



Chemistry and the material world

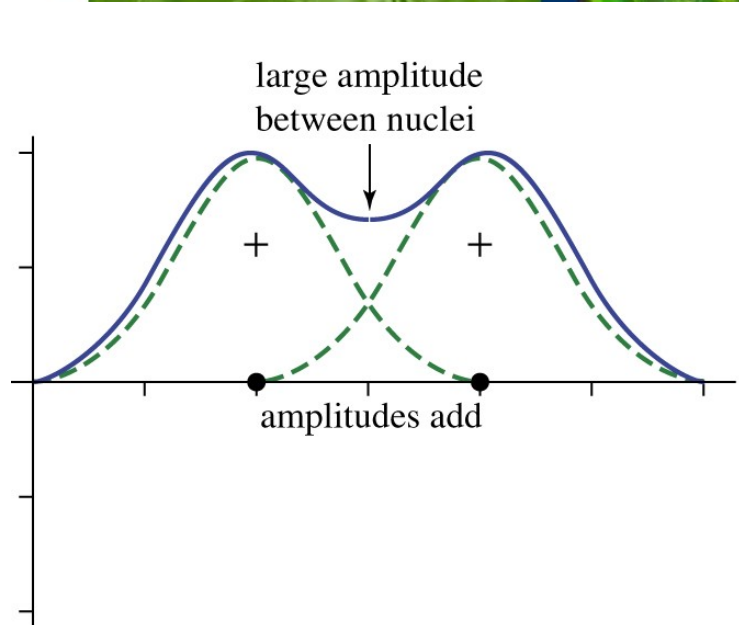
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Lecture 4
Matthias Lein

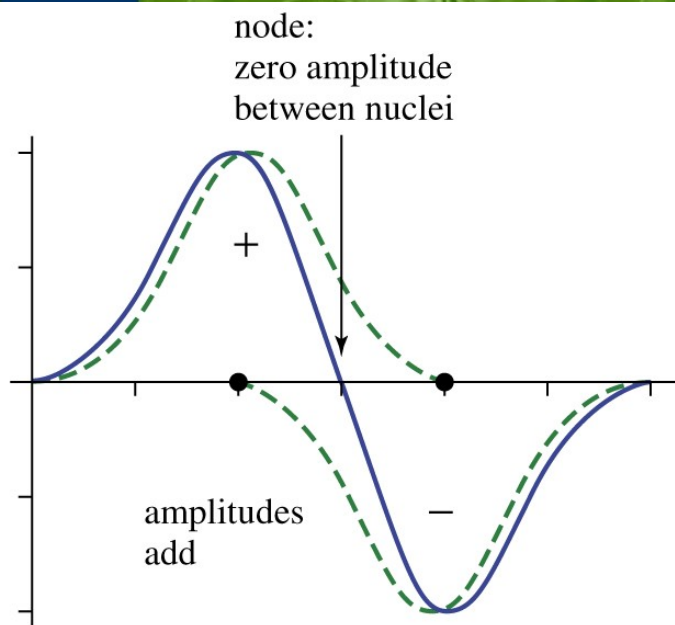


◆ Molecular Orbitals

- ◆ Constructive and destructive overlap of wavefunctions.
- ◆ Bonding and antibonding molecular orbitals.
- ◆ Symmetry labels for molecular orbitals.
- ◆ Construction of σ and π molecular orbitals.
- ◆ Symmetry restrictions and non interacting orbitals.
- ◆ Bond order in MO theory.
- ◆ Examples
 - ◆ H_2
 - ◆ He_2
 - ◆ Li_2

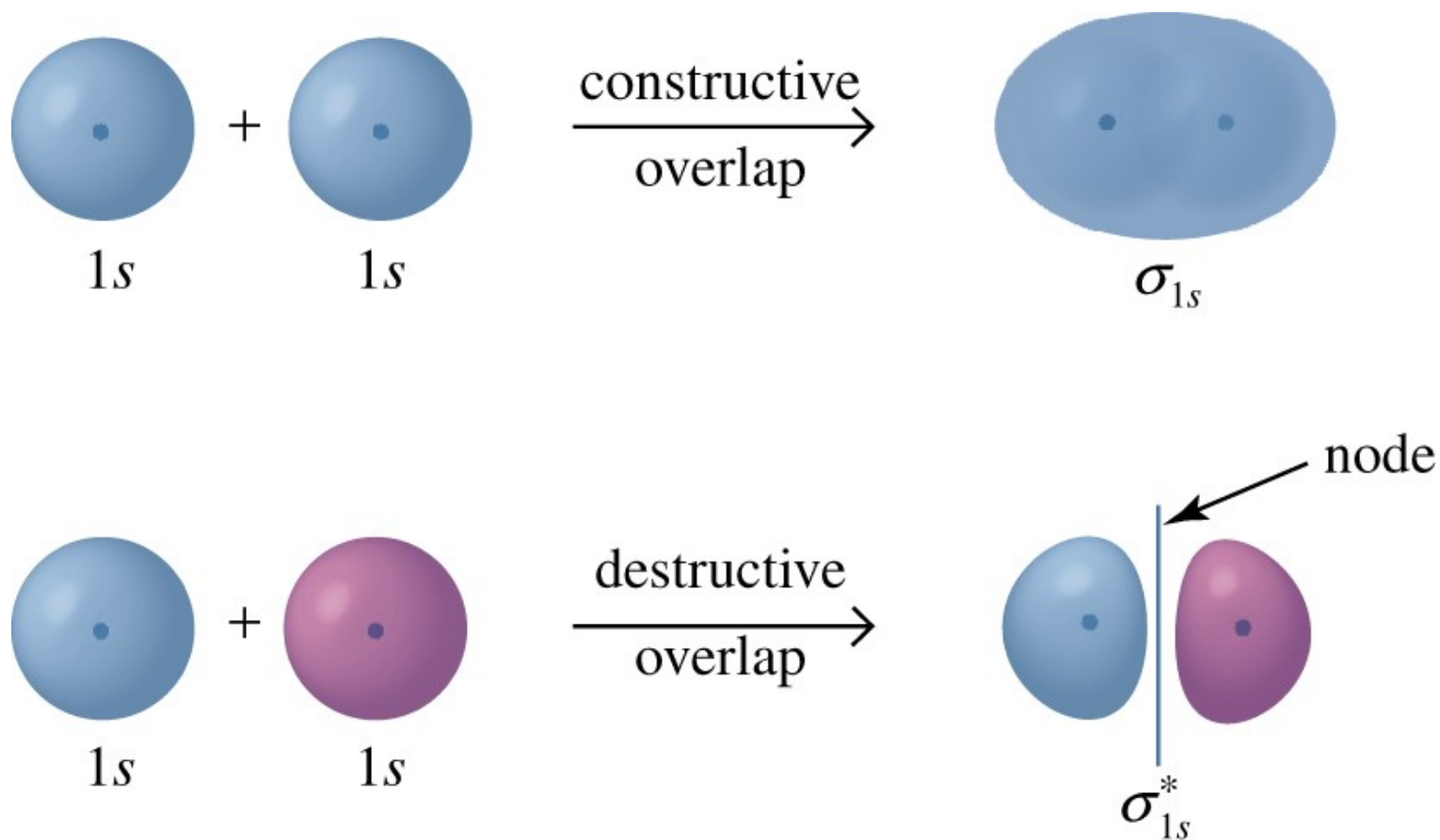


(a)

