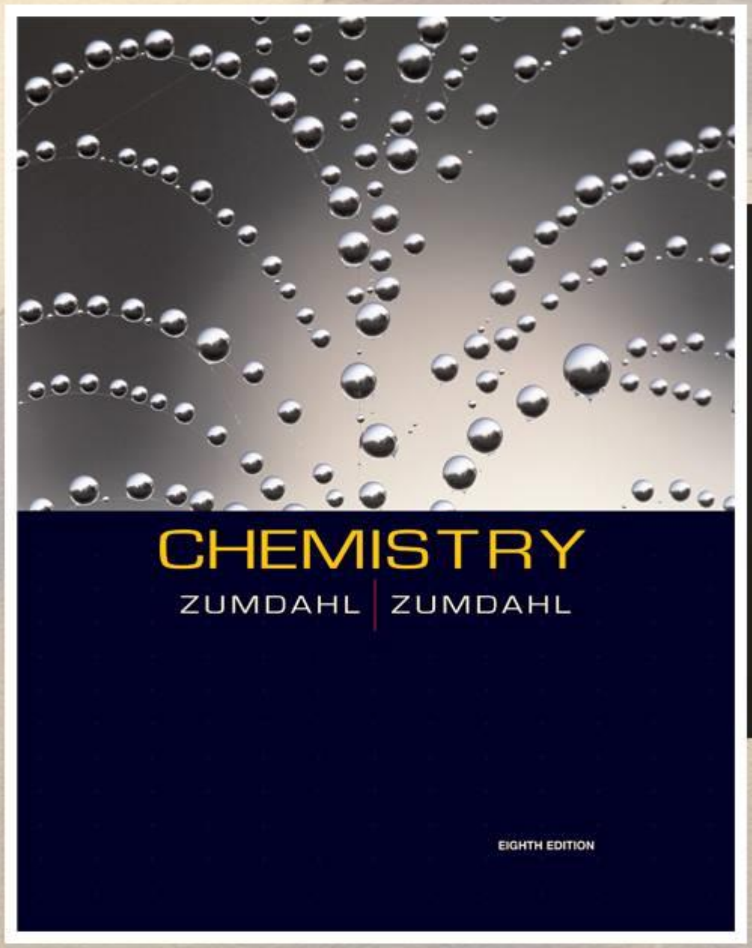
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Exercise

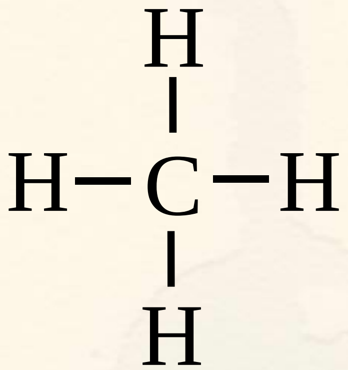
Draw the Lewis structure for methane, CH_4.

- What is the shape of a methane molecule?

  tetrahedral

- What are the bond angles?

  109.5°



Return to TOC

Hybridization and the Localized Electron Model

Concept Check

What is the valence electron configuration of a carbon atom?

s^2p^2

Why can't the bonding orbitals for methane be formed by an overlap of atomic orbitals?

Return to TOC

Hybridization and the Localized Electron Model

Bonding in Methane

- Assume that the carbon atom has four equivalent atomic orbitals, arranged tetrahedrally.

Return to TOC

Hybridization and the Localized Electron Model

Hybridization

- Mixing of the native atomic orbitals to form special orbitals for bonding.

Return to TOC

Hybridization and the Localized Electron Model

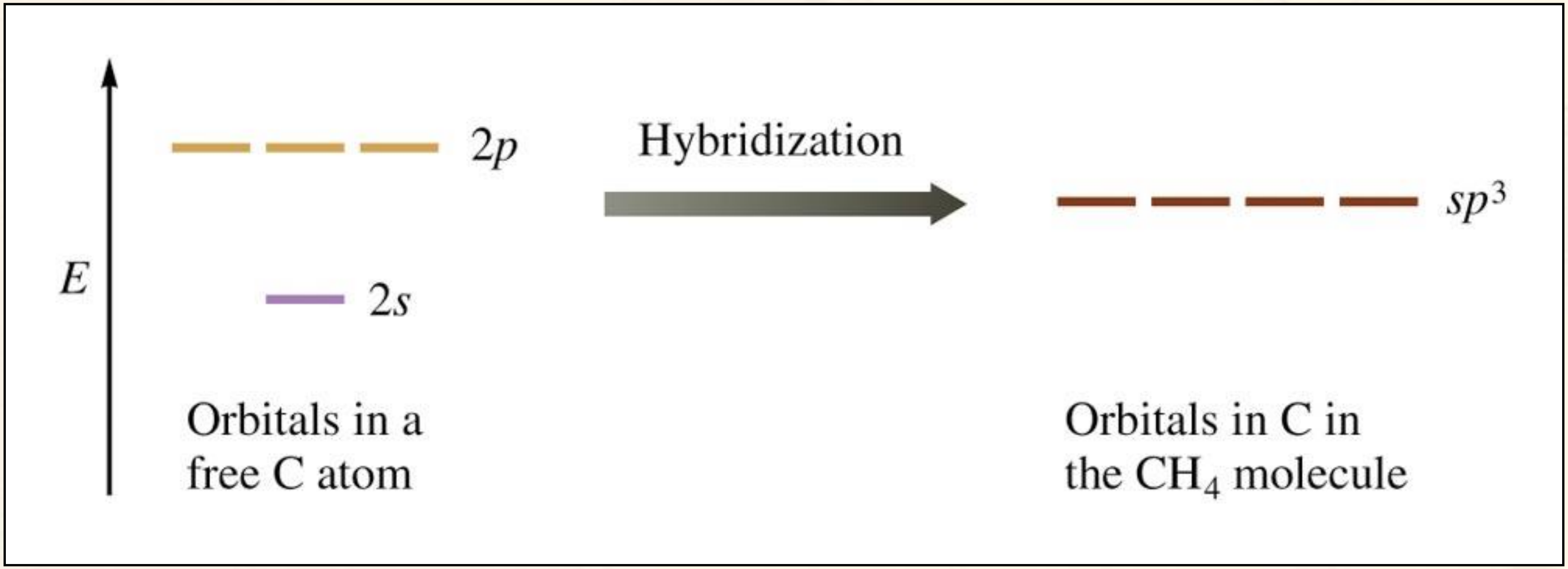
sp^3 Hybridization

- Combination of one *s* and three *p* orbitals.
- Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, the localized electron model assumes that the atom adopts a set of *sp*^{3} orbitals; the atom becomes *sp*^{3} hybridized.

Return to TOC

Hybridization and the Localized Electron Model

An Energy-Level Diagram Showing the Formation of Four *sp*³ Orbitals



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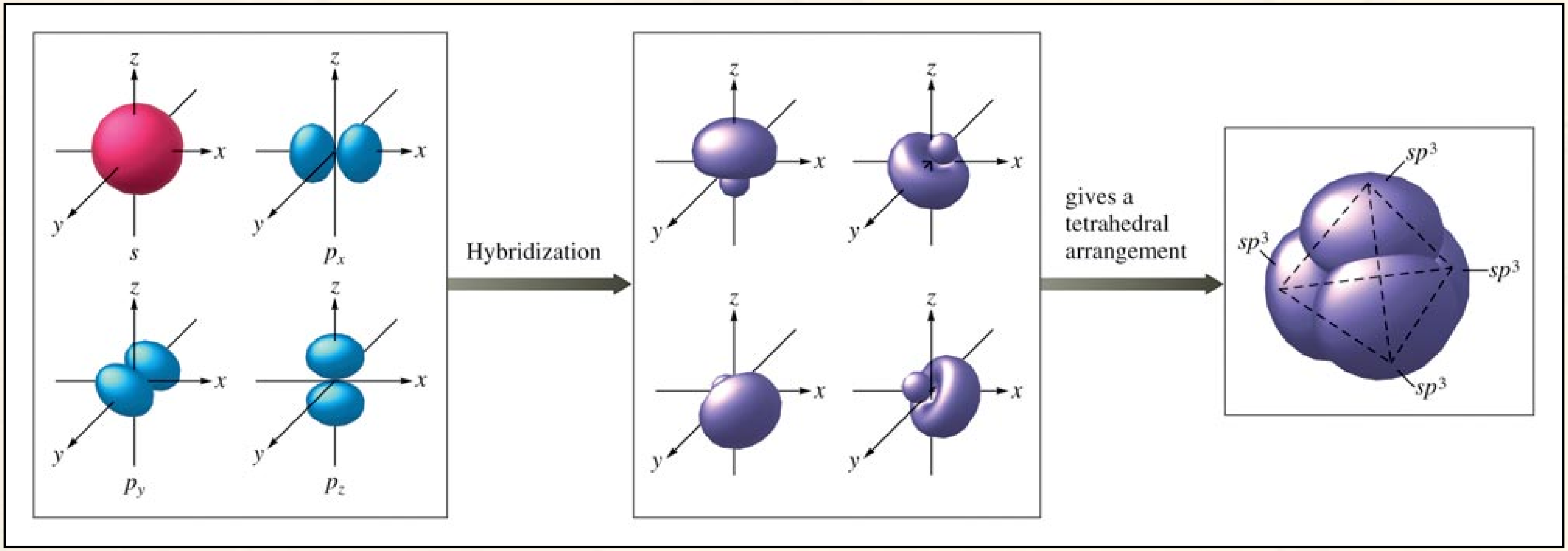
Hybridization and the Localized Electron Model

