Chemistry 4000

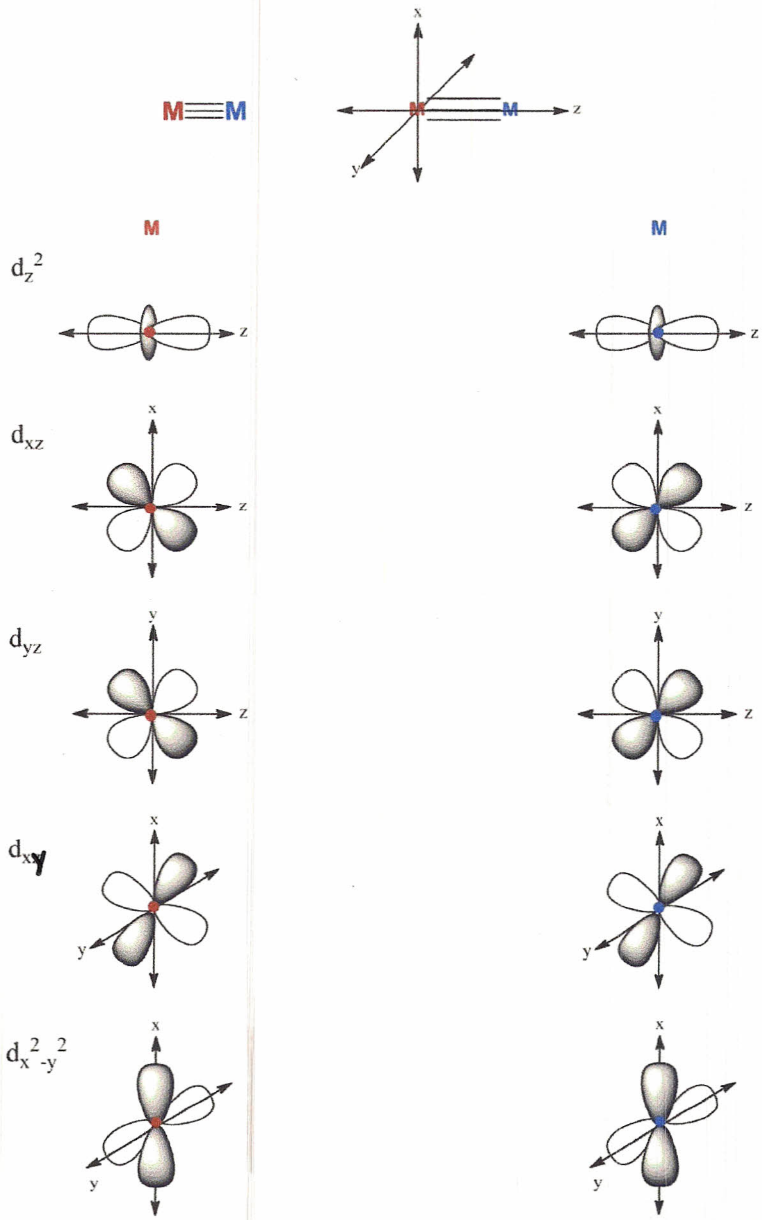
Introduction to Inorganic Chemistry: The Different Perspectives of Bonding

Exam 1

Name:

Show your work for maximum credit.

1. In class we talked about how to construct molecular orbitals. Let us construct molecular orbitals for a triple bond between two metals (they are the same). In the figure below I have drawn the triple bond interaction on a three axis coordinate system. To help you to visualize the formation of the molecular orbitals from the atomic orbitals of each metal, I have drawn the atomic orbitals on separate coordinate systems and have changed the perspective where appropriate. Take a moment to orient yourself. The questions begin on the next page. (30 points)

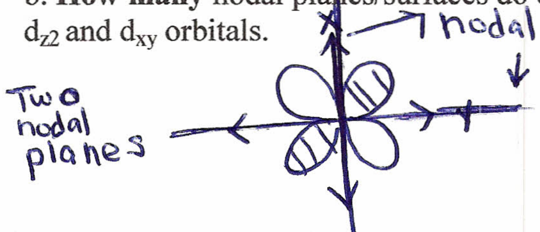


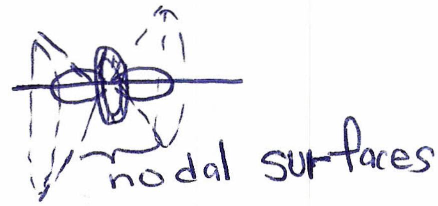
a. Considering the total number of atomic orbitals for the two metals, **how many** molecular orbitals can be constructed? **How many** are bonding and **how many** are antibonding?