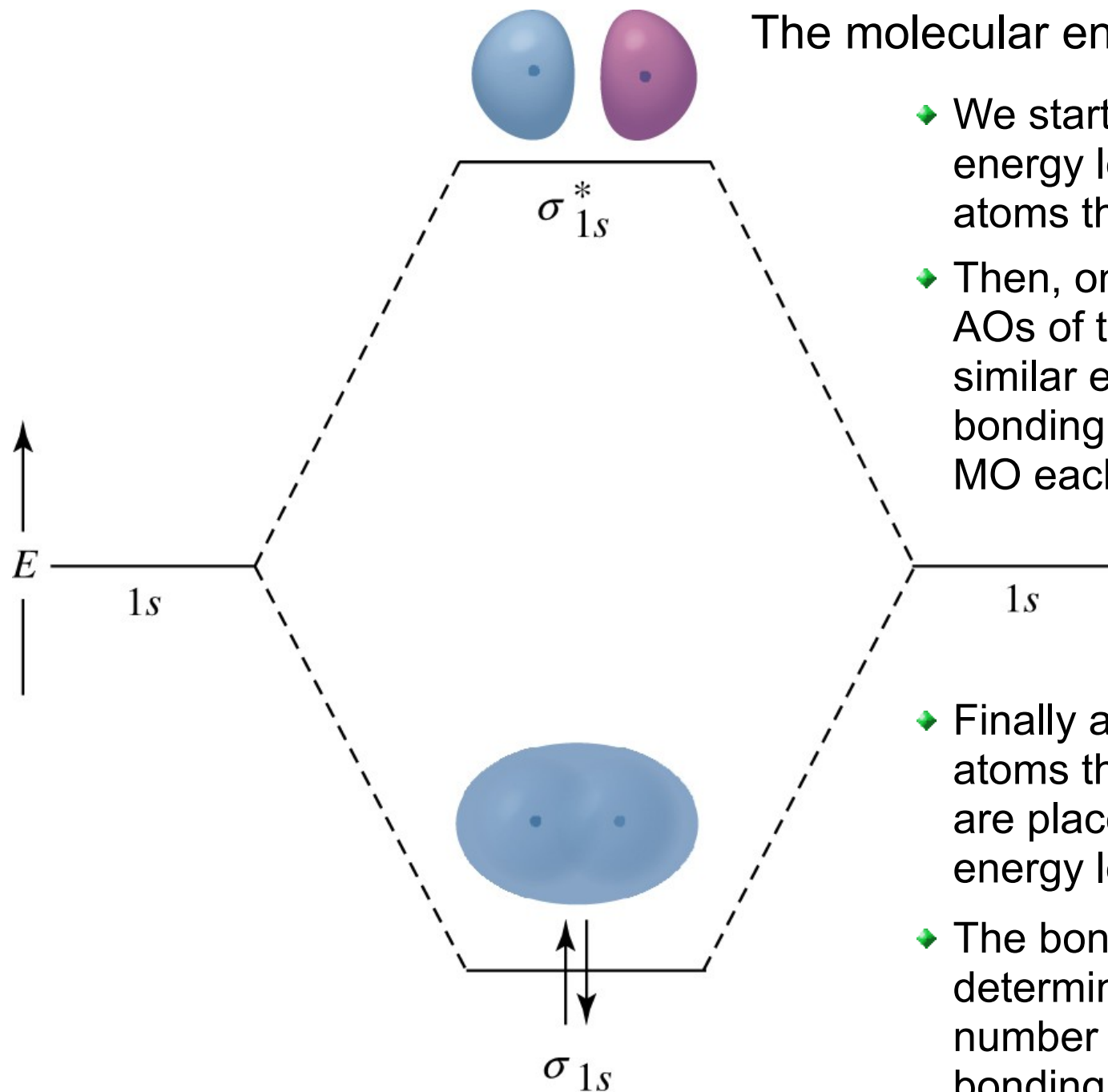


(b)

- Wave functions, just like other functions, can be added and subtracted
-
- ◆ In MO theory we always form all possible linear combinations, eg:
 - ◆ One MO through the positive linear combination of two AOs (a).
 - ◆ One MO through the negative linear combination of the same two AOs (b).
- ◆ When two lobes of equal sign are added:
 - ◆ They form a continuous new lobe over that region of space.
 - ◆ They are said to be bonding.
- ◆ When two lobes of opposite sign are added:
 - ◆ They cancel out in the region in between the original lobes (a node appears)
 - ◆ They are said to be antibonding (an asterisk* is added to the name)



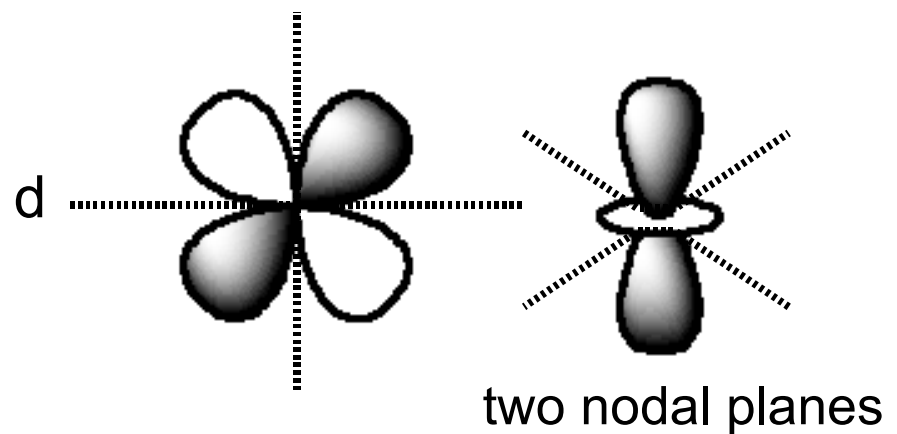
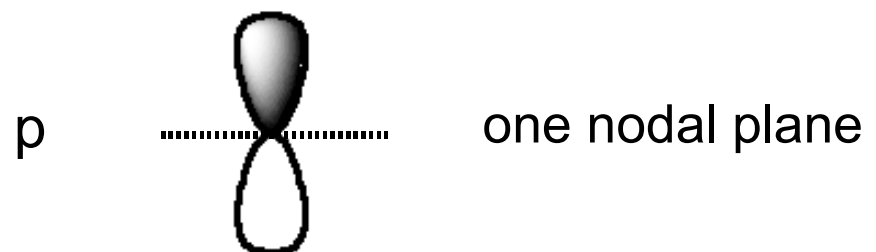
- The two different modes are called *constructive* and *destructive* respectively
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- In order to be able to combine AOs to form MOs the AOs need to
 - ◆ Be similar in energy.
 - ◆ Have the right symmetry with respect to the bond.