The Formation of sp^3 Hybrid Orbitals



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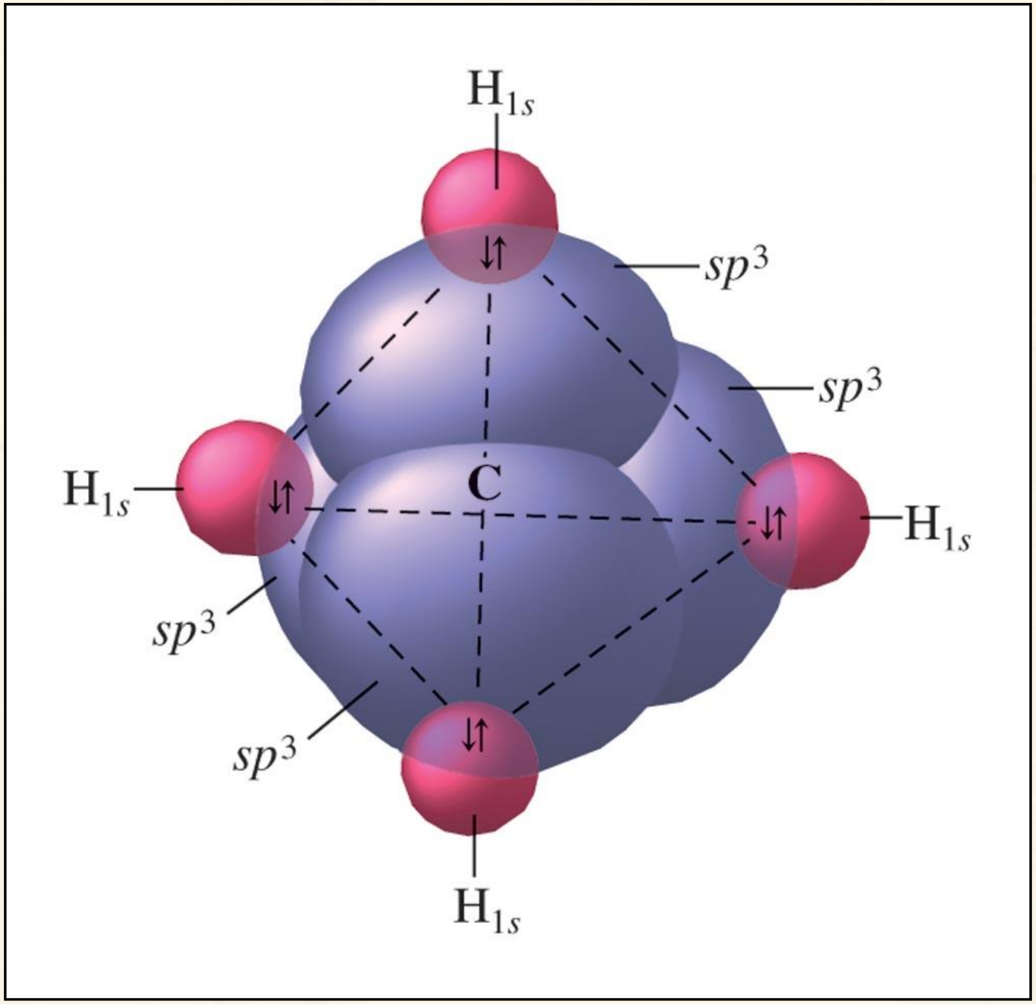
Hybridization and the Localized Electron Model

Tetrahedral Set of Four *sp*^{3} Orbitals



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Hybridization and the Localized Electron Model

Exercise

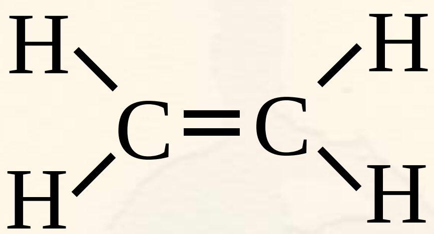
Draw the Lewis structure for C_2H_4 (ethylene)?

- What is the shape of an ethylene molecule?

  trigonal planar around each carbon atom

- What are the approximate bond angles around the carbon atoms?

  120^{o}



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Hybridization and the Localized Electron Model

Concept Check

Why can't sp^3 hybridization account for the ethylene molecule?

Return to TOC

Hybridization and the Localized Electron Model

sp^2 Hybridization

- Combination of one *s* and two *p* orbitals.
- Gives a trigonal planar arrangement of atomic orbitals.
- One *p* orbital is not used.
  - Oriented perpendicular to the plane of the *sp*^{2} orbitals.

Return to TOC

Hybridization and the Localized Electron Model

Sigma (σ) Bond

- Electron pair is shared in an area centered on a line running *between* the atoms.

Hybridization and the Localized Electron Model

Pi (π) Bond

- Forms double and triple bonds by sharing electron pair(s) in the space above and below the σ bond.
- Uses the unhybridized *p* orbitals.

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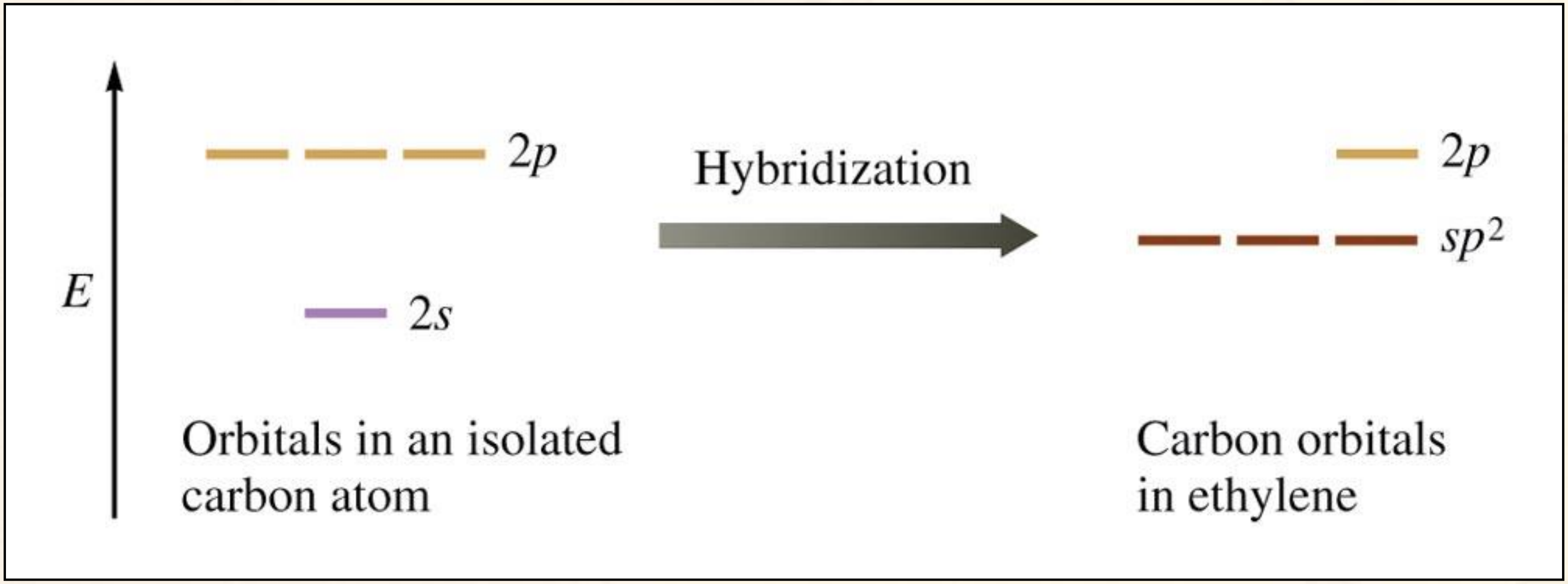
Hybridization and the Localized Electron Model

An Orbital Energy-Level Diagram for *sp*^{2} Hybridization



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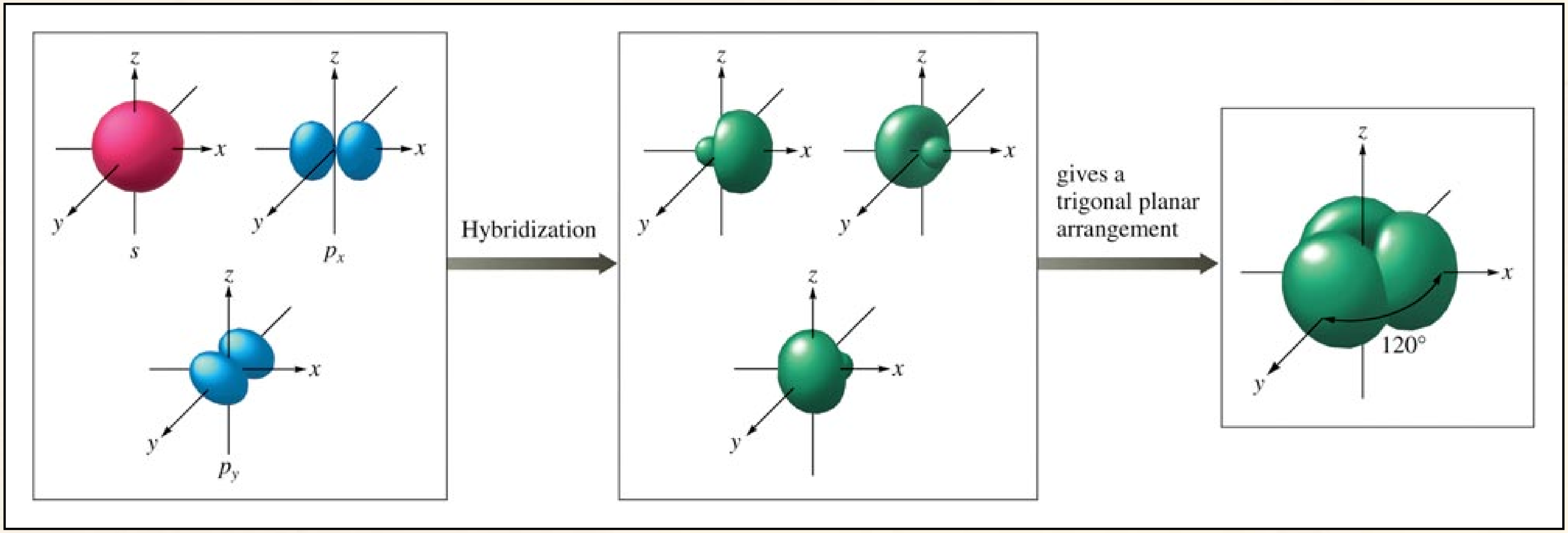
Hybridization and the Localized Electron Model

The Hybridization of the *s*, p_x, and p_y Atomic Orbitals



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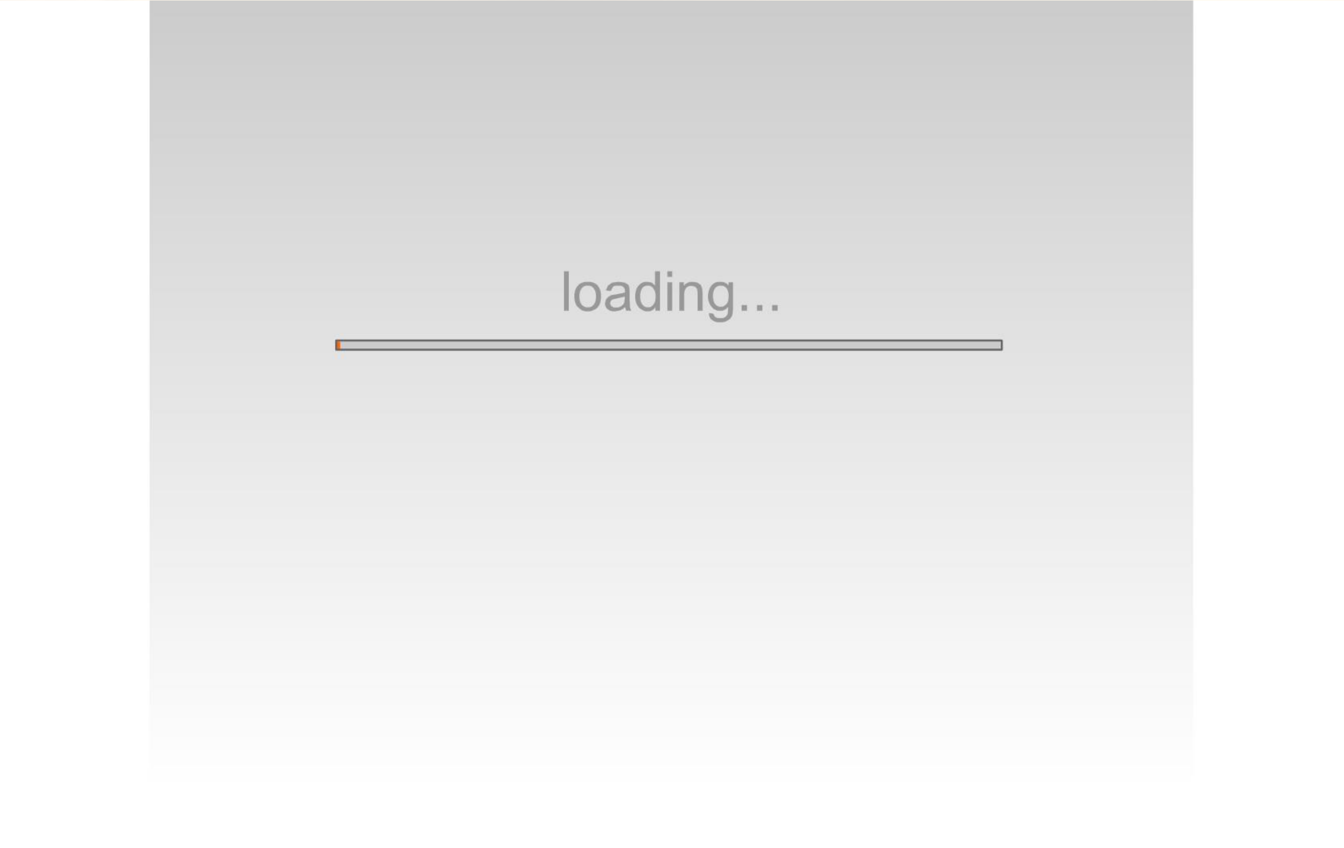
Hybridization and the Localized Electron Model

