Week 10: Molecular Structure

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Diskusjonsoppgaver

- Q13.5 On the basis of what you know about the indistinguishability of electrons and the difference between the wave functions for bonding electrons and lone pairs, discuss the validity and usefulness of the Lewis structure for the fluorine molecule.

- Q13.10 Why can localized orbitals not be represented in an MO energy diagram?

- Q13.8 Why are localized and delocalized models equally valid for describing bonding in closed-shell molecules? Why can experiments not distinguish between these models?

- Q13.15 A cyclic polyene is known to be nonplanar. Are the MO energy levels of this molecule well described by the Hückel model? Justify your answer.

Regneoppgaver gjort av meg

Figure 13.11
Schematic variation of molecular orbital energies for water as a function of bond angle. The symbols used on the left to describe the MOs are based on symmetry considerations and are valid for $2\theta < 180°$. This nomenclature is discussed in Chapter 16.
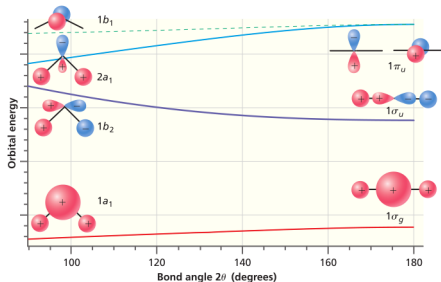
- **P13.13** Predict which of the bent molecules, BH_2 or NH_2, should have the larger bond angle on the basis of the Walsh correlation diagram in Figure 13.11. Explain your answer.
- **P13.5** Show that two of the set of four equivalent orbitals appropriate for sp^3 hybridization are orthgonal.

$$\psi_a = \frac{1}{2}(-\phi_{2s} + \phi_{2p_x} + \phi_{2p_y} + \phi_{2p_z}) \tag{1}$$

$$\psi_b = \frac{1}{2}(-\phi_{2s} - \phi_{2p_x} - \phi_{2p_y} + \phi_{2p_z}) \tag{2}$$

P13.16 The occupied MOs and MO energies of ethene are shown in the accompanying figure. Indicate which AOs are most important in each MO and indicate the relative phases of the AOs. Classify the MOs as localized or delocalized, σ or π bonds, and bonding, nonbonding, or antibonding.

−305.56 eV

−305.51 eV

−28.3 eV

−21.6 eV

−17.6 eV

−16.1 eV

−13.8 eV

−10.3 eV
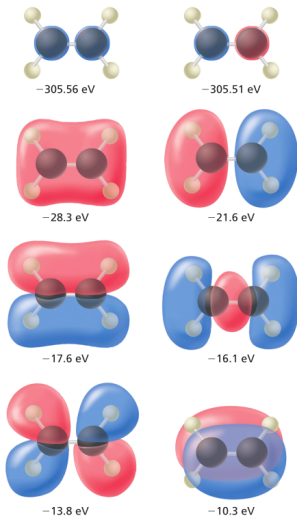
- **P13.6** Show that the water hybrid bonding orbitals given by

$$\psi_a = 0.55\phi_{2p_z} + 0.71\phi_{2p_y} - 0.45\phi_{2s} \qquad (3)$$

$$\psi_b = 0.55\phi_{2p_z} - 0.71\phi_{2p_y} - 0.45\phi_{2s} \qquad (4)$$

are orthogonal.

- **P13.10** Using your results from P13.6,
  - (a) Calculate the s and p character of the water lone pair hybrid orbitals.
  - (b) Show that the lone pair orbitals are orthogonal to each other and to the hybrid bonding orbitals.

P13.26 Use the geometrical construction shown in Example Problem 13.8 to derive the π electron MO levels for the cyclopentadienyl radical. What is the total π energy of the molecule? How many unpaired electrons will the molecule have?

One more

P13.19 The energy of the occupied valence MOs of H_2S is shown in the accompanying figure as a function of the H—S—H bond angle. Compare this diagram to the analogous diagram, Figure 13.11, for H_2O. Explain, based on the MO diagram, why H_2S is bent and why its bond angle ($92°$) is smaller than the bond angle in water. For comparison, also offer a bond-angle explanation based on hybridization rather than on the MO diagram.