

# 5 Molecular Structure and Orbitals

## Chapter Objectives:

- Learn the basics of Valence Bond Theory and Molecular Orbital Theory and how they are used to model covalent bonding.

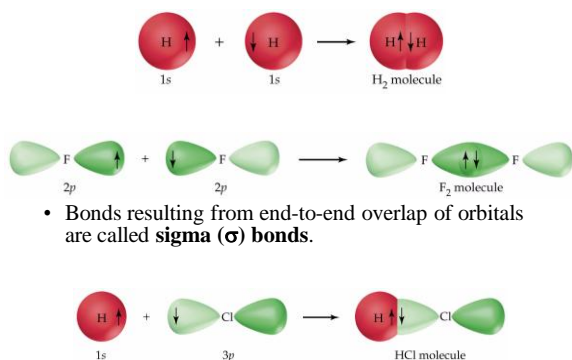
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## Valence Bond Theory (the Localized Electron Model)

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### Sigma ( $\sigma$ ) Bonds



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### Models of Bonding

- VSEPR theory accounts for the shapes of molecules, but does not tell us *how* those shapes come about.
- More advanced models of chemical bonding extend the concepts of quantum mechanics and wave functions/orbitals to describe molecules, and allow very precise calculations to be made about the properties of molecules.
  - Valence Bond (VB) theory** (or the *Localized Electron model*) is a relatively simple model which pictures covalent bonds as arising from the **overlap** of orbitals on adjacent atoms.
  - Molecular Orbital (MO) theory** is a more sophisticated model which pictures covalent bonds forming from *molecular orbitals* delocalized over the entire molecule.

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### Valence Bond Theory

- In valence bond theory, the orbitals which overlap on adjacent atoms are either the standard atomic orbitals (*s, p, d, f*), or *hybridized atomic orbitals* made by combining individual atomic orbitals.
- Covalent bonds result from the overlap of two half-filled orbitals in which the spins of the electrons are paired.
- Each of the bonded atoms maintains its own atomic orbitals, but the electron pair in the overlapping orbitals is shared by both atoms.
- The shape of the molecule is determined by the geometry of the overlapping orbitals.
- The greater the amount of overlap, the stronger the bond. This leads to a directional character to the bond when orbitals other than *s* are involved.

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### Hybrid Orbitals

- The shapes of *s, p,* and *d* orbitals do not account for the shapes of molecules, so we must use *different* orbitals in a molecule from those in isolated atoms.
  - [For instance, carbon's electron configuration has 2 half-filled *p* orbitals  $90^\circ$  from each other, yet carbon forms four bonds to hydrogen atoms to form  $\text{CH}_4$ , with bond angles of  $109.5^\circ$ .]
- The wave functions for the atomic orbitals derived from the Schrödinger equation are mathematically combined to form new wave functions called **hybrid atomic orbitals**.
- The number of hybrid orbitals equals the number of atomic orbitals which combine; we need one hybrid orbital for each electron pair (bond or lone pair).

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### Hybrid Orbitals

Electron groups	Hybrid orbitals	Molecular shape
2 electron groups	→ 2 $sp$ orbitals	→ linear (180°)
3 electron groups	→ 3 $sp^2$ orbitals	→ trigonal planar (120°)
4 electron groups	→ 4 $sp^3$ orbitals	→ tetrahedral (109.5°)
5 electron groups	→ 5 $sp^3d$ orbitals	→ trigonal bipyramidal (90°, 120°)
6 electron groups	→ 6 $sp^3d^2$ orbitals	→ octahedral (90°)

Multiple bonds count as one electron group when deciding which hybridization to use.

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### $sp^3$ Hybridization

- When the  $s$  and all three  $p$  orbitals combine, the resulting hybrid orbitals are  $sp^3$  hybrid orbitals.

