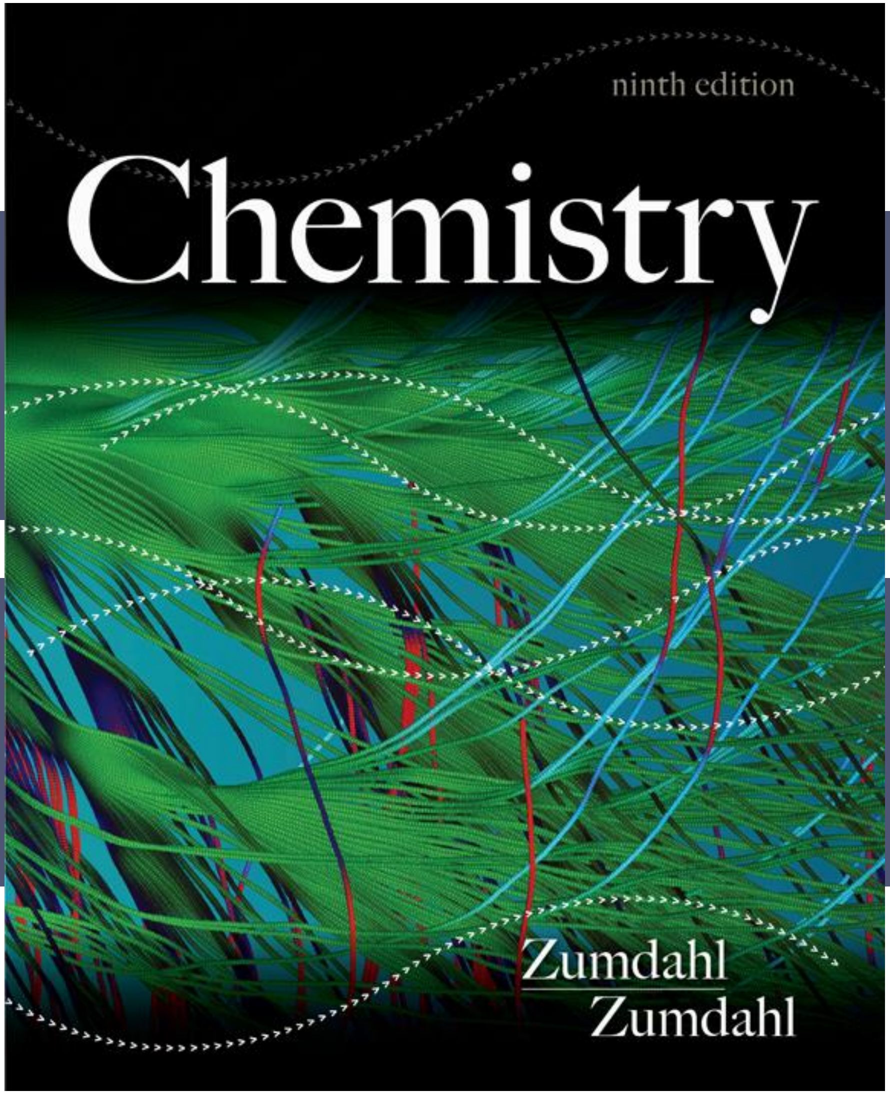


Chapter 9

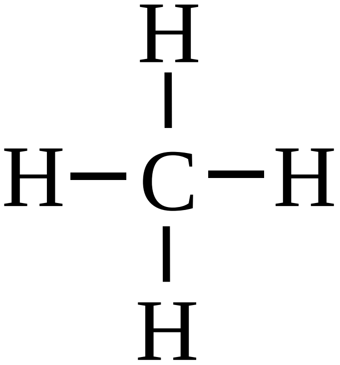
Covalent Bonding: Orbitals

EXERCISE!

Draw the Lewis structure for methane, CH_4.

- What is the shape of a methane molecule?

- What are the bond angles?



CONCEPT CHECK!

What is the valence electron configuration of a carbon atom?

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

Bonding in Methane

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

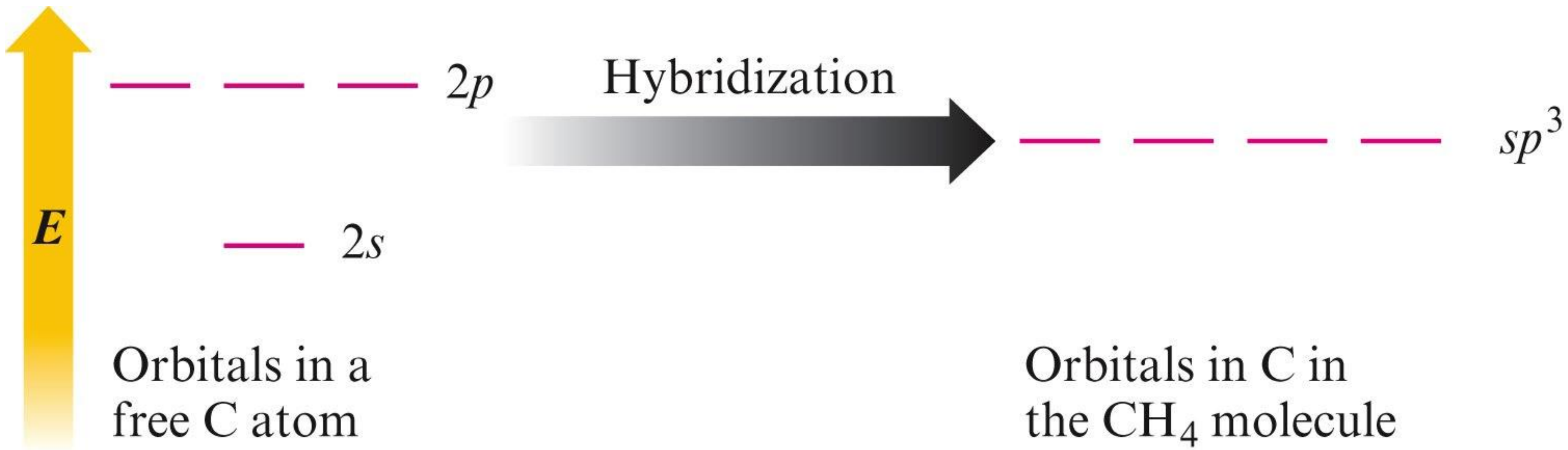
Hybridization

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

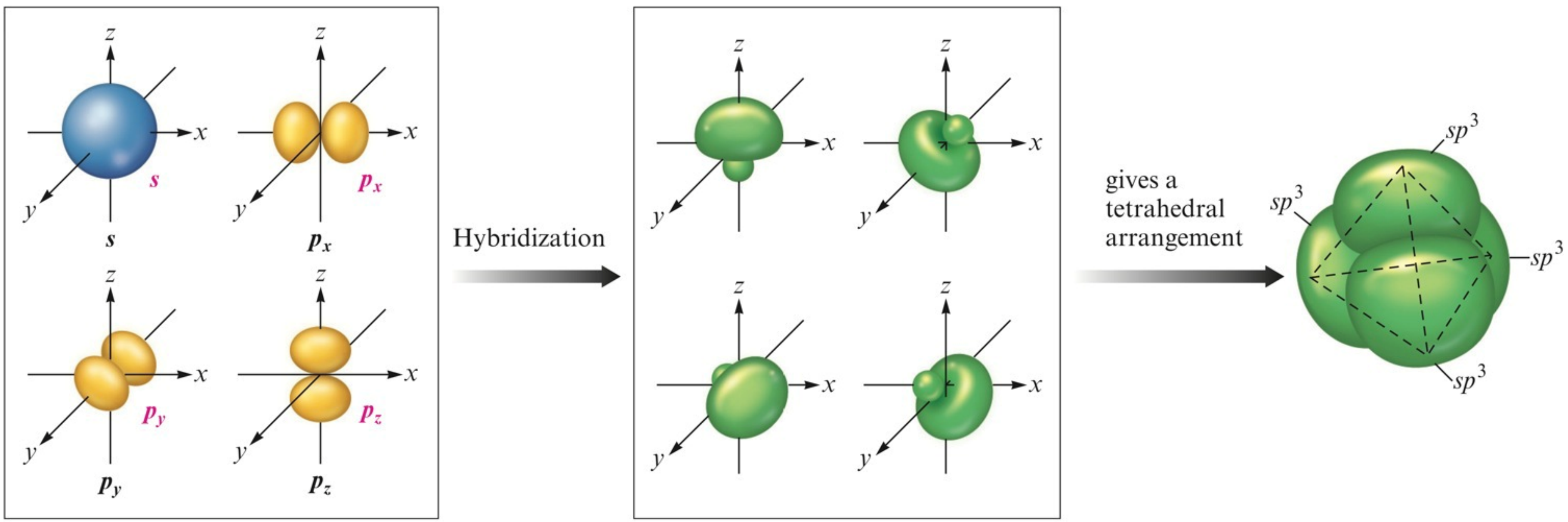
sp^3 Hybridization

- 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.
- The four orbitals are identical in shape.

