

Name: _____

Chemistry 1410: Physical Chemistry I

Exam #3:

8:00-9:50 am

- There are three questions worth a total of 300 points.
- Read all question first-answer the easiest first.
- Don't spend too much time on one question-if you get stuck move on.
- Justify any approximation you use.
- **Show all your work. No points will be given for answers without steps shown.**
- Good luck!

Cheat Sheet:

Fundamental Constants and factors:

Planck's constant	$h = 6.626 \times 10^{-34} \text{ Js}$
Boltzmann's constant	$k = 1.381 \times 10^{-23} \text{ JK}^{-1}$
Speed of light	$c = 2.998 \times 10^8 \text{ ms}^{-1}$
(Joule's to electron-volts)	$1\text{J} = 6.242 \times 10^{18} \text{ eV}$
Electronic charge	$e = -1.602177 \times 10^{-19} \text{ C}$
Mass of electron	$m_e = 9.1094 \times 10^{-31} \text{ kg}$
(amu to kg)	$1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$

Grade:

Question 1 [70 points]

(a) Consider $3p_z$ a H-atom wavefunction orbital.

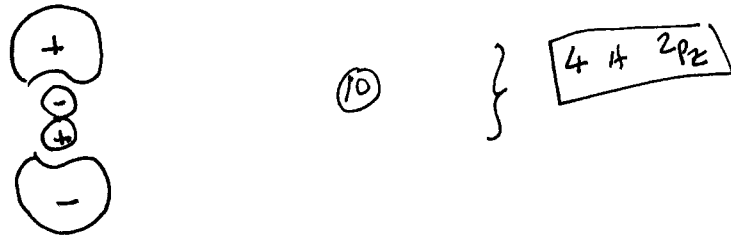
(i) How many nodes exist in the radial part of the orbital? [5 points]

$$\# \text{ nodes} = n - l - 1 = 3 - 1 - 1 = 1 \quad (5)$$

(ii) How many nodes exist in the angular part of $3p_z$ [5 points]

$$\# \text{ nodes} = l = 1 \quad (5)$$

(iii) Sketch the angular part of the $3p_z$ orbital? [10 points]



(iv) What is the energy of the H-atom in a $3p_z$ state – give your answer in eV? [5 points]

$$E = -\frac{13.6}{3^2} = -\frac{13.6}{9} \text{ eV} \quad /$$

(v) What is the total z-component of orbital angular momentum? [5 points]

$$l_z = m_l \hbar = 0 \quad /$$

(b) The radial part of 1s wavefunction for a H-atom has a maxima at $r=0$. However, the most probable distance between the electron and the nucleus is not at $r=0$. Explain? [10 points]

The RDF must averaged over all θ, ϕ . This adds a r^2 term which leads to the most probable distance NOT being at $r=0$

(c) Consider the H-atom wavefunction: $\psi \propto \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{i\phi}$.

(i) State the values of the quantum numbers, n and m_l . You must state the reasoning you used to determine these quantum numbers – just answers will not get you points. [10 points]

$$n = 3 \quad (2) \quad R_{nl} \psi = R_{nl} Y_l^{m_l} e^{im_l \phi} \quad (3)$$

$$m_l = +1 \quad (1) \quad R_{nl} \propto e^{-r/na_0} \quad (3)$$

(ii) What is the energy of this state in eV? [10 points]

$$E = -\frac{13.6}{n^2} = -\frac{13.6}{9}$$

(iii) What is the z-component of orbital angular momentum in this state? [10 points]

$$L_z = \hbar$$

Question 2 [90 points]

