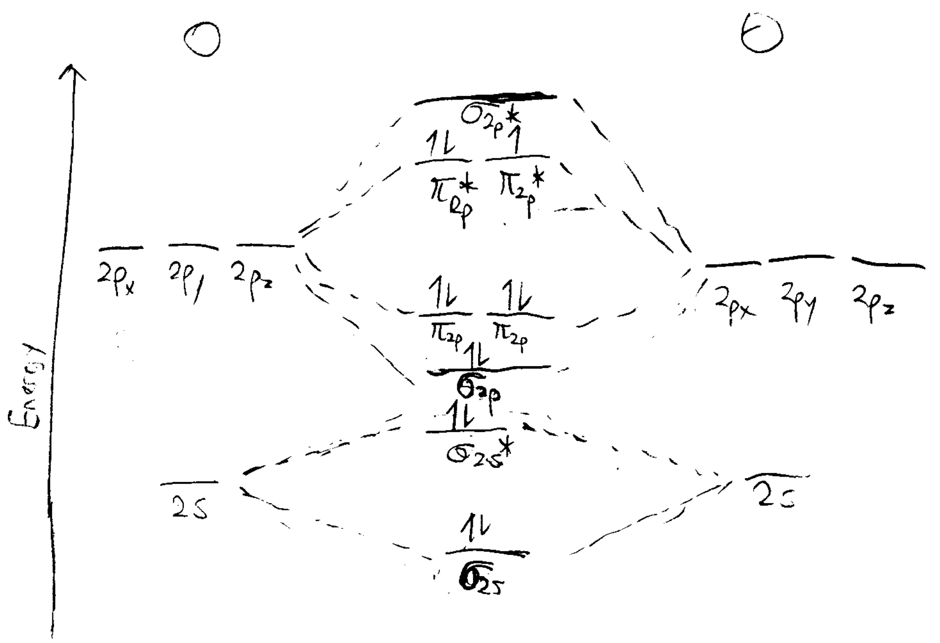
1. (5 points each) Consider the bonding in the superoxide ion O_2^-

A) Draw the correlation diagram, showing the electron occupancy.



O_2^-: 13 valence e⁻

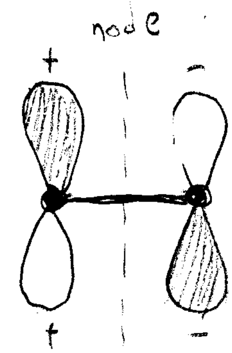
17 total e⁻

B) Write the valance electron configuration.

O_2^-: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$

C) Sketch the shape of the HOMO.

