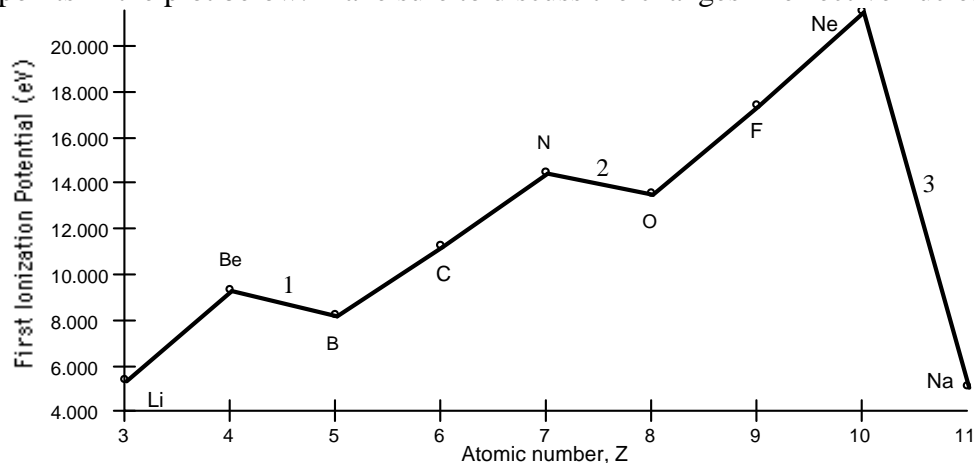


Answer 12 of the following 16 questions. Each question is 8 points each.

1. Give the electron configuration for V^{2+} ion:

2-3. What are the causes of the decreases in first ionization potential observed at numbered points in the plot below. Make sure to discuss the changes in effective nuclear charge.



2. Decrease 1:

3. Decrease 2:

4. Which orbital penetrates closer to the nucleus, a 2s or 2p? Why? Which orbital will feel a greater Z_{eff} in a multi-electron atom?

5. Match the descriptions with the *ab initio* wavefunctions at right. Each question may have more than one answer:

<u>Characteristics of basis set</u>	<u>Basis Sets</u>
a. has split valence shell _____	3-21G
b. has 10 gaussian primitives _____	6-31G
c. has polarization functions _____	6-31G*
d. used for s and p type orbitals _____	

6. What is the purpose of configuration interaction (e. g. MP2 or CI) calculations?

7. In class we used the molecular orbital diagram for N_2 to predict the bond order of the CN molecule. But, is it valid to use the molecular orbital diagram of a homonuclear diatomic to describe the molecular orbitals for a heteronuclear diatomic like CN? Below are reproduced the molecular orbital energies and coefficients for CN from MOPAC. Use this data to determine whether it was correct to use N_2 's molecular orbital diagram for CN. The internuclear axis is the x axis. You must give your reasoning for credit.

ROOT NO.	1	2	3	4	5	6
	<u>-36.81997</u>	<u>-16.22187</u>	<u>-13.39740</u>	<u>-13.39716</u>	<u>-2.89573</u>	<u>1.78345</u>
S C 1	-0.55867	0.56951	-0.00013	0.00000	0.51018	0.00000
PX C 1	-0.30060	-0.03626	0.00010	0.00000	-0.69765	0.00000
PY C 1	0.00000	0.00001	0.41748	-0.41222	0.00005	-0.57523
PZ C 1	0.00000	-0.00001	-0.41221	-0.41749	-0.00005	-0.56999
S N 2	-0.71743	-0.63645	0.00003	0.00000	0.09329	0.00000
PX N 2	0.28778	-0.51892	-0.00007	0.00000	0.49426	0.00000
PY N 2	0.00000	0.00005	0.57625	-0.56896	0.00010	0.41675
PZ N 2	0.00000	-0.00005	-0.56897	-0.57624	-0.00010	0.41297
ROOT NO.	7	8				
	<u>1.78350</u>	<u>6.77503</u>				
S C 1	0.00004	-0.32133				
PX C 1	-0.00001	-0.64932				
PY C 1	0.57000	-0.00001				
PZ C 1	-0.57523	0.00001				
S N 2	-0.00001	0.26744				
PX N 2	0.00000	-0.63530				
PY N 2	-0.41296	-0.00002				
PZ N 2	0.41675	0.00002				

8. The molecular orbitals for the CN diatomic molecule are given in problem 7. Calculate the % character in orbital 5 for the carbon atom.

