Organic Electronic Devices

Week 2: Electronic Structure
Lecture 2.1: Atomic and Molecular Orbitals

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Lecture Overview and Learning Objectives

- Concepts to be Covered in this Lecture Segment
  - The Origin of Atomic Orbital Levels with respect to the Hydrogen Atom
  - Extension of Atomic Orbital Theory to Molecular Orbital Theory
  - Origin of Transport Bands and Band gaps in Organic Semiconductors

- Learning Objectives
  By the Conclusion of this Presentation, You Should be Able to:

1. **Define** what is meant by an atomic orbital and molecular orbital and the corresponding energies of these levels.
2. **Explain** the interplay between atomic orbitals, molecular orbitals, and the electron densities of molecules. Furthermore, one should be able to **comment** on the concept of bonding and antibonding orbitals with respect to an energy band diagram.
3. **Describe** the origin of the Highest Occupied Molecular Orbital (HOMO) energy level, the Lowest Unoccupied Molecular Orbital (LUMO) energy level, and the band gap in organic electronic semiconducting materials.
Organic Electronic Descriptions Rely on Wave-Particle Duality

Thinking of Electrons as Particles is Useful in Some Contexts

1. Filling of orbitals with different quantum numbers usually discretizes the different electrons into countable particles that can be placed with 4 specific quantum numbers.

2. Often, we will think about electrons either having “spin up” or “spin down”. This is in the direct line of thinking with the Pauli exclusion principle. This principle states that no two electrons can occupy the same quantum state simultaneously.

3. Hund’s rule states that for degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.

4. In future lectures, we will talk about a charged particle moving through space in a solid-state organic electronic device.

Thinking of Electrons as Waves is Useful in Other Contexts

1. The mathematical description of orbitals is based on Schrödinger’s formulation of quantum mechanics and his equation for the wave equation (full details in the next lecture).

2. Solving Schrödinger’s equation allows one to describe the probability of finding an electron, given the quantum numbers of the system.

It Is Important to be able to Switch Between This Two Paradigms!
Recall the Electron Shell Nomenclature in Atoms
Orbital Dimensions Change Based on Electron Type

Three Dimensional Representation of Electron Probabilities for Atomic Orbitals

Atomic and Molecular Orbitals in Diatomic Hydrogen ($\text{H}_2$)

- The number of molecular orbitals is equal to the number of atomic orbitals that are used to form the molecular orbitals.
- Shaded blue regions indicate regions of electron probability.
- Electrons fill the molecular orbitals (MOs) in order of lower to higher energy.
**sp² Hybridization of Conjugated Carbon-Carbon Bonds**

Frontier Orbitals are Those in the Last Shell of the Atom or Molecule

Level 2 of Carbon is the Outermost Shell

**sp² Hybridization Increases Unpaired e⁻**

Energy

<table>
<thead>
<tr>
<th>Energy</th>
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<tbody>
<tr>
<td>2s</td>
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<tr>
<td>2p</td>
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<td>2p</td>
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3 x sp² AOs in the plane


Example of Conjugated Bonding in 1,3-Butadiene

1,3-Butadiene
4 Carbons with sp² Hybridized Orbitals

4 Frontier pₓ Orbitals for \( \pi \)-Bonding

Here, \( \pi_2 \) is the Highest Occupied Molecular Orbital (HOMO) Energy Level and \( \pi_3 \) is the Lowest Unoccupied Molecular Orbital (LUMO) Energy Level.

Extension of Molecular Orbital Theory to the Solid State

- Isolated molecules readily can demonstrate discrete energy levels, as depicted for the isolated case of 1,3-butadiene on the previous slide.

- However, this does not translate well to discrete energy levels because we will now have $> 10^{23}$ molecules present for macroscopic solid-state organic electronic devices.

|--------------|----------------------|----------------------|------------------|------------------|------------------------|

The relative proximity of each of the individual single molecule energy levels to one another indicates that they are very close in energy (recall that at room temperature there is $\sim 26$ meV of thermal energy available).

Therefore, bands of energy form to create the HOMO and LUMO energy levels observed in the solid state.
Analogies Between Inorganic and Organic Semiconductors

- The mechanism of bonding (and transport) in inorganic semiconductors (e.g., Si, GaAs) is different from organic semiconductors in a distinct manner.

- However, analogies can be (and often are) drawn between the inorganic semiconductor nomenclature and the organic semiconductor nomenclature. As such, we need to be aware of these similarities, but it should be noted that there is not a 1-to-1 similarity.

- The HOMO energy level is like the valence band in the inorganic semiconductor literature.

- The LUMO energy level is like the conduction band in the inorganic semiconductor literature.

- The bandgap energy difference between the HOMO and LUMO energy levels is similar to the bandgap energy for intrinsic inorganic semiconductor literature.
Atomic orbitals allow for the visualization of the probability of finding an electron near a nucleus for a given series of quantum numbers. These atomic orbitals can be extended to molecular orbitals in the case of compounds. Furthermore, orbitals can go from “pure” s, p, d, and f types to those that are hybridized. In this manner, unique sp-type hybridization can arise that allow conjugated materials to have unique optoelectronic properties.

The extension of the molecular orbital theory to conjugated materials allows for the concepts of the HOMO and LUMO energy levels to be defined. These are more well-defined for isolated molecules, but the concept can be translated to the solid state assuming that there are bands of molecular orbitals that are relatively close to one another in energy. This provides for HOMO and LUMO bands in solid state organic electronic materials.