Homo is π_{2p}^*



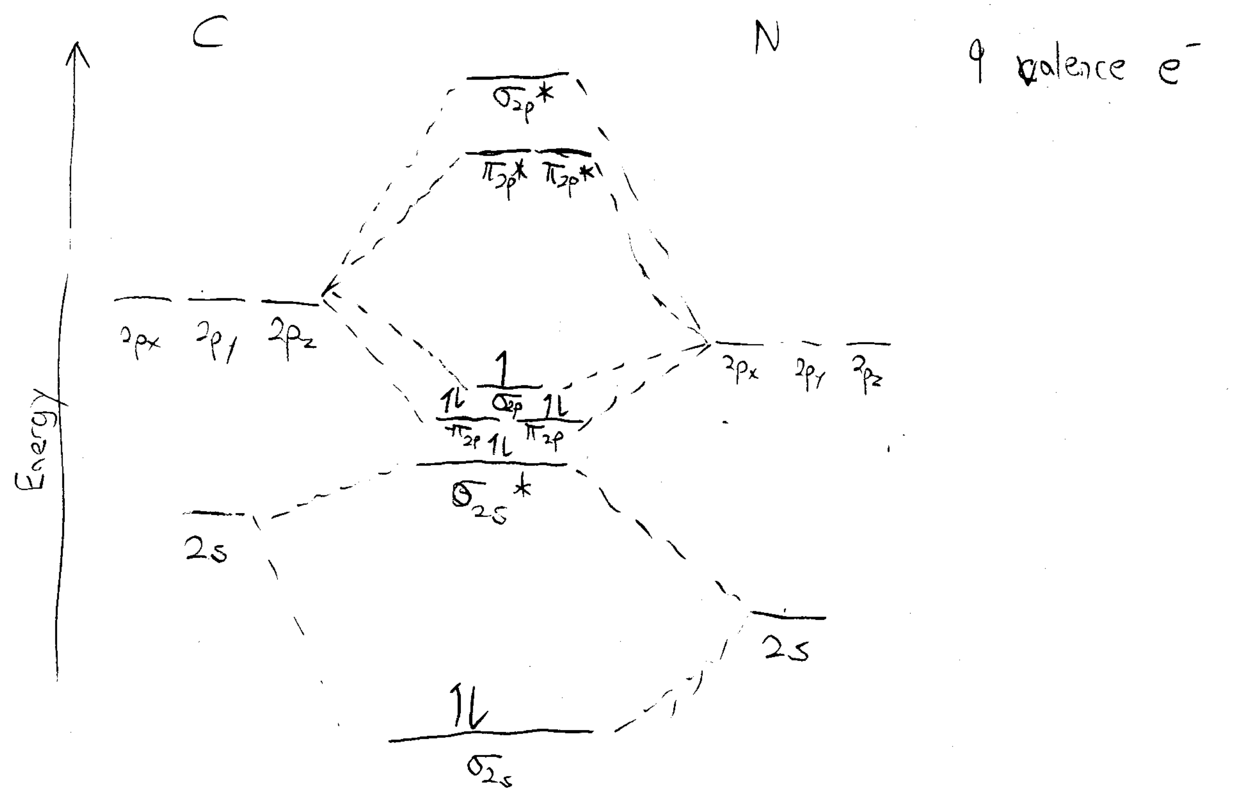
D) Specify the bond order and magnetic behavior.

B.O. = $\frac{1}{2}$(bonding e^- - antibonding e^-) = $\frac{1}{2}(8-5)$ = 1.5

O_2^- is paramagnetic

2. (10+5+5 points) Consider the bonding in the neutral cyanide radical CN

A) Draw the correlation diagram, showing the electron occupancy.



B) Write the valance electron configuration.

CN: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$

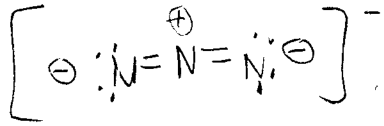
C) Specify the bond order and magnetic behavior.

B.O. = $\frac{1}{2}$(bonding e⁻ − antibonding e⁻) = $\frac{1}{2}(7-2)$ = 2.5

CN is paramagnetic

3. (5+10+5+5 points) Consider the bonding in the azide ion N_3^-

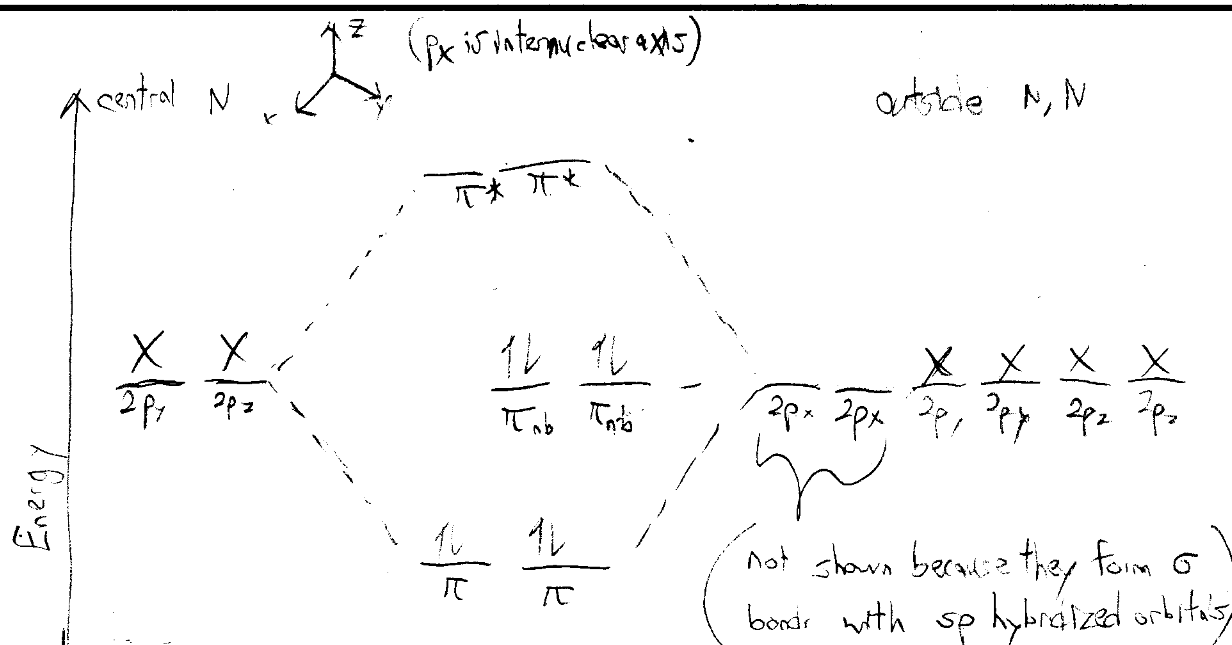
A) Use VSEPR to determine the geometry (sketch and label) and hybridization.