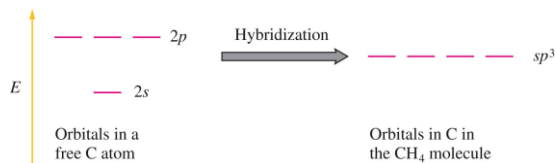


Figure 5.13

- These 4 orbitals point to the corners of a tetrahedron (109.5°).
- $sp^3$  orbitals are used to describe the C atoms in  $CH_4$  and  $C_2H_6$ , the N in  $NH_3$ , and the O in  $H_2O$ .

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### $sp^3$ Hybridization

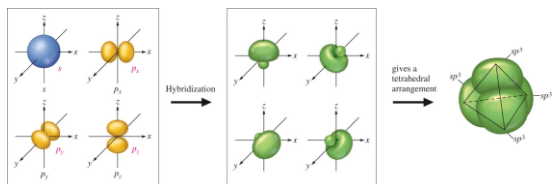


Figure 5.11

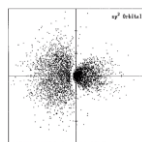


Figure 5.12

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### $sp^3$ Orbitals in Methane, $CH_4$

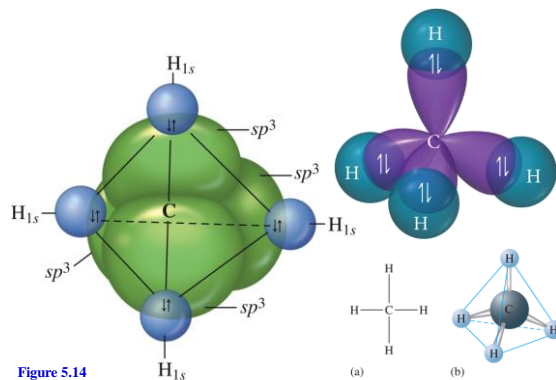


Figure 5.14

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### $sp^3$ Orbitals in Ammonia, $NH_3$

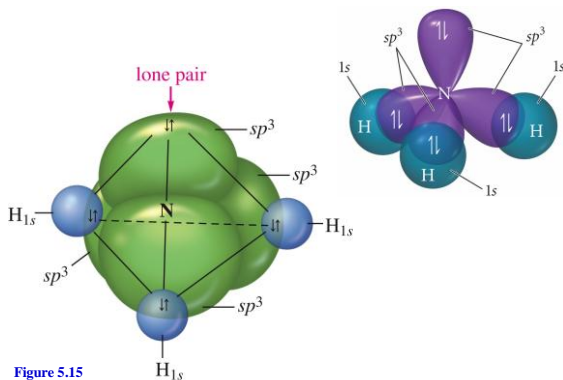
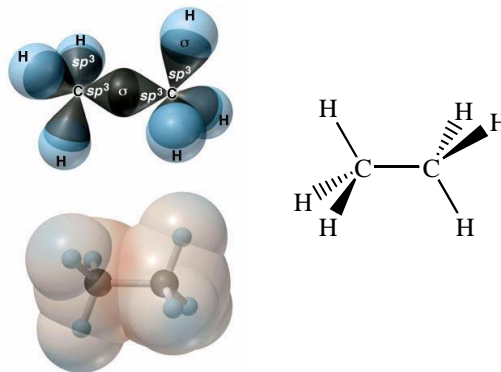


Figure 5.15

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### $sp^3$ Orbitals in Ethane, $C_2H_6$



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### $sp^2$ Hybridization

- When the  $s$  and *two* of the three  $p$  orbitals combine, the resulting hybrid orbitals are  $sp^2$  hybrid orbitals.

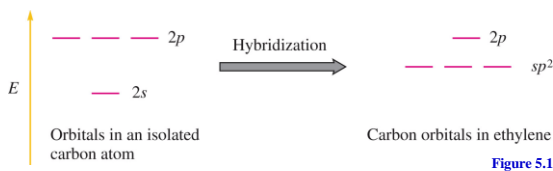


Figure 5.17

- These 3 orbitals point to the corners of an equilateral triangle ( $120^\circ$ ), with the unhybridized  $p$  orbital  $90^\circ$  from this plane.
- $sp^2$  orbitals are used to describe the B atom in  $BF_3$ , and the C atoms in ethylene,  $C_2H_4$ .

