Question: Which orbital interactions will be important in constructing the pictures and approximate MO (molecular orbital) energy level diagrams we have discussed in class?

There are three considerations here:

1. Symmetry: Only orbitals of the same symmetries (within the overall molecule's symmetry operators) can interact. Thus, \( \pi \) interactions are separated by symmetry from \( s \) interactions in e.g. the \( \text{N}_2 \) molecule.

   \[
   \text{Orbital:} \quad \begin{array}{cccc}
   2\text{Py} & 2\text{Pz} & 2\text{Px} & 2s \\
   \text{Symmetry*:} & \text{SA} & \text{AS} & \text{SS} & \text{SS} \\
   \end{array}
   \]

* Symmetric or antisymmetric with respect to \( \square_1 \) and \( \square_2 \)

2. Overlap: More overlap leads to larger splitting. Thus, the end-to-end \( p-\square \) is stronger than the side-on \( p-\square \) interaction due to greater interpenetration of the partner orbitals.

3. Energy Matching: Orbitals interact most strongly when they're of the same energy. This is one reason we never worry about the contribution of \( 1s \) orbitals on \( C \) to bonding - they're energetically out of reach of the valence orbitals, and their \( 1s-1s \) overlap is negligible. In general, badly matched orbitals don't bond much, in the sense of additional energy lowering \( \Delta E \) due to the interaction; for orbitals of differing energies, perturbation theory summarizes the interaction energy as

   \[
   \Delta E = \frac{\langle a | H | b \rangle}{E_1 - E_2}
   \]

   where \( \langle a | H | b \rangle \) is the so-called resonance integral (often just called \( I \)), roughly proportional to the overlap between orbitals \( \square_1 \) and \( \square_2 \), and \( E_1 \) and \( E_2 \) are the energies of the two orbitals before interaction. Since it is in the denominator, the larger the energy difference \( (E_1 - E_2) \), the smaller the interaction energy.