10 atomic orbitals ⇒ 10 molecular orbitals
- 5 bonding
- 5antibonding

} b/c of the requirement for comparable energy + symmetry is fulfilled

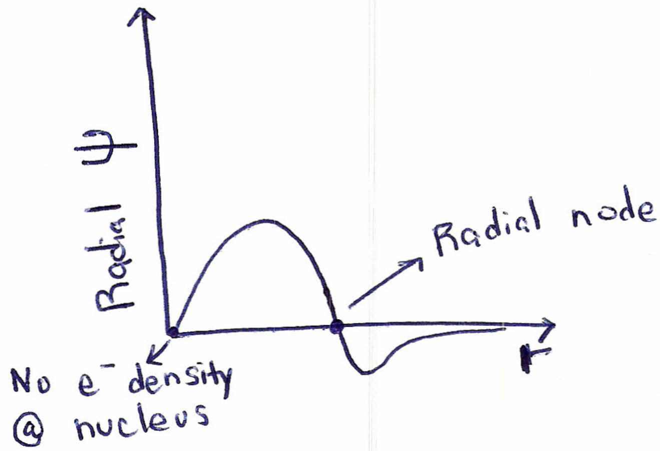
b. **How many** nodal planes/surfaces do d orbitals have? **Draw** these nodal planes/surfaces for the d_{z2} and d_{xy} orbitals.





c. If these were 4d orbitals, how many radial nodes do you expect each to have? Sketch the radial wave function plot versus radial distance for a 4d orbital.

Radial nodes: n-ℓ-1 = 4-2-1 = 1

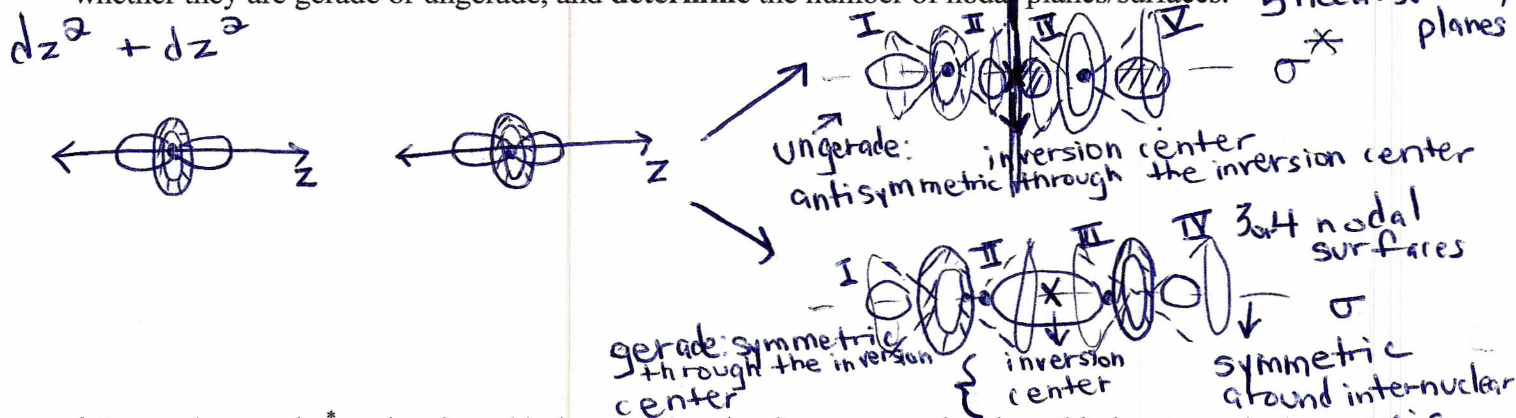


For the following set of questions, assume that six electrons are being shared by both metals.

