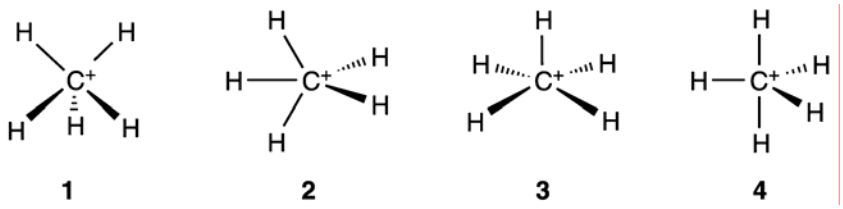
# Chemistry 5.04 (F04)
# Problem Set 4

Due Friday, 22 October

1. Derive the molecular orbital diagram of a linear $H_3$ ($D_{\infty h}$), isosceles triangular $H_3$ ($C_{2v}$) and equilateral trianglular $H_3$ ($D_{3h}$).

2. In Lecture 12 (see notes), the MO diagram for $NH_3$ is derived. We used the $C_3$ character table to determine the SALCs for $\psi^{e(+)}(L)$ and $\psi^{e(-)}(L)$. Now derive the SALCs using the $C_{3v}$ character table. The $\psi^{e(+)}(L)$ SALC will follow directly from the application of the projection operator. Use the Schmidt orthogonalization method to determine $\psi^{e(-)}(L)$.

3. The simplest molecule that can function as an electron pair donor (Lewis base) is $H_2$. Interaction with a vacant orbital will lead to a three-center, two-electron, donor-acceptor bond. Such is the case for $CH_5^+$ (a molecular species that has been known in the gas phase since 1952), which is the Lewis acid-base adduct formed from $H_2$ and $CH_3^+$. Paul von R. Schleyer and his colleagues (*J. Am. Chem. Soc.* **1981**, *103*, 5649) have calculated the relative energies of the four proposed structures shown below. Derive the qualitative MO diagrams of **1**-**4**.



**1** **2** **3** **4**

| *Molecule* | *Relative Energy/kcal mol$^{-1}$* |
|---|---|
| 1 | 0.0 |
| 2 | 3.0 |
| 3 | 7.5 |
| 4 | 16.4 |

4. Here's one I always give. Although the octahedral MO diagram provides a starting point for the construction of the electronic structure of many metal complexes, it is not inclusive. Not all complexes are conveniently referenced to octahedral geometry. Other important coordination geometries include tetrahedral, square planar, trigonal bipyramidal and pyramidal.

*Five coordinate complexes*

Stereochemical interconversion between trigonal bipyramidal and square-pyramidal $ML_5$ complexes is well known.

a. Find the total representation for the σ- and π- ligand group orbitals and decompose it into the irreducible representations.

b. Determine the symmetry adapted linear combinations of the σ-ligand group orbitals.

c. Draw the pictorial representations and label each one according to the irreducible representation for which it forms a basis. Also, indicate the metal orbitals that participate in σ-bonding.

d. Construct the qualitative MO diagrams for trigonal bipyramidal and square-pyramidal $ML_5$ complexes.

e. Draw a correlation diagram relating the d-orbital splitting diagrams of $ML_5$ complexes with σ-only, π-donor and π-acceptor ligand sets.

*Four coordinate complexes*

Four coordinate transition complexes, $ML_4$, generally exhibit tetrahedral or square planar geometries.

f. Construct the MO diagram for tetrahedral complexes featuring a homoleptic σ-bonding ligand coordination sphere.

g. Determine the MO diagram for a σ-bonded square planar complex.

h. Draw a correlation diagram relating the d-orbital splitting diagrams of $ML_4$ square planar and tetrahedral complexes with σ-only, π-donor and π-acceptor ligand sets.

i. $[NiCl_4]^{2-}$ is known to be tetrahedral and paramagnetic, while $[Ni(CN)_4]^{2-}$ is square planar. Use the appropriate MO diagrams to explain the difference in structures of the two complexes.

j. Even though $Ni(CO)_4$ contains π-acceptor ligands, the complex is tetrahedral. Using the appropriate MO diagram as a guideline, explain why $Ni(CO)_4$ is tetrahedral and $[Ni(CN)_4]^{2-}$ is square planar.

k. In the lowest energy d-d excited state, $[Ni(CN)_4]^{2-}$ undergoes a $D_{4h} \rightarrow D_{2d}$ distortion. Explain.