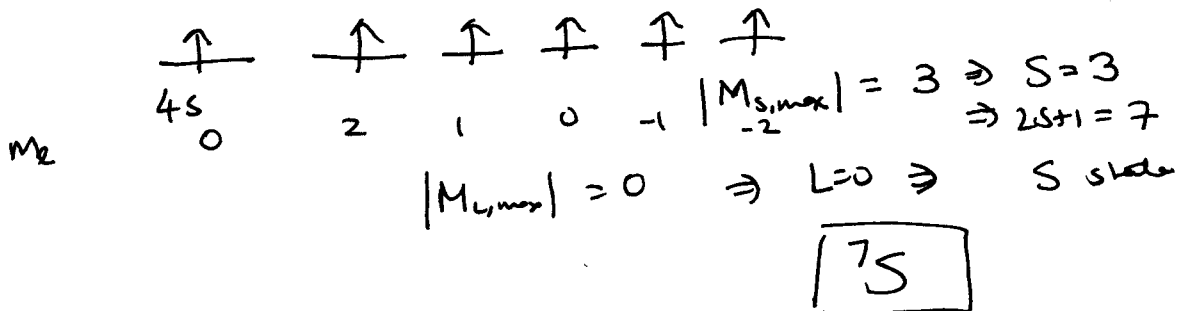
(a) Using the ground state of He atom explain why two electrons in an orbital must be spin paired. [10 points]

He = $1s^2$
 $\psi(1,2) = -\psi(2,1)$
 Given that $\psi(1,2) = \phi_1(1)\phi_1(2) \times \text{spin parts}$.
 (combination of $\alpha(1)\alpha(2) - \beta(1)\beta(2)$ cannot lead to antisymmetry since the spatial part is symmetric.
 only $\alpha(1)\beta(2)$ will lead to $\psi(1,2) = -\psi(2,1)$

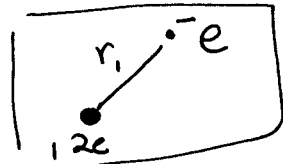
(b) Explain Cr has a ground state electron configuration of $[\text{Ar}]3d^5 4s^1$ rather than $[\text{Ar}]3d^4 4s^2$. [10 points]

$3d^5 4s^1$ leads to maximum multiplicity $(2S+1)$ value which leads to a lower energy than $3d^4 4s^2$ configuration

(c) Determine the Term Symbol for Cr in the ground state. [10 points]



(d) Write down the Hamiltonian for He^+ . The wavefunction $\psi = \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} e^{-2r/a_0}$ is the solution for the lowest energy state. By substituting into the Schrodinger's equation determine the energy of this state. [30 points]



H-atom Hamiltonian but

$$\hat{H} = \hat{K}_1 - \frac{2e^2}{4\pi\epsilon_0 r_1} \Rightarrow = -\frac{\hbar^2}{2m_e r^2} \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \theta} \sin^2 \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] - \frac{2e^2}{4\pi\epsilon_0 r_1}$$

10 points (-4 if Va missed)

$$\begin{aligned} \hat{H}\psi &= -\frac{\hbar^2}{2m_e r^2} \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} e^{-2r/a_0} + 0 + 0 \right] - \frac{2e^2}{4\pi\epsilon_0 r} \psi \\ &= -\frac{\hbar^2}{2m_e r^2} \left[\frac{\partial}{\partial r} \left[r^2 \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} \left(-\frac{2}{a_0}\right) e^{-2r/a_0} \right] \right] - \frac{2e^2}{4\pi\epsilon_0 r} \psi \\ &= -\frac{\hbar^2}{2m_e r^2} \left[-2r \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} \left(\frac{2}{a_0}\right) e^{-2r/a_0} + \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} \left(\frac{2}{a_0}\right)^2 r^2 e^{-2r/a_0} \right] - \frac{2e^2}{4\pi\epsilon_0 r} \psi \\ &= +\frac{2\hbar^2}{2m_e r} \left(\frac{2}{a_0}\right)^{3/2} \psi - \frac{\hbar^2}{2m_e r^2} \cdot \frac{4}{a_0^2} \psi - \frac{2e^2}{4\pi\epsilon_0 r} \psi \\ &= -\frac{4\hbar^2}{2m_e a_0^2} \psi + \left[\frac{2\hbar^2}{2m_e r a_0} - \frac{2e^2}{4\pi\epsilon_0 r} \right] \psi \\ &= -\frac{4\hbar^2}{2m_e a_0^2} \psi + \left[\frac{2\hbar^2}{2m_e r} \cdot \frac{2}{\epsilon_0 h^2} - \frac{2e^2}{4\pi\epsilon_0 r} \right] \psi \\ &= -\frac{4\hbar^2}{2m_e a_0^2} \psi + \left[\frac{2e^2}{4\pi\epsilon_0 r} - \frac{2e^2}{4\pi\epsilon_0 r} \right] \psi \\ &= -\frac{4\hbar^2}{2m_e a_0^2} \psi \end{aligned}$$