N_3^- has 16 valence e^-

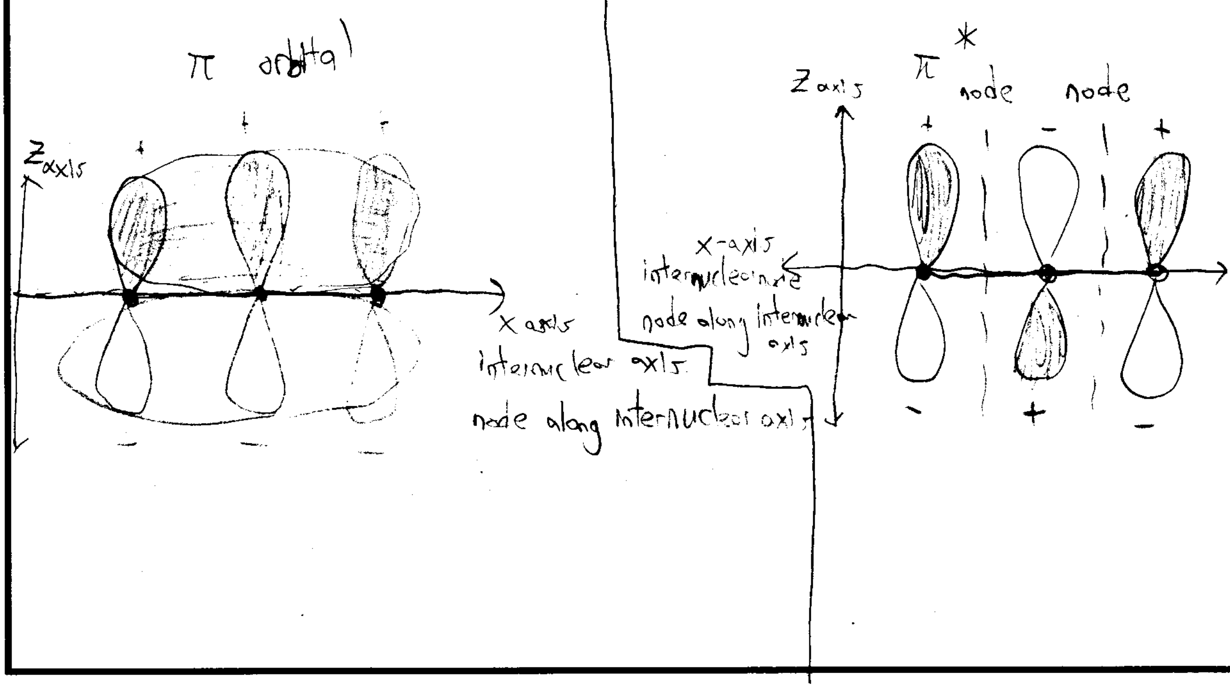
N_3^- is sp hybridized and the geometry is linear

B) Draw the correlation diagram for the pi molecular orbitals, showing the electron occupancy. Specify the number of sigma and pi bonds.