Formation of C=C Double Bond in Ethylene



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Exercise

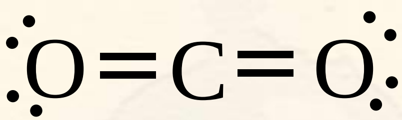
Draw the Lewis structure for CO_2.

- What is the shape of a carbon dioxide molecule?

  linear

- What are the bond angles?

  180^o



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Hybridization and the Localized Electron Model

sp Hybridization

- Combination of one *s* and one *p* orbital.
- Gives a linear arrangement of atomic orbitals.
- Two *p* orbitals are not used.
  - Needed to form the π bonds.

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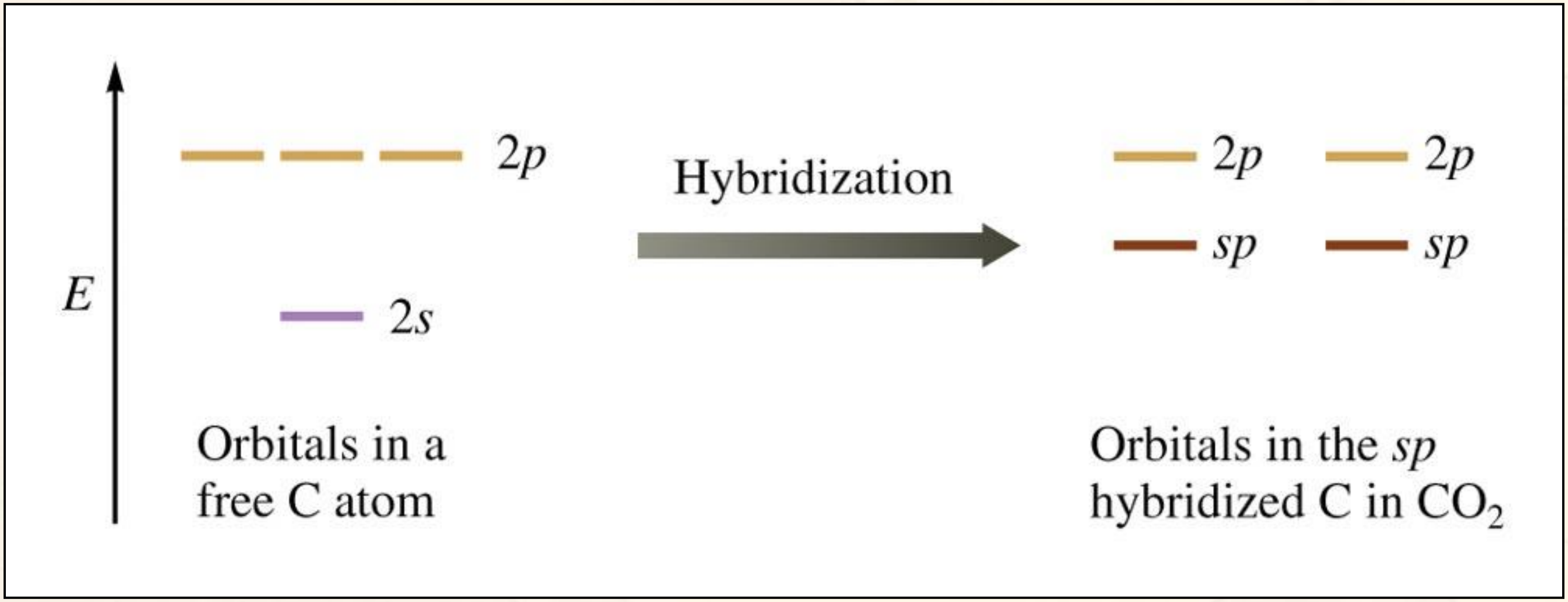
Hybridization and the Localized Electron Model

The Orbital Energy-Level Diagram for the Formation of *sp* Hybrid Orbitals on Carbon



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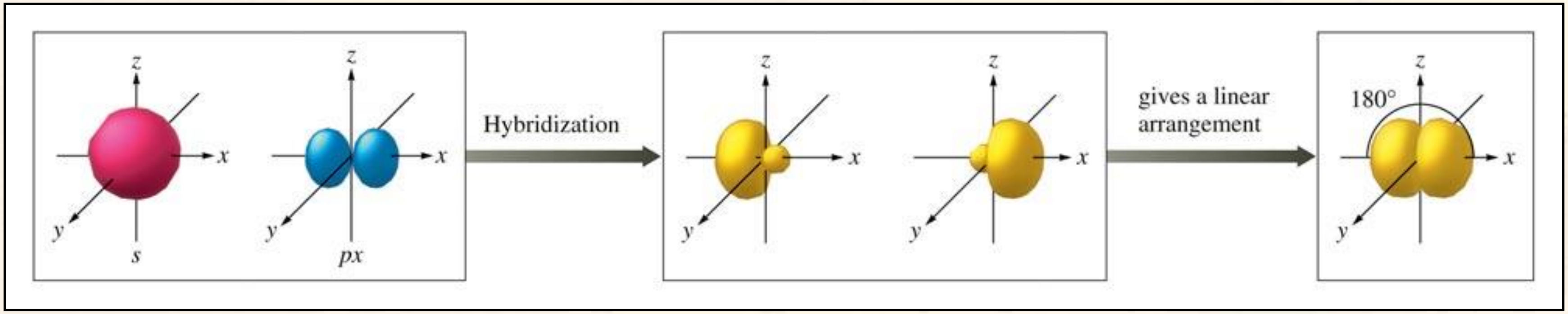
Hybridization and the Localized Electron Model

When One *s* Orbital and One *p* Orbital are Hybridized, a Set of Two *sp* Orbitals Oriented at 180 Degrees Results



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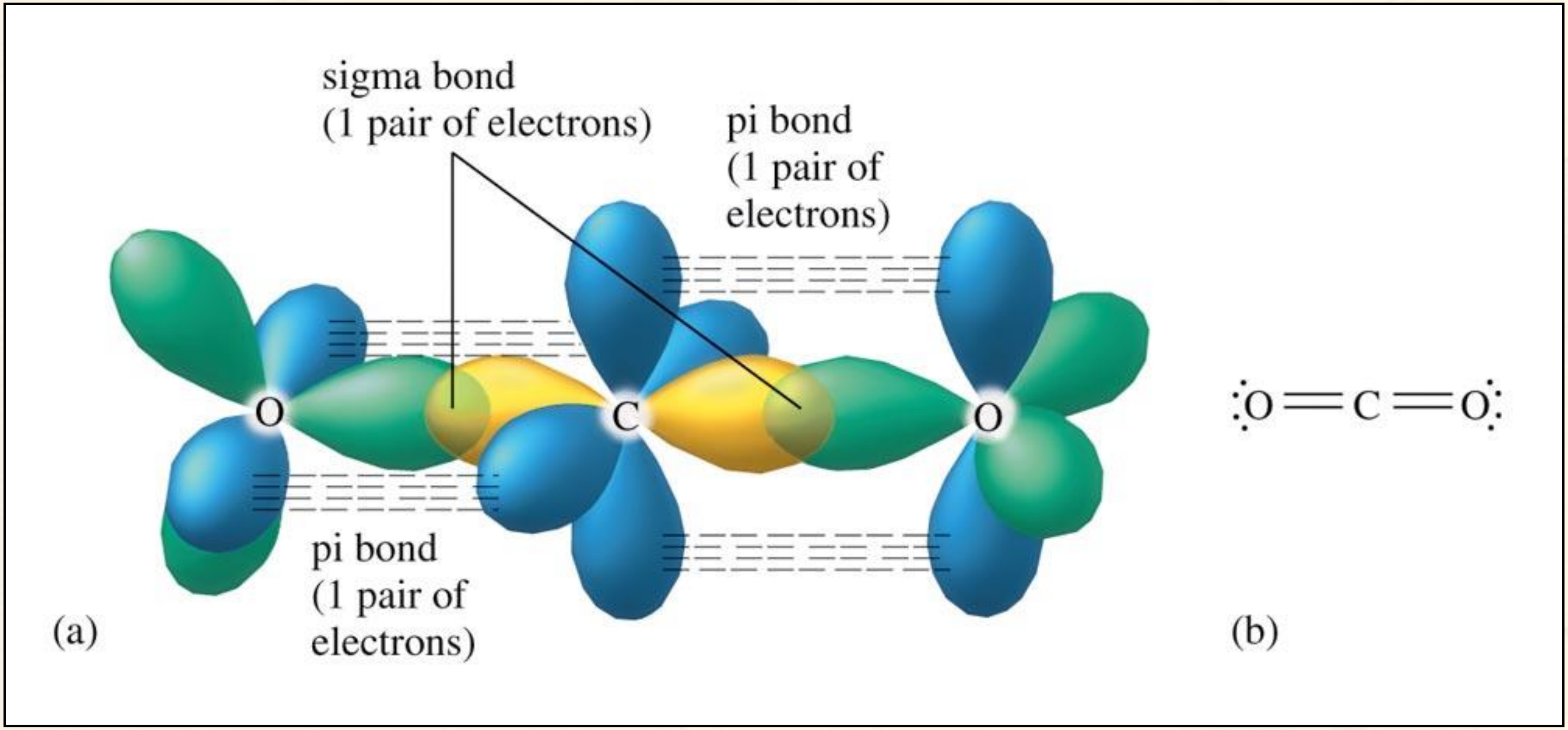
The Orbitals for CO_2



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Hybridization and the Localized Electron Model

Exercise

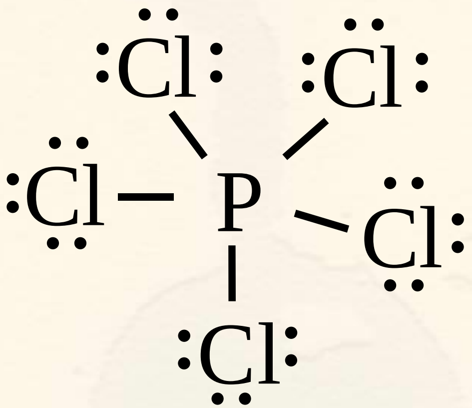
Draw the Lewis structure for PCl_5.