$$E = -\frac{4\hbar^2}{2m_e a_0^2}$$

(e) Consider the case of an excited atom of He with the configuration of $1s^1 2s^1$.

(i) Write down an equation for ψ_{singlet} . [5 points]

$$\begin{aligned}\psi_{\text{singlet}} &= \frac{1}{\sqrt{2}} [1s(1)2s(1) + 2s(1)1s(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ &= \phi_{\text{singlet}, s, s, \sigma} \cdot \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]\end{aligned}$$

(ii) Write down an equation for one of the three triplet wavefunctions (ψ_{triplet}). [5 points]

$$\begin{aligned}\psi_{\text{triplet}} &= \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] \alpha(1)\alpha(2) \\ &= \phi_{\text{triplet}} \alpha(1)\alpha(2)\end{aligned}$$

} $\begin{matrix} \text{or} \\ \beta(1)\beta(2) \\ \text{or} \\ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{matrix}$

(iii) Determine whether ψ_{singlet} is orthogonal to ψ_{triplet} . ? [20 points]

$$\begin{aligned}\int \psi_{\text{singlet}}^* \psi_{\text{triplet}} d\tau &= \frac{1}{\sqrt{2}} \int \phi_{\text{singlet}}^* \phi_{\text{triplet}} \int (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \alpha(1)\alpha(2) d\tau \\ &= \frac{1}{\sqrt{2}} \int \phi_{\text{singlet}}^* \phi_{\text{triplet}} \left[\int \alpha(1)\alpha(2) d\tau_1, \int \beta(1)\alpha(2) d\tau_2 - \int \beta(1)\alpha(1) d\tau_1, \int \alpha(2)\alpha(2) d\tau_2 \right] \\ &= 0\end{aligned}$$

They are orthogonal.

Question 3 [90 points]

(a) In this question you will consider a molecular ion.

(i) Write down the molecular electron configuration and the wavefunction for the He_2^+ ion - you can use a Slater determinant to write down the wavefunction.

[10 points]

3 electrons
electron configuration = $(1\sigma_g)^2 (1\sigma_u^*)^1$

$$\Psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} |1\sigma_g(1)\alpha(1) & |1\sigma_g(1)\beta(1) & |1\sigma_u^*(1)\alpha(1) \\ |1\sigma_g(2)\alpha(2) & |1\sigma_g(2)\beta(2) & |1\sigma_u^*(2)\alpha(2) \\ |1\sigma_g(3)\alpha(3) & |1\sigma_g(3)\beta(3) & |1\sigma_u^*(3)\alpha(3) \end{vmatrix}$$

[could be $\sigma_u^*(1)\beta(1)$
or
can have
4 columns]

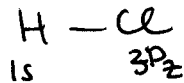
(ii) Using 2 sentences each describe the Hartree Fock Self Consistent Field Method to determine the optimized molecular orbitals and energy diagram for a molecule like He_2^+ .

[10 points]

- ① Create 1-electron M.O. (i.e. consider only 1 electron in MO) - σ_i
Use these to average out repulsive terms.
Solve separate $\hat{H}_i \phi_i = \epsilon_i \sigma_i$ to get better MO's
These σ_i have adjustable terms
- ② Use Slater || to get Ψ .
- ③ Determine $E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau}$; and minimize E
by optimizing adjustable terms
- ④ Go to 1 and iterate till convergence in E results.

