1.19: Bonding in Polyatomics- Constructing Molecular Orbitals from SALCs

In the previous section we showed how to use symmetry to determine whether two atomic orbitals can form a chemical bond. How do we carry out the same procedure for a polyatomic molecule, in which many atomic orbitals may combine to form a bond? Any SALCs of the same symmetry could potentially form a bond, so all we need to do to construct a molecular orbital is take a linear combination of all the SALCs of the same symmetry species. The general procedure is:

1. Use a basis set consisting of valence atomic orbitals on each atom in the system.
2. Determine which irreducible representations are spanned by the basis set and construct the SALCs that transform as each irreducible representation.
3. Take linear combinations of irreducible representations of the same symmetry species to form the molecular orbitals. E.g. in our NH_3 example we could form a molecular orbital of A_1 symmetry from the two SALCs that transform as A_1,

$$\begin{aligned} \Psi(A_1) &= c_1\phi_1 + c_2\phi_2 \\ &= c_1 s_N + c_2 \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3) \end{aligned} \tag{19.1}$$

Unfortunately, this is as far as group theory can take us. It can give us the functional form of the molecular orbitals but it cannot determine the coefficients c_1 and c_2. To go further and obtain the expansion coefficients and orbital energies, we must turn to quantum mechanics. The material we are about to cover will be repeated in greater detail in later courses on quantum mechanics and valence, but they are included here to provide you with a complete reference on how to construct molecular orbitals and determine their energies.