***Chemistry***

**8: Advanced Theories of Covalent Bonding**

**8.4: Molecular Orbital Theory**

33. How are the following similar, and how do they differ?

(a) σ molecular orbitals and π molecular orbitals

(b) *ψ* for an atomic orbital and ψ for a molecular orbital

(c) bonding orbitals and antibonding orbitals

Solution

(a) Similarities: Both are bonding orbitals that can contain a maximum of two electrons. Differences: σ orbitals are end-to-end combinations of atomic orbitals, whereas π orbitals are formed by side-by-side overlap of orbitals. (b) Similarities: Both are quantum-mechanical constructs that represent the probability of finding the electron about the atom or the molecule. Differences: *ψ* for an atomic orbital describes the behavior of only one electron at a time based on the atom. For a molecule, *ψ* represents either a mathematical combination of atomic orbitals. (c) Similarities: Both are orbitals that can contain two electrons. Differences: Bonding orbitals result in holding two or more atoms together. Antibonding orbitals have the effect of destabilizing any bonding that has occurred.

35. Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

Solution

An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.

37. Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

Solution

Bonding orbitals have electron density in close proximity to more than one nucleus. The interaction between the bonding positively charged nuclei and negatively charged electrons stabilizes the system.

39. Explain why an electron in the bonding molecular orbital in the H2 molecule has a lower energy than an electron in the 1*s* atomic orbital of either of the separated hydrogen atoms.

Solution

The pairing of the two bonding electrons lowers the energy of the system relative to the energy of the nonbonded electrons.

41. Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.

(a) H2, , 

(b) O2, , 

(c) Li2, , 

(d) F2, , 

(e) N2, , 

Solution

The bond order is equal to half the difference between the number of bonding electrons and the number of antibonding electrons. The bond with the greatest bond order is predicted to be the strongest. (a) H2 bond order = 1,  bond order = 0.5,  bond order = 0.5, strongest bond is H2; (b) O2 bond order = 2,  bond order = 3;  bond order = 1, strongest bond is ; (c) Li2 bond order = 1,  bond order = 0.5, Be2 bond order = 0, Li2 have the same strength bond; (d) F2 bond order = 1,  bond order = 1.5, bond order = 0.5, strongest bond is ; (e) N2 bond order = 3,  bond order = 2.5,  bond order = 2.5, strongest bond is N2.

43. Compare the atomic and molecular orbital diagrams to identify the member of each of the following pairs that has the highest first ionization energy (the most tightly bound electron) in the gas phase:

(a) H and H2

(b) N and N2

(c) O and O2

(d) C and C2

(e) B and B2

Solution

(a) H2; (b) N2; (c) O; (d) C2; (e) B2

45. A friend tells you that the 2*s* orbital for fluorine starts off at a much lower energy than the 2*s* orbital for lithium, so the resulting σ2*s*molecular orbital in F2 is more stable than in Li2. Do you agree?

Solution

Yes, fluorine is a smaller atom than Li, so atoms in the 2*s* orbital are closer to the nucleus and more stable.

47. What charge would be needed on F2 to generate an ion with a bond order of 2?

Solution

2+

49. Explain why  is diamagnetic, while , which has the same number of valence electrons, is paramagnetic.

Solution

N2 has s-p mixing, so the π orbitals are the last filled in . O2 does not have s-p mixing, so the σ*p* orbital fills before the π orbitals.

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