9. Is the diatomic orbital below σ , π , or δ , bonding or anti-bonding, and g or u? The x axis is the internuclear axis.



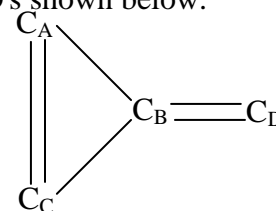
10. Calculate the bond order between atoms B and D for the molecule and MO's shown below.

$$E_4 = \alpha - 1.4812 \beta \quad \psi_4 = 0.3020 p_A - 0.7494 p_B + 0.3020 p_C + 0.5059 p_D$$

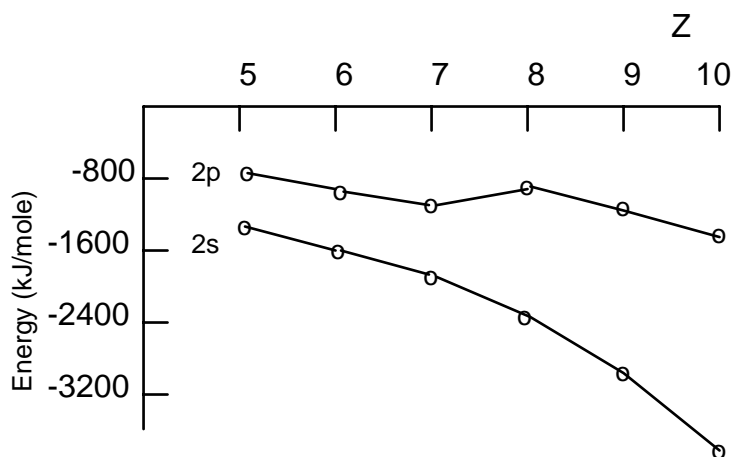
$$E_3 = \alpha - 1.0000 \beta \quad \psi_3 = 0.7071 p_A + 0.0000 p_B - 0.7071 p_C + 0.0000 p_D$$

$$E_2 = \alpha + 0.3111 \beta \quad \psi_2 = 0.3682 p_A - 0.2536 p_B + 0.3682 p_C - 0.8152 p_D$$

$$E_1 = \alpha + 2.1701 \beta \quad \psi_1 = 0.5227 p_A + 0.6116 p_B + 0.5227 p_C + 0.2818 p_D$$



11. Use the atomic energy level diagram at right to explain why the molecular orbital diagram for N_2 is different from O_2 .



12. Take as a trial function for the ground state of the hydrogen atom e^{-kr} . Use the variation principle to find the optimum value of k . Just set up the calculations, but remember to include all information that is necessary to do the integrals and/or other calculations.

15. An excited state configuration of He is $1s^1 2p^1$. If the spatial wavefunction is $(1s(1)2p(2) - 1s(2)2p(1))$, what is/are the allowable spin wavefunction(s)?

14-16. The molecular orbital printout for NO_2^+ with a 180° bond angle is given on the last page. Answer the following questions based on this printout.

14. Which orbitals are the bonding π orbitals?

15. What is the π bond order for NO_2^+ ? Draw the Lewis Dot structure for NO_2^+ and predict the bond order. How well do the MOPAC and the Lewis Dot structure prediction agree?

16. Which orbital is the HOMO? Is this orbital σ or π , and is it bonding, non-bonding, or anti-bonding?

MNDO Printout for linear NO₂⁺ ion.