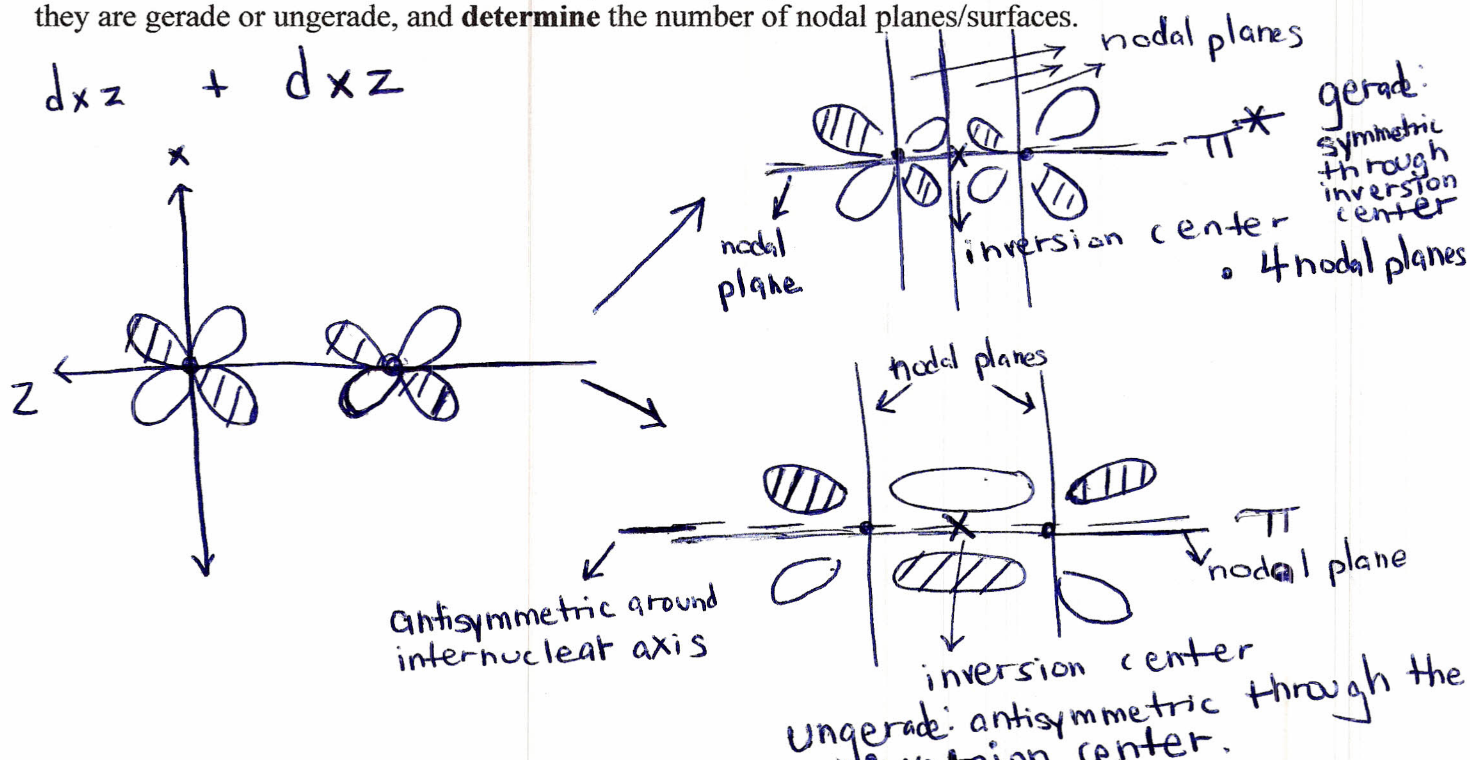
d. How many bonding molecular orbitals will there be for the triple bond?

To accommodate six e⁻ in a triple bond you will need three bonding m.o.s.

e. **Draw** the σ and σ* molecular orbitals, **explain** why they are σ molecular orbitals, **state** whether they are gerade or ungerade, and **determine** the number of nodal planes/surfaces.