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### $sp^2$ Hybridization

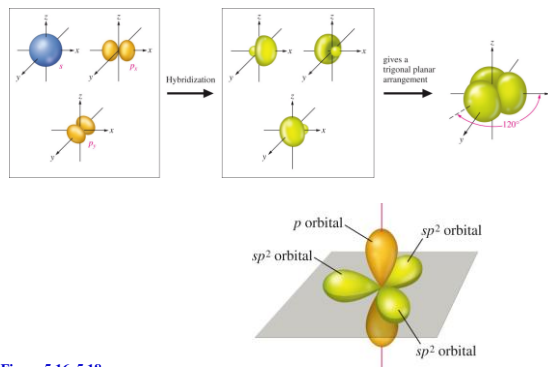
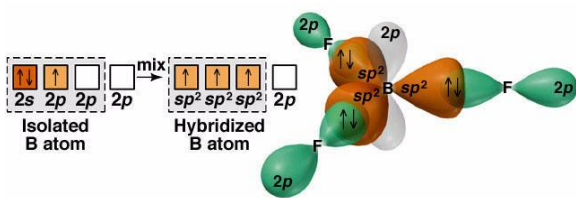


Figure 5.16, 5.18

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### $sp^2$ Orbitals in $BF_3$



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### $sp^2$ Hybridization and $\pi$ Bonds

- When two  $sp^2$ -hybridized atoms are joined, a **double bond** is formed from two types of overlap:
  - a **sigma ( $\sigma$ ) bond** resulting from end-on-end overlap of the  $sp^2$  orbitals.
  - a **pi ( $\pi$ ) bond** resulting from the side-to-side overlap of the  $p$  orbitals.

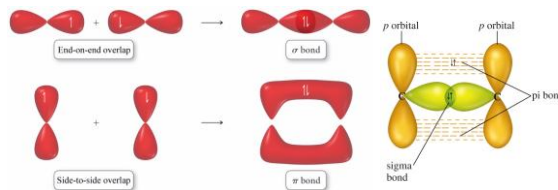


Figure 5.20

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### Single Bonds and Double Bonds in VB Theory

- A **sigma ( $\sigma$ ) bond** results from the **end-to-end** overlap of cylindrical ( $p$ ,  $sp$ ,  $sp^2$ ,  $sp^3$ , etc.) or spherical ( $s$ ) orbitals.
  - $\sigma$ -bonds are *cylindrically symmetrical*, and there is free rotation around them.
  - All single bonds are  $\sigma$ -bonds.
- A **pi ( $\pi$ ) bond** results from the **side-to-side** overlap of  $p$  orbitals on  $sp^2$ - or  $sp$ - hybridized atoms.
  - $\pi$ -bonds have regions of electron density above and below the  $\sigma$ -bond axis; free rotation is not allowed around a  $\pi$ -bond.
  - A double bond is a  $\sigma$ -bond + a  $\pi$ -bond.
  - A triple bond is a  $\sigma$ -bond + 2  $\pi$ -bonds.

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### $sp^2$ Orbitals in Ethylene, $C_2H_4$