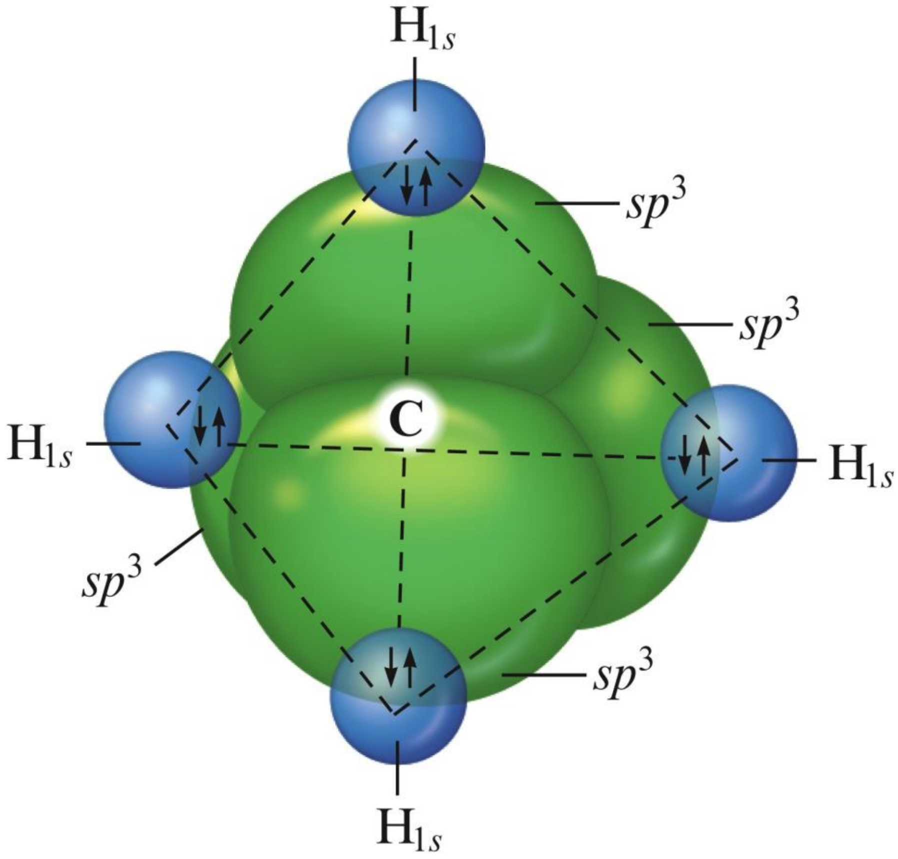
An Energy-Level Diagram Showing the Formation of Four *sp³* Orbitals



The Formation of *sp³* Hybrid Orbitals



Tetrahedral Set of Four sp^3 Orbitals



EXERCISE!

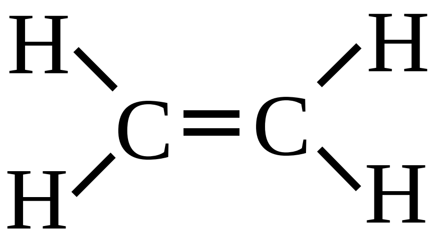
Draw the Lewis structure for C_2H_4 (ethylene)?

- 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



CONCEPT CHECK!

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

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.

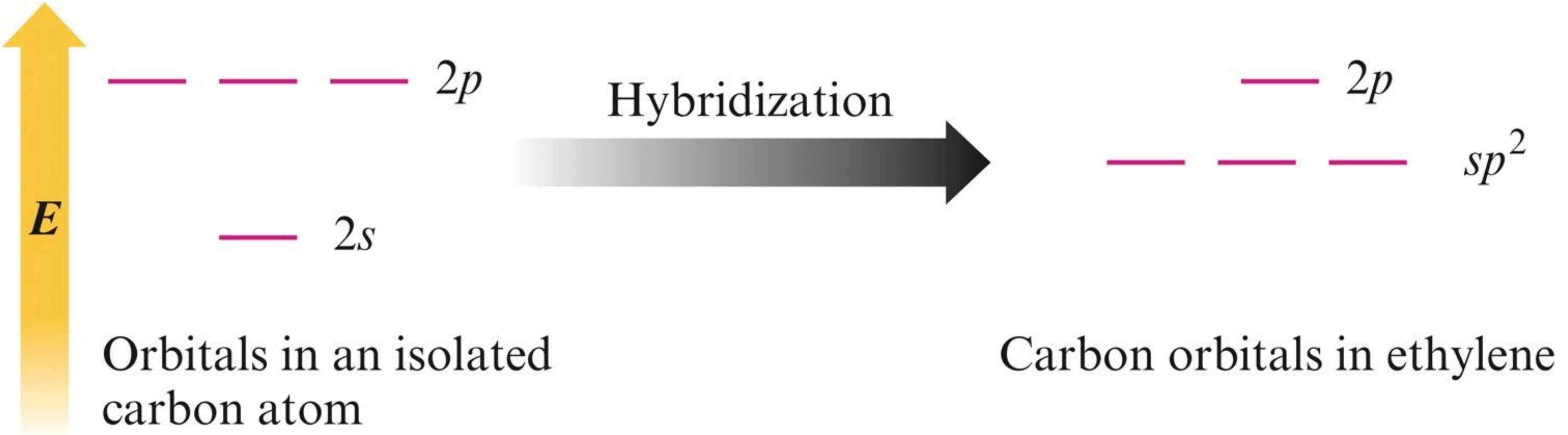
Sigma (Σ) Bond

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

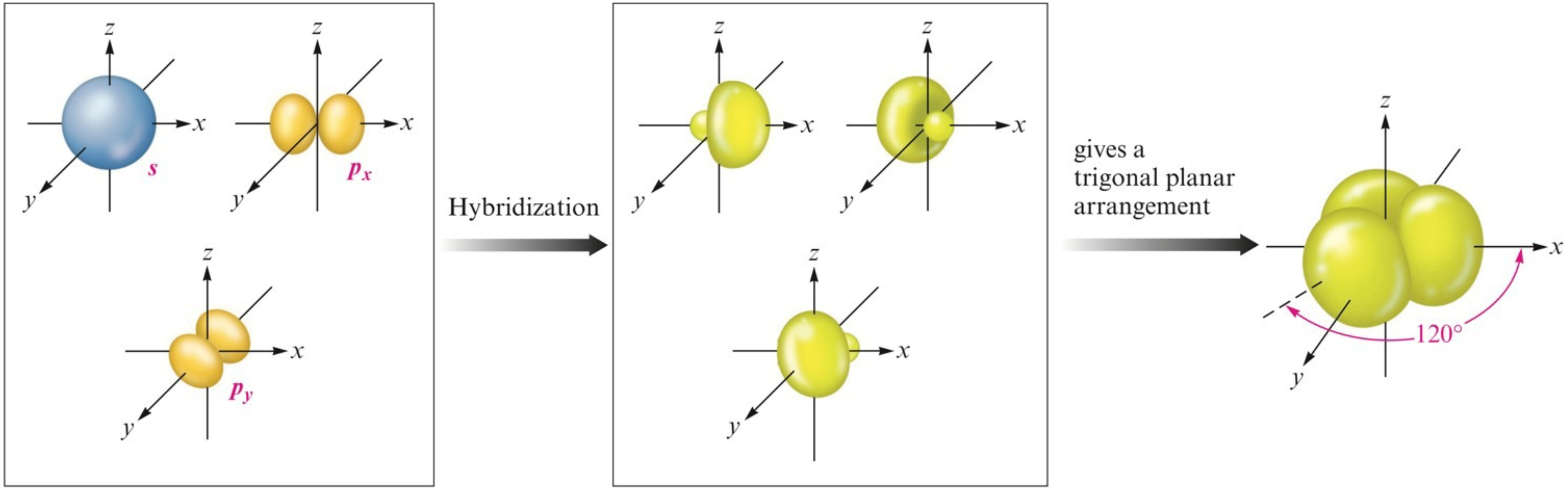
Pi (Π) Bond

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

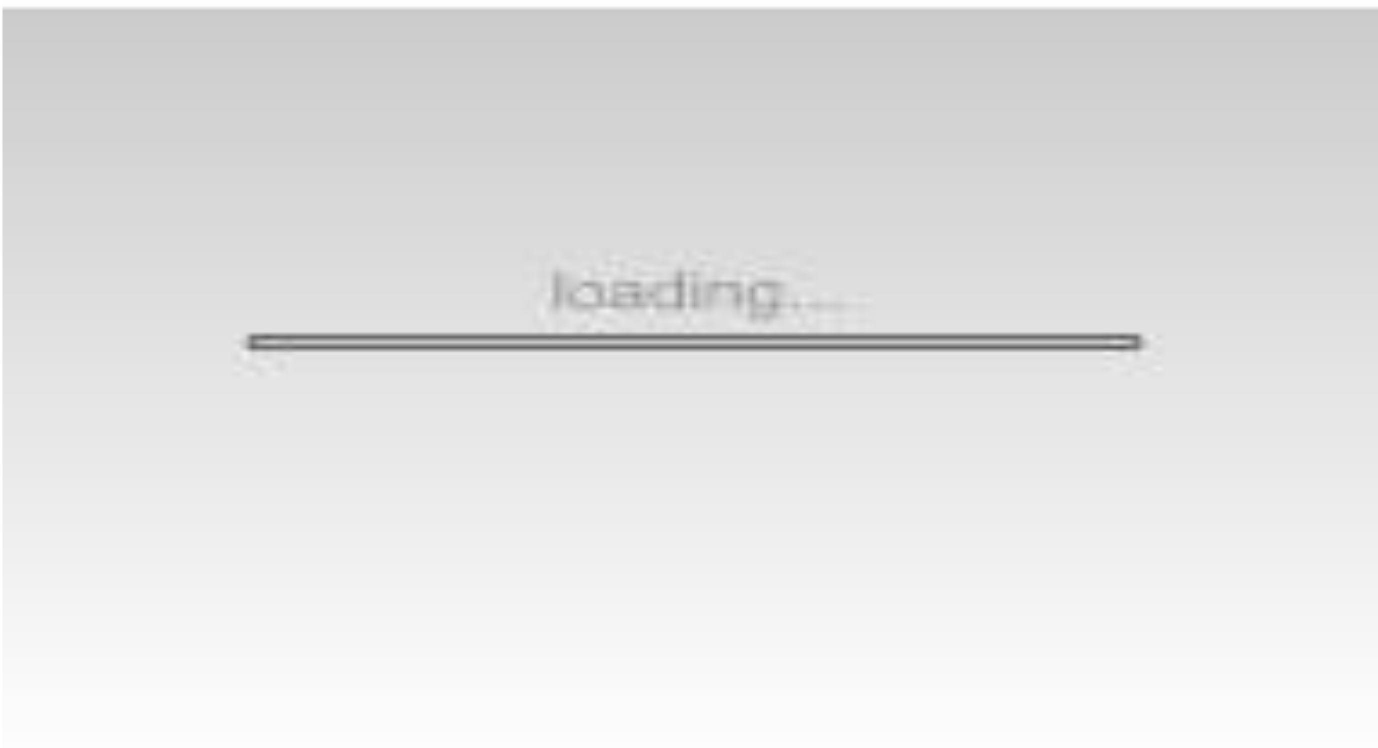
An Orbital Energy-Level Diagram for sp^2 Hybridization