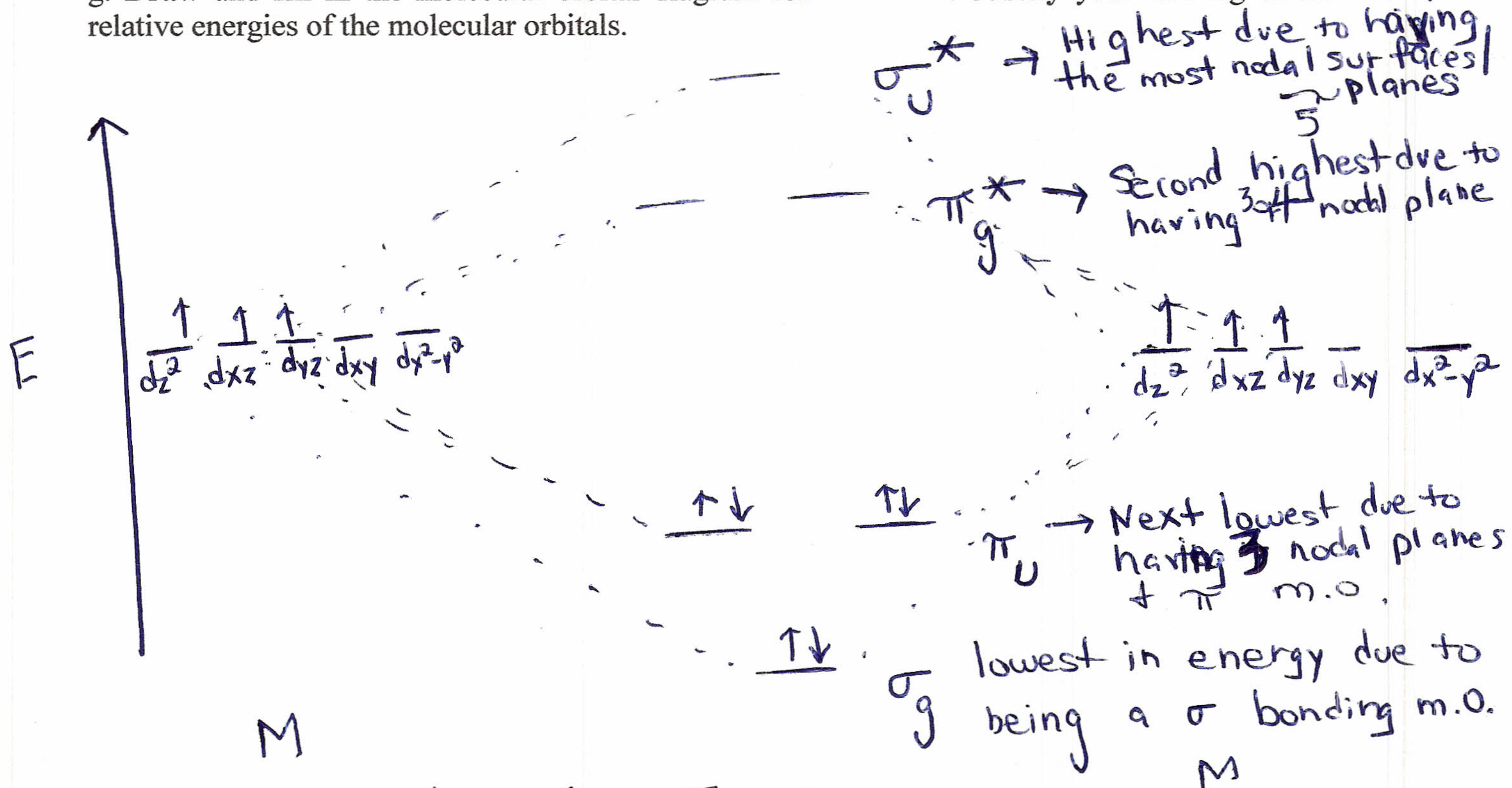
f. **Draw** the π and π* molecular orbitals, **explain** why they are π molecular orbitals, **state** whether they are gerade or ungerade, and **determine** the number of nodal planes/surfaces.



• 3 nodal planes

dyz + dyz ⇒ gives comparable molecular orbitals as dxz + dxz

g. **Draw** and **fill in** the molecular orbital diagram for M≡M. **Justify** your ranking of the relative energies of the molecular orbitals.



Bond order $= \frac{1}{2}[6] = 3$

h. Would the bond length increase or decrease if you were to add one electron to this molecule? **Explain.**

Bond order $= \frac{1}{2}[6-1] = 2.5$ bond length would increase b/c the bond is weakened.

i. After adding the one electron, would the system be paramagnetic or diamagnetic?

