Problem Set #12

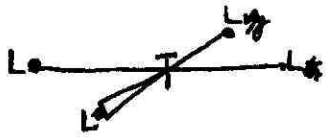
① Zumdahl Chapter 20 problems

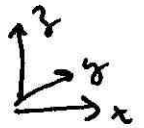
38, 39, 41, 42, 43, 45, 48, 49, 50

For the last three of the Zumdahl problems it may be useful to solve the following two MO problems.

② Beside octahedral TL_6 species (T = transition metal, L = ligand) two of the most common geometries are

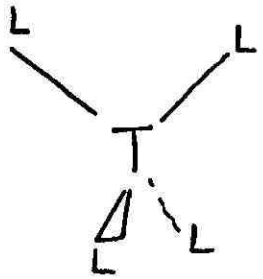
square planar :





(use these axes.

and tetrahedral

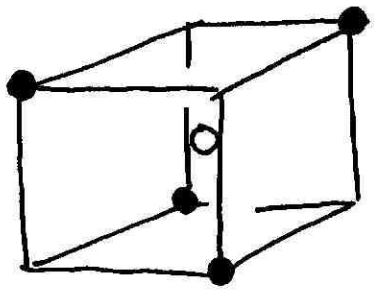


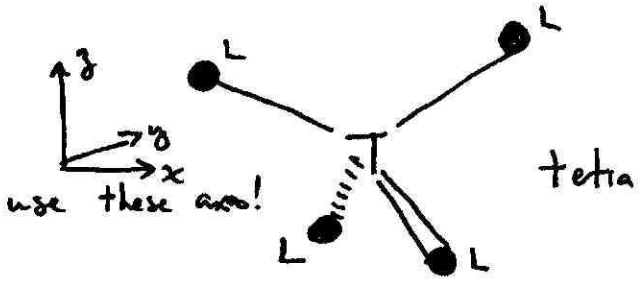
(i) Derive an MO diagram for square planar TL_4 with L a σ-donor (a halide for example)

(ii) Derive TL_4 diagram for a σ-donor, π acceptor (CO for example)

(iii) Rationalize that d^8 systems are often observed as square planar geometries and not octahedral geometries.

③ The tetrahedral geometry is harder to visualize than the square planar geometry. For deriving the MO diagram of a tetrahedral species it is easiest if one observes a tetrahedron is a cube with half the corners missing.





(i) We know the d orbitals have the values of $2z^2-x^2-y^2$, xy, xz, yz and x^2-y^2. Evaluate the values of these functions at the four points where the tetrahedral atoms are located: Assume that the cube is centered at the origin and has a side of length 2. Use the axes shown.

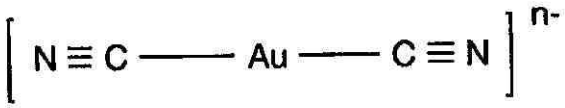
(ii) For those values = 0 in (i) there is no σ-interaction between the T and L and hence if L is a σ-donor only, no T-L interaction. Why is this so? Derive a TL_4 MO diagram for L = σ-donor only. What is a most stable d-electron count for

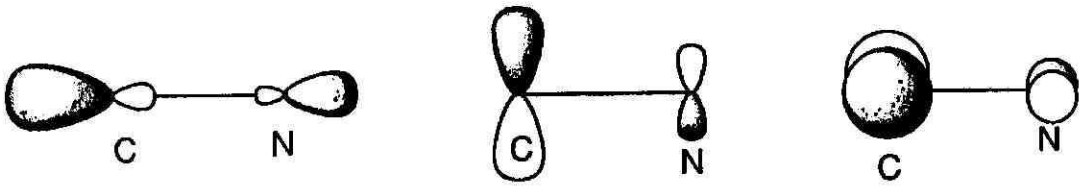
④ As we saw for  reduction by H^-, qualitative MO arguments work easily for atoms in the same row of the periodic table, but not so easily for atoms in different rows. (For atoms in different rows we have both changes in size of the orbitals and energies of the orbital while for atoms in the same row we can concentrate just on the energies of the orbital.) Explain using MO theory why

$$NH_3 > H_2O > F^-$$

in the spectrochemical series.

5a (36 pts) Please consider the **linear** ion $[Au(CN)_2]^{n-}$. Assume the **Au** atom has **only valence s and d** orbitals and that the atomic orbital **energy of these s and d orbitals are the same.** Assume that for the **cyanide** ligand one needs **only consider the three orbitals** shown below. In the answer box provided please draw the MOs for this system. **Please indicate which orbitals have the same or nearly the same energy.**





SEE NEXT PAGE FOR ANSWER BOX

5b (6 pts) If all bonding and non-bonding orbitals are filled what is the value of n in the chemical formula $[Au(CN)_2]^{n-}$?

ANSWER: | n = |

ANSWER BOX for Sa:

HIGHEST ENERGY

N ≡ C —— Au —— C ≡ N

N ≡ C —— Au —— C ≡ N

N ≡ C —— Au —— C ≡ N

N ≡ C —— Au —— C ≡ N

N ≡ C —— Au —— C ≡ N

N ≡ C —— Au —— C ≡ N

N ≡ C —— Au —— C ≡ N

N ≡ C —— Au —— C ≡ N

N ≡ C —— Au —— C ≡ N

N ≡ C —— Au —— C ≡ N

N ≡ C —— Au —— C ≡ N

LOWEST ENERGY