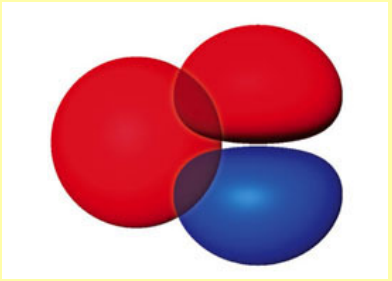
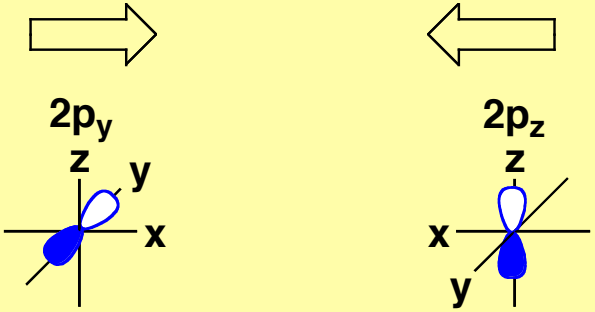
Pairwise Orbital Combinations

- ✓ Continue to follow the convention
- ✓ Identify the disallowed combinations
  - No net orbital overlap

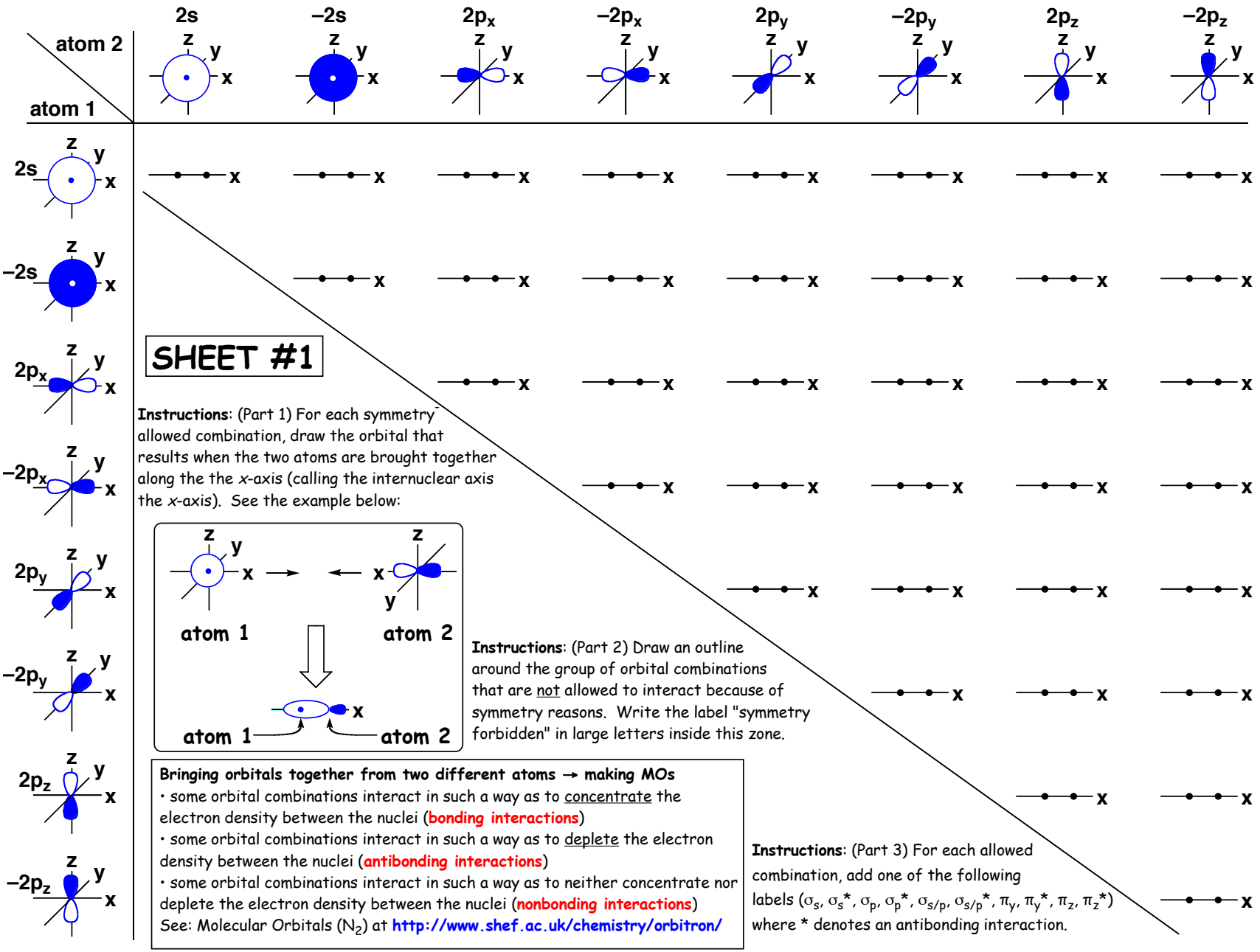


  - Perpendicular orbitals



- ✓ Attempted LCAO on disallowed combinations results in "no orbital interaction"

Identify All the "Disallowed" Combinations



SHEET #1

Instructions: (Part 1) For each symmetry-allowed combination, draw the orbital that results when the two atoms are brought together along the the *x*-axis (calling the internuclear axis the *x*-axis). See the example below:

Instructions: (Part 2) Draw an outline around the group of orbital combinations that are <u>not</u> allowed to interact because of symmetry reasons. Write the label "symmetry forbidden" in large letters inside this zone.

Instructions: (Part 3) For each allowed combination, add one of the following labels (σ_s, σ_s^*, σ_p, σ_p^*, $\sigma_{s/p}$, $\sigma_{s/p}^*$, π_y, π_y^*, π_z, π_z^*) where * denotes an antibonding interaction.

Bringing orbitals together from two different atoms → making MOs

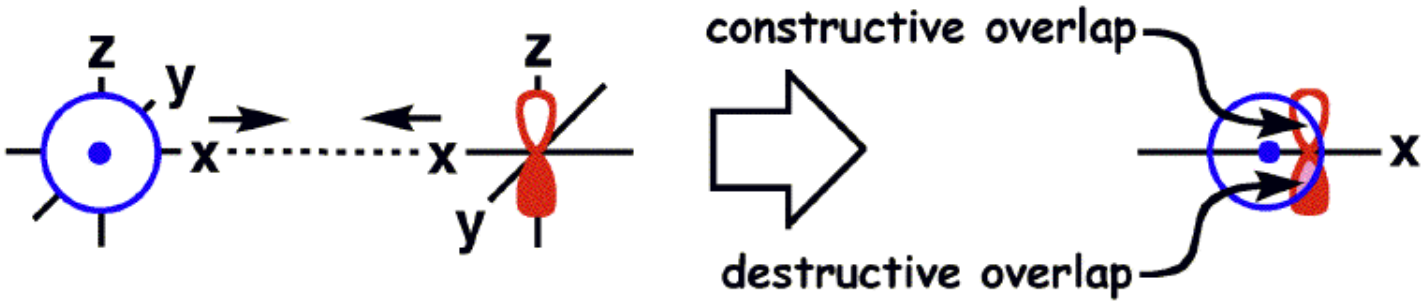
- some orbital combinations interact in such a way as to <u>concentrate</u> the electron density between the nuclei (**bonding interactions**)