There would be one unpaired e⁻ ⇒ paramagnetic

2. **Determine** the Lewis dot structure for the following three molecules **including** the resonance structures. **Identify** the optimal structure or resonance hybrid. **Define** the expected geometry. **Predict** the bond angles. The central atom in each molecule is in **bold**. (25 points):

a. **B**$(OH)_3$

B O H

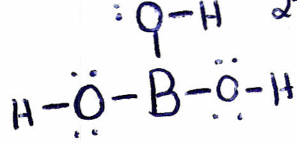
Have $3 + 3(6 + 1) = 24\,e^-$

Need $6 + 3(8 + 2) = 36\,e^-$

exception here

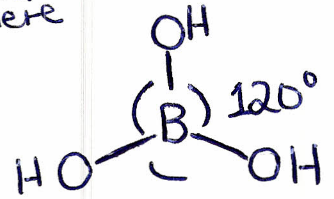
$36e^- - 24e^- = 12e^- \div 2 = 6$ bonds

$24e^- - 12e^- = 12$ free e^-



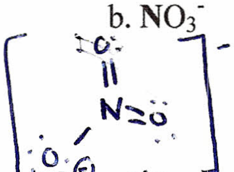
Steric #: 3

All bonded pairs



Trigonal planar

b. NO_3^-



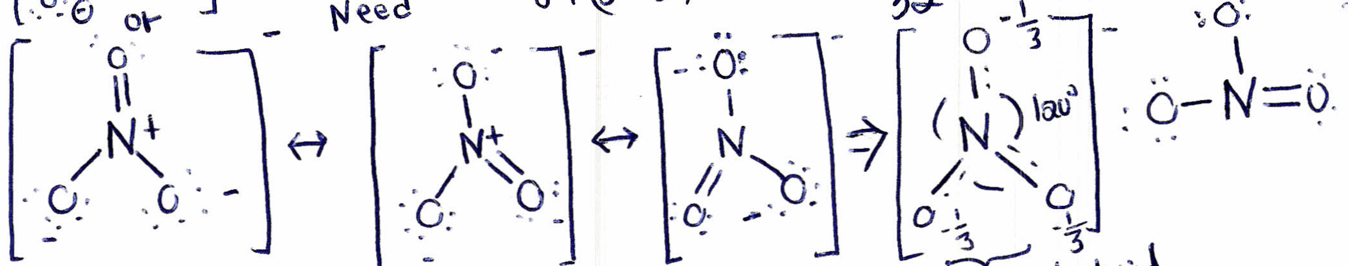
N 3O

Have $5 + (3\times6) + 1 = 24e^-$

Need $8 + (3\times8) = 32$

$32e^- - 24e^- = 8e^- \div 2 = 4$ bonds

$24e^- - 8e^- = 16e^-$ free



Res. hybrid

Trigonal planar

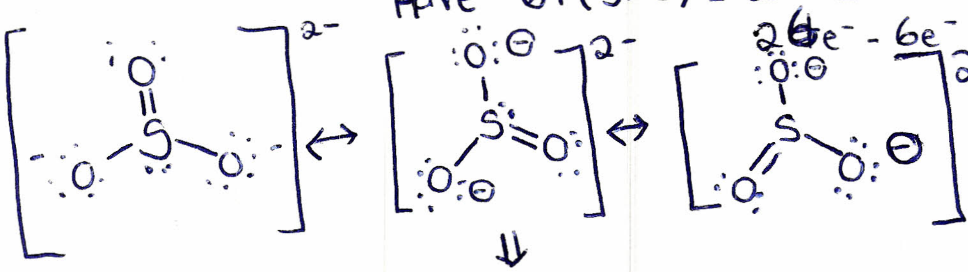
c. SO_3^{2-}

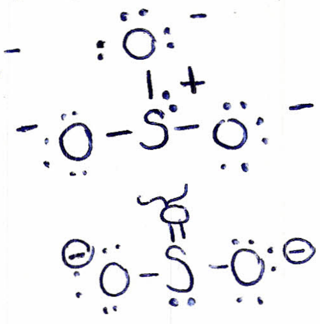
S 3O

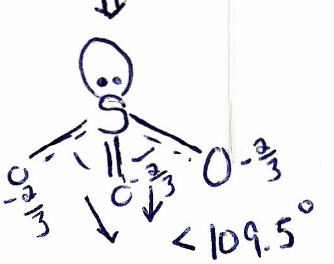
Have $6 + (3\times6) + 2e^- = 26e^-$

$26e^- - 6e^- = 20e^-$

Minimum # of bonds = 3





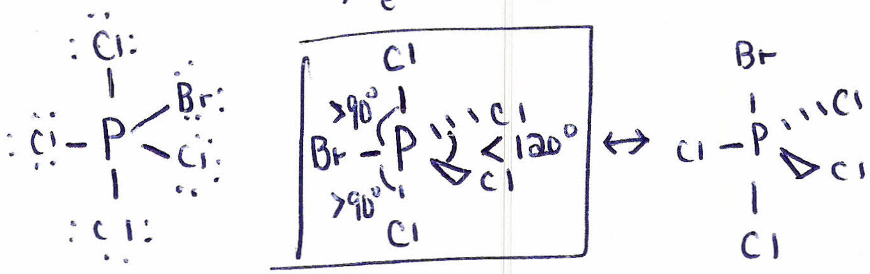


P 4 Cl Br

Have $5+4\times(7)+7 = 40$ valence e^-

d. PCl_4Br Minimum # of bonds: 5

$40_{e^-} - 10\ e^- = 30\ e^-$



$\chi_{Br} < \chi_{Cl}$ → Main structure · Trigonal bipyramidal

Provide an explanation for the following set of questions (3-7).

3. Circle the atom/ion with the higher ionization energy (5 points):

a. (Mg) or Al → Filled 2s

b. O or (O^+) → Second I.E.

4. Circle the atom/ion with the larger atomic radius (5 points):