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



Formation of C=C Double Bond in Ethylene



EXERCISE!

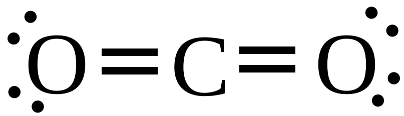
Draw the Lewis structure for CO_2.

- What is the shape of a carbon dioxide molecule?

  linear

- What are the bond angles?

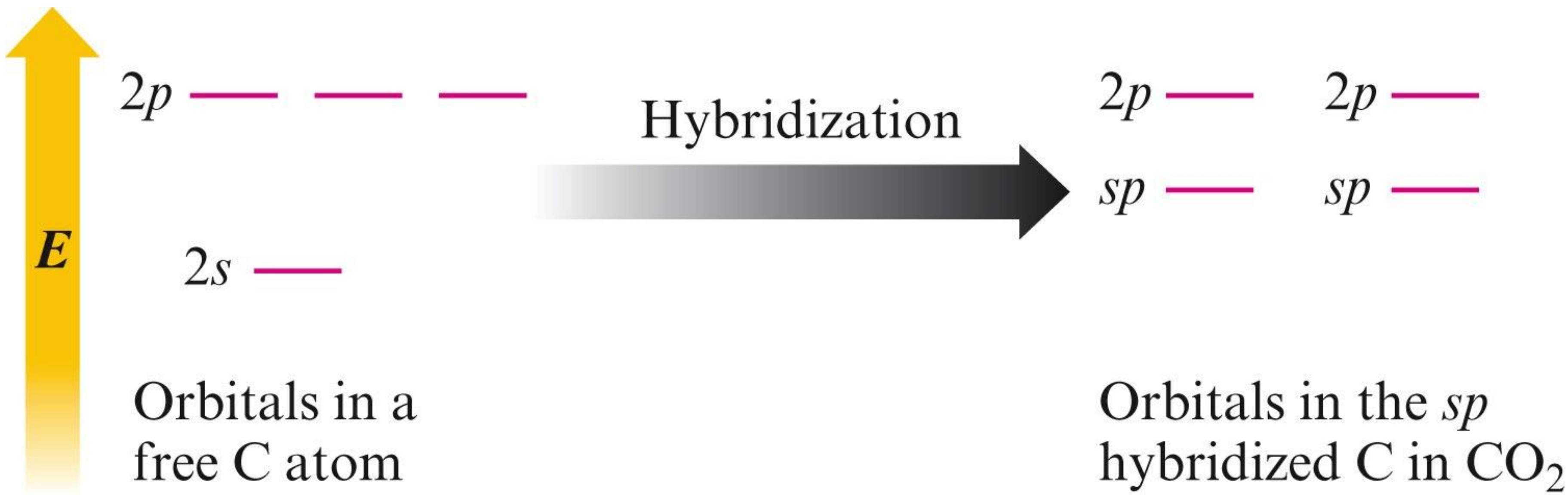
  180º



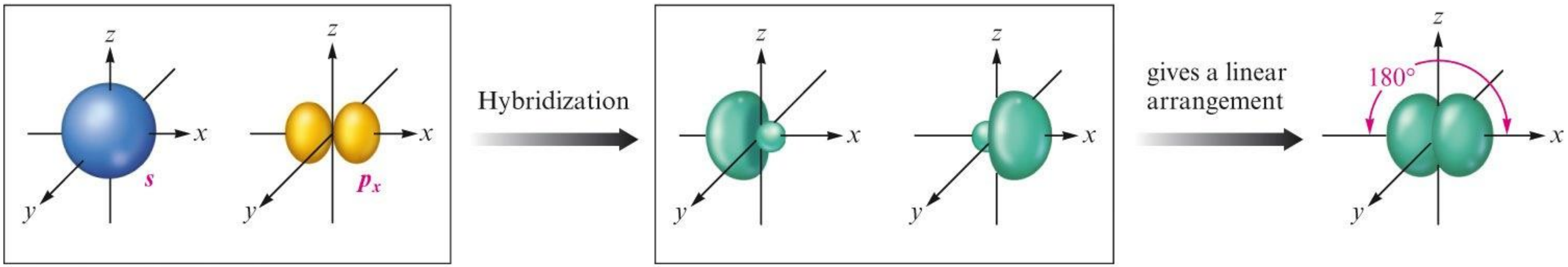
sp Hybridization

- 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.

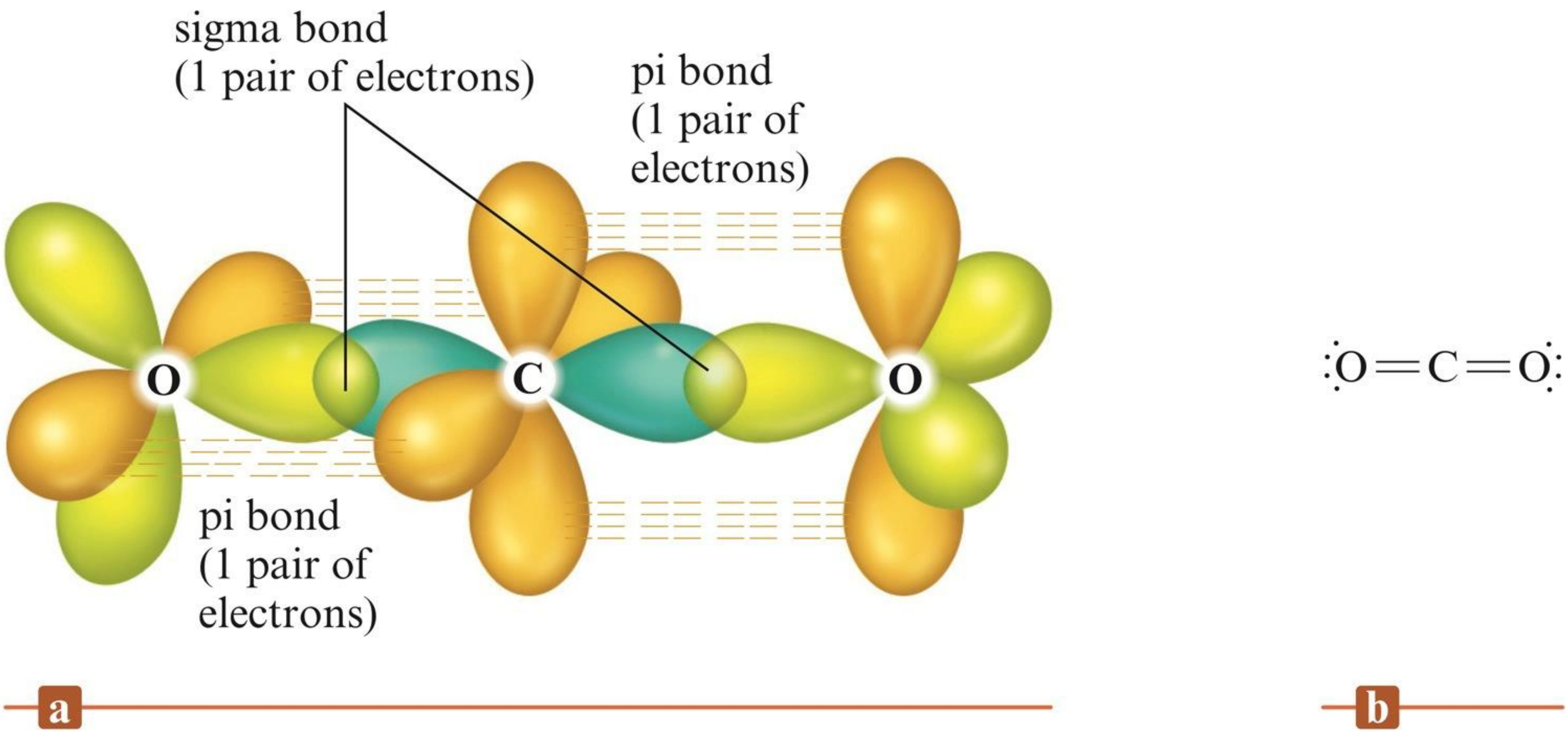
The Orbital Energy-Level Diagram for the Formation of *sp* Hybrid Orbitals on Carbon



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



The Orbitals for CO_2



EXERCISE!