- What is the shape of a phosphorus pentachloride molecule?

  trigonal bipyramidal

- What are the bond angles?

  90^o and 120^o



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Hybridization and the Localized Electron Model

dsp^3 Hybridization

- Combination of one *d*, one *s*, and three *p* orbitals.
- Gives a trigonal bipyramidal arrangement of five equivalent hybrid orbitals.

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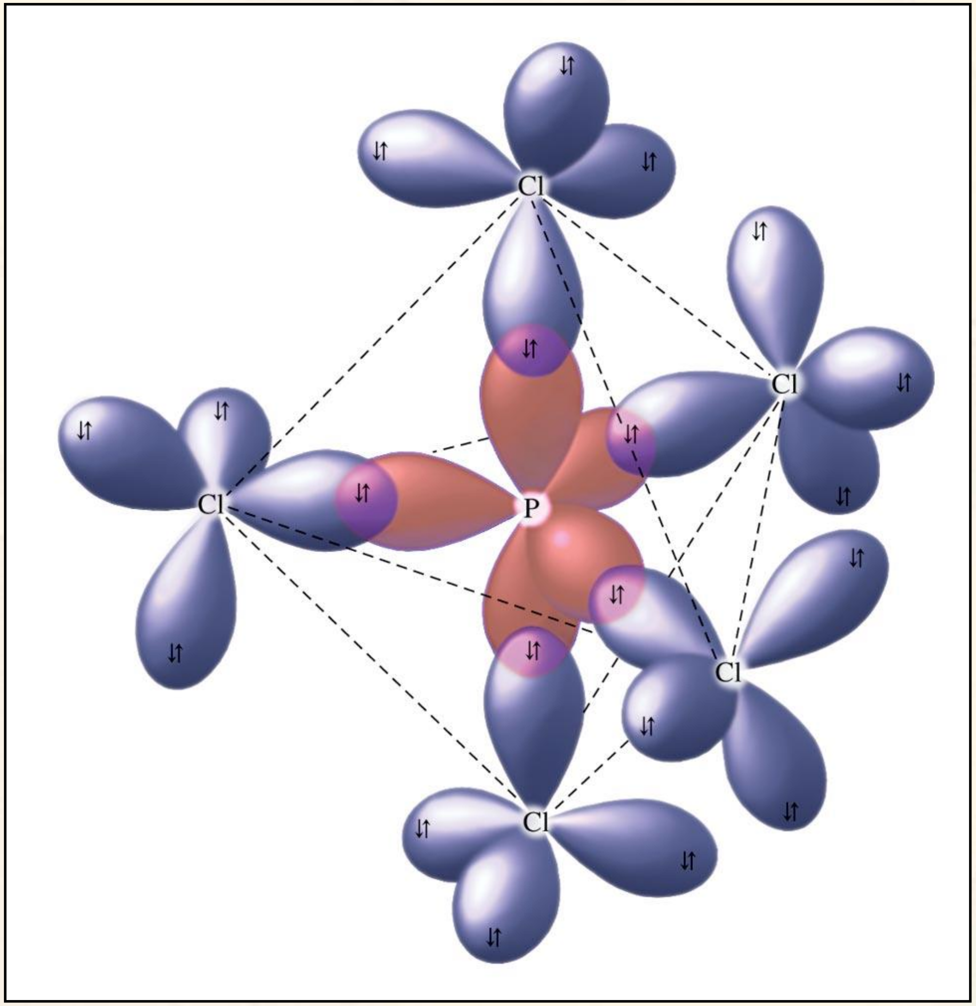
Hybridization and the Localized Electron Model

The Orbitals Used to Form the Bonds in PCl_5



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Hybridization and the Localized Electron Model

Exercise

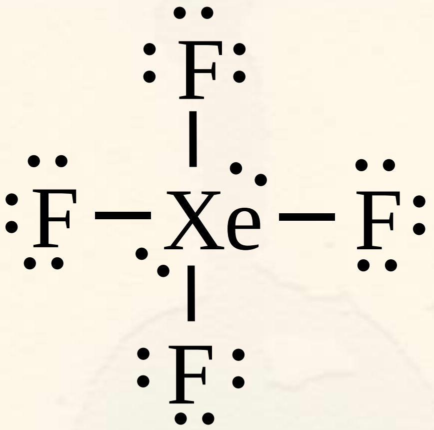
Draw the Lewis structure for XeF_4.

- What is the shape of a xenon tetrafluoride molecule?

  octahedral

- What are the bond angles?

  90^{o} and 180^{o}



Return to TOC

Hybridization and the Localized Electron Model

d^2sp^3 Hybridization

- Combination of two *d*, one *s*, and three *p* orbitals.
- Gives an octahedral arrangement of six equivalent hybrid orbitals.

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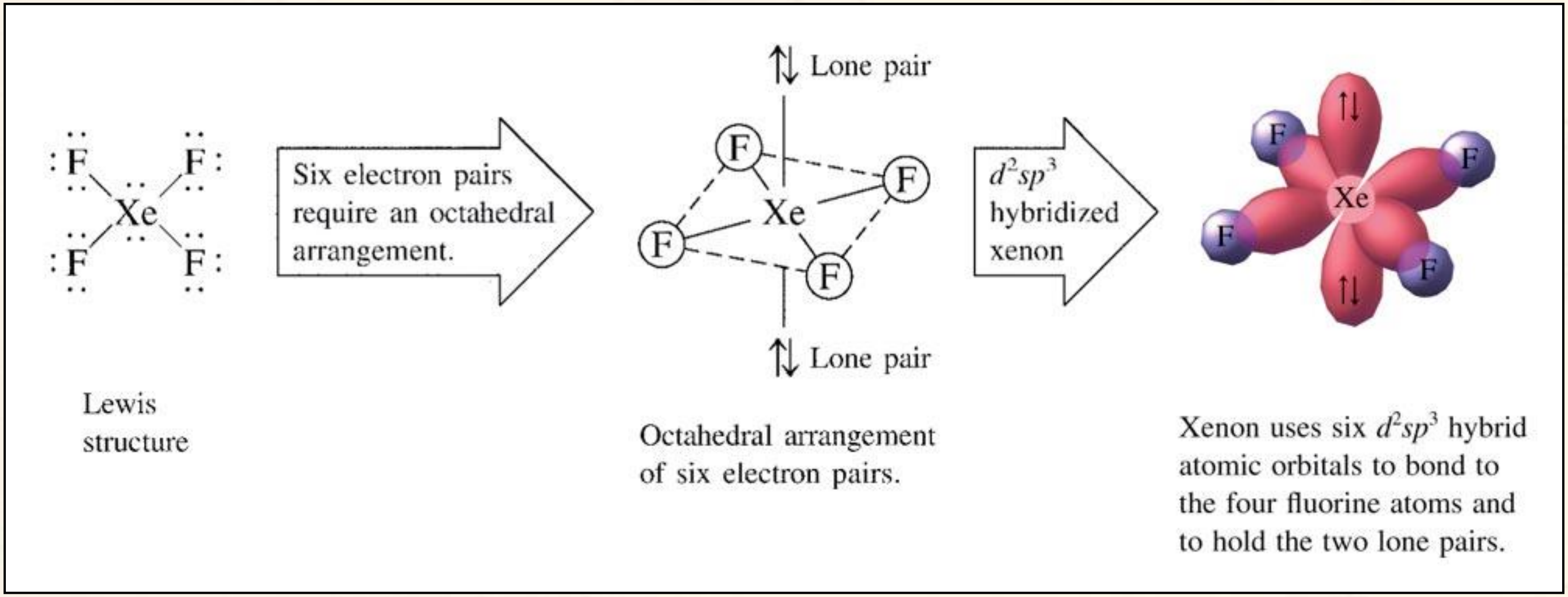
Hybridization and the Localized Electron Model

How is the Xenon Atom in XeF_4 Hybridized?



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Concept Check

Draw the Lewis structure for HCN.

Which hybrid orbitals are used?

Draw HCN:

- Showing all bonds between atoms.
- Labeling each bond as σ or π.

Return to TOC

Hybridization and the Localized Electron Model

Concept Check

Determine the bond angle and expected hybridization of the central atom for each of the following molecules:

NH_3 SO_2 KrF_2

CO_2 ICl_5

NH_3 – 109.5^{o}, sp^3

SO_2 – 120^{o}, sp^2

KrF_2 – 90^{o}, 120^{o}, dsp^3

CO_2 – 180^{o}, sp

ICl_5 – 90^{o}, 180^{o}, d^2sp^3

Return to TOC

Hybridization and the Localized Electron Model

Using the Localized Electron Model

- Draw the Lewis structure(s).
- Determine the arrangement of electron pairs using the VSEPR model.
- Specify the hybrid orbitals needed to accommodate the electron pairs.

Return to TOC

The Molecular Orbital Model

- Regards a molecule as a collection of nuclei and electrons, where the electrons are assumed to occupy orbitals much as they do in atoms, but having the orbitals extend over the entire molecule.
- The electrons are assumed to be delocalized rather than always located between a given pair of atoms.