a. (Fe^{2+}) or Fe^{3+} → lower Z^*

b. F or (Cl) → Higher "n" level

5. Circle the atom with the higher electron affinity (5 points):

a. (H) or Ne → Noble gas

b. (Cr) or Mn Cr: [Ar] $4s^1 3d^5$ (Mn: [Ar] $4s^2 3d^5$) filled half-filled

6. Circle the one with the higher effective nuclear charge (5 points):

a. (a 2p e^- in Cu^{2+}) or a 3d e^- in Cu^{2+} → More penetrating

b. a 2s e^- in Na or a (2s e^- in K)

Na: $(1s^2)(2s^2 2p^6)\ 3s^1$

K: $(1s^2)(2s^2 2p^6)(3s^2 3p^6)\ 4s^1$

$Z^* = Z - S$

S will be the same

$Z_K > Z_{Na}$

7. Circle the free ion with the higher magnetic moment (5 points):

a. Fe^{2+} or (Fe^{3+}) Fe^{2+}: [Ar] $3d^6$ ↑↓ ↑ ↑ ↑ ↑

b. (Ti^{4+} or V^{5+}) Fe^{3+}: [Ar] $3d^5$ (↑ ↑ ↑ ↑ ↑) higher # of unpaired e^-

→ Neither has unpaired e^-

8. a. In the Schrödinger equation, what does the wave function define? (5 points)

$H\Psi = E\Psi$

Ψ: Helps to define the e^- as a wave. It takes into consideration the angular + radial components of the atomic orbitals. Each a.o. has a distinct Ψ.

b. In general terms, what do the kinetic and potential energy components of the Hamiltonian operator describe? (5 points)

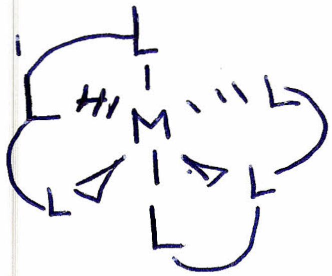
K.E. → Describes the e^- in motion

P.E. → Describes the electrostatic attraction between e^- + nucleus

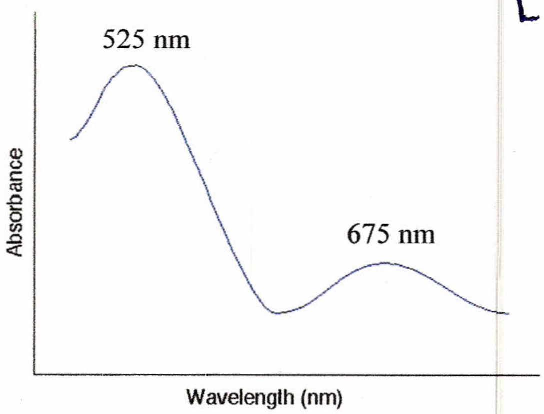
(10 points)

9. On the first day of class we performed a demonstration that introduced you to coordination chemistry. We briefly discussed that certain metal ions have a preferred coordination number of 6. **How** can a tridentate ligand satisfy this coordination number? **Provide** a drawing showing the geometry.

