

Organic Electronic Devices

Week 2: Electronic Structure

Lecture 2.1: Atomic and Molecular Orbitals

Bryan W. Boudouris
Chemical Engineering
Purdue University

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.

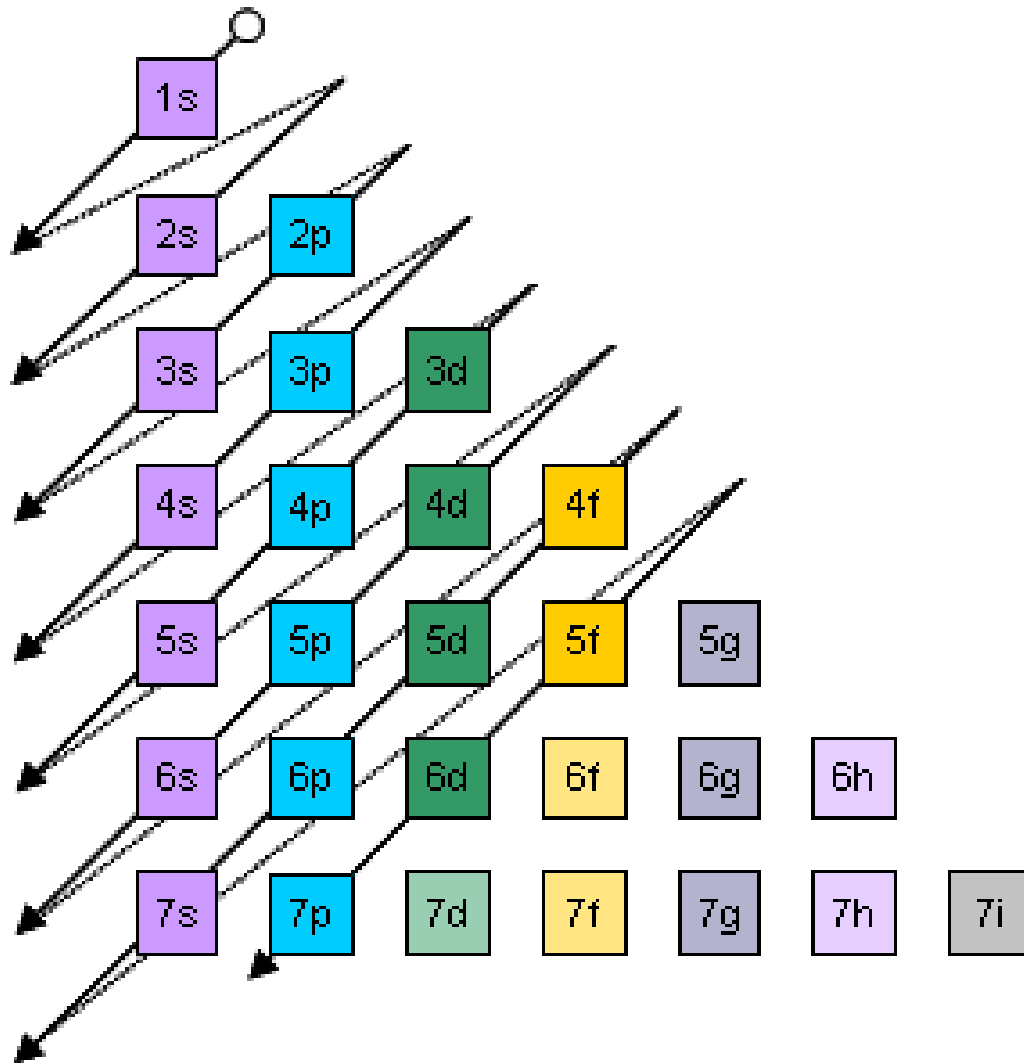
Thinking of Electrons as Waves is Useful in Other Contexts

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

hydrogen 1 H 1.0079	
lithium 3 Li 6.941	beryllium 4 Be 9.0122
sodium 11 Na 22.990	magnesium 12 Mg 24.305
potassium 19 K 39.098	calcium 20 Ca 40.078
rubidium 37 Rb 85.468	strontium 38 Sr 87.62
caesium 55 Cs 132.91	barium 56 Ba 137.33
francium 87 Fr [223]	radium 88 Ra [226]