(b) In this question you will consider bonding in a heteronuclear diatom.

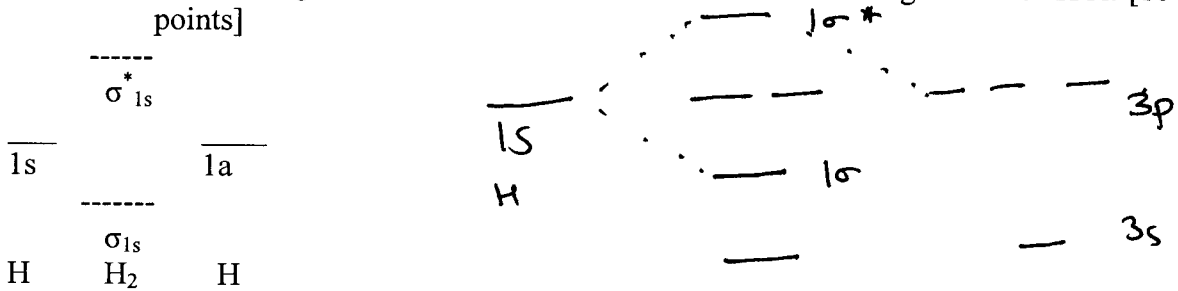
(i) Write an equation that describes the Valence Bond view of bonding in HCl. [10 points]



$$\psi \propto \left[1s_{\text{H}(1)} 3p_{z,\text{Cl}}(2) + 1s_{\text{H}(2)} 3p_{z,\text{Cl}}(1) \right] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

(iii) The energy level diagram for H₂ based on Molecular Orbital Theory is shown.

Draw a similar energy level diagram that illustrates the energies of the Molecular Orbitals of HCl. You must show the atomic orbital energies. Based on this diagram write down the molecular electron configuration of HCl. [10 points]



8 electrons

$$(1\sigma)^2 (3s)^2 (3p_x)^2 (3p_y)^2$$

or

$$(1\sigma)^2 (3s)^2 (3p_x)^2 (3p_y)^2$$

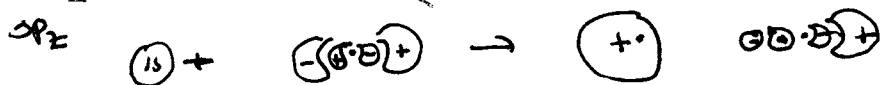
(iii) Sketch the HOMO and LUMO orbitals of HCl. [10 points]

HOMO is $3p_x$ or $3p_z$ of Cl

LUMO is $1\sigma^*$



LUMO



3p orbitals instead of 3p_z

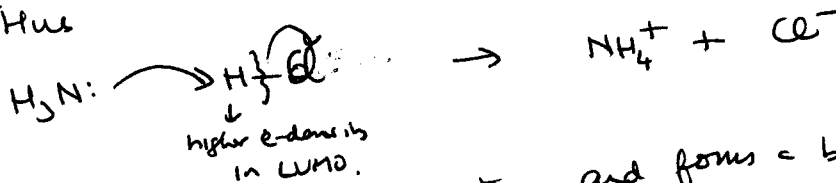
- (iv) HCl reacts with NH_3 to form NH_4^+ and Cl^- in aqueous solution. Using the MO's for HCl explain the reaction mechanism – you do not need the MOs for NH_3 . You should indicate where the electrons go, justify the direction of arrow in the reaction mechanism, and also describe which bond cleaves and why. [10 points]

Lone Pair of NH_3 is placed on LUMO of HCl
 [since LUMO of HCl has a lower energy than HOMO of NH_3]
 Now configuration is $(1s)^2 (2s)^2 (2p_x)^2 (2p_y)^2 (2p_z)^2 (1\sigma^*)^2$

$$\text{B.O.} = \frac{1}{2}(2 - 2) = 0$$

Thus H-Cl bond breaks. NOTE that in $1\sigma^*$ e-density is highest on H-atom.

