

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 21: Polyatomic, conjugated molecules, and introduction to band theory

References

1. Levine, *Physical Chemistry*, 19.1–19.5, 23.11

Key Concepts

- The geometry of more complex molecules cannot be explained by molecular orbital theory alone.
- In methane, 4 equivalent bonds are necessary to achieve the tetrahedral structure you would expect. It is therefore necessary to create hybrid atomic orbitals by mathematically combining the wave functions of the atomic orbitals of carbon.

$$\Psi_a = c_1\psi_{2p_z} + c_2\psi_{2p_x} + c_3\psi_{2p_y} + c_4\psi_{2s}$$

where Ψ_a is one of four hybrid sp^3 atomic orbitals while the original orbital wave functions are represented by ψ . These hybrid orbitals can make 4 equivalent σ bonds with 4 hydrogen to make methane.

- In conjugated molecules like 1,3-butadiene, we had described the π electrons as particles in a box with a length equal to the length of the molecule. This description enabled us to predict the wavelength associated with the transition from what we at the time called the HOMO to the LUMO.
- This picture fits in with our LCAO-MO model. By take combinations of the unhybridized p orbitals on each carbon we can construct 4 molecular orbitals with different energies and bonding character. This picture resembles the first 4 solutions to the PIB, which gives support to the “simple” PIB and its predictions.
- When we start putting together large numbers of atoms to form solid, our molecular orbital pictures evolves into band structure.
- Where molecules have discrete transitions from one electronic energy state to another, when large numbers of atoms are considered a continuous set of energies, or a band, is obtained
- The conductivity of a solid is dependent on the structure and electron occupancies of the bands.
 - In a conductor, like a metal, there is partially filled band that has empty electron states contained within it. This can occur when two bands overlap to produce a large range of electron energies that are not all occupied.
 - In an insulator, the electron energy states in a band are completely filled. There is also a large energy gap (E_g) between the filled band and the next available energy in the next band. The lower, full band is called the valence band, while the higher energy, empty band is called the conduction band. For an insulator, $E_g \gg k_bT$, i.e. it is highly unlikely that thermal energy will allow promotion of an electron from the valence band to the conduction band.
 - If the band gap energy is on the order of k_bT ($E_g \sim k_bT$) then the solid is a semiconductor. This leads to the conductivity to be a strong function of temperature. The probability of promoting an electron from the valence band to the conduction band is given by:

$$e^{-E_g/k_bT}$$

At low temperature, there is not enough thermal energy to promote many electrons to available states in the conduction band, leading to insulating behavior. At higher temperatures, the probability of finding an electron in the conduction band is much larger leading to conducting behavior.