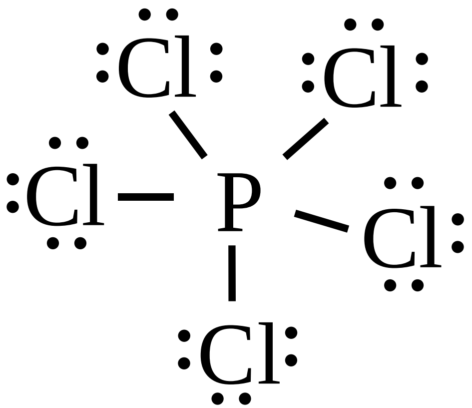
Draw the Lewis structure for PCl_5.

- What is the shape of a phosphorus pentachloride molecule?

  trigonal bipyramidal

- What are the bond angles?

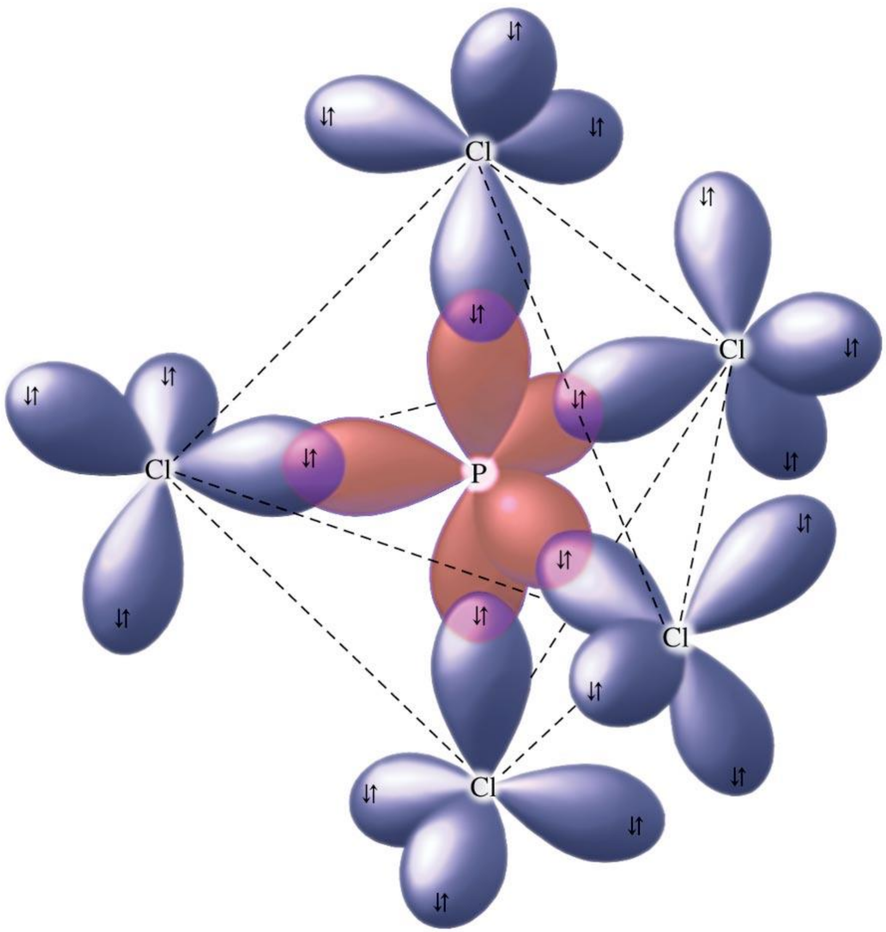
  90^o and 120^o



dsp^3 Hybridization

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

The Orbitals Used to Form the Bonds in PCl_5



EXERCISE!

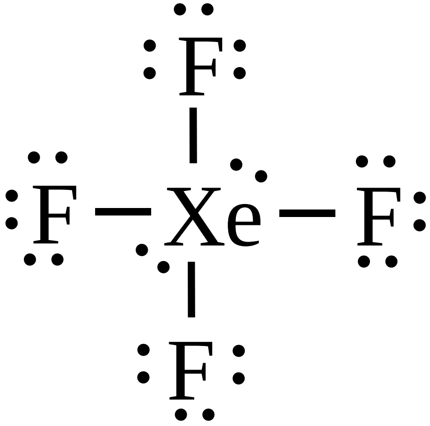
Draw the Lewis structure for XeF_4.

- What is the shape of a xenon tetrafluoride molecule?

  octahedral

- What are the bond angles?

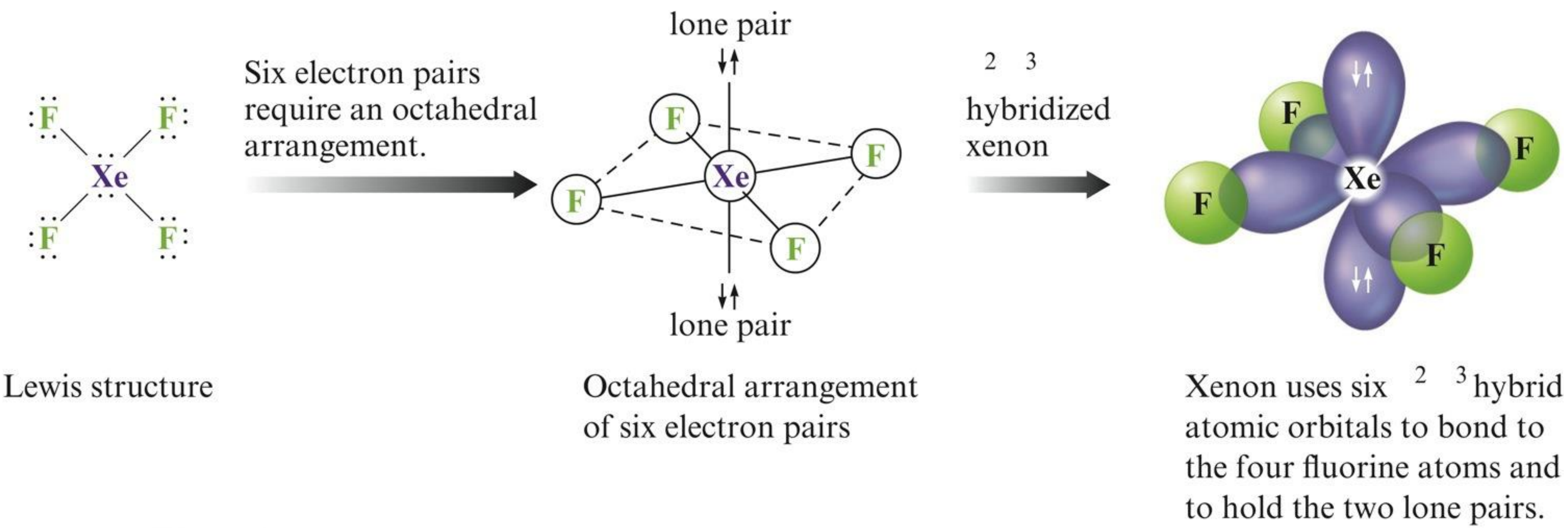
  90^o and 180^o



d^2sp^3 Hybridization

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

How is the Xenon Atom in XeF_4 Hybridized?



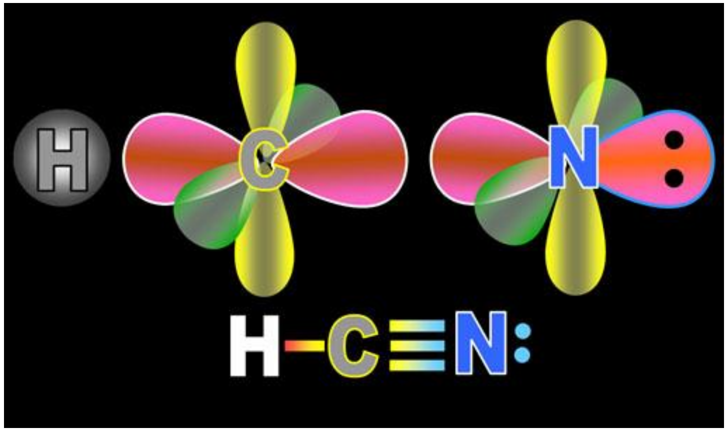
CONCEPT CHECK!

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.