* Lanthanide

** Actinide se

					helium 2 He 4.0026
boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
	ununquadium 114 Uuq [289]				

holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Orbital Dimensions Change Based on Electron Type

Three Dimensional Representation of Electron Probabilities for Atomic Orbitals

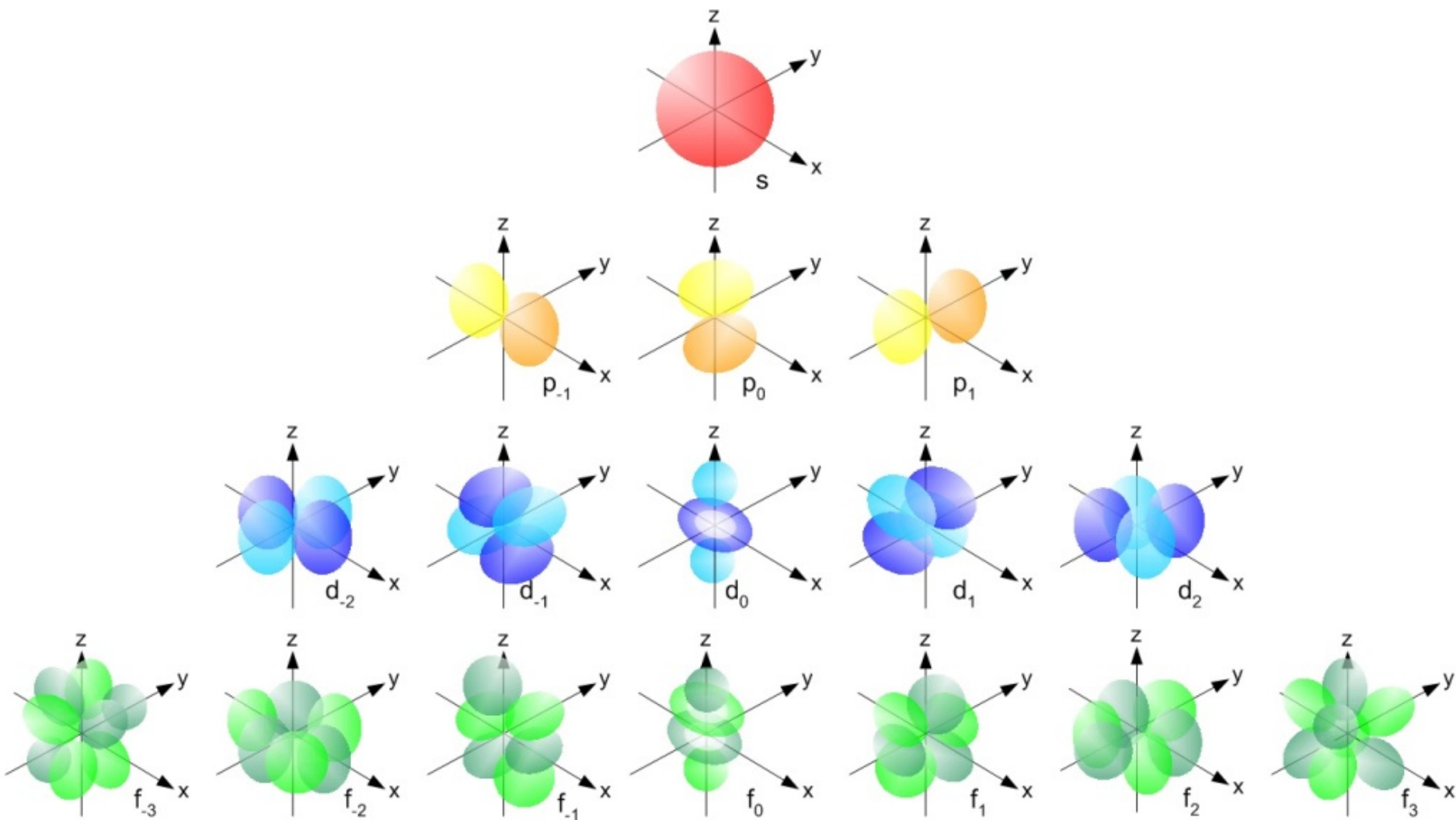
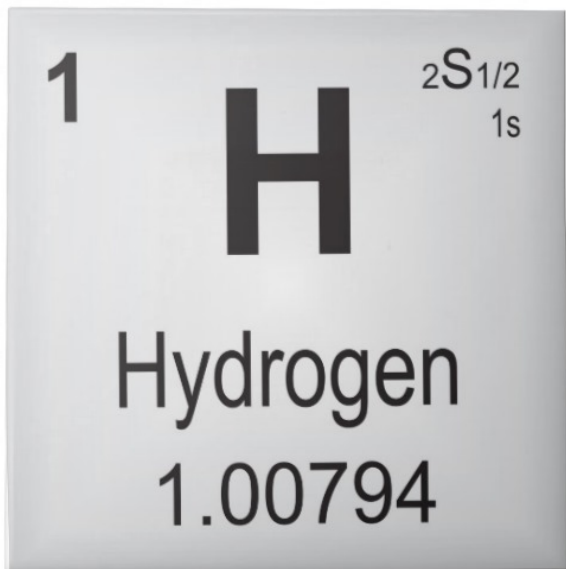
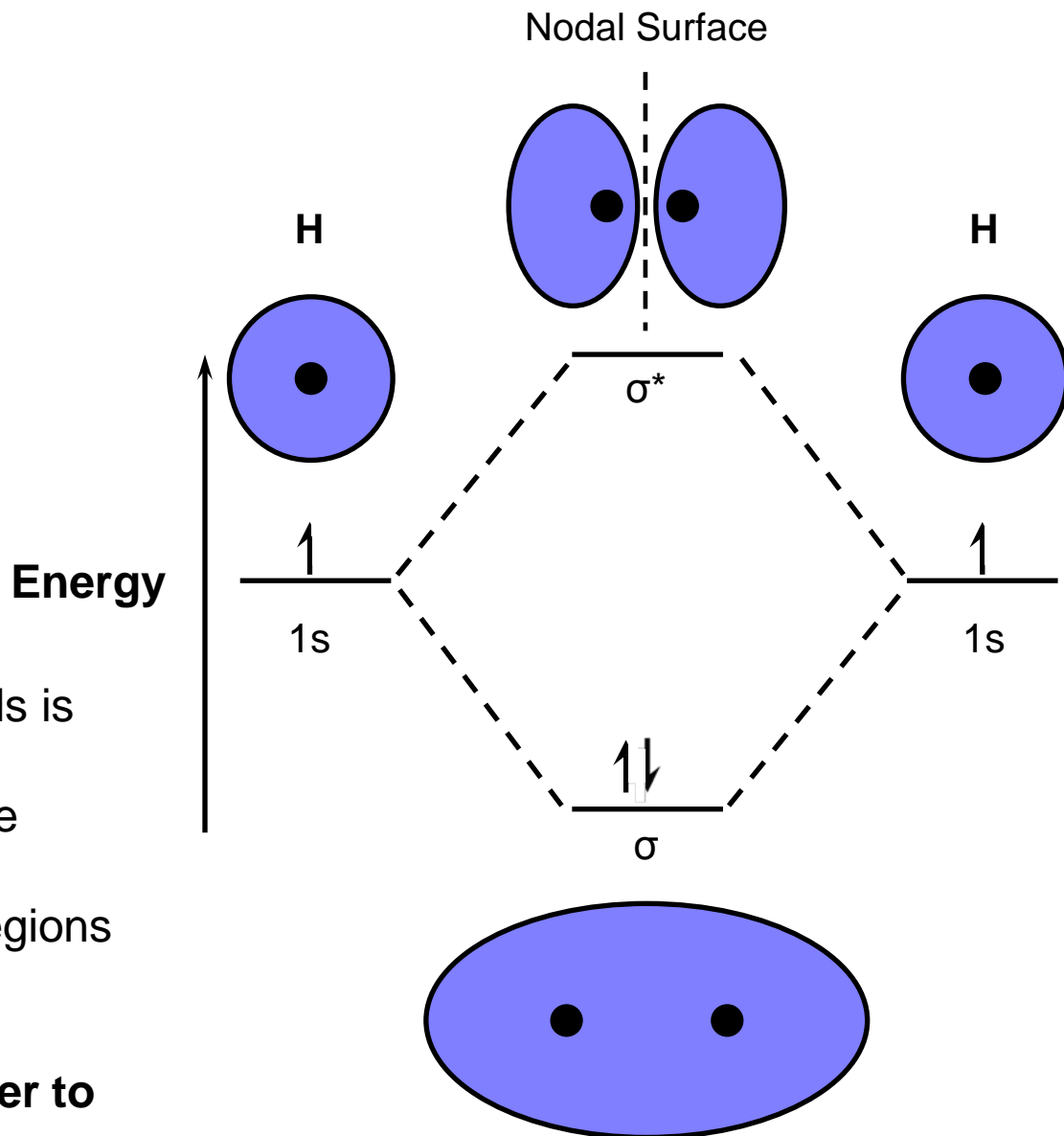