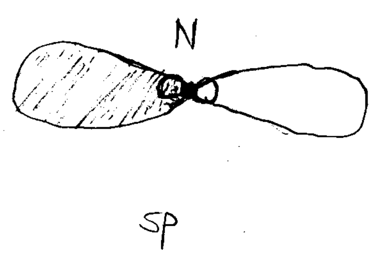


There are 2 π bonds and 2 σ bonds

C) Sketch the shapes of the π and π* molecular orbitals, labeling the axes and nodes.

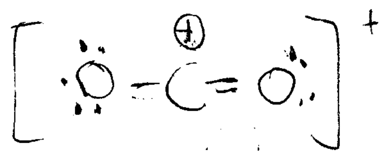


D) Sketch the hybrid orbitals localized on the central nitrogen.



4. (5+10+5+5 points) Consider the bonding in the $CO_2{}^+$ molecular ion;

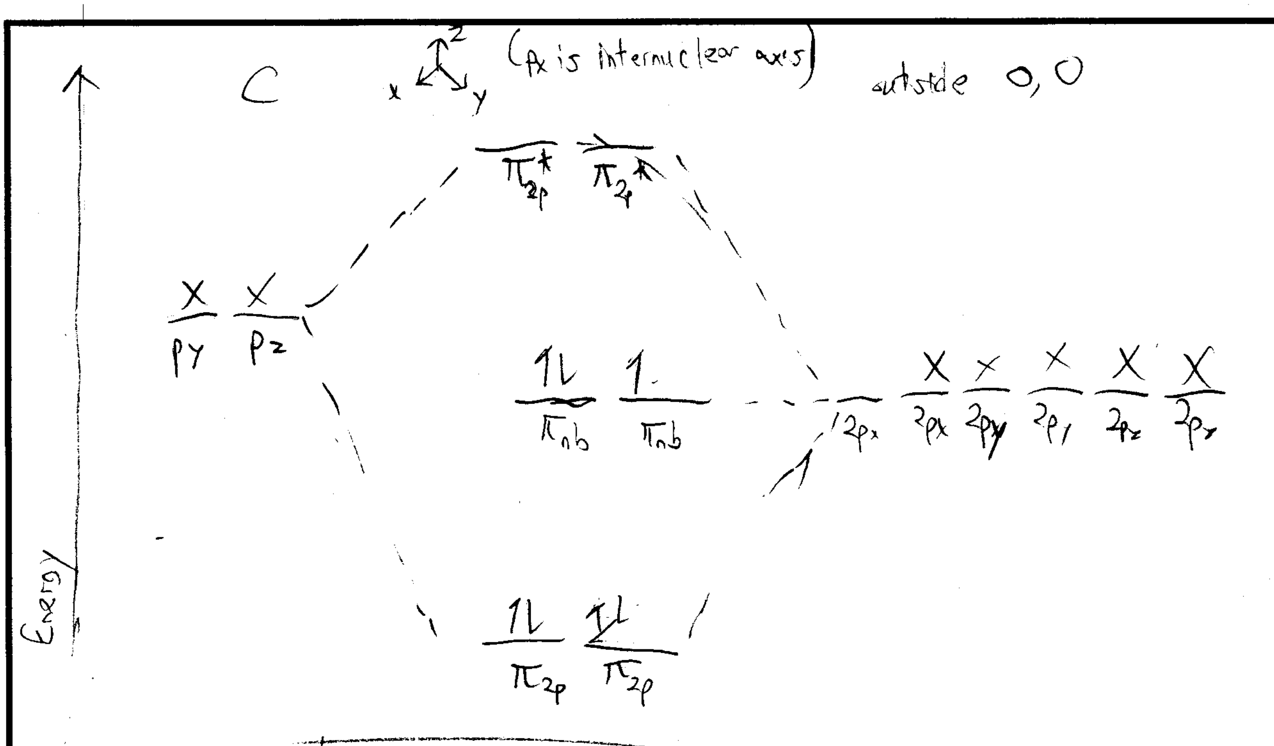
A) Use VSEPR to determine the geometry (sketch and label) and hybridization.