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 – 109.5º, sp^3

SO_2 – 120º, sp^2

KrF_2 – 90º, 120º, dsp^3

CO_2 – 180º, sp

ICl_5 – 90º, 180º, d^2sp^3

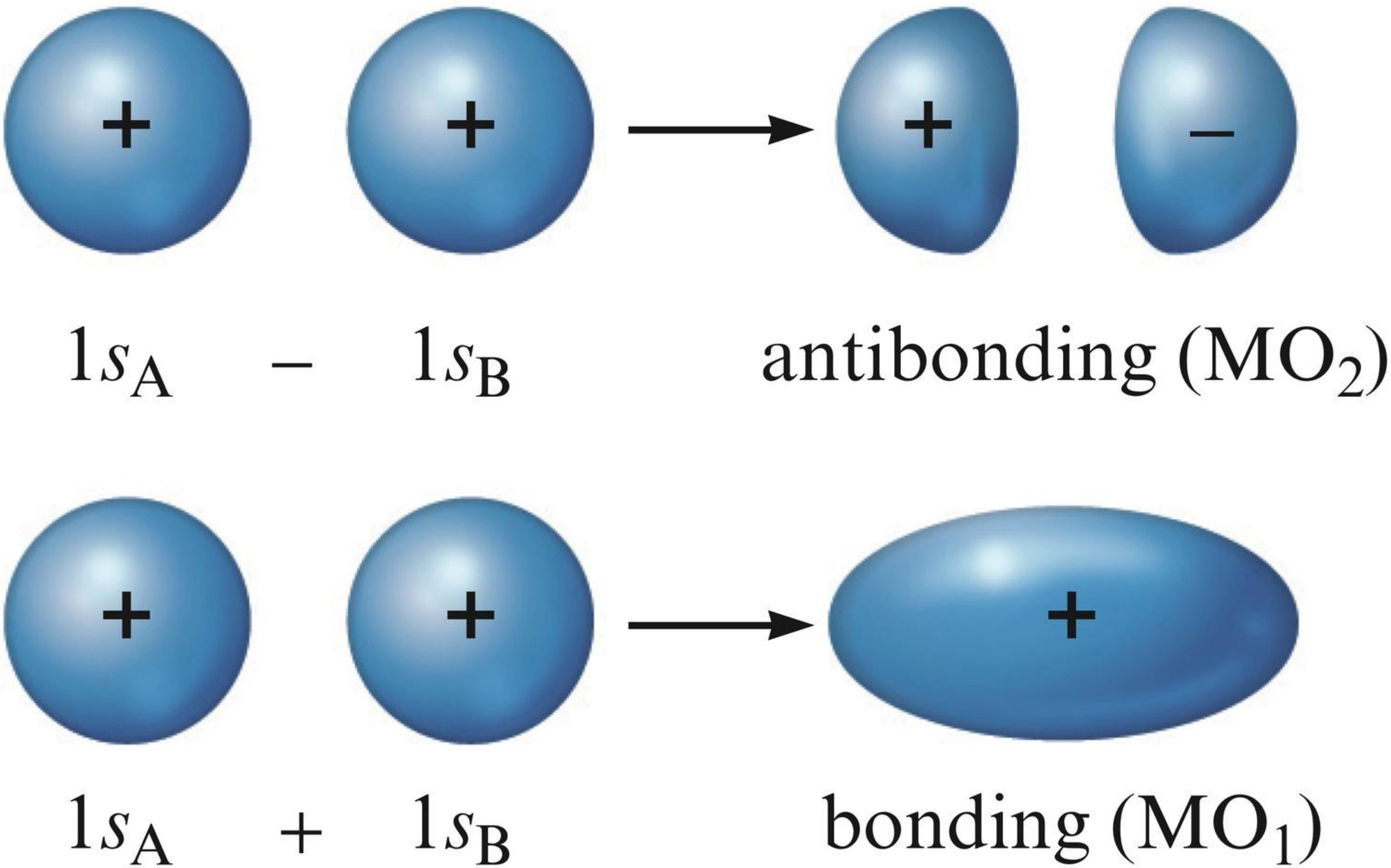
Using the Localized Electron Model

- 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.

- 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.

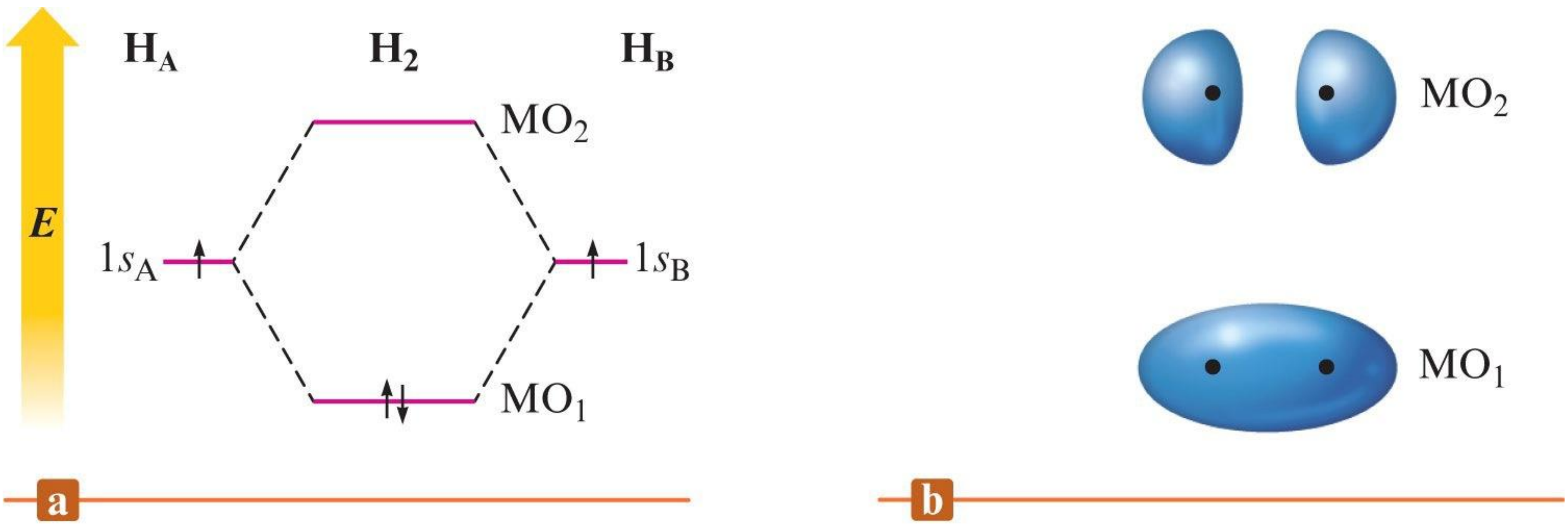
- The electron probability of both molecular orbitals is centered along the line passing through the two nuclei.
  - Sigma (σ) molecular orbitals (MOs)
- In the molecule only the molecular orbitals are available for occupation by electrons.

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



- 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

MO Energy-Level Diagram for the H_2 Molecule



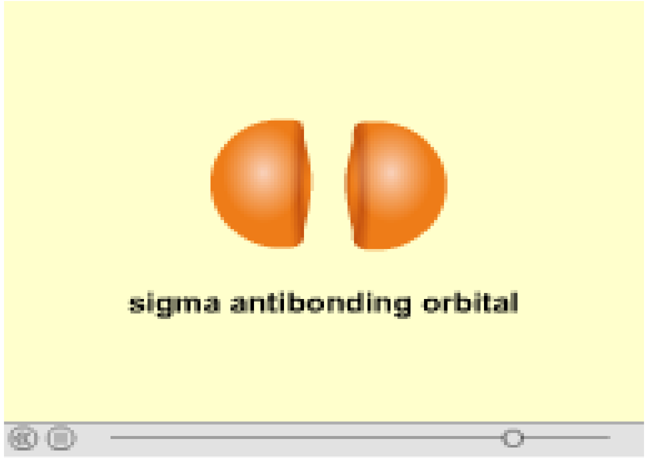
Energy diagram

Electron probability distribution

- 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.

- Molecular electron configurations can be written in much the same way as atomic electron configurations.
- Each molecular orbital can hold 2 electrons with opposite spins.
- The number of orbitals are conserved.

Sigma Bonding and Antibonding Orbitals



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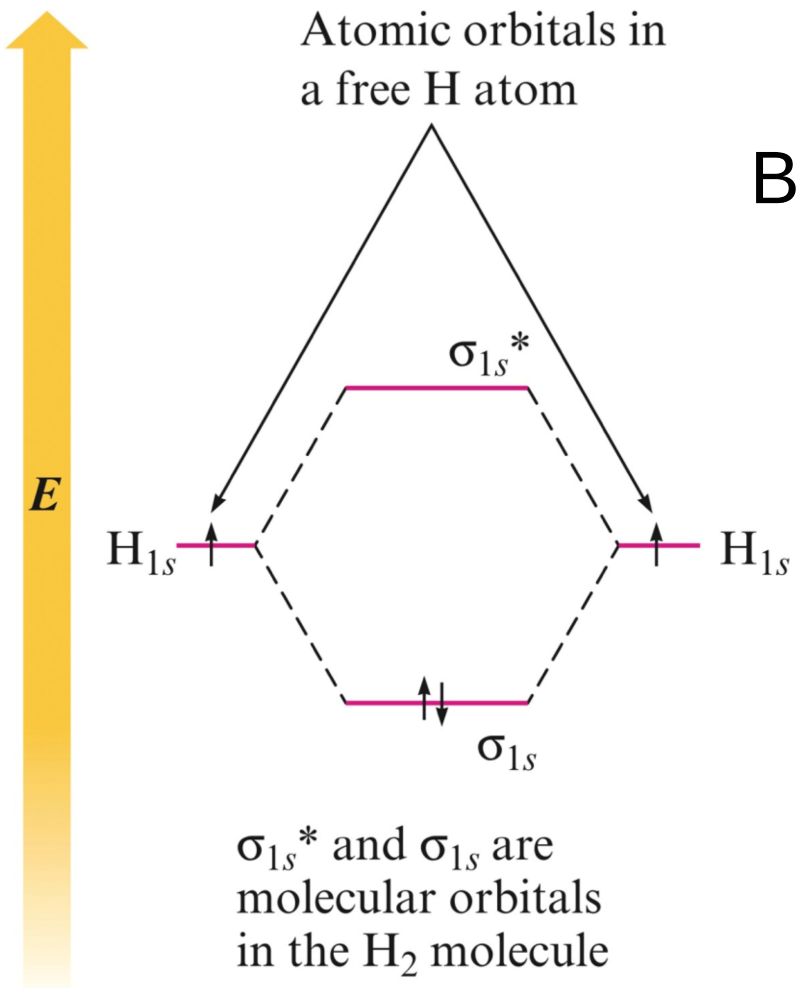
Bond Order

- Larger bond order means greater bond strength.