Image Reproduced From: University of California, David ChemWiki Page. <http://chemwiki.ucdavis.edu/>.

Atomic and Molecular Orbitals in Diatomic Hydrogen (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.**



sp^2 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

sp^2 Hybridization Increases Unpaired e^-

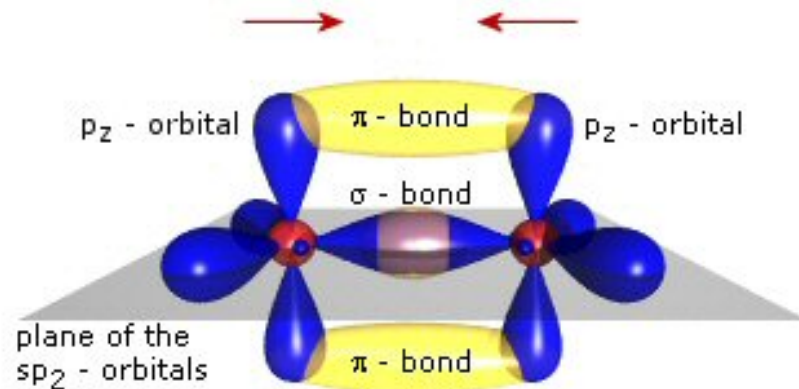
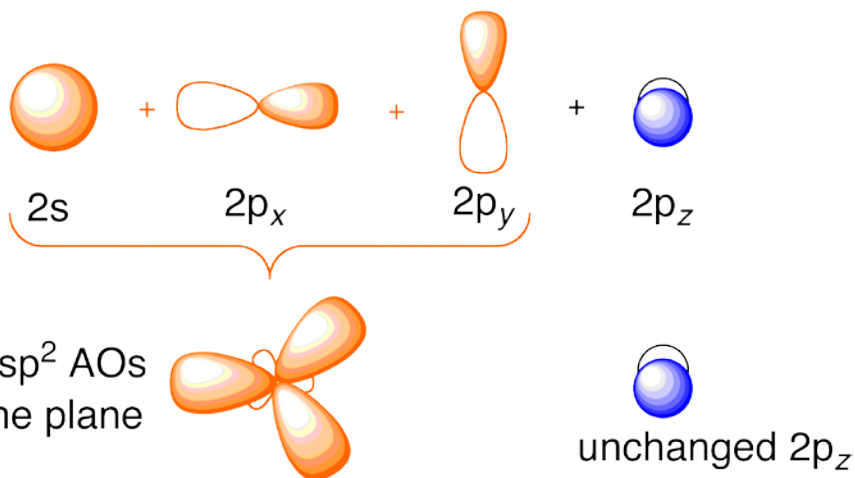
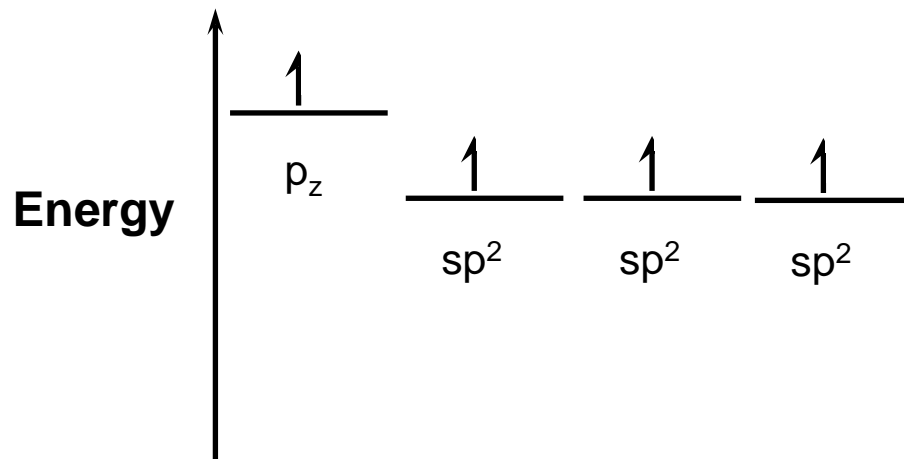
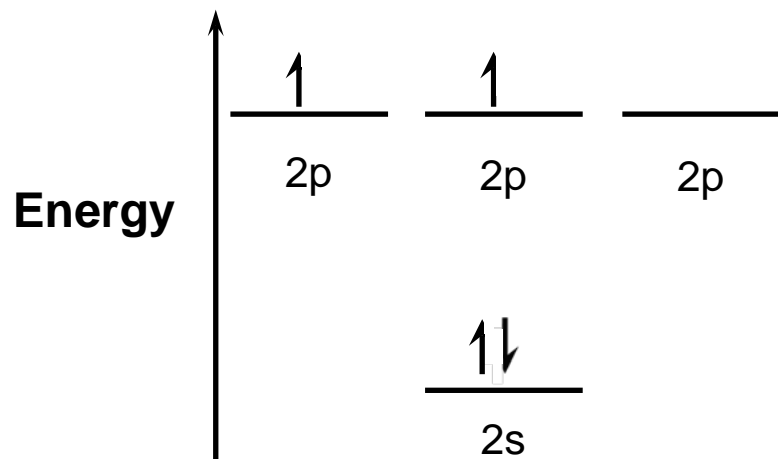