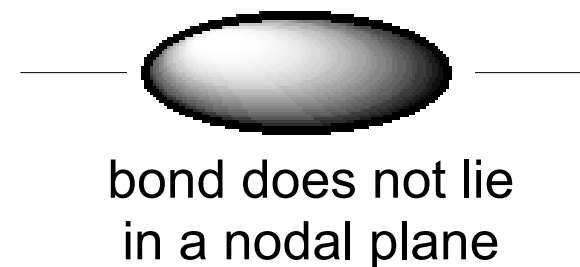
The molecular energy level diagram of H_2

- ◆ We start by drawing the atomic energy level diagram of both atoms that form the molecule
- ◆ Then, one by one, we combine AOs of the right symmetry with similar energies to form one bonding and one antibonding MO each.
- ◆ Finally all electrons (from both atoms that form the molecule) are placed into the molecular energy level diagram.
- ◆ The bond order can be determined by comparing the number of electrons occupying bonding and antibonding MOs.

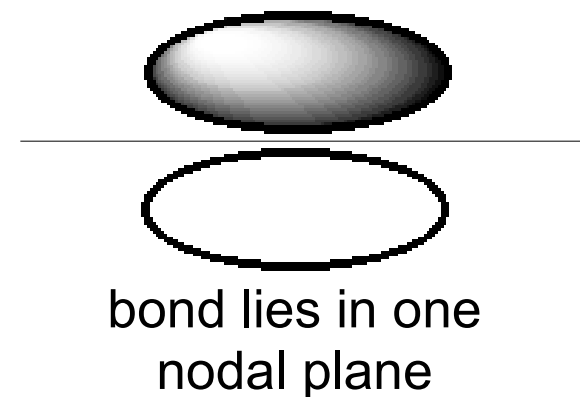
Orbitals have different symmetries:



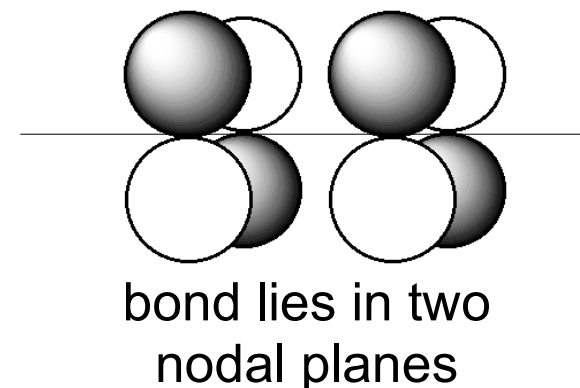
σ
(sigma)