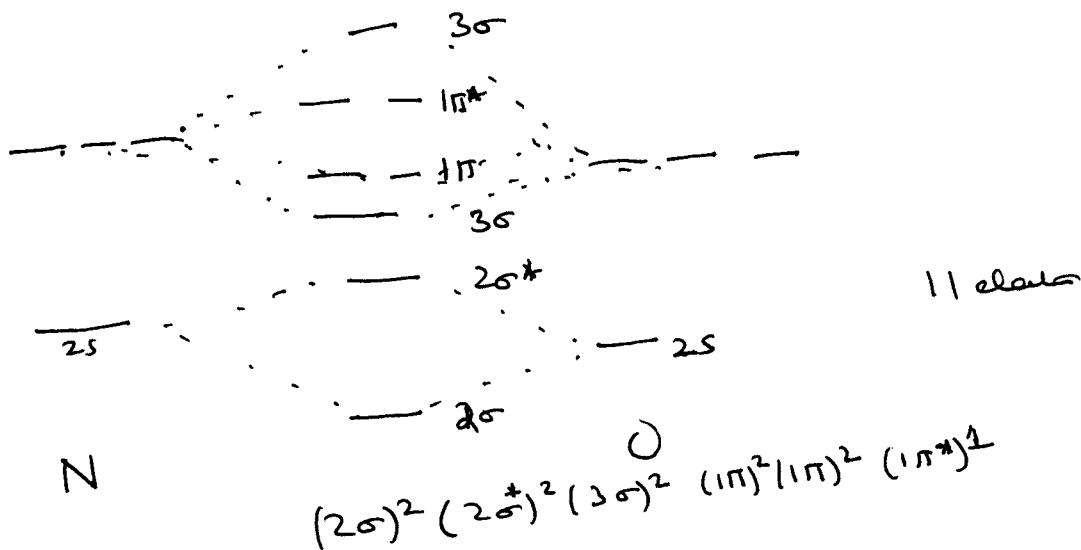
Thus



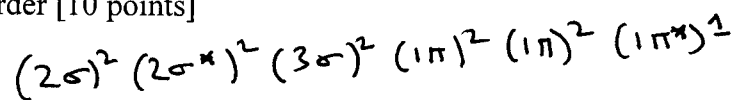
NH_3 takes up the H^+ atom and forms a bond. This delocalizes its L.P. and stabilizes it.

- (c) In this question you will consider the molecule NO.

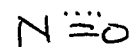
- (i) Draw an energy level diagram that illustrates the energies of the Molecular Orbitals (MOs) of NO. Your diagram should also include the energies of the relevant atomic orbitals (AOs) [see Question 3b for an illustration]. Each MO should be connected by dashed lines to the AOs used to construct them. Include all possible Molecular Orbitals. [10 points]



(ii) Write down the molecular electron configuration of NO. Determine the bond order [10 points]



$$B.O. = \frac{1}{2}(8 - 3) = \frac{1}{2}(5) = 2.5$$

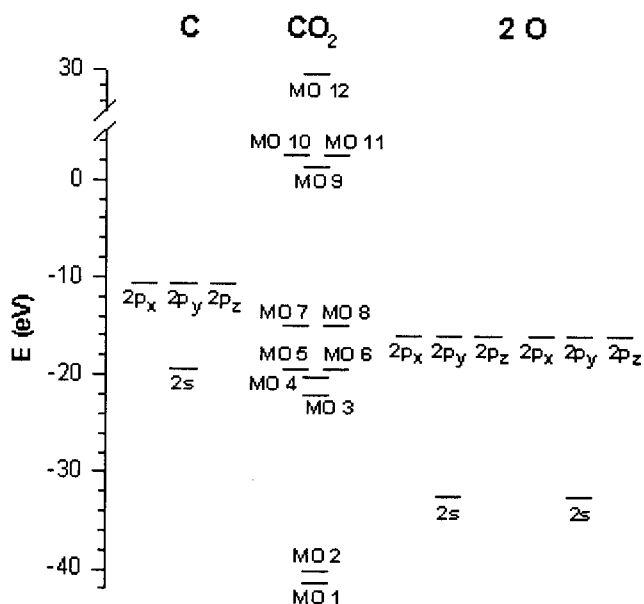


(iii) Based on molecular electron configuration predict the magnetic properties of NO. [10 points]

There is an unpaired electron -
NO will be paramagnetic.