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

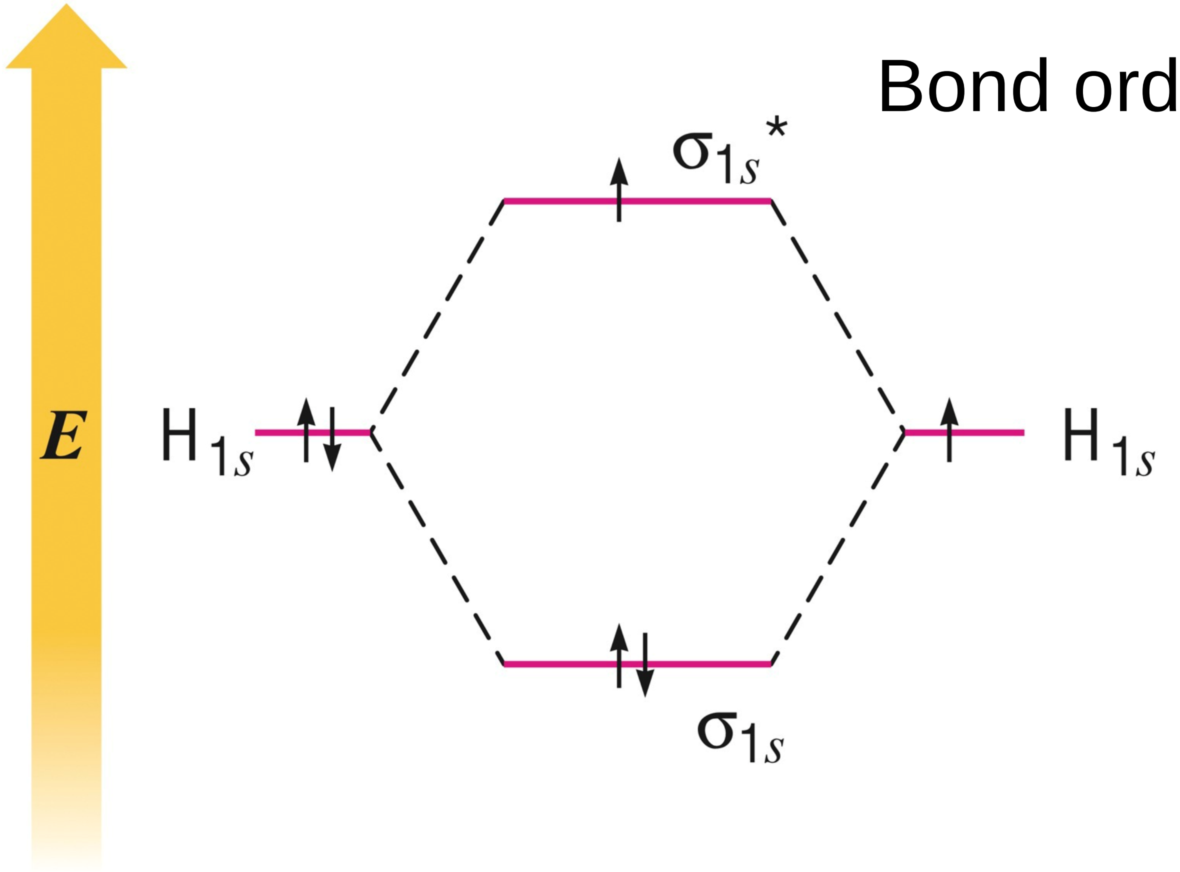
Example: H_2



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

Example: H_2^-

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



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.

Pi Bonding and Antibonding Orbitals

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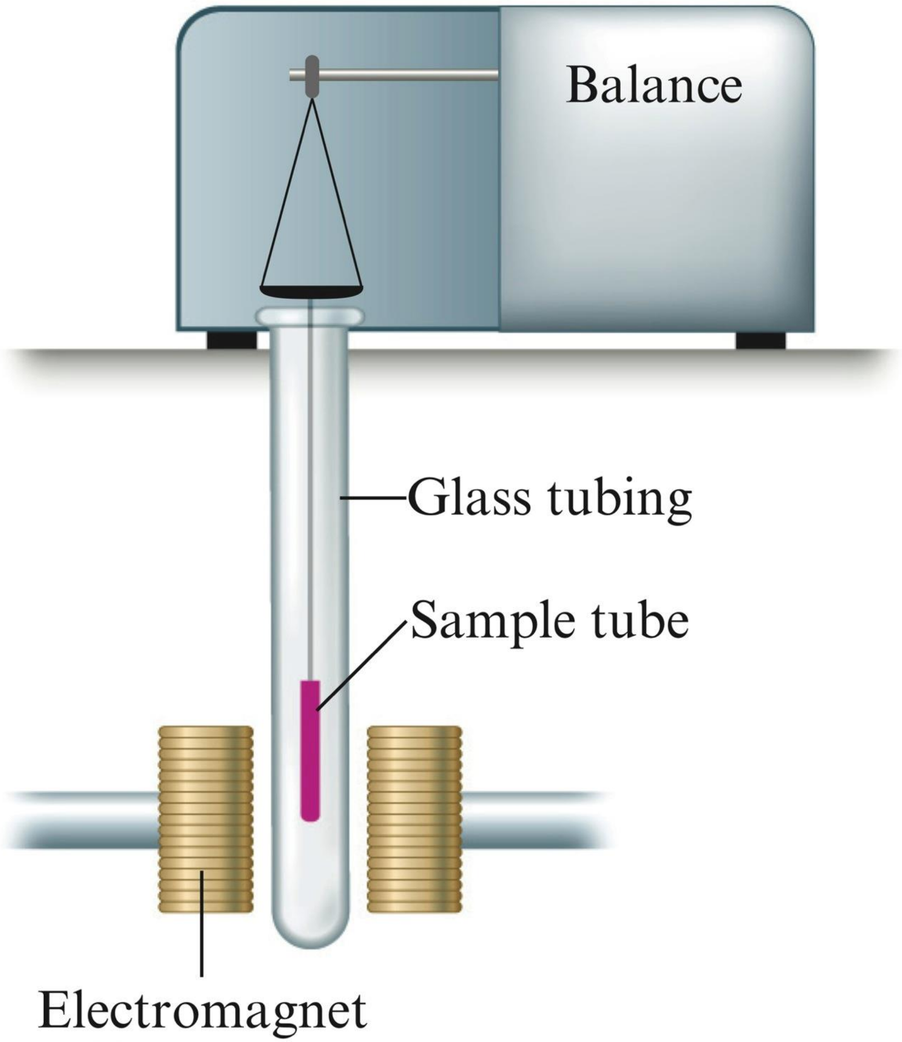
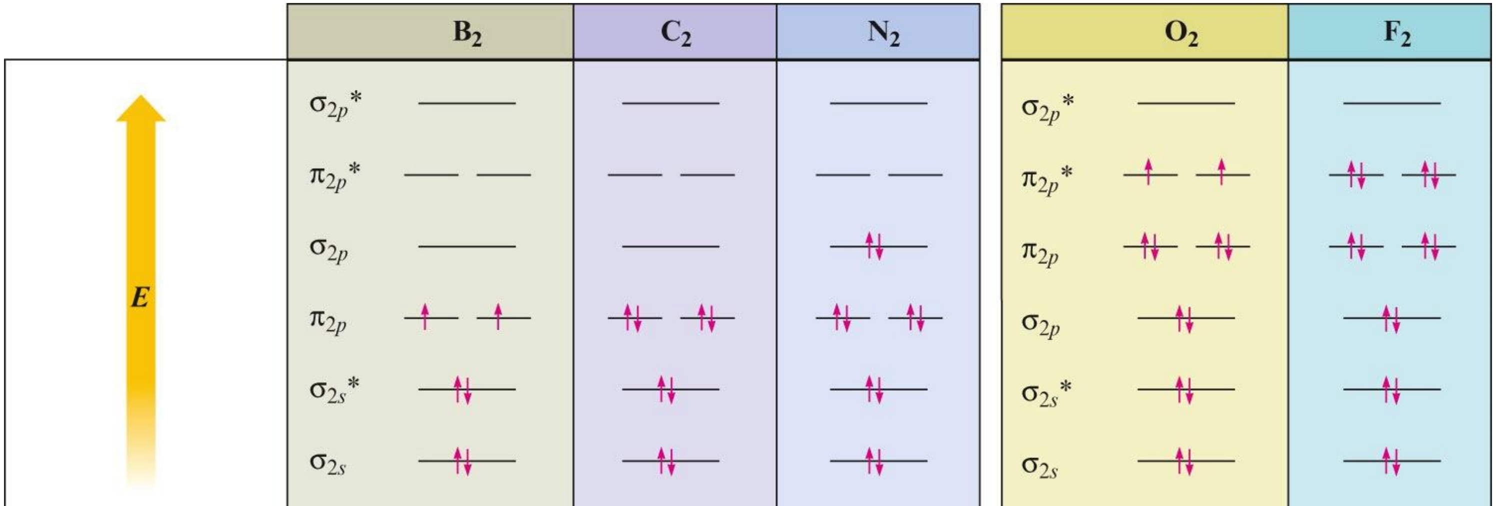
Paramagnetism