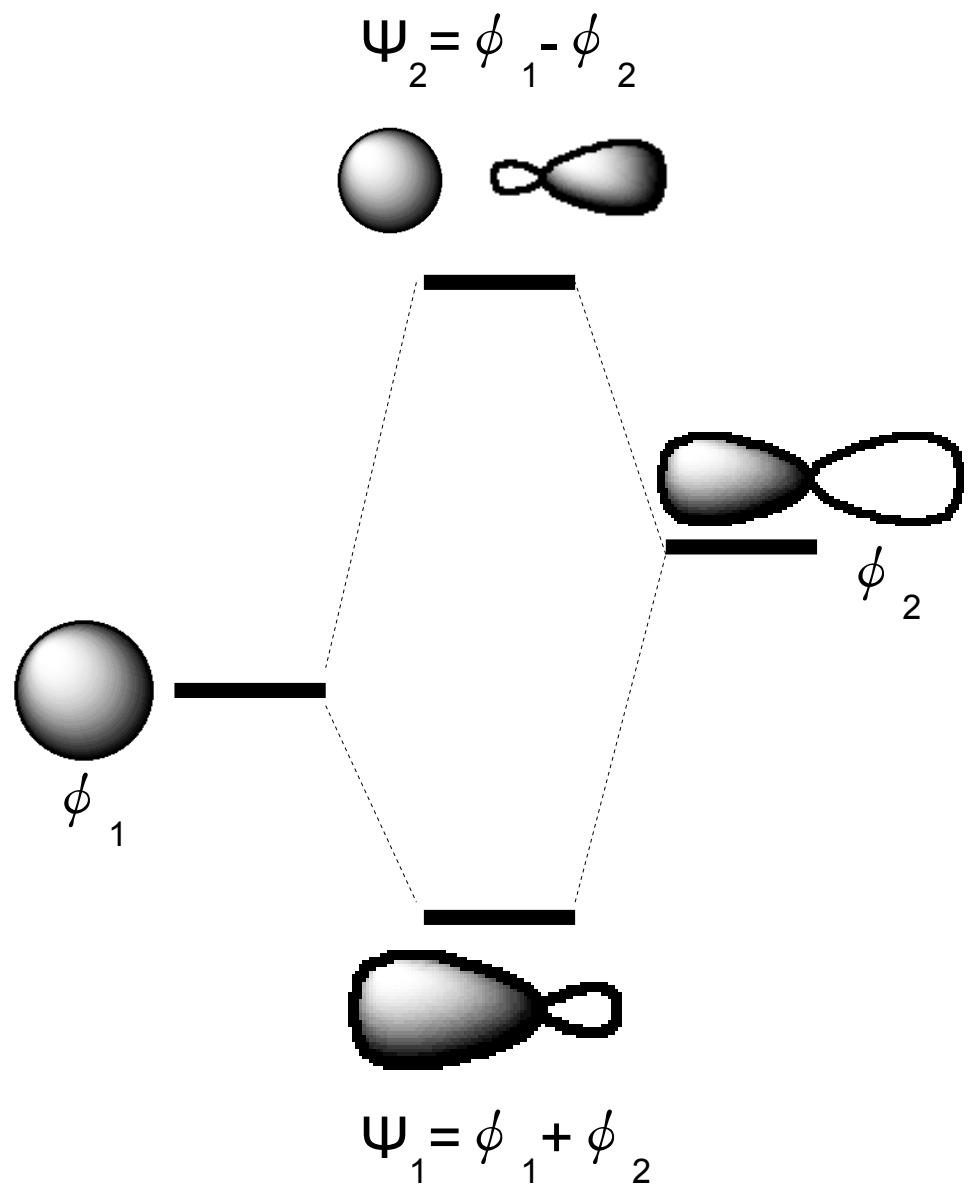
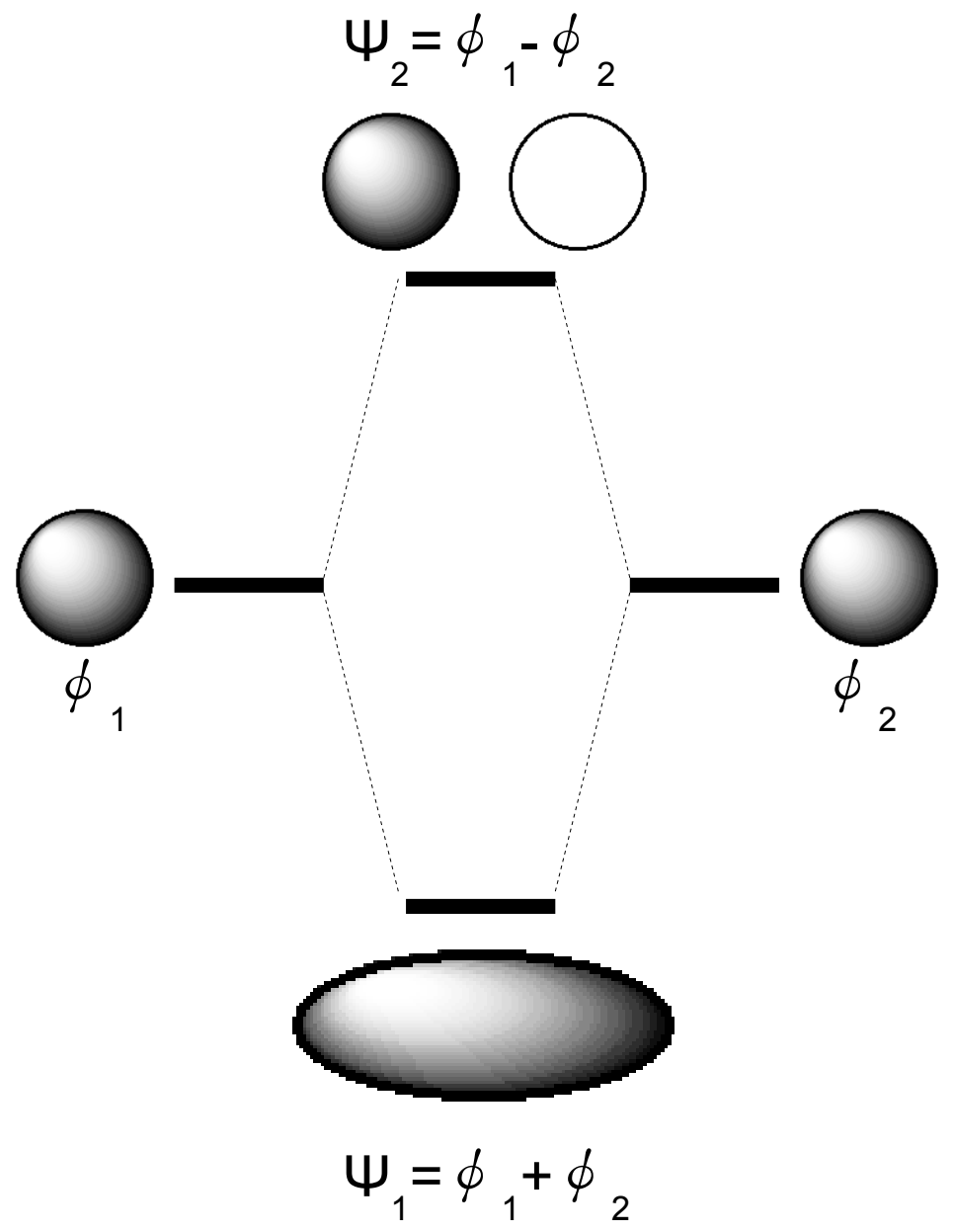