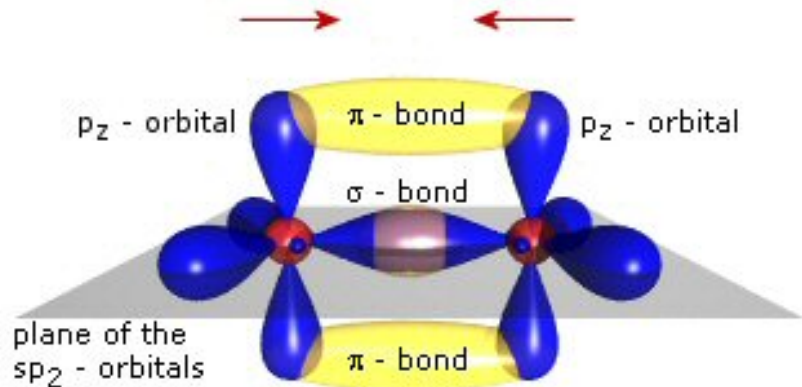
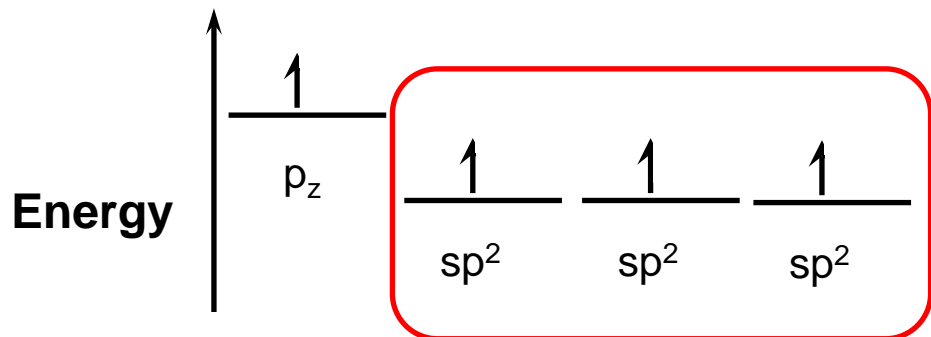
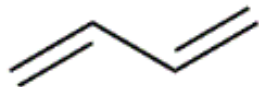
Image Reproduced From: University of Liverpool ChemTube 3D Page. <http://www.chemtube3d.com/>.