Return to TOC

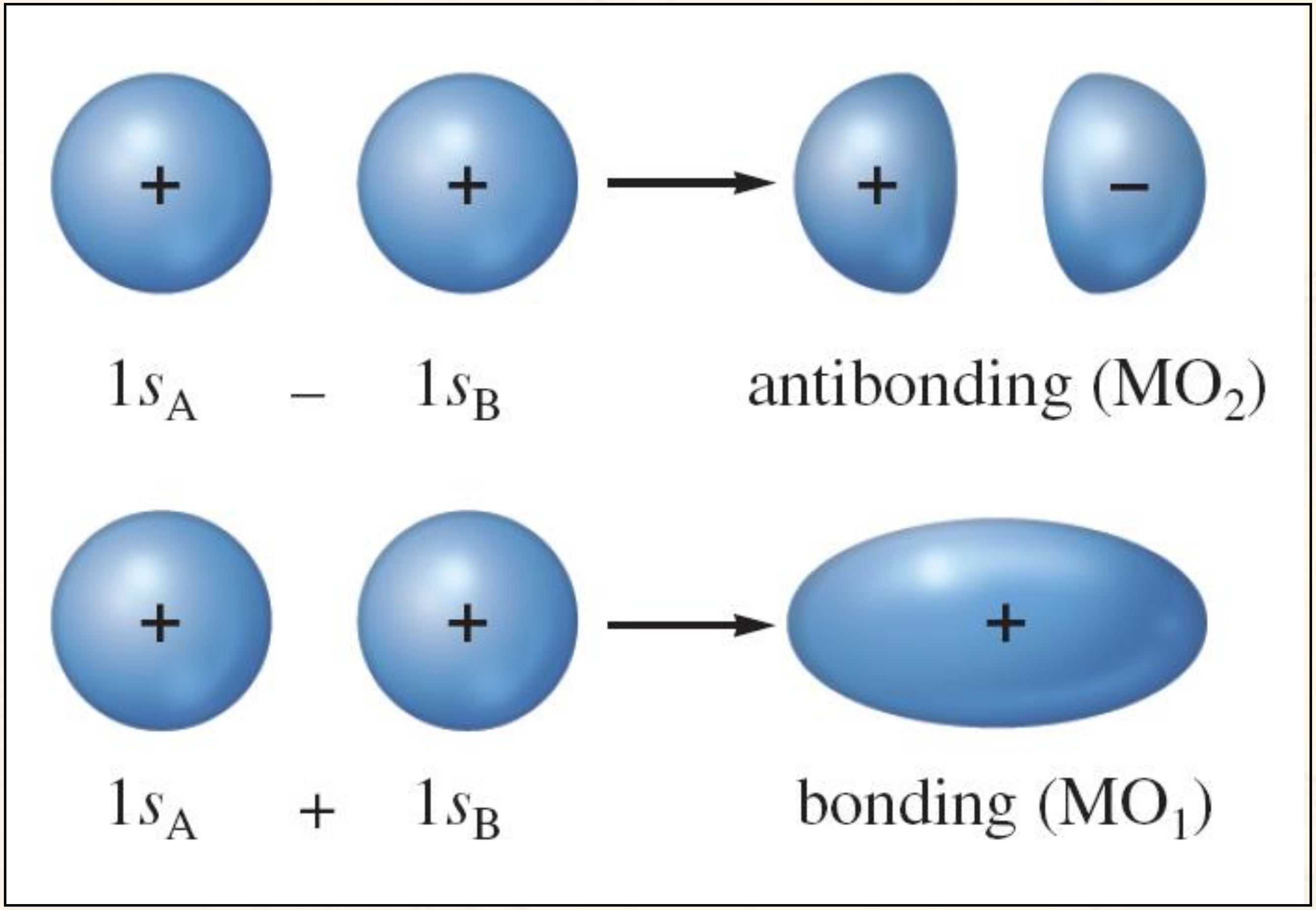
The Molecular Orbital Model

- The electron probability of both molecular orbitals is centered along the line passing through the two nuclei.
  - Sigma (σ) molecular orbitals (MOs)
- In the molecule only the molecular orbitals are available for occupation by electrons.

Return to TOC

The Molecular Orbital Model

Combination of Hydrogen 1*s* Atomic Orbitals to form MOs



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The Molecular Orbital Model

- MO_1 is lower in energy than the *s* orbitals of free atoms, while MO_2 is higher in energy than the *s* orbitals.
  - Bonding molecular orbital – lower in energy
  - Antibonding molecular orbital – higher in energy

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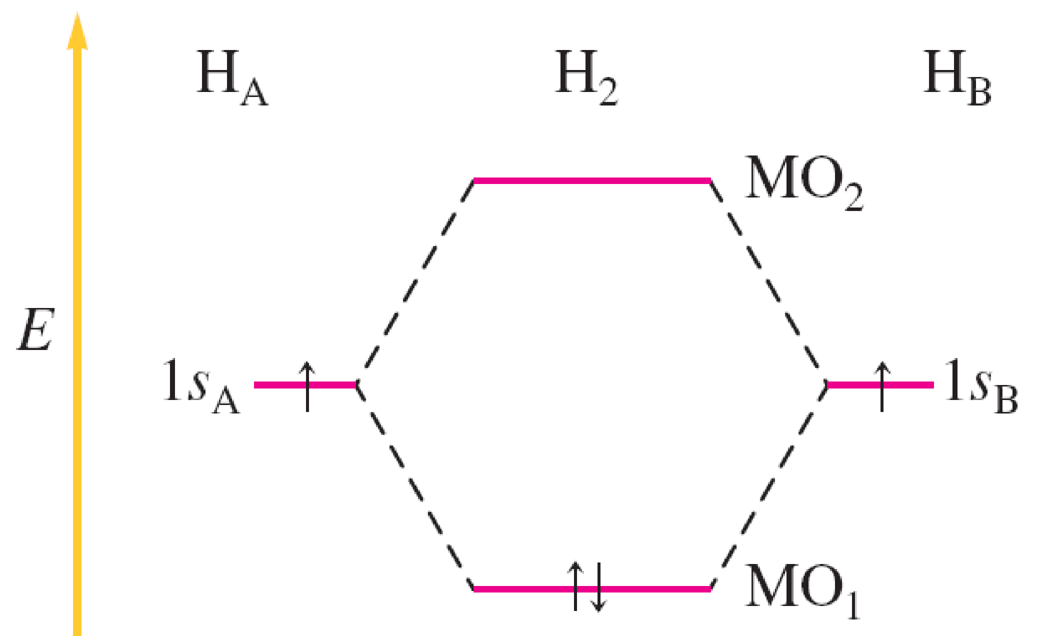
The Molecular Orbital Model

MO Energy-Level Diagram for the H_2 Molecule



(a) Energy diagram

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The Molecular Orbital Model

- The molecular orbital model produces electron distributions and energies that agree with our basic ideas of bonding.
- The labels on molecular orbitals indicate their symmetry (shape), the parent atomic orbitals, and whether they are bonding or antibonding.

Return to TOC

The Molecular Orbital Model

- Molecular electron configurations can be written similar to atomic electron configurations.
- Each molecular orbital can hold 2 electrons with opposite spins.
- The number of orbitals are conserved.

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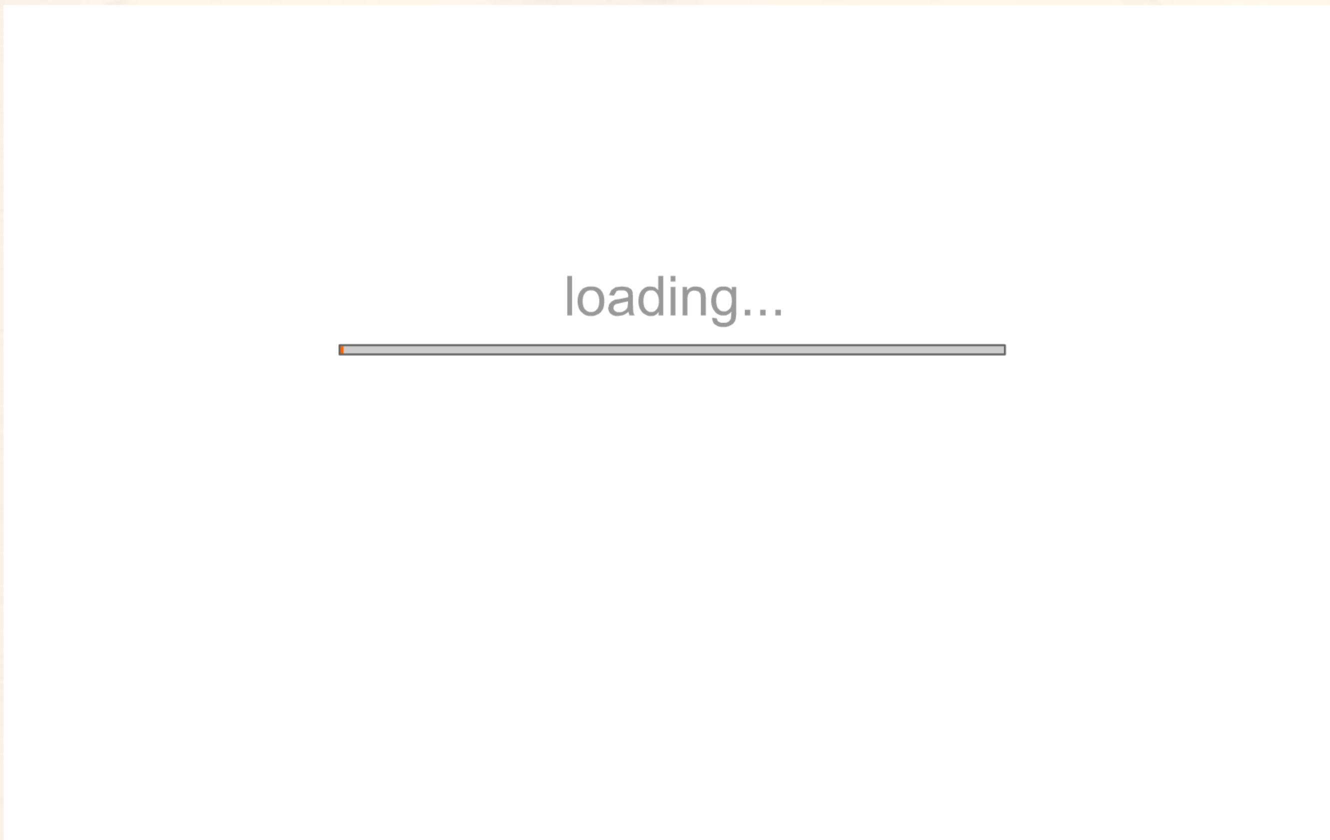
The Molecular Orbital Model

Bonding in H_2



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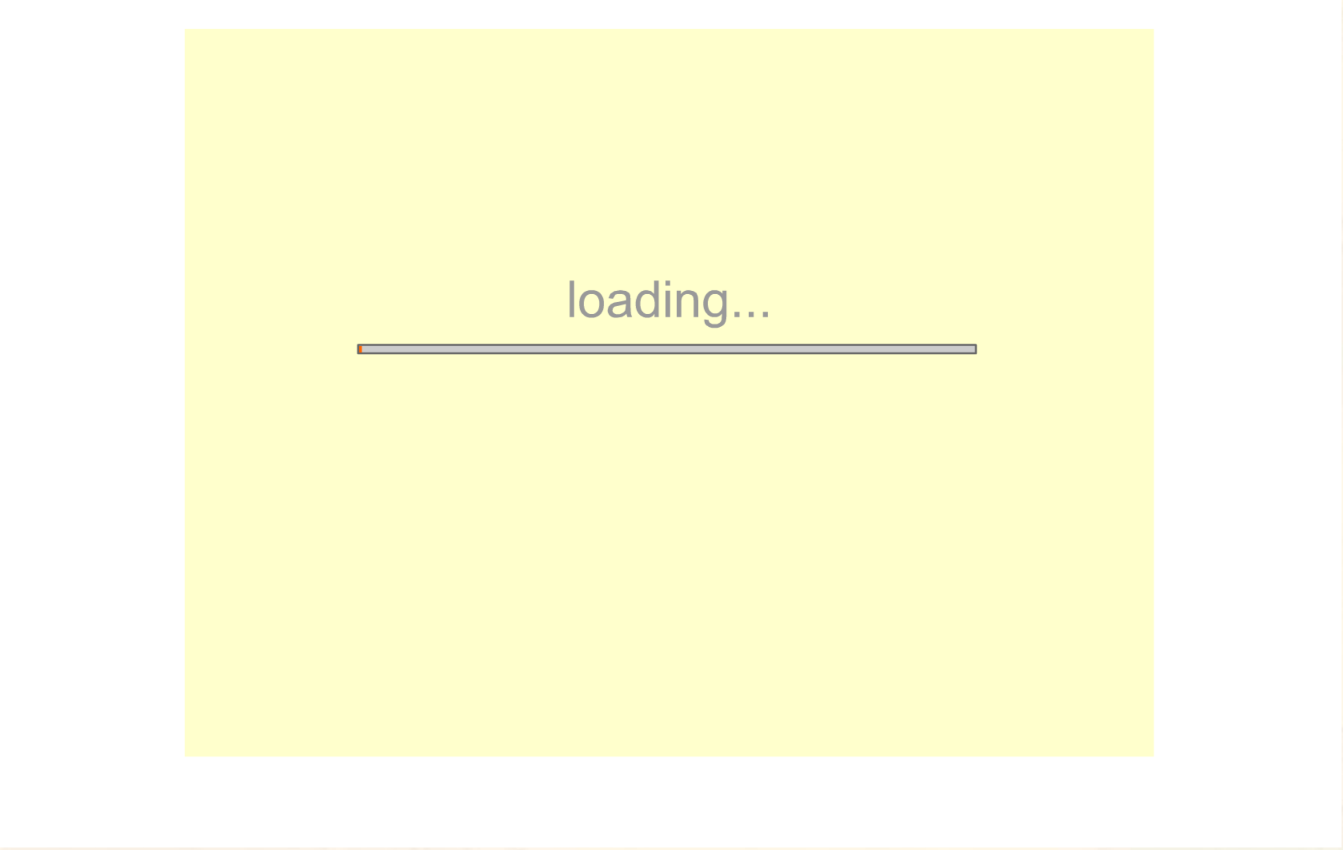
The Molecular Orbital Model