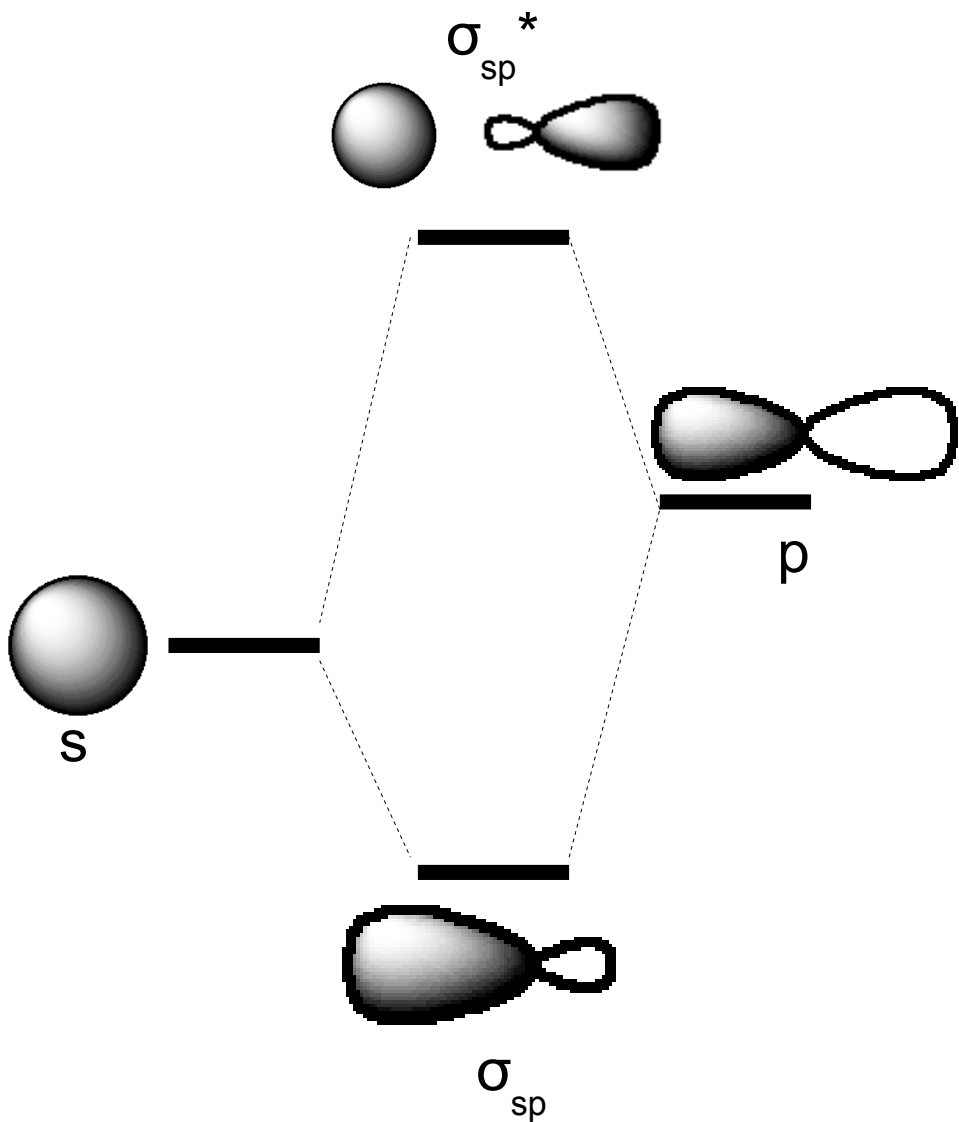
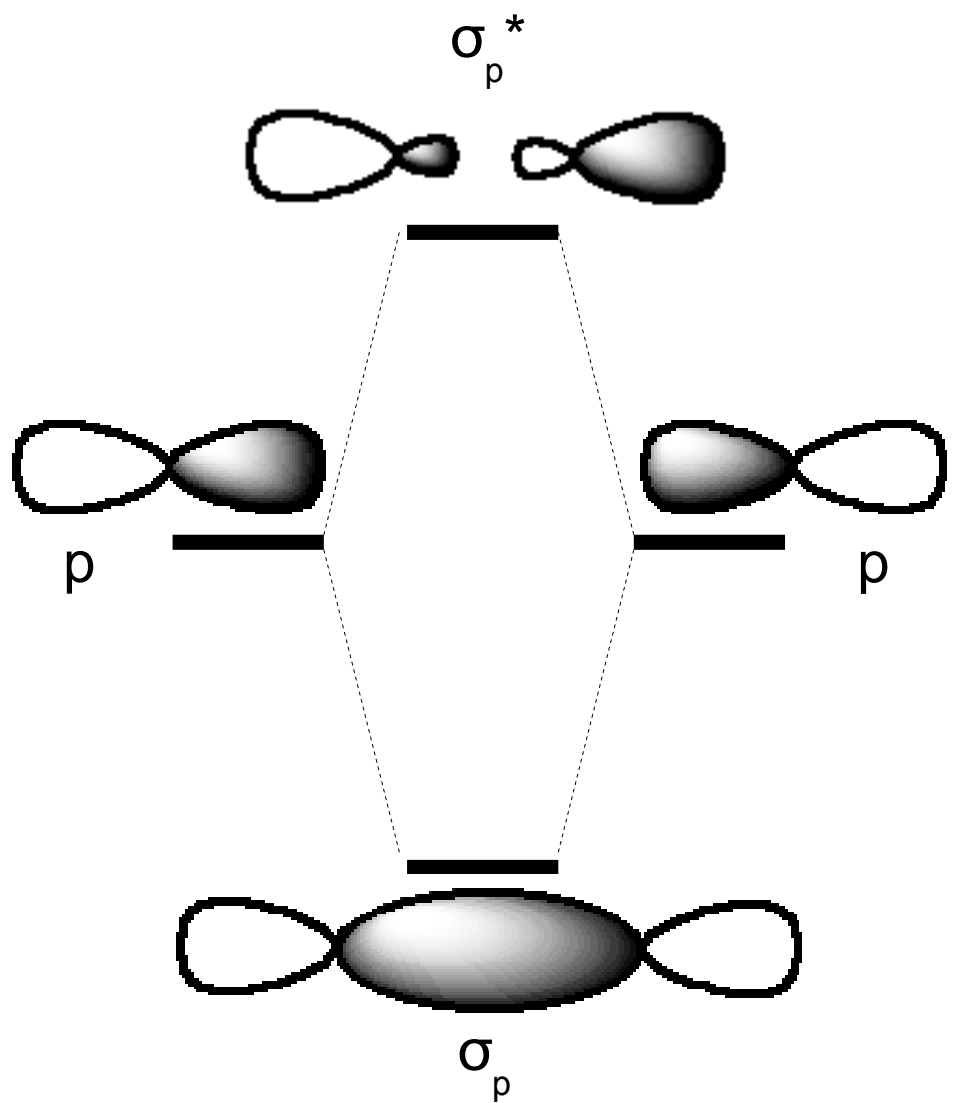
π
(pi)