Image Reproduced From: Organic Semiconductor World. <http://www.iapp.de/orgworld/>.

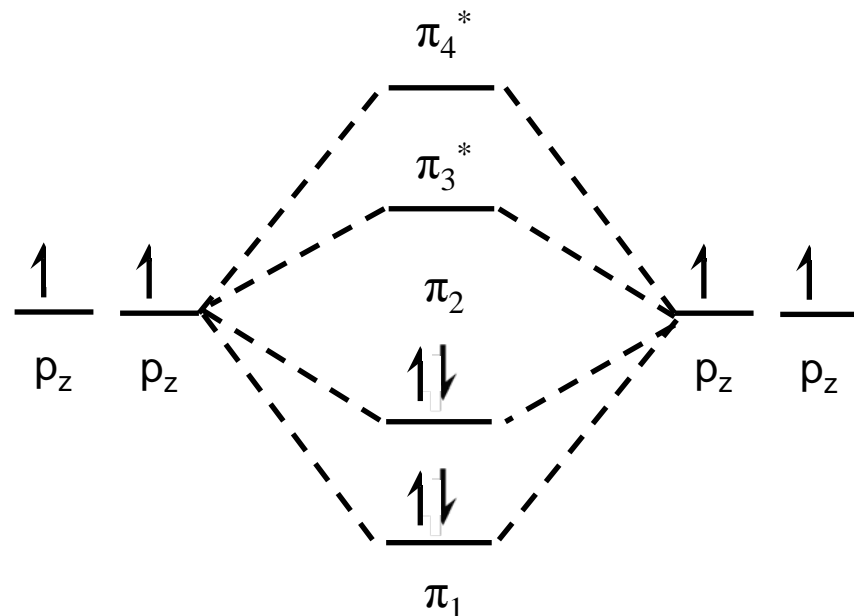
Example of Conjugated Bonding in 1,3-Butadiene

