**In-Class Activity: Molecular Orbitals of Square-Planar Complexes**

In groups of 3 or 4, please work through the following problems related to bonding in two square planar complexes using the principles of group theory and MO theory. You should only need your character tables and chemical intuition to answer most of the questions.

Previously in class, we derived the MO diagram for tetrahedral methane. Now let's turn our attention to the hypothetical square planar CH4 molecule. We will work through #1 & 2 together, then you can move forward as a group.



1. What is the point group for square-planar methane?
2. For starters, we need to derive a set of ligand-group orbitals (LGOs) for the 4 hydrogen 1*s* orbitals. To do this, follow the steps below (also listed in your handout on creating LGOs):
   1. Form a reducible representation for these 4 equivalent orbitals by determining the character of the matrix for which they form a basis under each class of symmetry operation in the point group of interest. This will correspond to the number of orbitals whose position remains unchanged under a particular class of operation.
   2. Now create a SALC for each of these LGOs. Some you should be able to do by inspection or by using a carbon-based orbital as a "generator function". If you can't find a symmetry match in the *p* and *s* orbitals, you can always use a *d* orbital as a generator function even if that orbital doesn't exist on the atom of interest (we're just using a shortcut to get at the desired symmetry). Alternatively, you can always use the projection operator to get the answer you want.
3. For the purposes of our discussion, we will focus on valence orbitals only, meaning the 2*s* and 2*p* orbitals on C and the 4×1*s* orbitals of the hydrogen atoms. To what irreducible representations do the valence orbitals of carbon belong in this point group?
4. Finally, draw an MO diagram for the complex, making sure to follow the rules of MO theory (especially that each MO must form a basis for an irreducible representation of the point group and that # orbitals in = # orbitals out).
5. Can you see a reason from the MO diagram why planar CH4 would be unfavorable? What is the nature of the HOMO in this molecule? How many bonds are there in planar CH4?
6. Now let's move onto a known (if relatively unusual) square planar molecule, NiH42– (see *J. Am. Chem. Soc.* **2010**, 13684). Create an MO diagram for NiH42– with planar CH4 as a starting point, keeping in mind the following points:
   1. The nickel 3*d*, 4*s*, and 4*p* orbitals are the only ones to be considered for bonding.
   2. Since Ni is less electronegative than H, all of the Ni valence orbitals are higher in energy than the H 1*s* orbitals.
   3. Be sure to account for all of the valence electrons present (4 from H atoms, 10 from Ni, and 2 from the charge).

We can assume that the 4*s* and 4*p* orbitals of nickel have the same symmetry as carbon's 2*s* and 2*p* orbitals. What irreducible representations are spanned by the nickel 3*d* orbitals?

How does the addition of nickel 3*d* orbitals affect the MO picture you get? How many bonds are there in NiH42–?