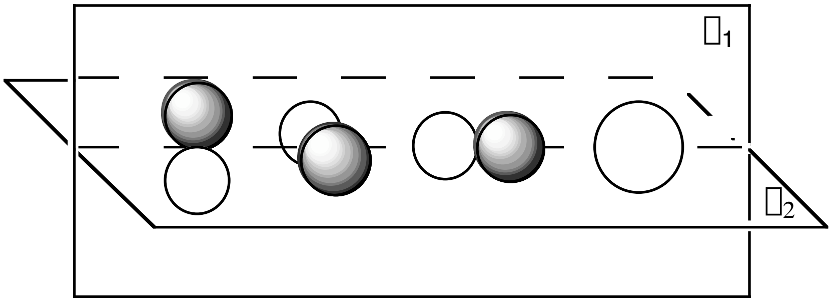
CEM 851 Handout 1
Building Orbitals of Organic Molecules

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:

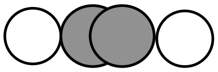
1. Symmetry: Only orbitals of the same symmetries (within the overall molecule's symmetry operators) can interact. Thus, π interactions are separated by symmetry from □ interactions in e.g. the N_2 molecule.

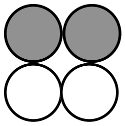


	2Py	2Pz	2Px	2s
Orbital:				
Symmetry*:	SA	AS	SS	SS

* Symmetric or antisymmetric with respect to □1 and □2

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


p-□


p-□

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 □□ due to the interaction; for orbitals of differing energies, perturbation theory summarizes the interaction energy as $\square\square = \dfrac{\langle \square_1 | H | \square_2 \rangle^2}{E_1 \square E_2}$ where $\langle \square_1 | H | \square_2 \rangle$ is the so-called resonance integral (often just called □), 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.