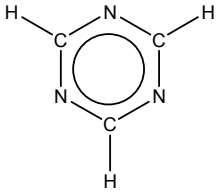
Question	Mark
1	**/9**
2	**/ 6**
3	**/ 7**
4	**/5**
5	**/ 4**
6	**/ 11**
7	**/18**
Total	**/60**

1. (**9 points)** Determine the point group for each of the following molecules/shapes.

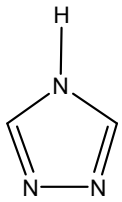
A.



B.

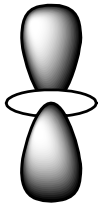


C.

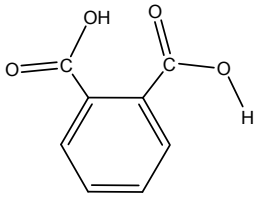


Point Group: A.____C2v_____ B.___D3h_____ C.___C2v_____

D.



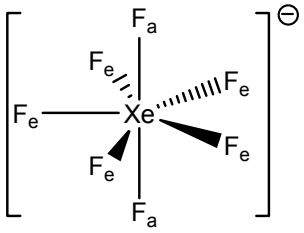
E.



F. $S(O)F_4$

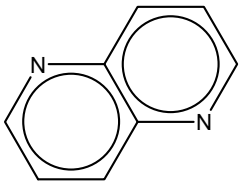
Point Group: D.___D∞h_____ E.___Cs_____ F._____C2v____

G.



F_e = equitorial
F_a = axial

H.



I. SO_3

Point Group: G. ___D5h____ H. ____C2h___ I. _D3h _____

2. **(6 points; ½ point per blank)** Determine the irreducible representations (i.e. set of characters) corresponding to the p_y, the d_{xy}, and the d_{xz} orbitals on the central atom of a molecule in the C_{2v} point group. Please write your answers in the character table below. (It is not necessary to show your derivations. You may use the back of one of the exam pages for your scratch work.) It is ***not necessary to determine the symmetry labels.***

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
	1	1	-1	-1	xy
	1	-1	1	-1	xz
	1	-1	-1	1	y

3. **(7 points, no partial marks)** In the left column of the character tables below, write the symmetry labels corresponding to each of the irreducible representations.

C_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1
A_u	1	1	-1	-1
B_g	1	-1	1	-1
B_u	1	-1	-1	1

Students may put a ′on Ag and Bu and a ″ on Au and Bg

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
B_1	1	-1	1	1	-1
E	2	0	-2	0	0

4. **(5 points)** The molecule ammonia, NH_3, has C_{3v} symmetry. List **all** of the symmetry operations for this molecule.

Answer: E, C_3, C_3^2, $3\sigma_v$. (must list that there are 3 planes or only 4 points)

5. **(4 points; no partial marks)**
(a) Which of the following diatomics has the highest bond order? Which has the lowest bond order?

O_2, SN^-, SiO, BrO^-, N_2^+

Answer:

Molecule	number of valence electrons
O_2	12
SN^-	12
SiO	10
BrO^-	14
N_2^+	9

Regardless of the level of secondary orbital mixing, SiO will have the highest bond order.
Regardless of the level of secondary orbital mixing, ClO^- will have the lowest bond order.

Highest bond order: _____

Lowest bond order: _____

(b) Which of the species in part (a) should be diamagnetic.