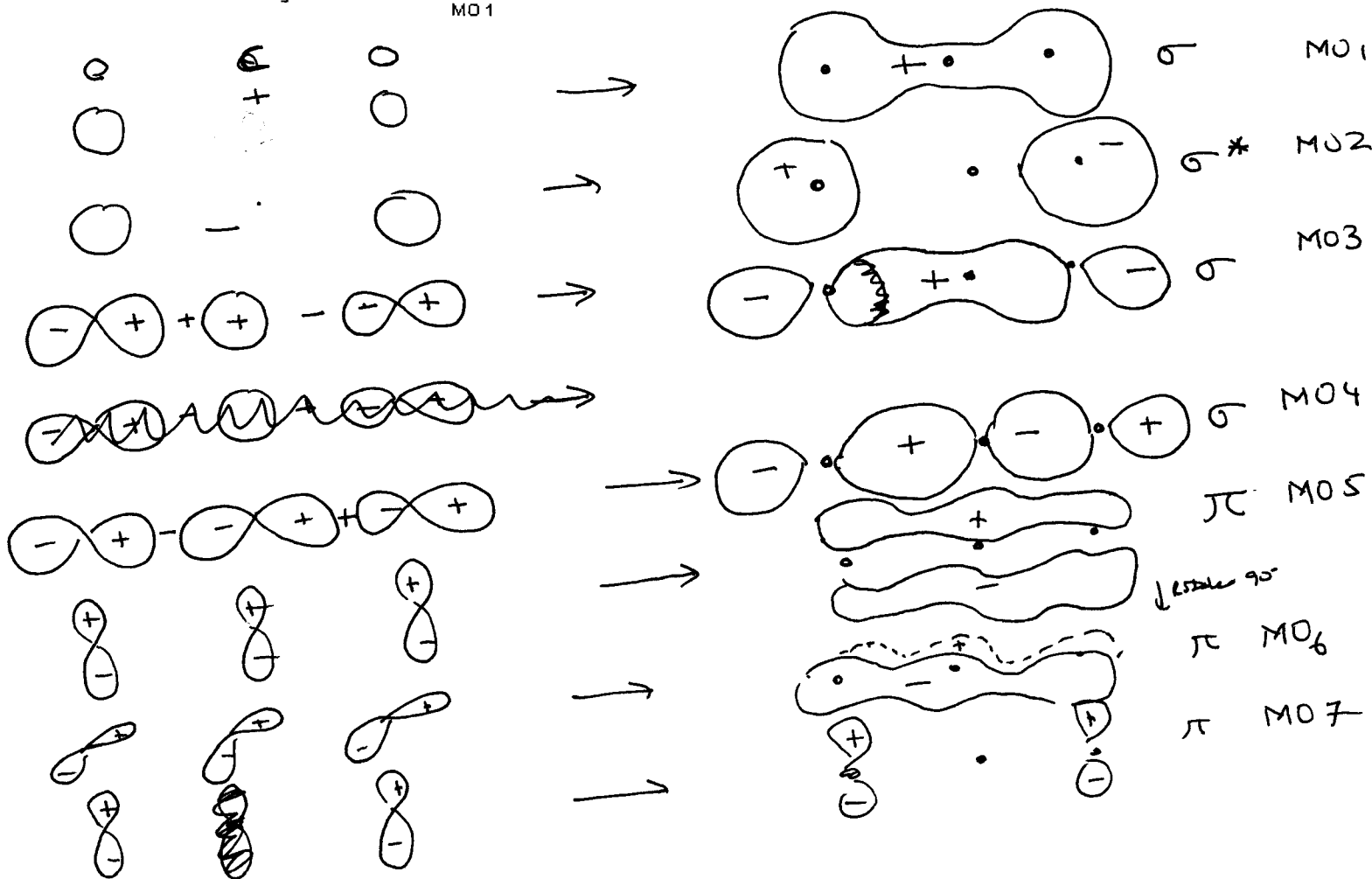
Question 4 [50 points]