Sigma Bonding and Antibonding Orbitals



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The Molecular Orbital Model

Bond Order

- Larger bond order means greater bond strength.

$$\text{Bond order} = \frac{\#\text{ of bonding } e^{-} \; - \; \#\text{ of antibonding } e^{-}}{2}$$

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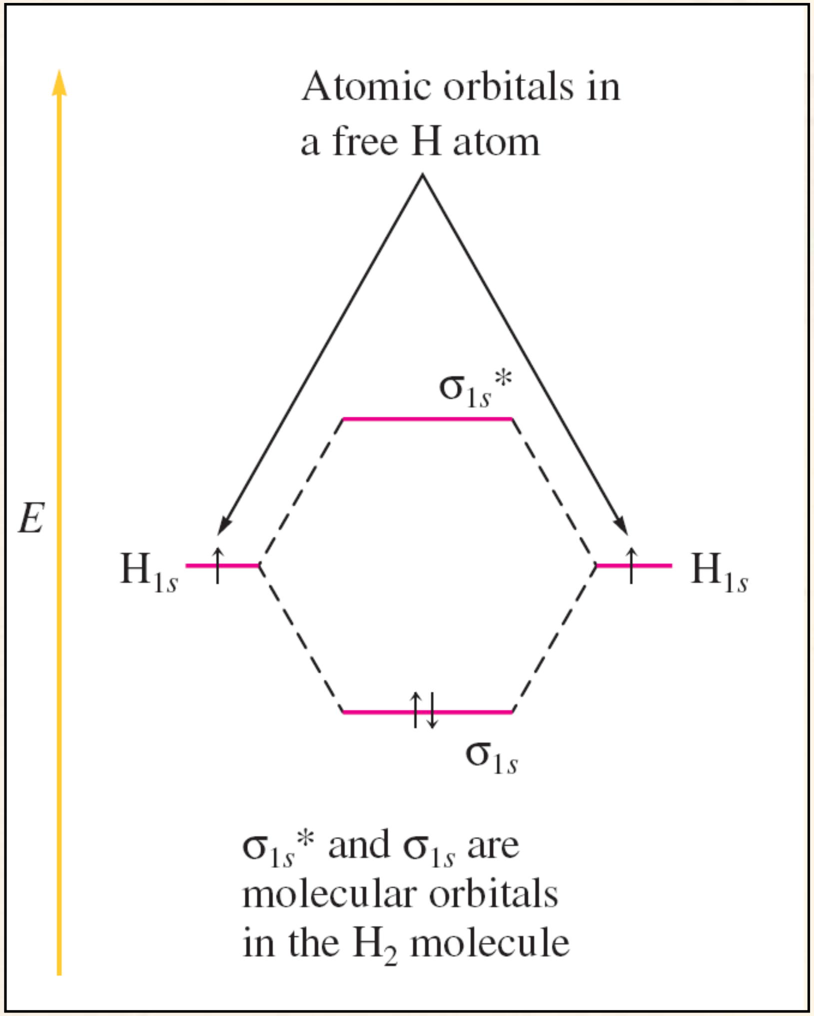
The Molecular Orbital Model

Example: H_2



$$\text{Bond order} = \frac{2 - 0}{2} = 1$$

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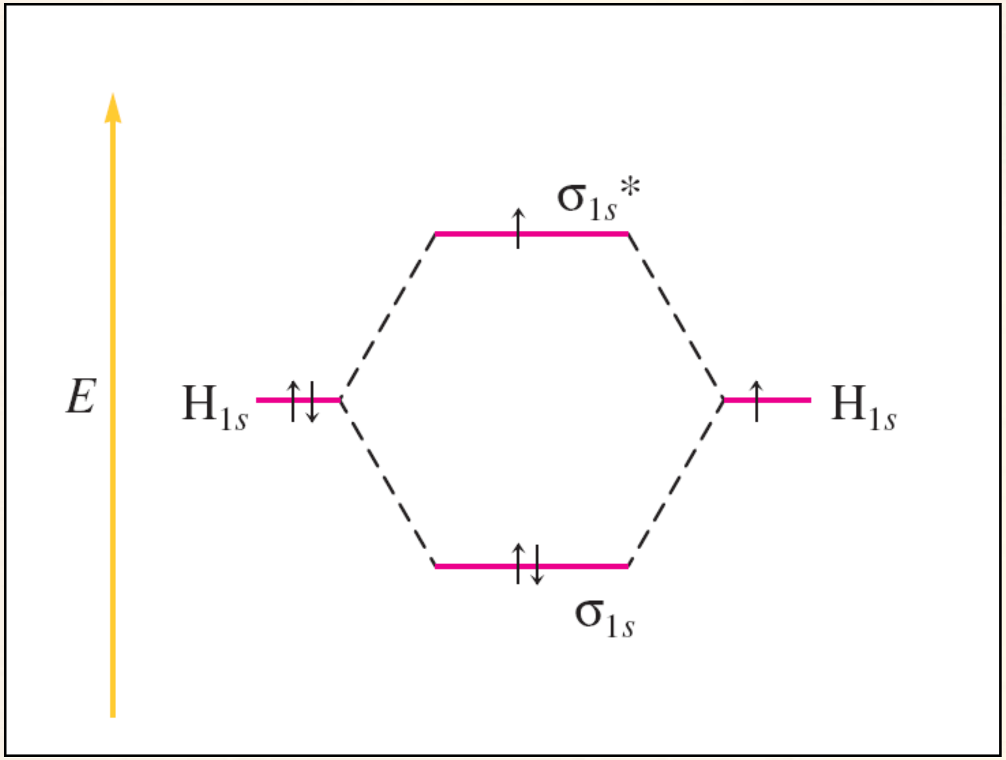
The Molecular Orbital Model

Example: H_2^-

$$\text{Bond order} = \frac{2 - 1}{2} = \frac{1}{2}$$



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Bonding in Homonuclear Diatomic Molecules

Homonuclear Diatomic Molecules

- Composed of 2 identical atoms.
- Only the valence orbitals of the atoms contribute significantly to the molecular orbitals of a particular molecule.

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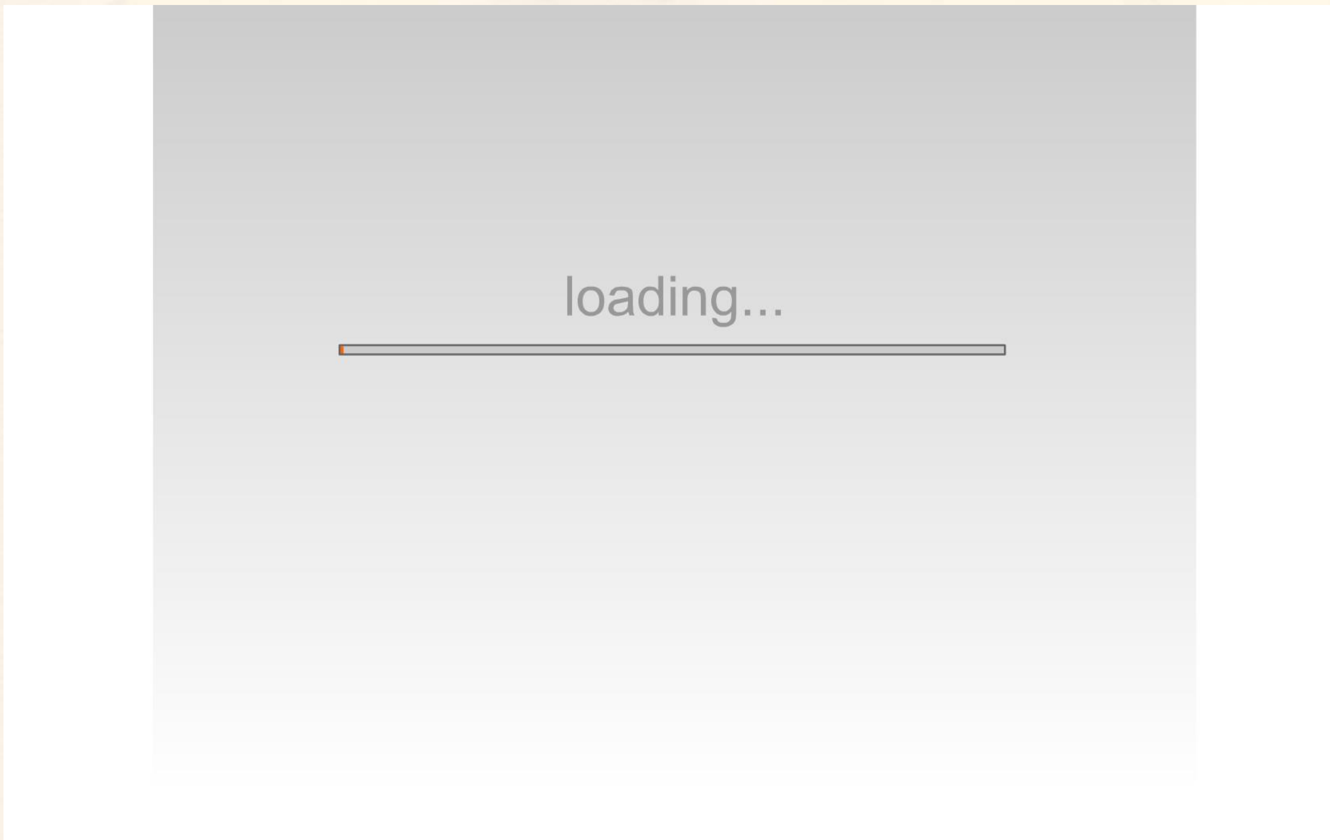
Bonding in Homonuclear Diatomic Molecules