CARTESIAN COORDINATES								
NO.	ATOM	X	Y	Z				
1	O	-1.1322	0.0000	0.0000				
2	N	0.0000	0.0000	0.0000				
3	O	1.1322	0.0000	0.0000				
ROOT NO.		1	2	3	4	5	6	
		-57.08707	-54.46867	-33.49827	-29.01234	-28.94768	-28.94768	
S	O	1	-0.49158	0.56897	-0.49728	0.38374	0.00000	0.00000
PX	O	1	-0.20912	0.19547	0.33125	-0.49599	0.00000	0.00000
PY	O	1	0.00000	0.00000	0.00000	0.00000	-0.43660	-0.24833
PZ	O	1	0.00000	0.00000	0.00000	0.00000	0.24833	-0.43660
S	N	2	-0.65517	0.00000	0.53477	0.00000	0.00000	0.00000
PX	N	2	0.00000	-0.52547	0.00000	0.46202	0.00000	0.00000
PY	N	2	0.00000	0.00000	0.00000	0.00000	-0.61183	-0.34799
PZ	N	2	0.00000	0.00000	0.00000	0.00000	0.34799	-0.61183
S	O	3	-0.49158	-0.56897	-0.49728	-0.38374	0.00000	0.00000
PX	O	3	0.20912	0.19547	-0.33125	-0.49599	0.00000	0.00000
PY	O	3	0.00000	0.00000	0.00000	0.00000	-0.43660	-0.24833
PZ	O	3	0.00000	0.00000	0.00000	0.00000	0.24833	-0.43660
ROOT NO.		7	8	9	10	11	12	
		-21.88253	-21.88253	-9.13976	-9.13976	-7.65529	0.20642	
S	O	1	0.00000	0.00000	0.00000	0.00000	0.10519	-0.17032
PX	O	1	0.00000	0.00000	0.00000	0.00000	0.58868	-0.46452
PY	O	1	0.34987	-0.61449	0.38267	-0.31824	0.00000	0.00000
PZ	O	1	0.61449	0.34987	-0.31824	-0.38267	0.00000	0.00000
S	N	2	0.00000	0.00000	0.00000	0.00000	-0.53364	0.00000
PX	N	2	0.00000	0.00000	0.00000	0.00000	0.00000	-0.71443
PY	N	2	0.00000	0.00000	-0.54615	0.45419	0.00000	0.00000
PZ	N	2	0.00000	0.00000	0.45419	0.54615	0.00000	0.00000
S	O	3	0.00000	0.00000	0.00000	0.00000	0.10519	0.17032
PX	O	3	0.00000	0.00000	0.00000	0.00000	-0.58868	-0.46452
PY	O	3	-0.34987	0.61449	0.38267	-0.31824	0.00000	0.00000
PZ	O	3	-0.61449	-0.34987	-0.31824	-0.38267	0.00000	0.00000

SIGMA-PI BOND-ORDER MATRIX							
		S-SIGMA	P-SIGMA	P-PI	S-SIGMA	P-SIGMA	P-PI
		O 1	O 1	O 1	N 2	N 2	N 2
S-SIGMA	O 1	0.074301					
P-SIGMA	O 1	0.000000	0.904887				
P-PI	O 1	0.000000	0.000000	1.490829			
S-SIGMA	N 2	0.012605	0.394752	0.000000	0.814714		
P-SIGMA	N 2	0.059226	0.440557	0.000000	0.000000	0.999566	
P-PI	N 2	0.000000	0.000000	0.999917	0.000000	0.000000	1.999833
S-SIGMA	O 3	0.001288	0.001182	0.000000	0.012605	0.059226	0.000000
P-SIGMA	O 3	0.001182	0.068396	0.000000	0.394752	0.440557	0.000000
P-PI	O 3	0.000000	0.000000	0.490912	0.000000	0.000000	0.999917
		S-SIGMA	P-SIGMA	P-PI			
		O 3	O 3	O 3			
S-SIGMA	O 3	0.074301					
P-SIGMA	O 3	0.000000	0.904887				
P-PI	O 3	0.000000	0.000000	1.490829			