- some orbital combinations interact in such a way as to <u>deplete</u> the electron density between the nuclei (**antibonding interactions**)
- some orbital combinations interact in such a way as to neither concentrate nor deplete the electron density between the nuclei (**nonbonding interactions**)

See: Molecular Orbitals (N_2) at **http://www.shef.ac.uk/chemistry/orbitron/**

A Word About Symmetry

Two orbitals are allowed to interact if both transform the same with respect to the entire set of relevant symmetry operations (i.e., for any particular operation, both orbitals must transform symmetrically or both must transform antisymmetrically). Two orbitals are forbidden from interacting if the two transform differently with any member of the symmetry operations in the set (i.e., if one transforms symmetrically and the other transforms antisymmetrically, the combination is disallowed).

Table 2. The combination of 2s and $2p_z$ is unsuitable for both sigma and pi bonding. All of the constructive overlap is canceled by the destructive overlap resulting in no net overlap. This is consistent with the symmetry analysis shown below.



symmetry operator	2s	$2p_z$	Same / different orbital symmetry	Result
$C_\infty(x)$	symmetrical	does not possess $C_\infty(x)$	different	not suitable for σ bonding
$C_2(x)$	symmetrical	antisymmetrical	different	not suitable for pi bonding
$\sigma(xy)$	symmetrical	antisymmetrical	different	
$\sigma(xz)$	symmetrical	symmetrical	same	