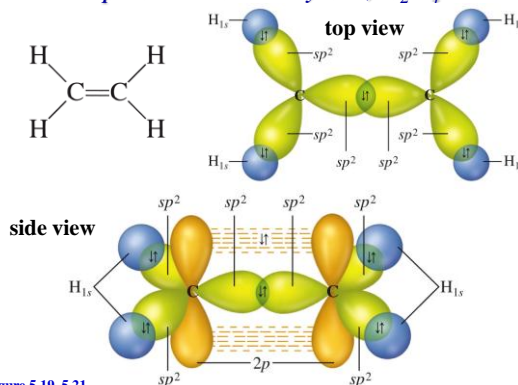
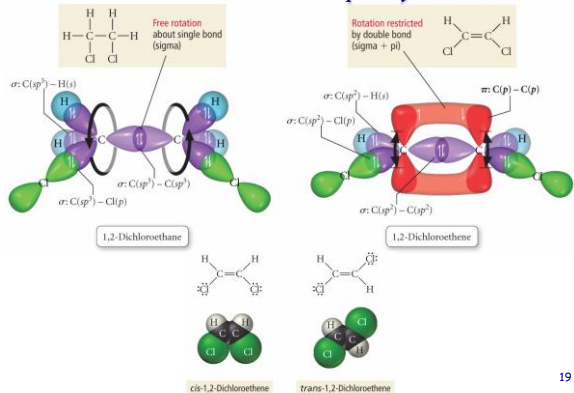


Figure 5.19, 5.21

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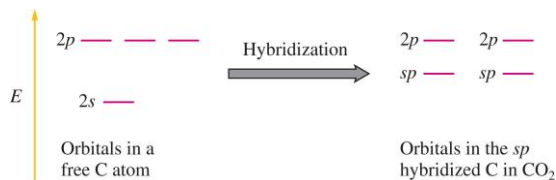
### Cis and Trans Isomers in $sp^2$ -Hybridization



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### $sp$ Hybridization

- When the  $s$  and *one* of the three  $p$  orbitals combine, the resulting hybrid orbitals are  $sp$  hybrid orbitals.



- These 2 orbitals point 180° from each other, with the unhybridized  $p$  orbitals at 90° angles from this line.
- $sp$  orbitals are used to describe the Be atom in  $BeCl_2$ , and the C atoms in acetylene,  $C_2H_2$ .

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### $sp$ Hybridization

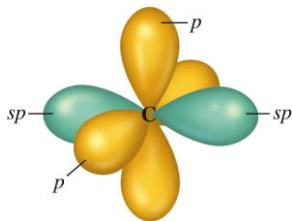
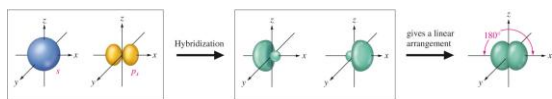
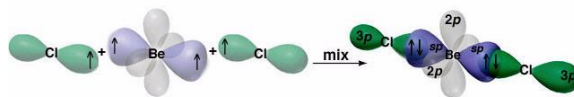


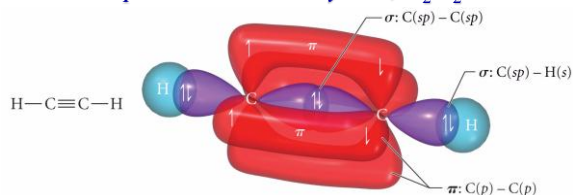
Figure 5.22, 5.25

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### $sp$ Orbitals in $BeCl_2$



### $sp$ Orbitals in Acetylene, $C_2H_2$



### $sp$ Orbitals in $CO_2$

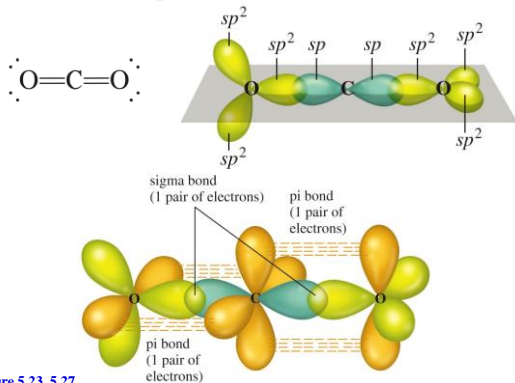


Figure 5.23, 5.27

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### $sp$ Orbitals in $N_2$

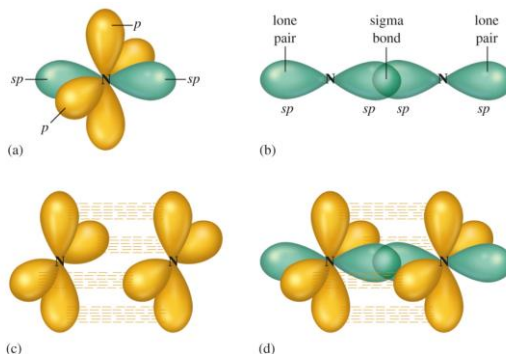


Figure 5.28

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### $sp^3d$ and $sp^3d^2$ Hybridization