You would need two tridentate ligand to satisfy C.N. = 6



ii. A coordination complex displays the following UV-Vis absorbance. **Calculate** the energy of the absorbances.



$E = h\nu = h\frac{c}{\lambda}$

$h = 6.626 \times 10^{-34}$ Js

$c = 3.0 \times 10^{8}$ m/s

For 525 nm

$E = \frac{(6.626 \times 10^{-34} \text{ Js})(3.0 \times 10^{8} \text{ m/s})}{525 \times 10^{-9} \text{ m}}$

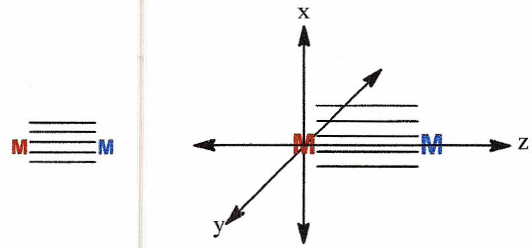
$= 3.79 \times 10^{-19}$ J

For 675 nm

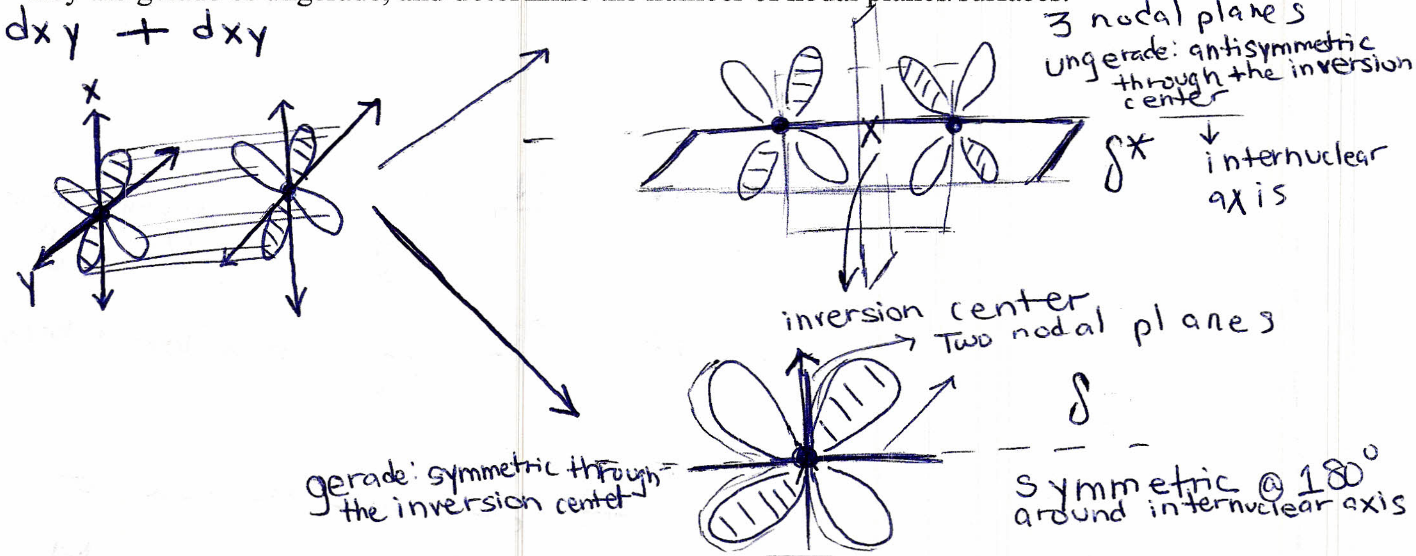
$E = 2.94 \times 10^{-19}$ J

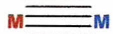
Extra Credit (10 points):

Let's revisit question 1. It turns out that a quintuple bond (five bonds) can exist between two metals. This was a finding reported by YC Tsai et al. in the 2009 JACS manuscript "Journey from Mo-Mo quadruple bonds to quintuple bonds." Using molecular orbital theory, this would require the construction of an additional type of molecular orbital known as the delta molecular orbital (δ). This type of molecular orbital involves a pair of d-orbitals oriented in such a way that they are parallel to one another.

