Wave Equations of Molecules

- Approximate wave functions are sought by combining atomic wave functions for the bonded atoms.

- Several different approaches have been taken to constructing trial wave functions.

- Valence Bond (VB) - Heitler & London (1927)

  $$\Psi_{\text{bond}} = \psi_a \psi_b$$

  - Hybrid orbitals - Pauling (1920s)

- Molecular Orbital (MO) - Hund, Mulliken (1920s)

  $$\Psi_{\text{MO}} = a\psi_A \pm b\psi_B$$

  - LCAOs - Lennard-Jones (1929)

Normalization Requirement

- From the Copenhagen interpretation we associate the probability of finding the electron in a vanishingly small volume element ("a point") as
$$P \propto \Psi\Psi^*$$

- The electron has unit probability over all space:
$$\int \Psi\Psi^* d\tau = 1$$

- To ensure that any trial wave function, ψ, meets this criterion we generally must multiply by a *normalization constant*, N, such that

$$\int (N\psi)(N\psi^*) d\tau = N^2 \int \psi\psi^* d\tau = 1$$

- If ψ is a solution to the Schrödinger equation, then so too is $N\psi$, and E in $\mathcal{H}\psi = E\psi$ is unaffected.

Slater Overlap Criterion

● When two orbitals on different atoms A and B overlap, the nature and effectiveness of their interaction is given by the *Slater overlap integral*

$$S = \int \Psi_A \Psi_B d\tau$$

which can be evaluated precisely only for H_2.

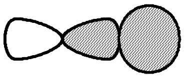
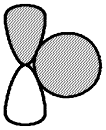
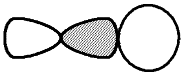
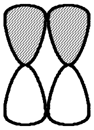
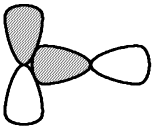
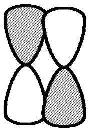
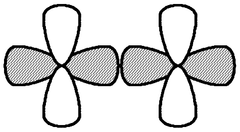
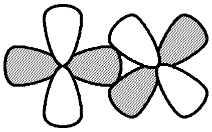
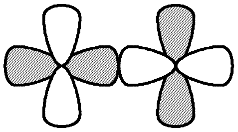
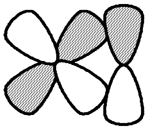
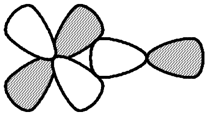
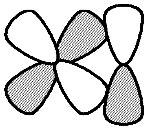
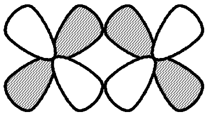
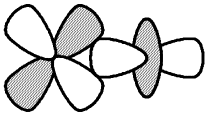
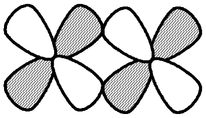
☞ For our purposes we only need to recognize when certain interactions of orbitals have $S > 0$, $S = 0$, or $S < 0$

- $S > 0$ – bonding interaction
- $S = 0$ – nonbonding interaction
- $S < 0$ – antibonding interaction

● The sense of S is evident from simple pictures of interacting orbitals.

- $S > 0$ – reenforcing overlap between nuclei
- $S = 0$ – equally reenforcing and cancelling overlaps
- $S < 0$ – cancelling overlap between nuclei

Examples of *S* > 0, *S* = 0, and *S* < 0

$S > 0$	$S = 0$	$S < 0$
		
		
		
		
		

AO Shape and Symmetry

- All AOs with the same value of *l* have the same symmetry, regardless of *n*.

- As isolated orbitals, each type can be identified with a particular point group.

  $s = R_3$
  $p = C_{\infty v}$
  $d = D_{2h}$ ("cloverleaf") or $D_{\infty h}$ (d_{z^2})

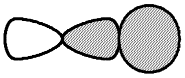
- Orbitals that have bonding combinations usually have the same kind of symmetry with respect to the internuclear axis.

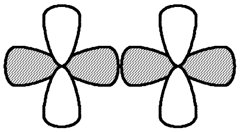
- If a bonding combination can be identified for any pair of orbitals, there must also be an antibonding combination.

- Nonbonding orbitals are oriented relative to each other such that they do not have the same kind of symmetry relative to the internuclear axis.

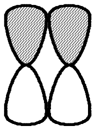
Symmetry Definition of Sigma, Pi, and Delta Interactions

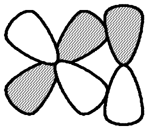
- Sigma interactions are symmetrical relative to a C_2 axis collinear with the internuclear axis.

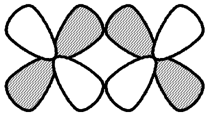




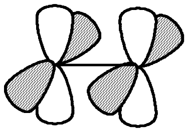
- Pi interactions are antisymmetric (Ψ changes sign) with respect to C_2 collinear with the internuclear axis and with respect to σ_v coplanar with the shared nodal plane.



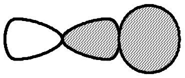




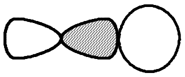
- Delta interactions are symmetric to C_2 and antisymmetric to C_4.



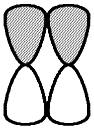
- Bonding and antibonding interactions of the same type have the same symmetry with respect to the internuclear axis.



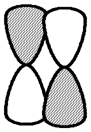
σ bonding



σ^* antibonding



π bonding



π^* antibonding