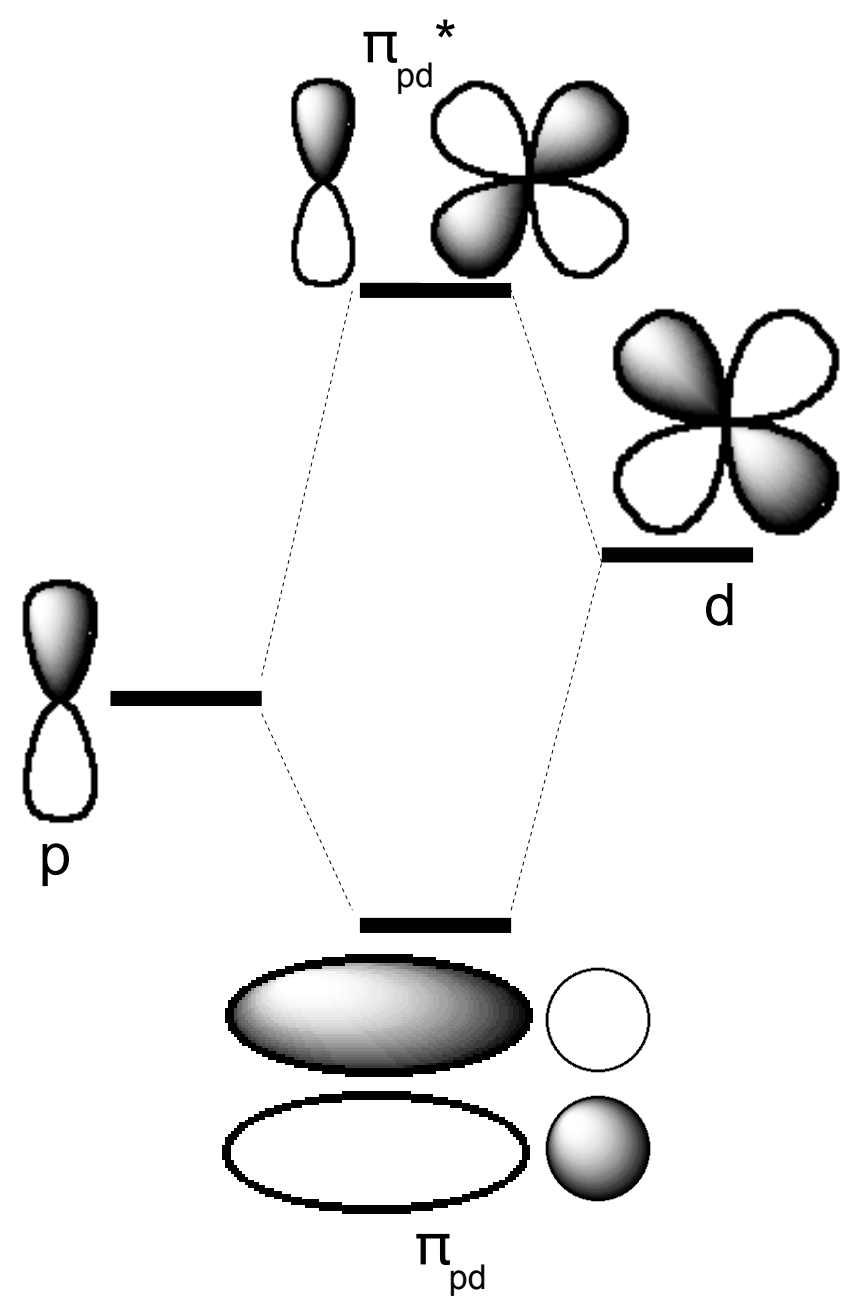
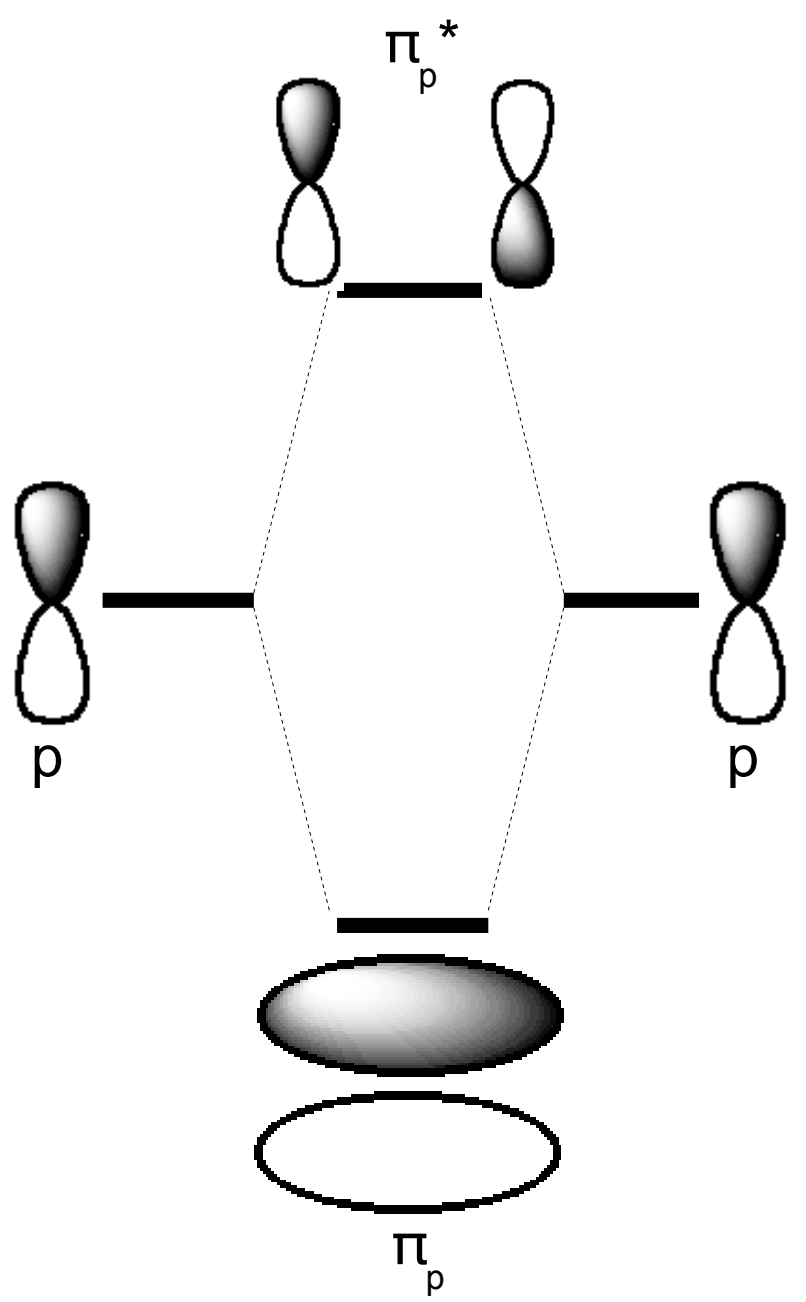


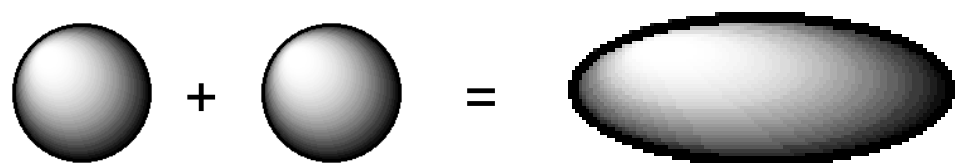
δ
(delta)



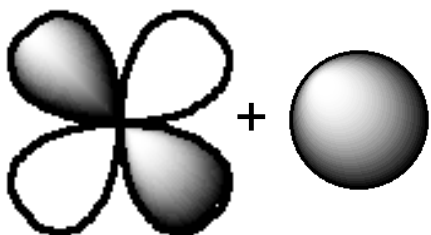
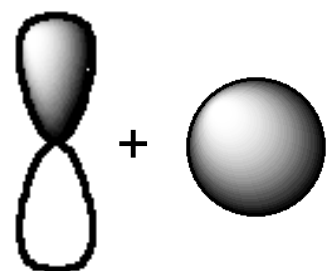
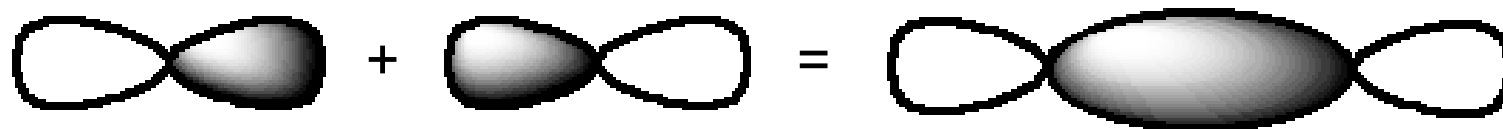