- 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)

Apparatus Used to Measure the Paramagnetism of a Sample



Molecular Orbital Summary of Second Row Diatomic Molecules



	B_2	C_2	N_2	O_2	F_2
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

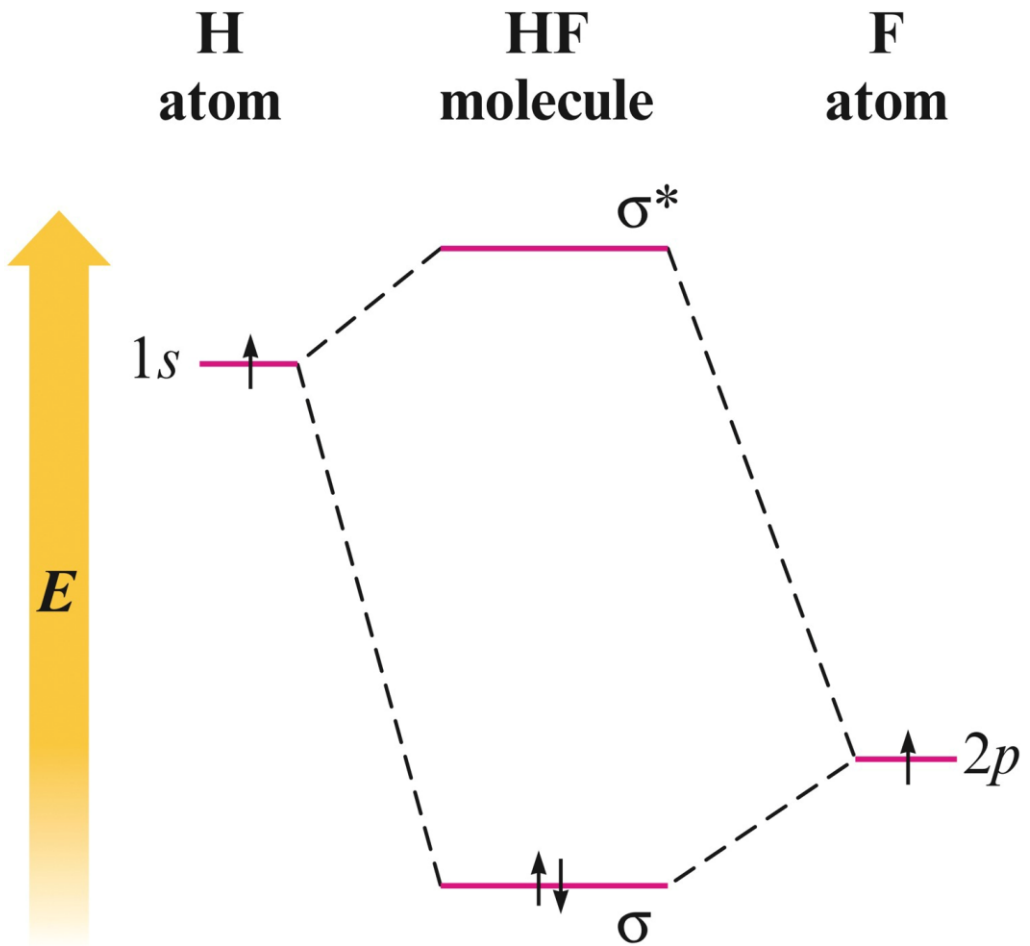
Heteronuclear Diatomic Molecules

- Composed of 2 different atoms.

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.

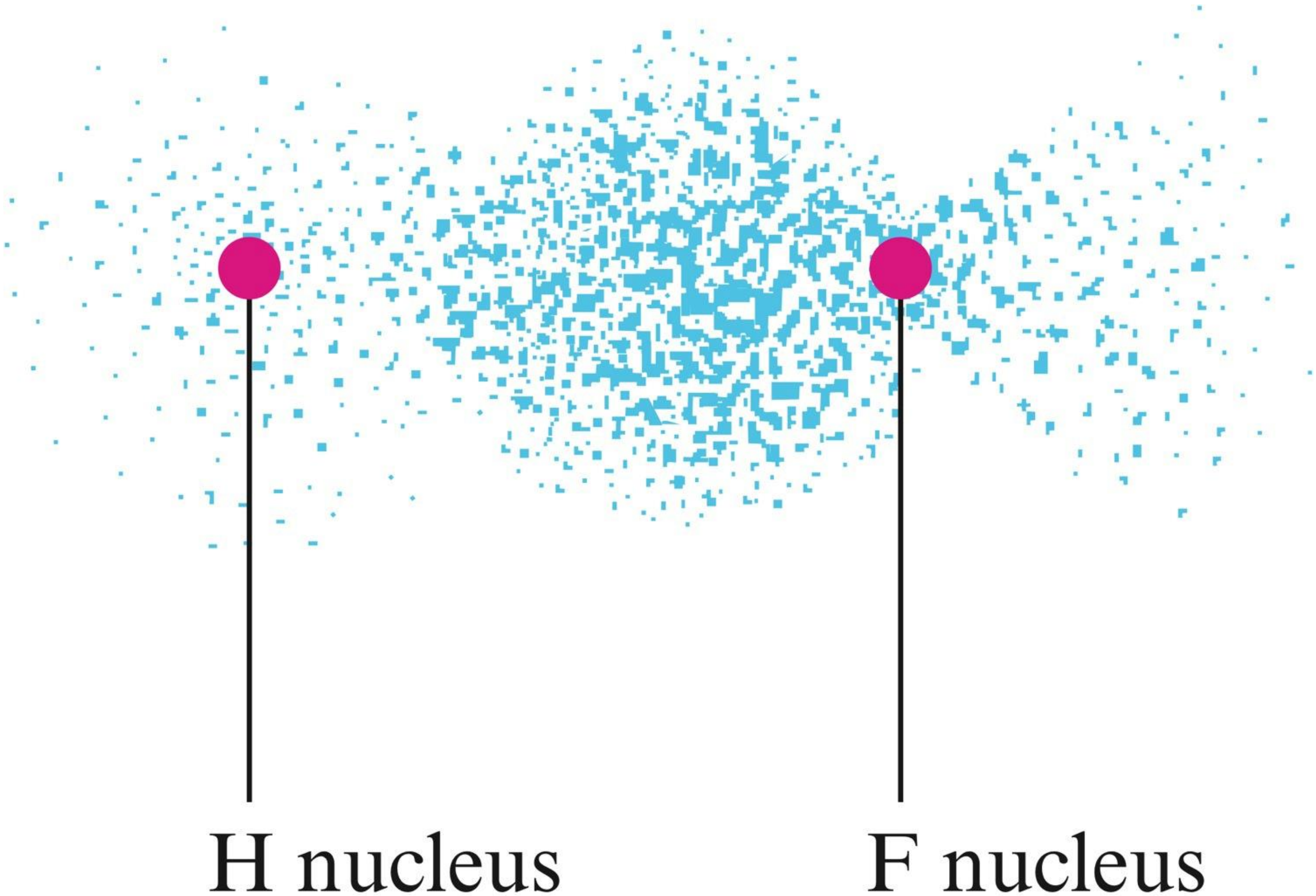
Orbital Energy-Level Diagram for the HF Molecule



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.