CO_2^+ has 15 e^-

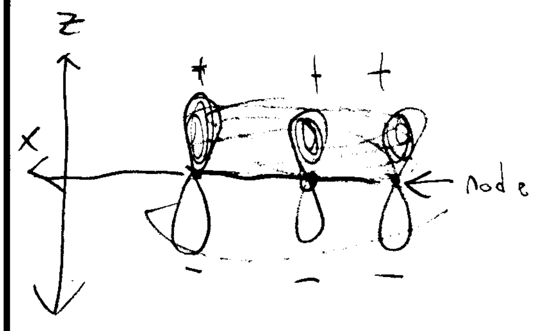
CO_2^+ is linear geometry and sp hybridized

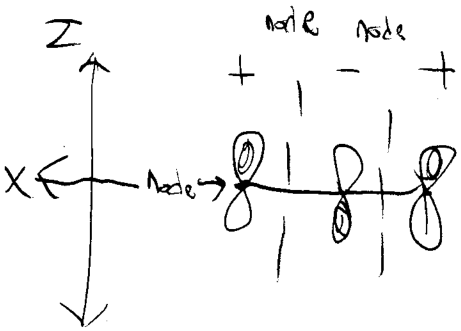
B) Draw the correlation diagram for the pi molecular orbitals, showing the occupancy. Specify the number of sigma and pi bonds.



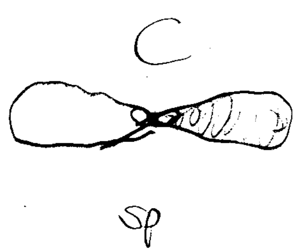
2 σ bonds, 2 π bonds

C) Sketch the shapes of the π and π^* molecular orbitals, labeling the axes and nodes.





D) Sketch all the hybrid orbitals localized on the carbon.



5. (5 points each)

The two naturally occurring isotopes of bromine are ^{79}Br and ^{81}Br, with masses of 78.918 and 80.196 u, respectively. The wavelength of the J = 0 to J = 1 rotational transition in $^{79}Br^{81}Br$ is measured to be 6.18 cm. Use this information to calculate the bond length in the Br_2 molecule.

$\lambda = 6.18\,cm = 0.0618\,m$

$\nu = \frac{c}{\lambda} = \frac{3\times10^8}{0.0618} = 4.85\times10^9\ Hz$

$\Delta E = h\nu = E_1 - E_0 = \frac{h^2}{8\pi^2 I}\left((1)(1+1) - (0)(0+1)\right) = \frac{h^2}{4\pi^2 I}$

$\nu = \frac{h}{4\pi^2 I}$

$I = \frac{h}{4\pi^2\nu} = \frac{6.626\times10^{-34}}{4\pi^2 \cdot 4.85\times10^9} = 0.0346\times10^{-43} = 3.46\times10^{-45} = \mu R_e^2$

$\mu = \frac{78.918 \cdot 80.196}{78.918 + 80.196} = 39.776\ amu$

$39.776\ amu \cdot 1.67\times10^{-27}\ kg/amu = 6.64\times10^{-26}\ kg$

$\frac{3.46\times10^{-45}}{6.64\times10^{-26}} = 5.2\times10^{-20} = R_e^2$

$R_e = 2.28\times10^{-10}\ m = \boxed{2.3\ Å}$

The wavelength of the vibrational transition in the $^{79}Br^{81}Br$ molecule is 3.09×10^{-5} m. Calculate the force constant for the bond in this molecule

$\nu = \frac{c}{\lambda} = \frac{3\times10^8}{3.09\times10^{-5}} = 9.7\times10^{12}\ Hz = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

$\mu(2\pi\nu)^2 = k$

$6.64\times10^{-26} \cdot 4\pi^2 \cdot \nu^2 = k$

$24664\times10^{-2}\ N/m = \boxed{250\ N/m}$