Answer
SiO.BrO^-

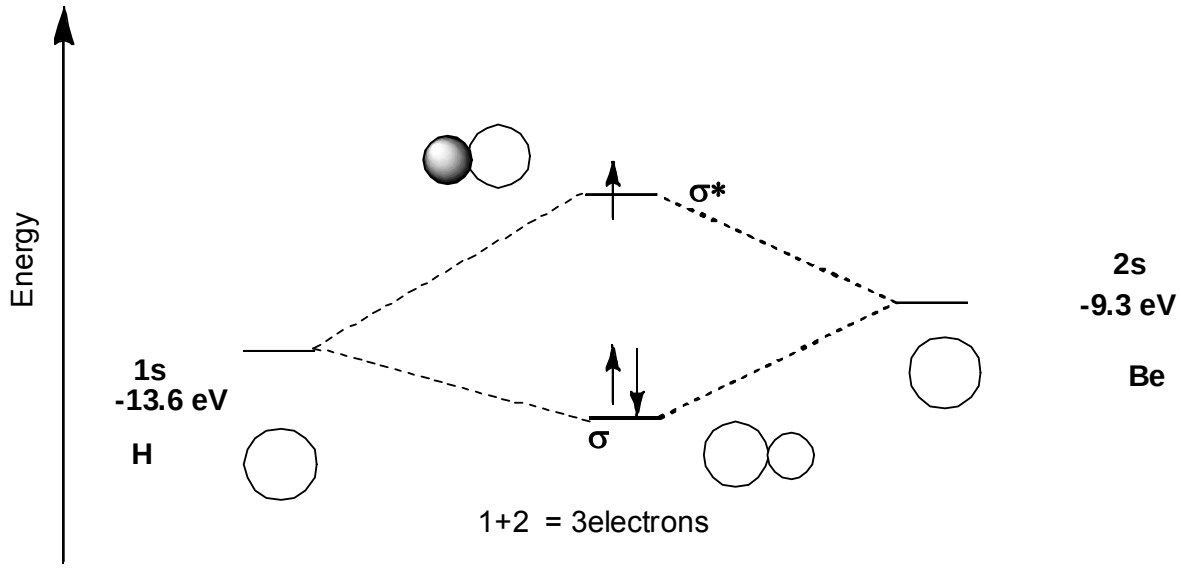
6. (**8 points**) (5 points) Prepare a molecular orbital energy level diagram for the molecule BeH. Then answer <u>all</u> of the following questions.

(i) (1 point) What is the bond order for this species ?

(ii) (1 point) Would you expect the bond to be polar and if so indicate the location of the δ+ and δ- charges.

(iii)(1 point) Use your diagram to comment on the stabilities and bond orders of BeH^+ and BeH^- relative to BeH.

Orbital Potential Energy (eV)			
Element	**1s**	**2s**	**2p**
H	-13.6		
He	-24.5		
Li		-5.5	
Be		-9.3	
B		-14.0	-8.3



Bond order is 0.5 = ½(2-1)

Should be polar with δ- on H and δ+ on Be.

BeH^+ would hav a bond order of 1 while BeH^- would have a zero bond order. In fact, BeH^- would be repulsive.

7. (**11 points**) Boron phosphide (BP) is a simple diatomic species for which we can prepare a molecular orbital diagram.

(a) (**9 points**) Using only the valence s and p-orbitals and ***neglecting*** secondary orbital mixing (i.e. s/p mixing), propose a molecular orbital energy diagram for BP.

Atomic Orbital Energies

	2s (eV)	2p(eV)			3s (eV)	3p (eV)
B	-14.05	-8.30		P	-18.84	-9.65

Include the following in your diagram:

(i) Energy axis

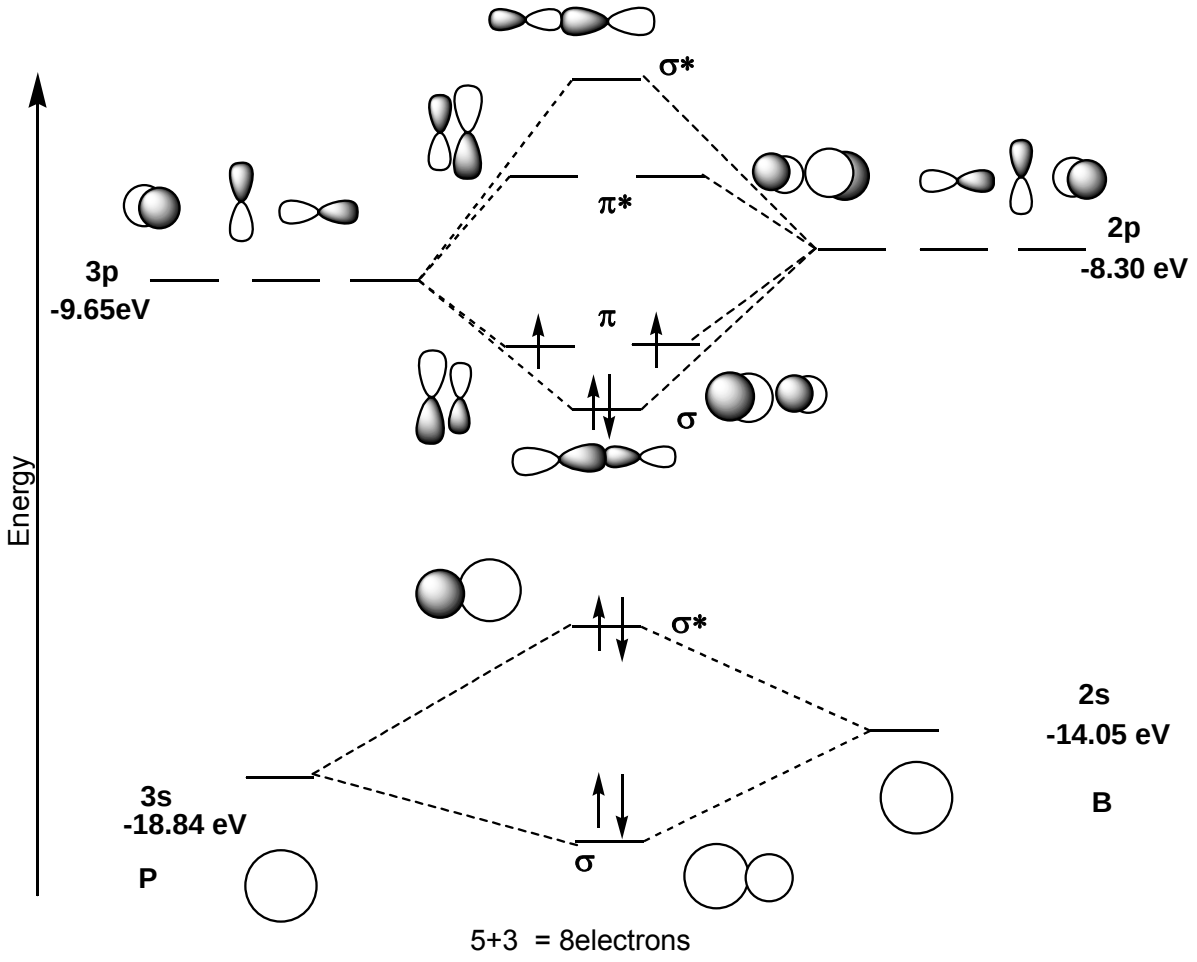
(ii) Atomic orbitals at the appropriate energies (include a sketch of each orbital) **(2)**

(iii) Molecular orbitals at the appropriate energies (include a sketch of each orbital) **(4)**