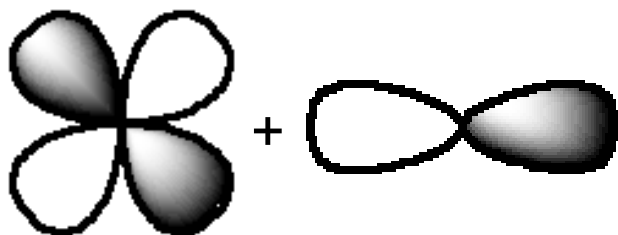
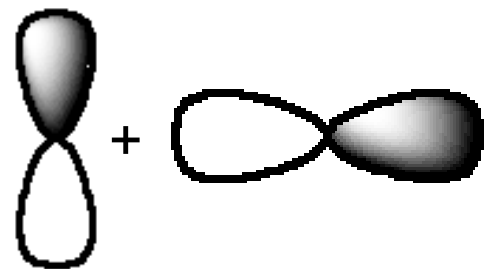


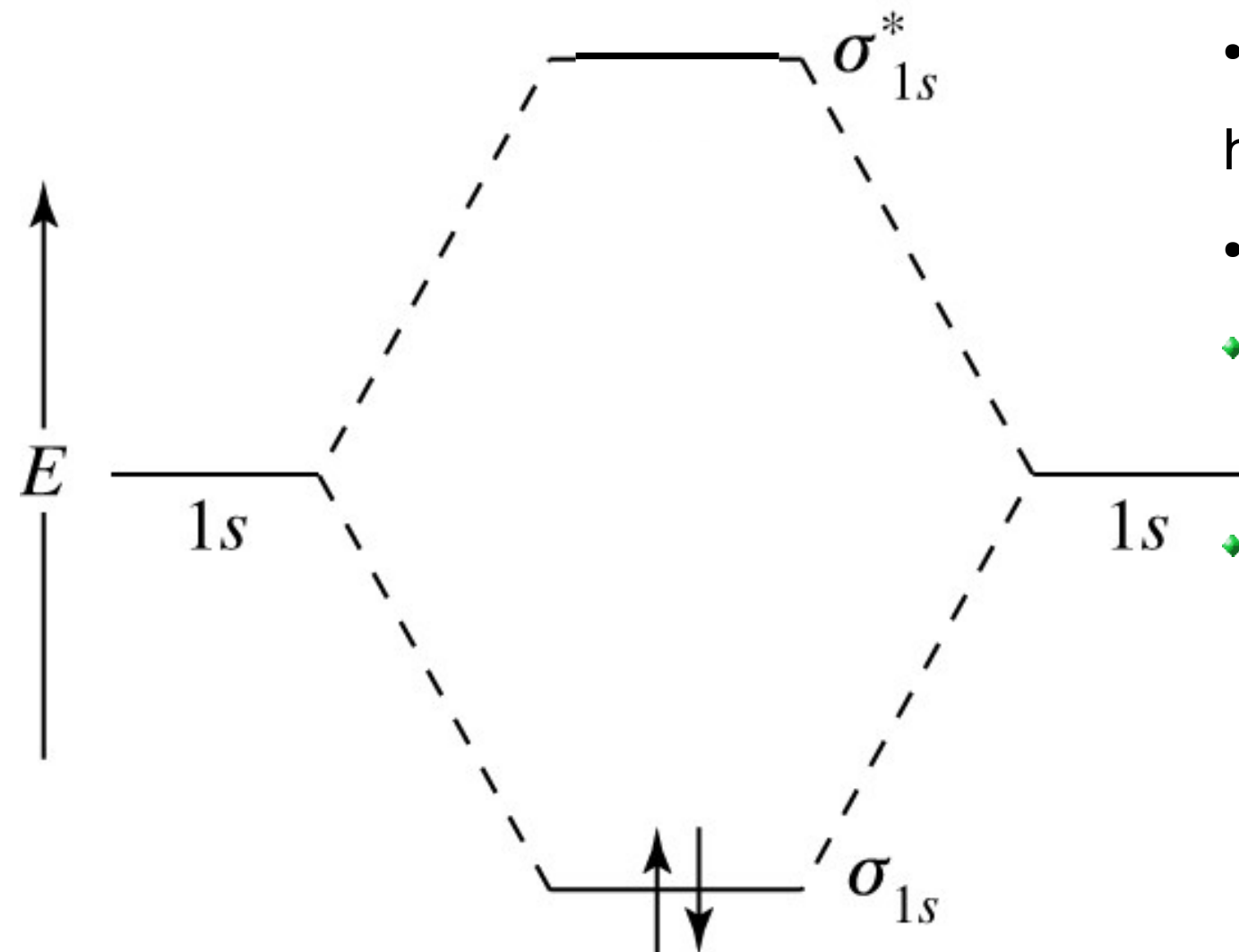


Interaction is often easily understood through overlap.