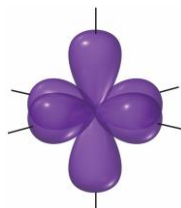
- The  $s$  and the three  $p$  orbitals can also combine with  $d$  orbitals in molecules with expanded octets:

$$-s + p + p + p + d = sp^3d \text{ hybrid orbitals}$$

$$-s + p + p + p + d + d = sp^3d^2 \text{ hybrid orbitals}$$



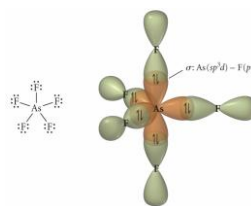
$sp^3d$  hybrid orbitals (shown together)



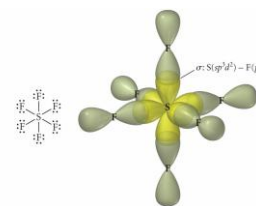
$sp^3d^2$  hybrid orbitals (shown together)

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### $sp^3d$ Orbitals in $AsF_5$ ; $sp^3d^2$ Orbitals in $SF_6$



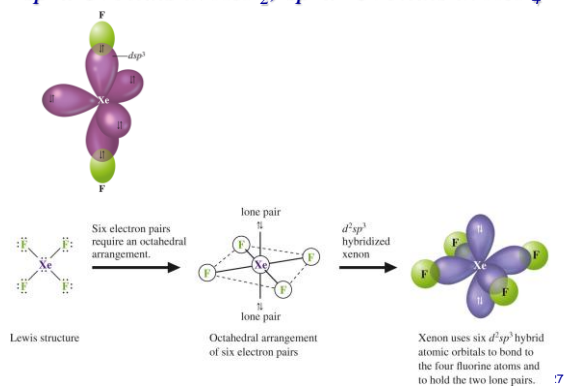
$sp^3d$  hybrid orbitals in  $AsF_5$



$sp^3d^2$  hybrid orbitals in  $SF_6$

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### $sp^3d$ Orbitals in $XeF_2$ ; $sp^3d^2$ Orbitals in $XeF_4$



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### Summary of Hybrid Orbitals

Number of Effective Pairs	Arrangement of Pairs	Hybridization Required
2	Linear	$sp$
3	Trigonal planar	$sp^2$
4	Tetrahedral	$sp^3$
5	Trigonal bipyramidal	$d^2sp^3$
6	Octahedral	$d^2sp^3$

Figure 5.32

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### Examples: Shape and Hybridization

- Write Lewis structures for the following molecules. Determine their electron-group shape and molecular shape, state whether or not the molecules will be polar, and the hybridization on the central atom.

- $BF_3$
- $NH_3$
- $SF_2$
- $CF_4$
- $NO_3^-$

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### Examples: Shape and Hybridization

- Write Lewis structures for the following molecules. Determine their electron-group shape and molecular shape, state whether or not the molecules will be polar, and the hybridization on the central atom.

- $PF_3$
- $HCN$
- $I_3^-$
- $SF_4$
- $XeF_4$

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# Molecular Orbital Theory

## Molecular Orbital Theory

- The valence bond model is easy to visualize, and works well for most molecules, but it does not describe magnetic and spectral properties well. A more complex model must be used to explain these phenomena.
- In **Molecular Orbital (MO) theory**, electrons occupy **molecular orbitals** that belong to the *entire molecule* rather than to an individual atom.
- Atomic or hybrid orbitals overlap with each other to form molecular orbitals. This overlap results in both *constructive* and *destructive* interference between the orbitals.
- The number of molecular orbitals formed is the same as the number of atomic orbitals which are combined.