Pi Bonding and Antibonding Orbitals



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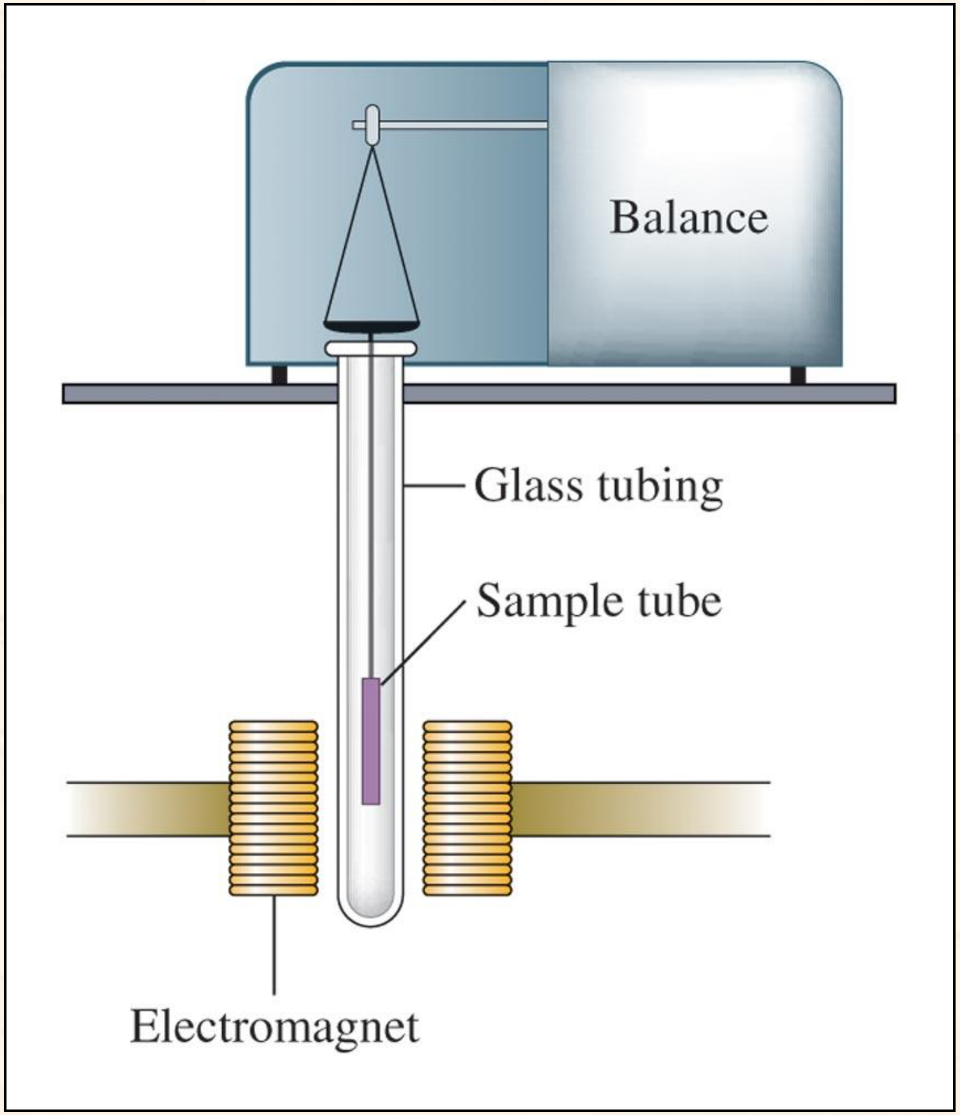
Bonding in Homonuclear Diatomic Molecules

Interesting effects are observed when these elements are placed in the presence of an external magnetic field.

Some elements are attracted to the magnet, others repelled



Apparatus Used to Measure the Paramagnetism of a Sample

Return to TOC

Bonding in Homonuclear Diatomic Molecules

Paramagnetism

- Paramagnetism – substance is attracted into the inducing magnetic field.
  - Unpaired electrons (O_2)
- Diamagnetism – substance is repelled from the inducing magnetic field.
  - Paired electrons (N_2)

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Bonding in Homonuclear Diatomic Molecules

Molecular Orbital Summary of Second Row Diatomic Molecules

E		B_2	C_2	N_2		O_2	F_2
↑	σ_{2p}^*	—	—	—	σ_{2p}^*	—	—
	π_{2p}^*	— —	— —	— —	π_{2p}^*	↑ ↑	↑↓ ↑↓
	σ_{2p}	—	—	↑↓	π_{2p}	↑↓ ↑↓	↑↓ ↑↓
	π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓
	σ_{2s}^*	↑↓	↑↓	↑↓	σ_{2s}^*	↑↓	↑↓
	σ_{2s}	↑↓	↑↓	↑↓	σ_{2s}	↑↓	↑↓
Magnetism		Paramagnetic	Diamagnetic	Diamagnetic		Paramagnetic	Diamagnetic
Bond order		1	2	3		2	1
Observed bond dissociation energy (kJ/mol)		290	620	942		495	154
Observed bond length (pm)		159	131	110		121	143

Return to TOC

Bonding in Heteronuclear Diatomic Molecules

Heteronuclear Diatomic Molecules

- Composed of 2 different atoms.

Return to TOC

Bonding in Heteronuclear Diatomic Molecules

Heteronuclear Diatomic Molecule: HF

- The 2*p* orbital of fluorine is at a lower energy than the 1*s* orbital of hydrogen because fluorine binds its valence electrons more tightly.
  - Electrons prefer to be closer to the fluorine atom.
- Thus the 2*p* electron on a free fluorine atom is at a lower energy than the 1*s* electron on a free hydrogen atom.

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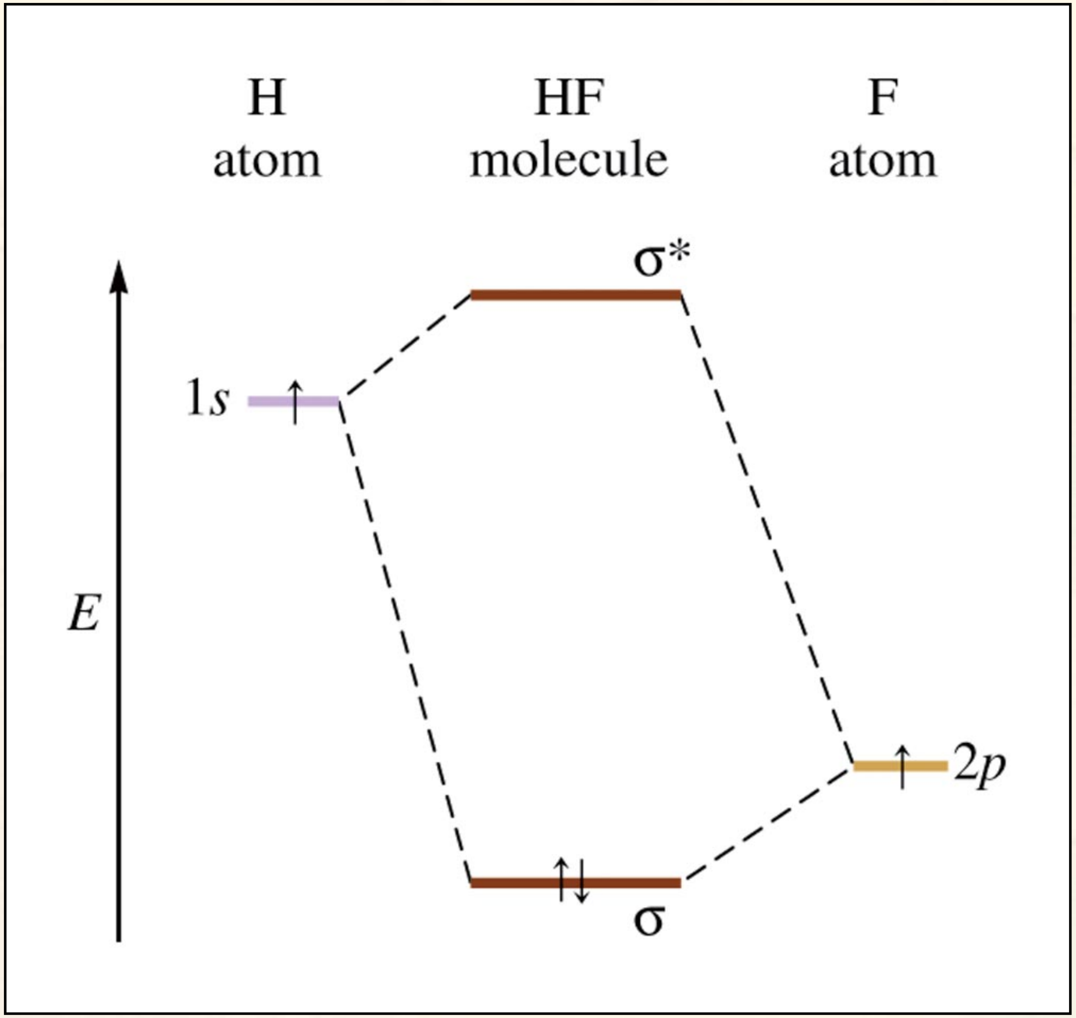
Bonding in Heteronuclear Diatomic Molecules

Orbital Energy-Level Diagram for the HF Molecule



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Bonding in Heteronuclear Diatomic Molecules

Heteronuclear Diatomic Molecule: HF

- The diagram predicts that the HF molecule should be stable because both electrons are lowered in energy relative to their energy in the free hydrogen and fluorine atoms, which is the driving force for bond formation.