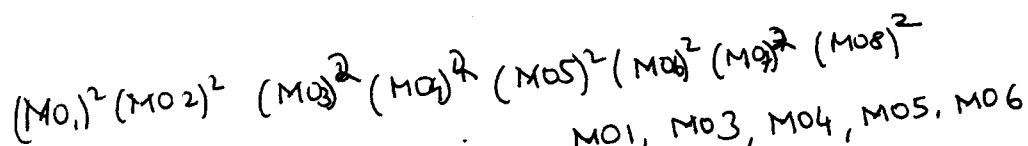
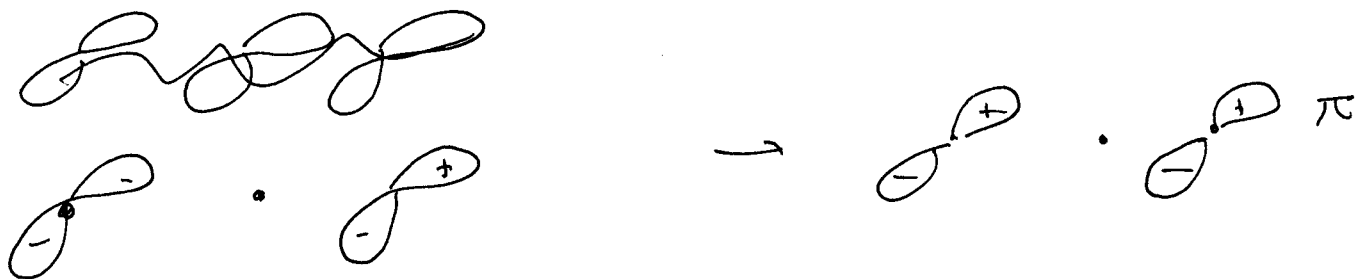
In this question we will consider the LCAO treatment of CO_2 , which is a linear molecule. Since there are 4 valence electrons for Carbon and 6 valence electrons in each Oxygen atom, we need to generate the eight lowest energy Molecular Orbitals to hold 16 electrons. These Molecular orbitals can be generated by recognizing that 2s Atomic Orbitals of C do not overlap with the 2s Atomic Orbitals of O since the energy of the C-2s is much higher. Using the energy level diagram that is provided determine the shapes of the 8 Molecular Orbitals with the lowest energies. Label the Orbitals as σ or π . Clearly show your reasoning by drawing out AO's and the appropriate additions or subtractions.



of the 8 Molecular Orbitals with the lowest energies. Label the Orbitals as σ or π . Clearly show your reasoning by drawing out AO's and the appropriate additions or subtractions.

(Hint: MO1 and MO2 involve only the 2s orbitals of O, since the C-2s are too high in energy. MO3 is a combination of C-2s and O-2pz. MO4 involves C-2pz and O-2pz. MO5 involves the 2px of all atoms, and MO6 involves the other 2py of atoms. MO7 involves only the 2px orbitals of O, and MO8 involves only the 2py orbitals of O.)





BOND electrons in

$MO_1, MO_3, MO_4, MO_5, MO_6$

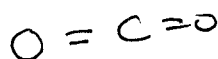
$\rightarrow 10 e^-$

ANTI BONDING electrons in MO_2

$\rightarrow 2$

NON-BONDING electrons in $MO_7, MO_8 \rightarrow 4$

$$B.O. = \frac{1}{2} (10 - 2) = 4$$



$$CO_2 = 4 + 6 + 6 = 16 e^-$$

10 bonds