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



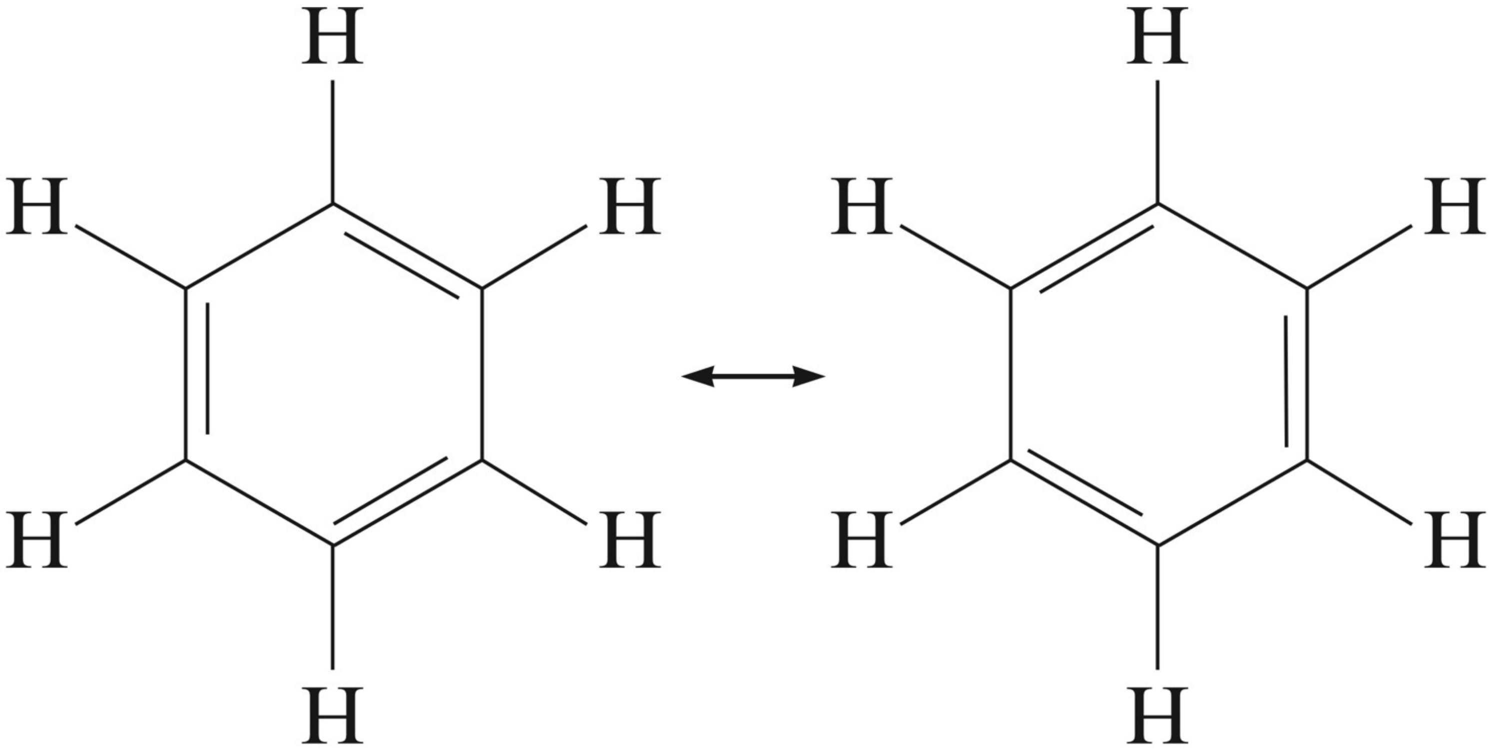
Heteronuclear Diatomic Molecule: HF

- 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.

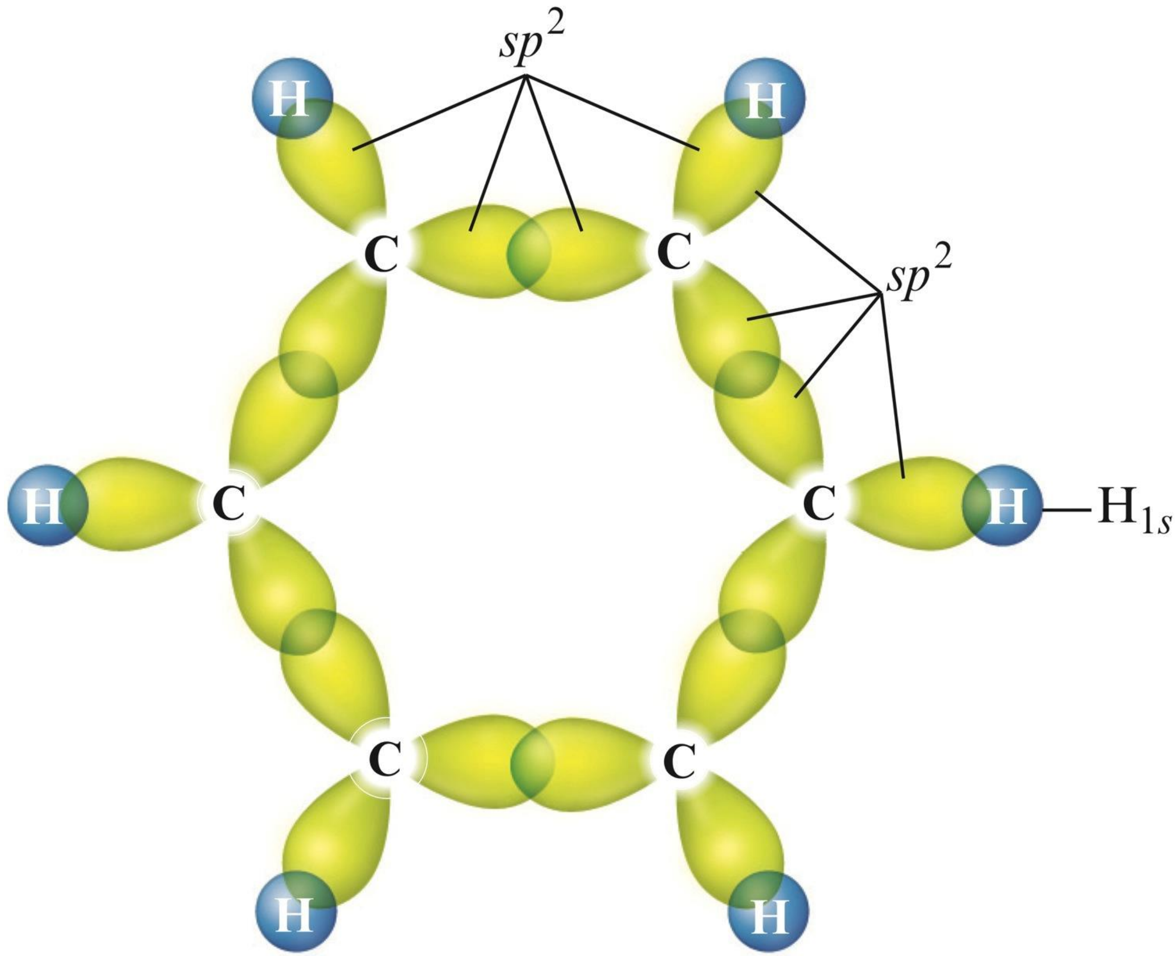
Delocalization

- 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.

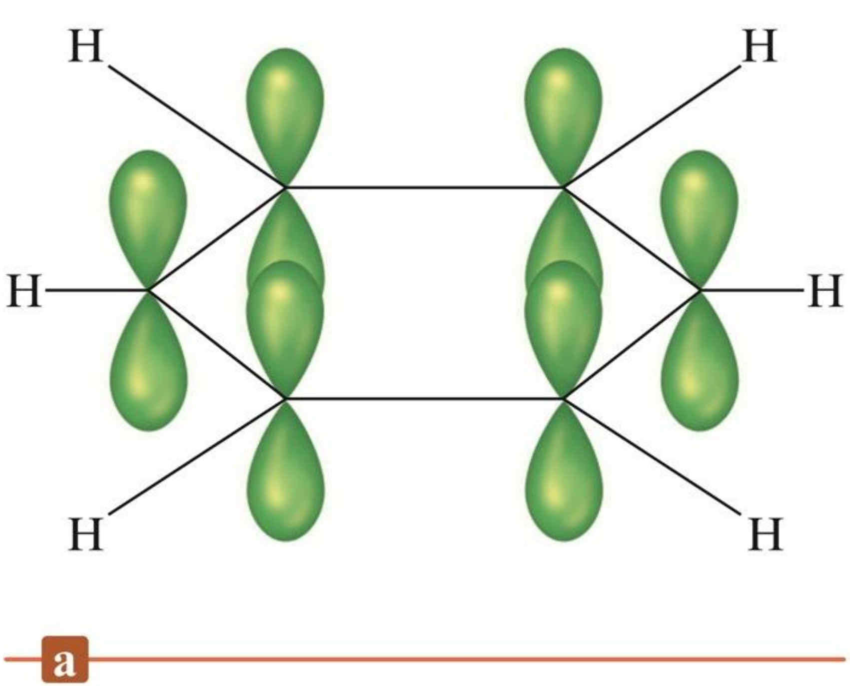
Resonance in Benzene

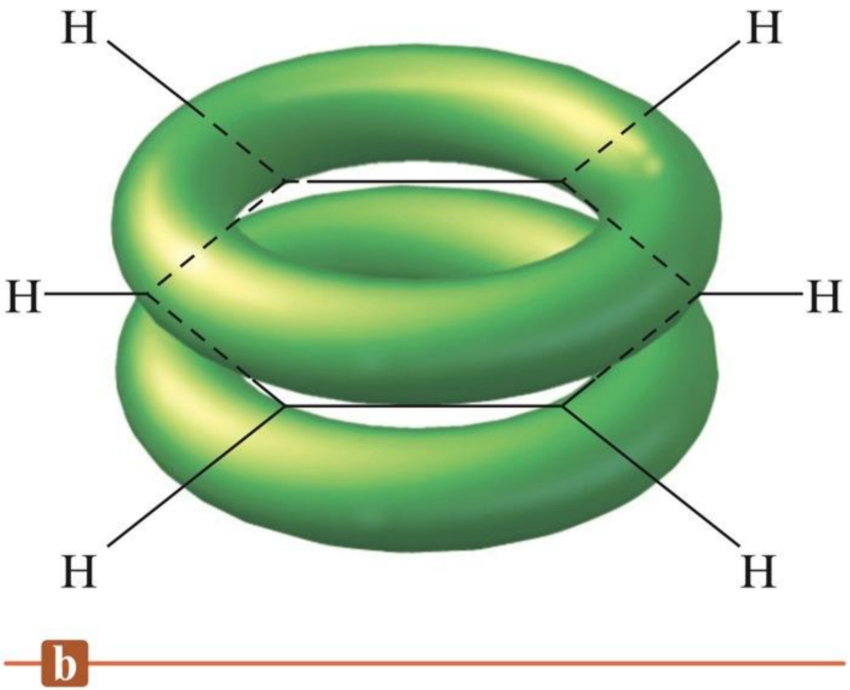


The Sigma System for Benzene



The Pi System for Benzene





Pi Bonding in the Nitrate Ion

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- Can be used to determine the relative energies of electrons in individual atoms and molecules.
- High-energy photons are directed at the sample, and the kinetic energies of the ejected electrons are measured.