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## Constructive and Destructive Interference

- Additive combinations** (resulting from *constructive* interference between atomic orbitals) form **bonding molecular orbitals** ( $\sigma$ ,  $\pi$ ).
  - These are *lower* in energy than the atomic orbitals.
  - The electrons in these orbitals spend most of their time in the region *in between* the nuclei, helping to bond the atoms together.
- Subtractive combinations** (resulting from *destructive* interference between atomic orbitals) form **antibonding molecular orbitals** ( $\sigma^*$ ,  $\pi^*$ ).
  - These are *higher* in energy than the atomic orbitals.
  - The electrons in these orbitals can't occupy the node in the central region and don't contribute to bonding.

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## Molecular Orbitals in the $H_2$ Molecule

- When two isolated H atoms interact with each other, their  $1s$  orbitals blend together, and the electrons spread out over both atoms, in both additive and subtractive combinations:

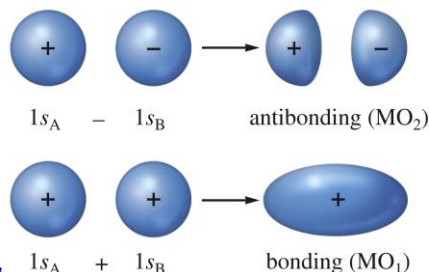


Figure 5.33

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## Molecular Orbitals in the $H_2$ Molecule

- The two electrons which used to be in the separate  $1s$  orbitals now reside in the  $\sigma$  bonding molecular orbital, resulting in a molecule which is lower in energy than the separate H atoms:

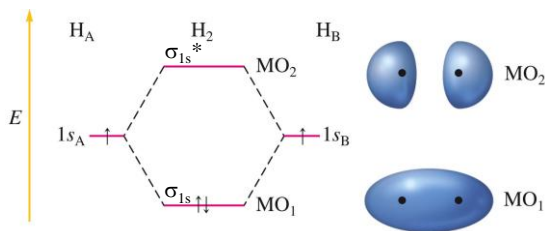


Figure 5.34

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## Why Doesn't $He_2$ Form?

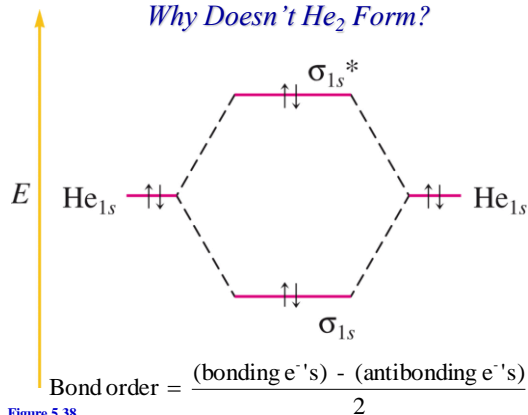
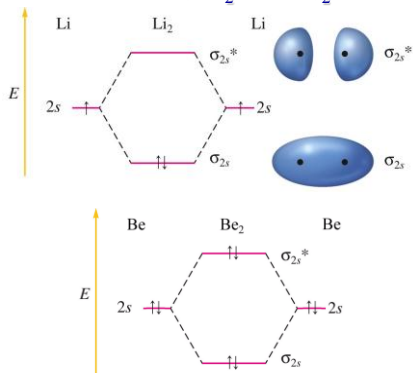


Figure 5.38

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*Diatomic Li<sub>2</sub> and Be<sub>2</sub>*