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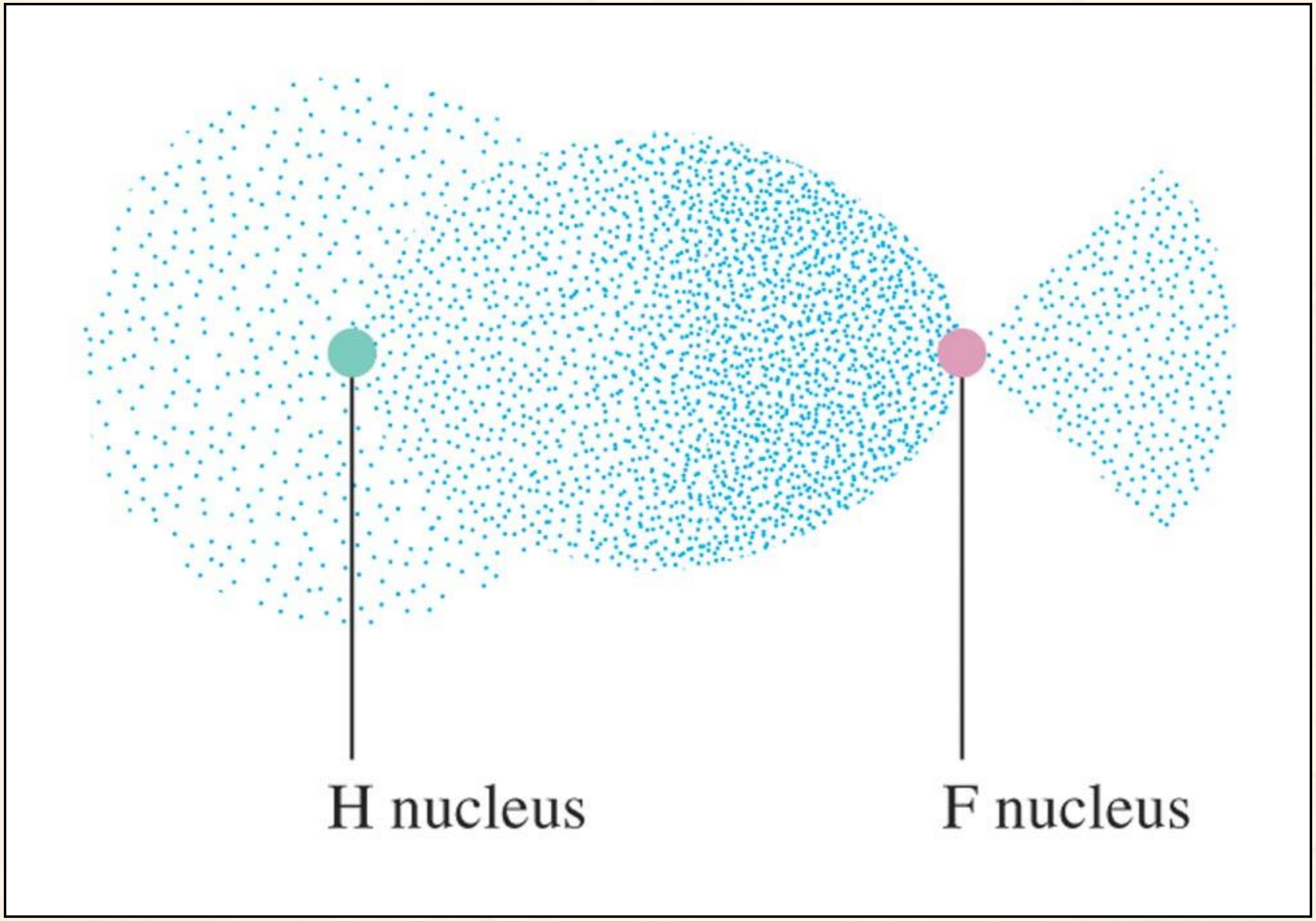
Bonding in Heteronuclear Diatomic Molecules

The Electron Probability Distribution in the Bonding Molecular Orbital of the HF Molecule



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Bonding in Heteronuclear Diatomic Molecules

Heteronuclear Diatomic Molecule: HF

- The σ molecular orbital containing the bonding electron pair shows greater electron probability close to the fluorine.
- The electron pair is not shared equally.
- This causes the fluorine atom to have a slight excess of negative charge and leaves the hydrogen atom partially positive.
- This is exactly the bond polarity observed for HF.

Return to TOC

Delocalization

- Describes molecules that require resonance.
- In molecules that require resonance, it is the π bonding that is most clearly delocalized, the σ bonds are localized.
- *p* orbitals perpendicular to the plane of the molecule are used to form π molecular orbitals.
- The electrons in the π molecular orbitals are delocalized above and below the plane of the molecule.

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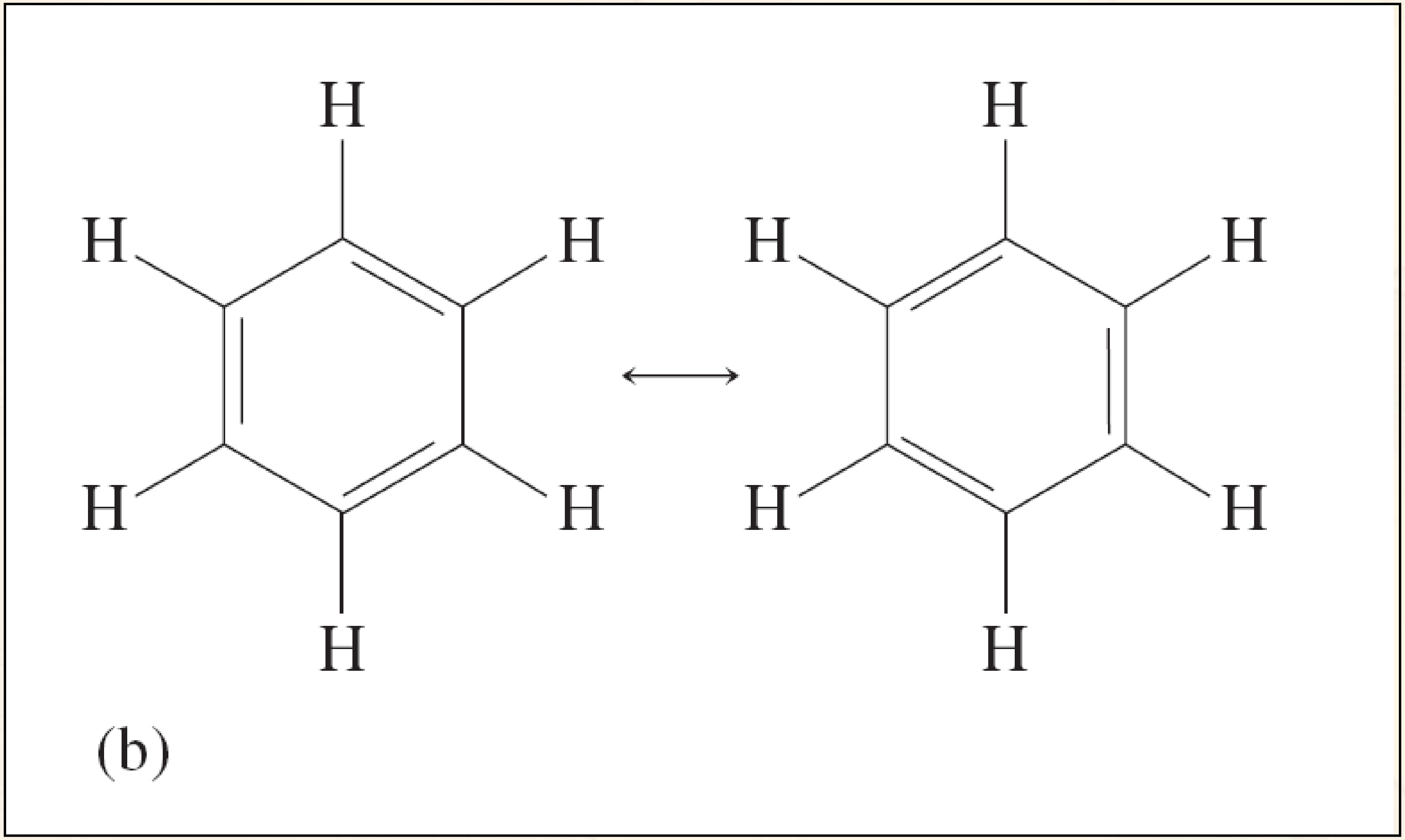
Combining the Localized Electron and Molecular Orbital Models

Resonance in Benzene



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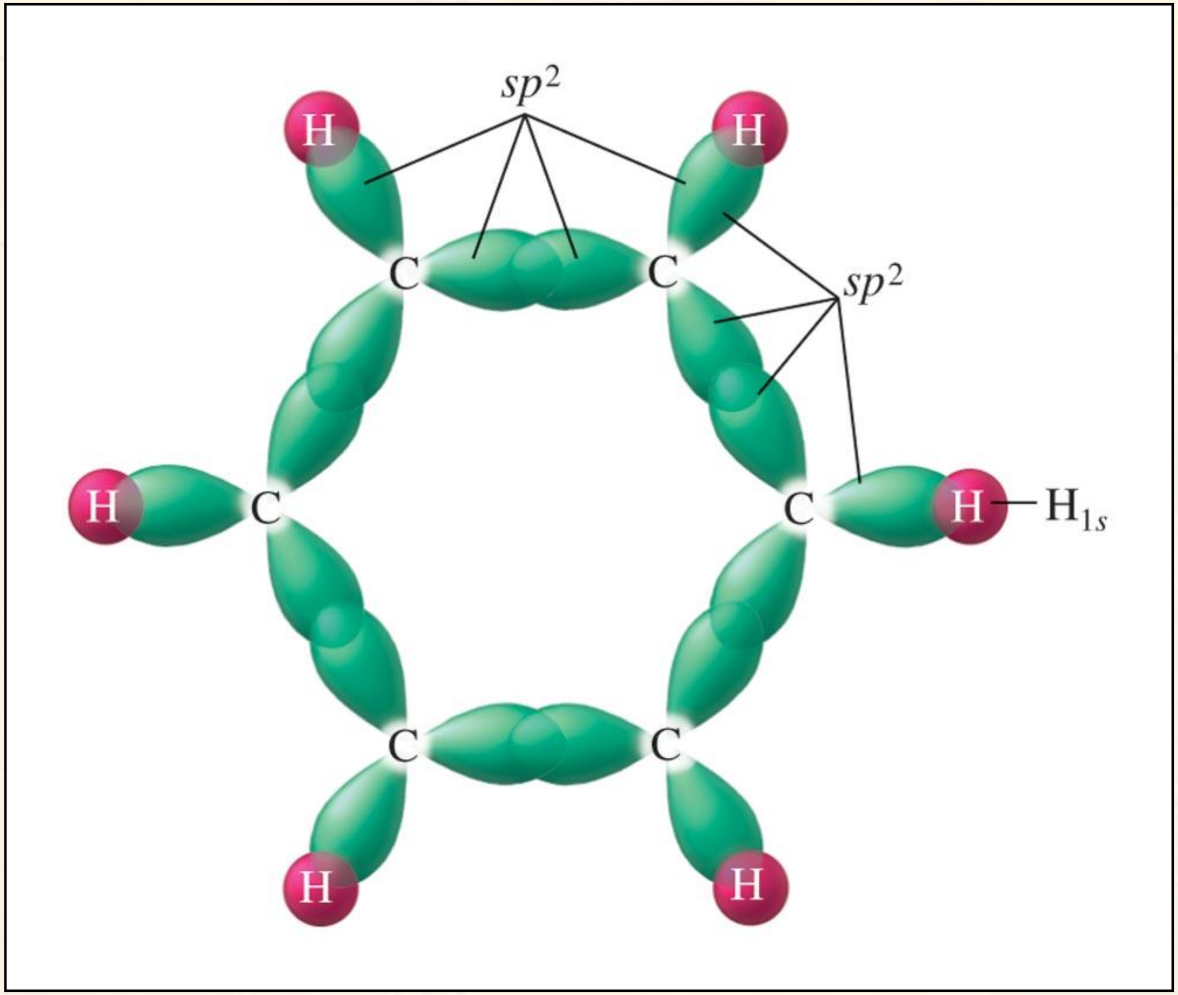
Combining the Localized Electron and Molecular Orbital Models

The Sigma System for Benzene



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Combining the Localized Electron and Molecular Orbital Models

The Pi System for Benzene