1,3-Butadiene

4 Carbons with sp^2 Hybridized Orbitals



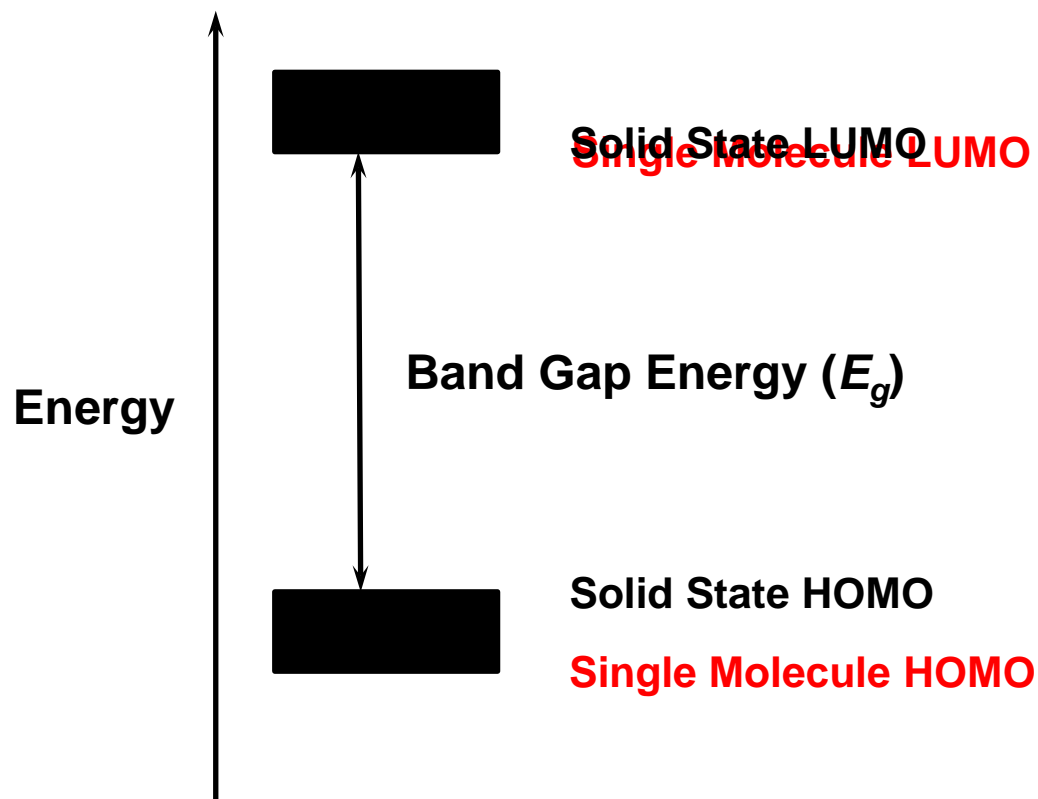
4 Frontier p_z Orbitals for π -Bonding



Here, π_2 is the Highest Occupied Molecular Orbital (HOMO) Energy Level and π_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.



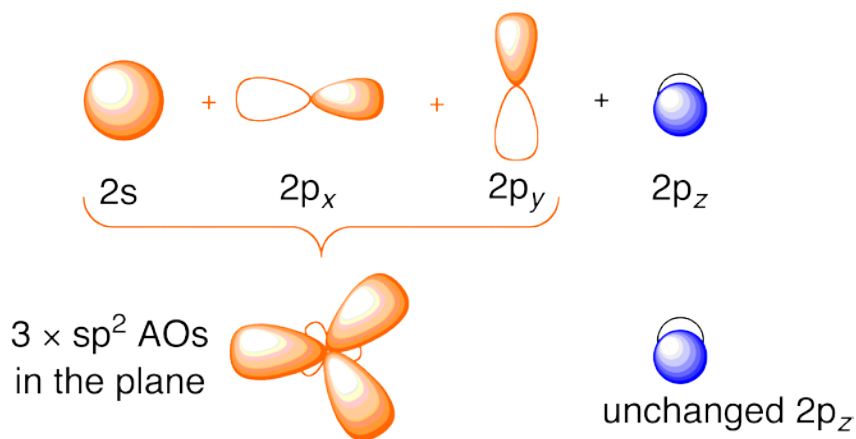
The relative proximity of each of the individual single molecule energy levels to one another indicates that they are very close in energy (recall that at room temperature there is ~ 26 meV of thermal energy available).

Therefore, bands of energy form to create the HOMO and LUMO energy levels observed in the solid state.

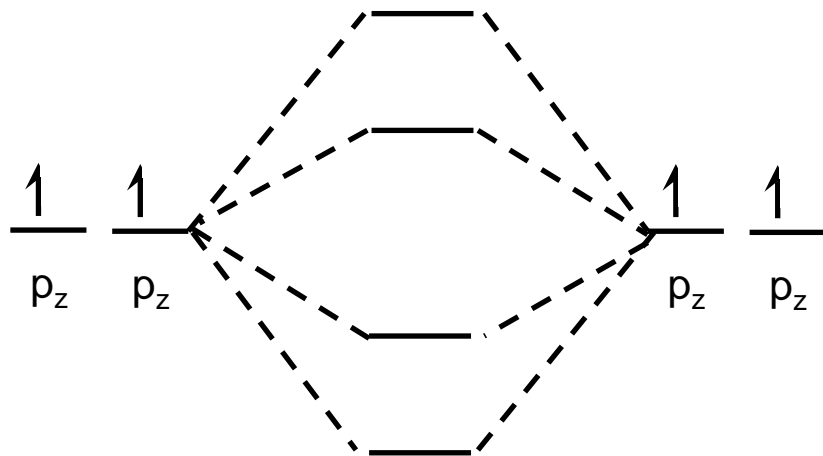
Analogies Between Inorganic and Organic Semiconductors

- **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.**

Summary and Preview of the Next Lecture



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.

Next Time: Using Quantum Mechanics to Calculate Electron Energies