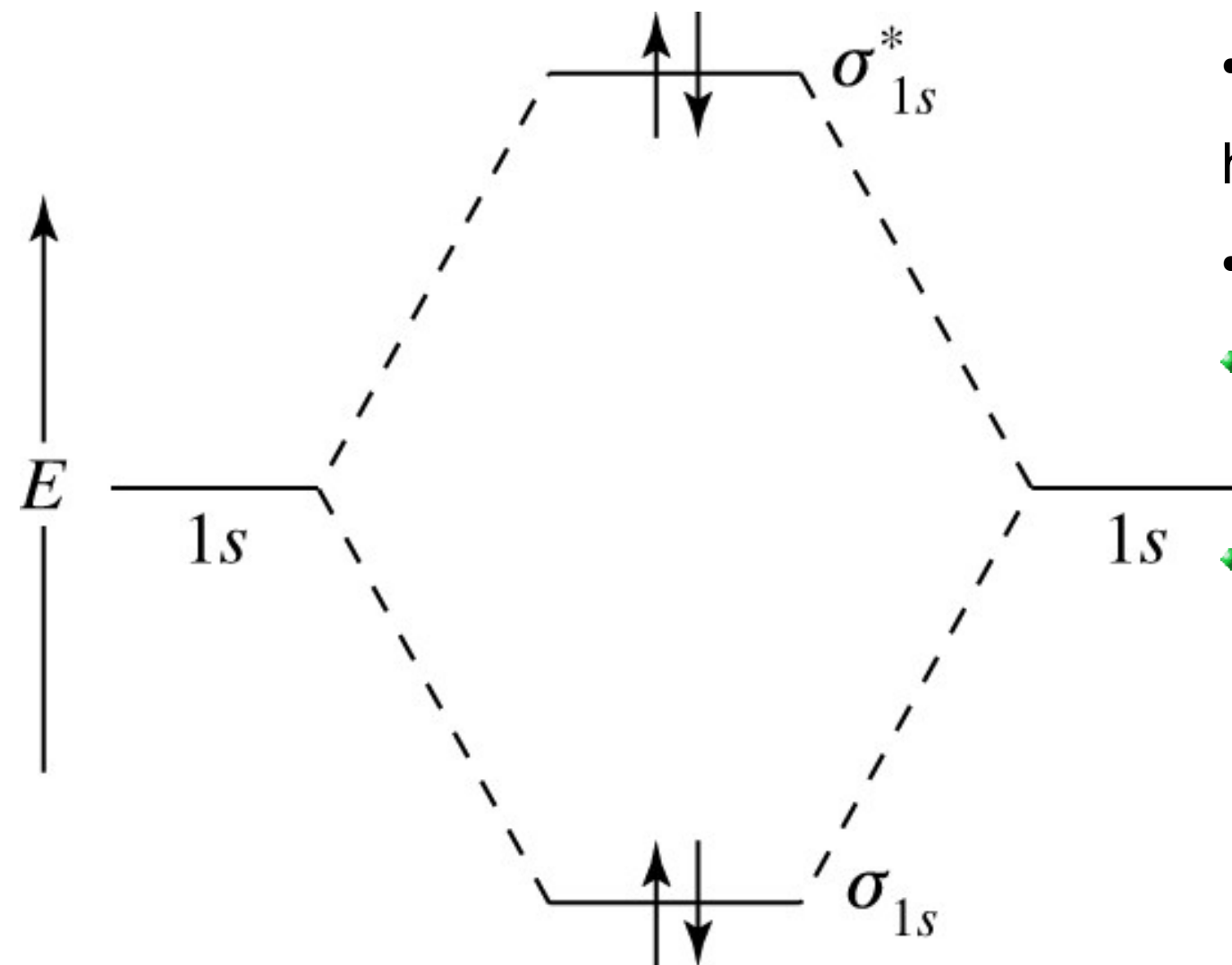


Some orbitals cannot interact because of symmetry considerations. They will overlap constructively on one side just as much as destructively on the other side.

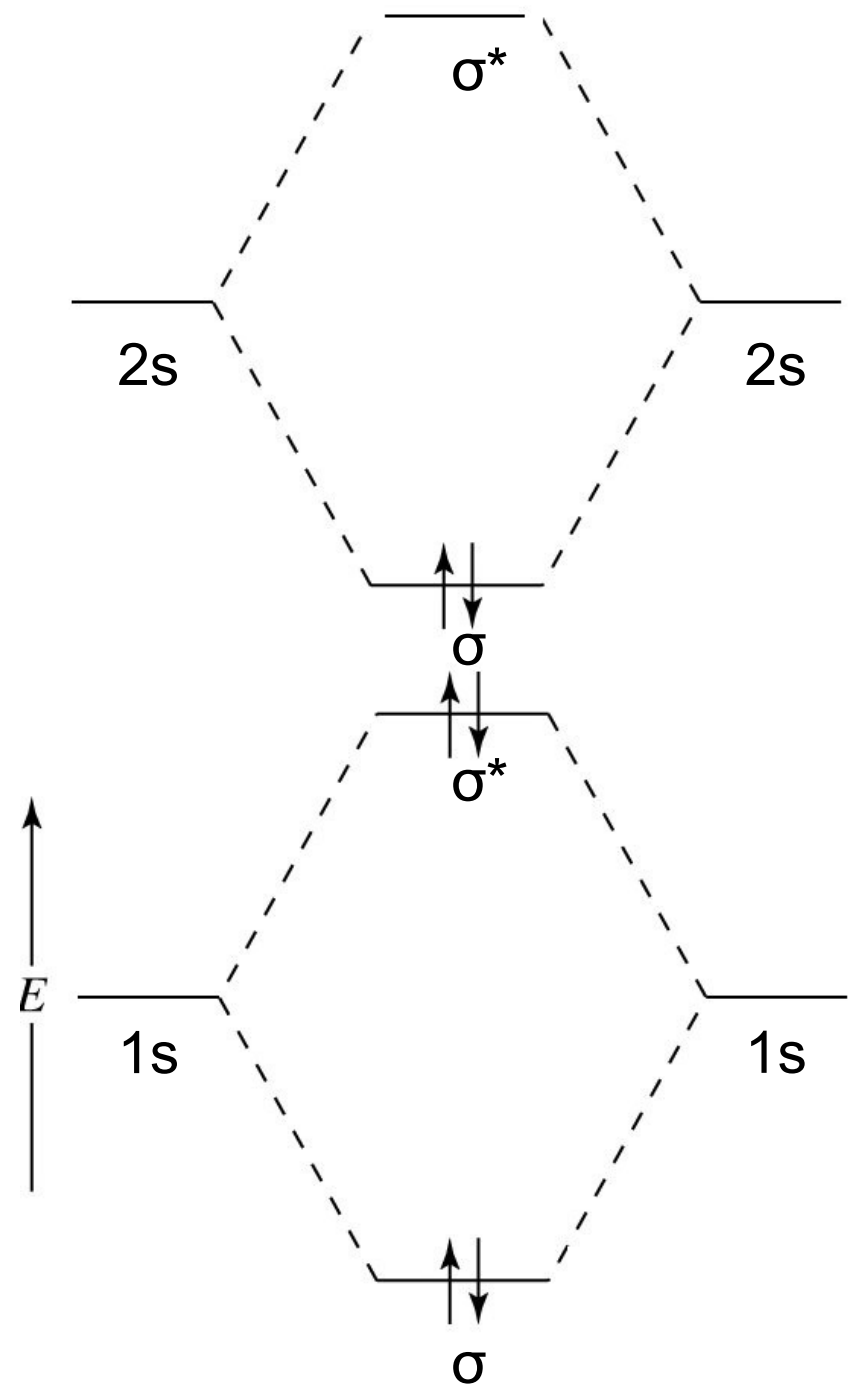




- The bond order in the hydrogen molecule is 1.
- There are
 - ◆ 2 electrons in a bonding orbital.
 - ◆ no electrons in an anti-bonding orbital.



- The bond order in the dihelium molecule is 0.
- There are
 - ♦ 2 electrons in a bonding orbital.
 - ♦ 2 electrons in an antibonding orbital.



- The bond order in the di-lithium molecule is 1.
- There are
 - ◆ 4 electrons in bonding orbitals.
 - ◆ 2 electrons in an anti-bonding orbital.



- ◆ Today we covered
 - ◆ Wavefunctions can overlap constructively in areas where they have equal sign and destructive where they have opposite sign.
 - ◆ MOs which are constructed from AOs which overlap constructively between the atoms are called bonding.
 - ◆ The opposite is called antibonding.
 - ◆ Symmetry labels for molecular orbitals are similar to the symmetry labels of atomic orbitals $s, p, d \rightarrow \sigma, \pi, \delta$
 - ◆ Symmetry restrictions and non interacting orbitals.
 - ◆ Bond order is determined by the number of electrons in bonding/antibonding orbitals.
 - ◆ Examples: H_2, He_2, Li_2