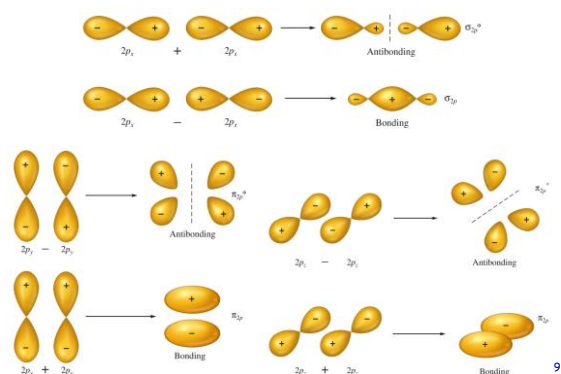
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*MO Theory and Other Diatomic Molecules*

- We will only look at **homonuclear diatomic molecules**, which are composed of two identical atoms (e.g., H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub>).
- In the simple VB model, the electrons in the O<sub>2</sub> molecule are all paired; experimentally, however, O<sub>2</sub> is found to be paramagnetic.
- The more mathematically sophisticated MO model predicts the correct electronic properties for O<sub>2</sub>.
- In the following slides, the  $\sigma_{2s}$  and  $\sigma_{2s}^*$  orbitals are produced from overlapping  $2s$  orbitals; the  $\sigma_{2p}$  and  $\sigma_{2p}^*$  orbitals are produced from end-to-end overlap of  $2p$  orbitals; the  $\pi_{2p}$  and  $\pi_{2p}^*$  orbitals are produced from side-to-side overlap of  $2p$  orbitals.

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*$\sigma$ ,  $\sigma^*$ ,  $\pi$ , and  $\pi^*$  MO's from  $p$  Atomic Orbitals*



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*MO Energy Diagrams for B<sub>2</sub> through Ne<sub>2</sub>*

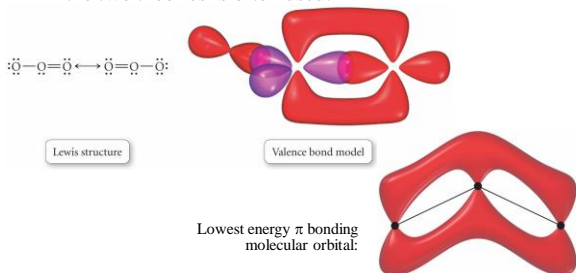
	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>
↑ E	$\sigma_{2p}^*$ —	—	—	$\sigma_{2p}^*$ —	—
	$\pi_{2p}^*$ —	—	—	$\pi_{2p}^*$ + + + +	+ + + +
	$\sigma_{2p}$ —	—	—	$\pi_{2p}$ + + + +	+ + + +
	$\pi_{2p}$ + + + +	+ + + +	+ + + +	$\sigma_{2p}$ —	—
	$\sigma_{2p}^*$ + + + +	+ + + +	+ + + +	$\sigma_{2p}^*$ + + + +	+ + + +
	$\sigma_{2s}$ + + + +	+ + + +	+ + + +	$\sigma_{2s}$ + + + +	+ + + +
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

Figure 5.46

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*Combining VB and MO Theory*

- Valence bond theory is conceptually simpler, and works well for describing  $\sigma$  bonds; but molecular orbital theory is more accurate, and is better at describing  $\pi$  bonds. In practice, a combination of the two theories is often used.



*Molecular Orbitals in Benzene, C<sub>6</sub>H<sub>6</sub>*

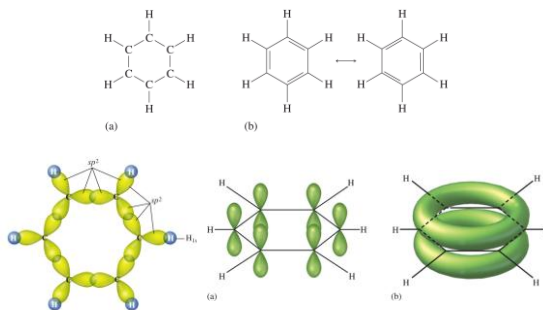


Figure 5.53, 5.54, 5.55

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