(iv) Labels for all atomic orbitals (e.g. 2s, 3p, etc...) **(1)**

(v) Labels for all molecular orbitals (e.g. σ^*, σ_g, π_u, etc...) **(1)**

(vi) Electrons in appropriate orbitals **(1)**



(b) (**1 point**) Predict the bond order in BP

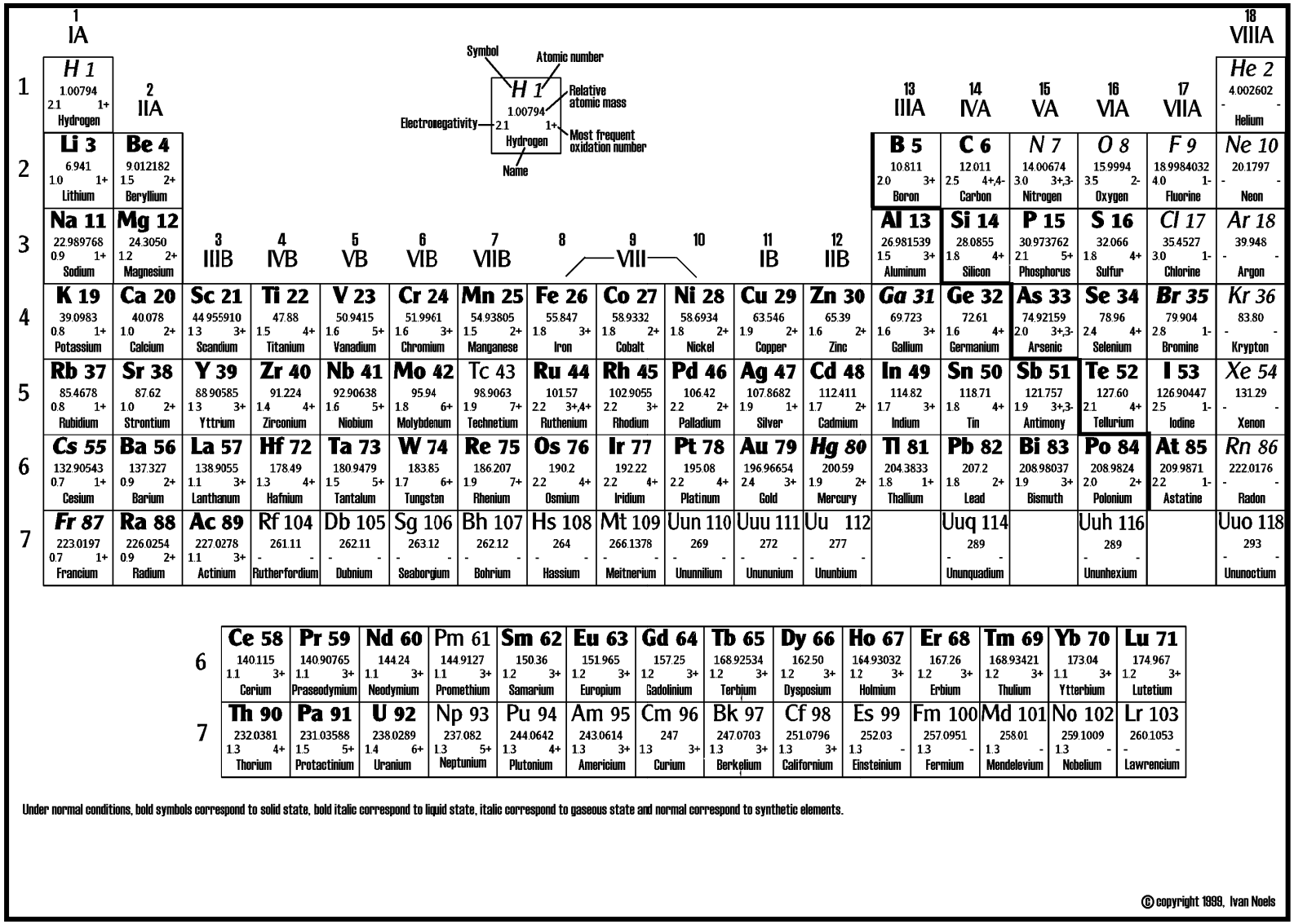
Bond order = 2

(c) (**1 points**) Identify the Highest Occupied Molecular Orbital (HOMO). Toward which atom would the HOMO be polarized and why?

Answer
The highest occupied MO are the π pair that are occupied each singly occupied.
These MO's should be polarized toward the P center.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_4^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
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	
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ(xy)	σ(xz)	σ(yz)	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z, xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y, xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x, yz
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x



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