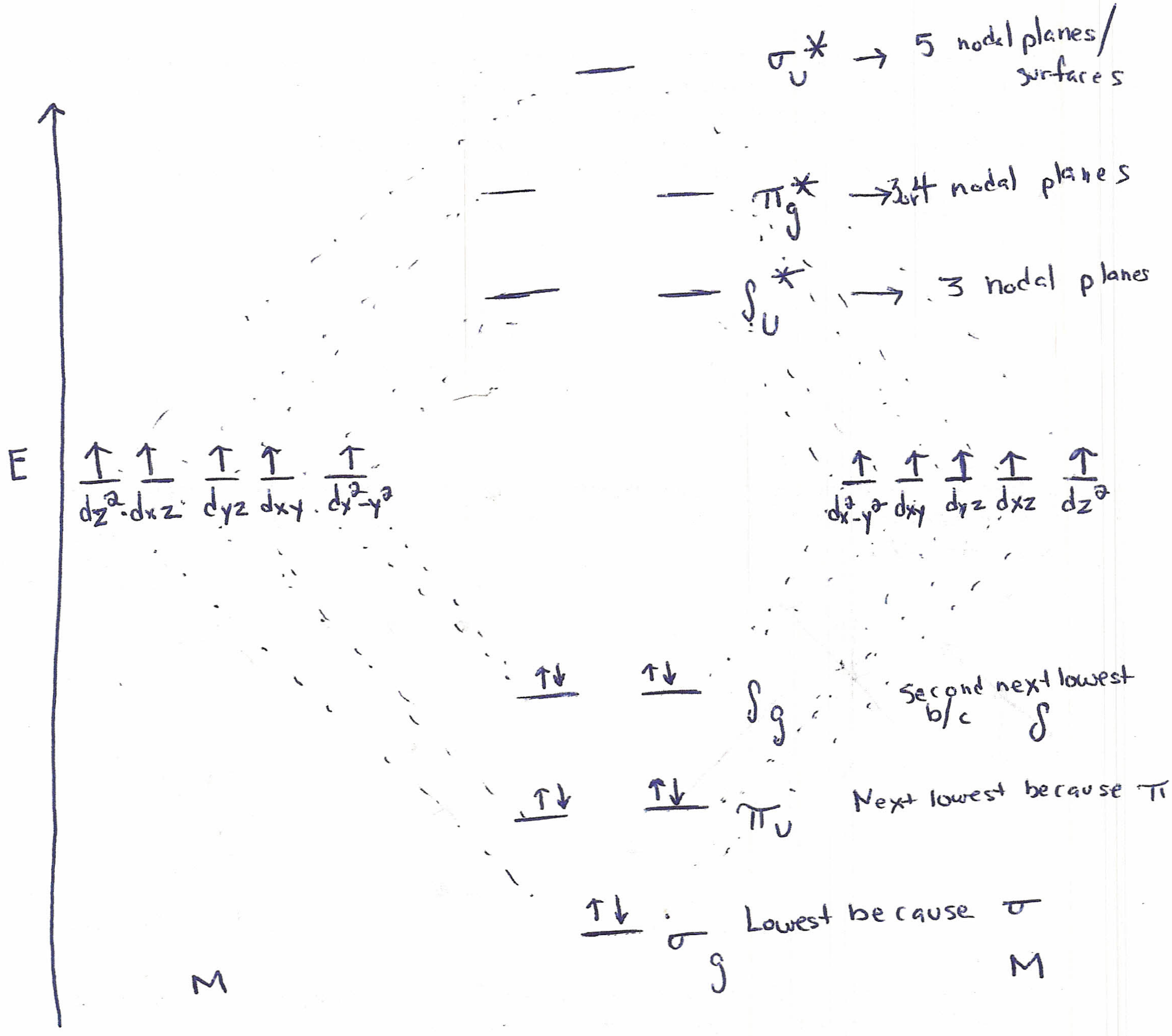


a. **Draw** the δ and δ* molecular orbitals, **explain** why they are δ molecular orbitals, **state** whether they are gerade or ungerade, and **determine** the number of nodal planes/surfaces.



g. **Draw** and **fill in** the molecular orbital diagram for  assuming that both metals are the same. **Justify** your ranking of the relative energies of the molecular orbitals.

⟹ See the next page.



$$\text{Bond order} = \frac{10}{2} = 5$$