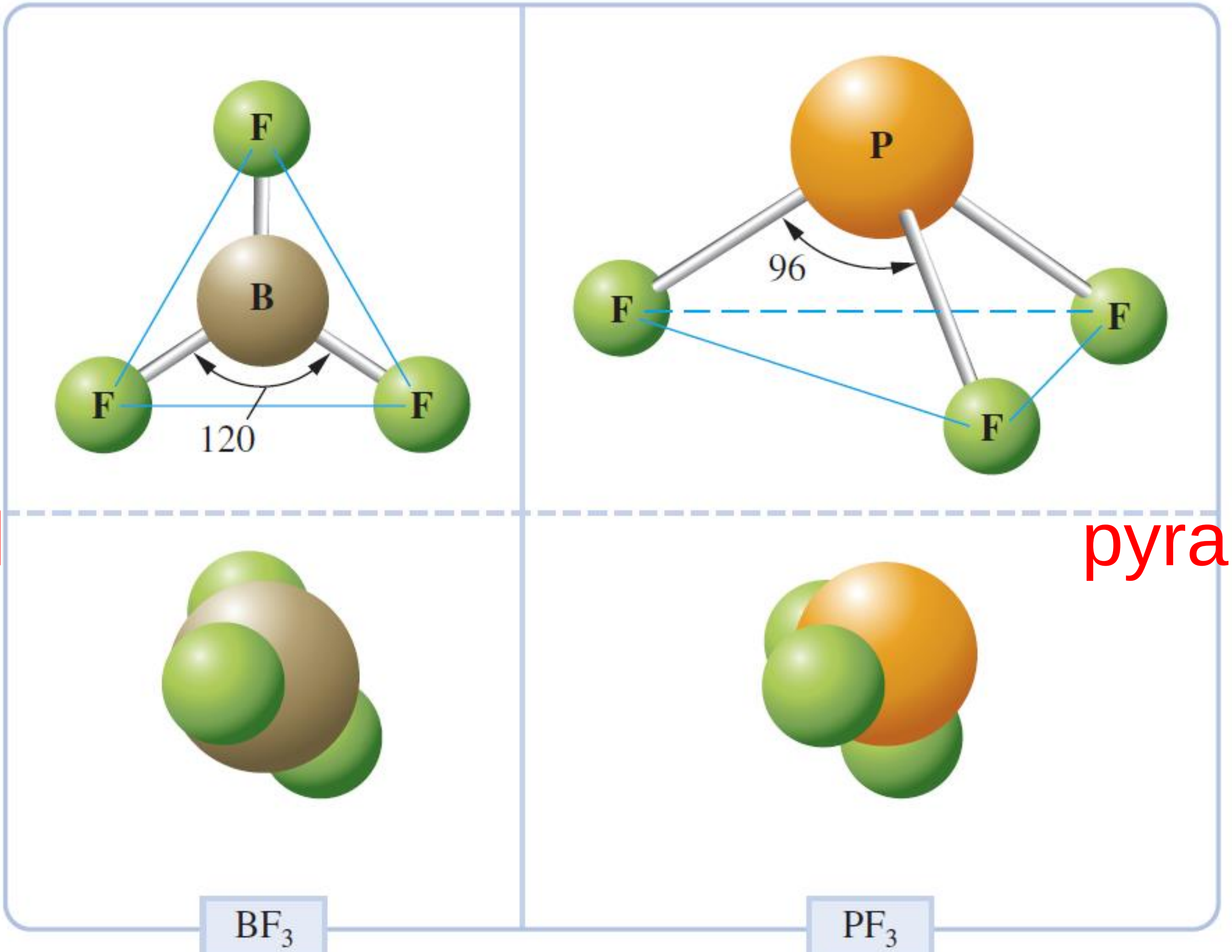
CHAPTER 10 MOLECULAR GEOMETRY AND CHEMICAL BONDING THEORY

Dr. Yuan Dan

10. Molecular Geometry and Chemical Bonding Theory

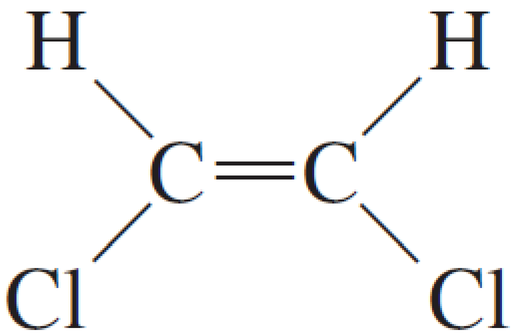
trigonal planar



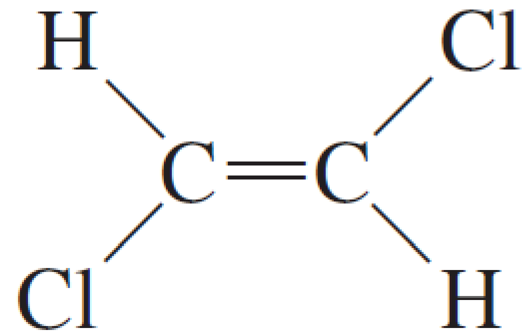
pyramidal

10. Molecular Geometry and Chemical Bonding Theory

isomers



cis-1,2-Dichloroethene



trans-1,2-Dichloroethene

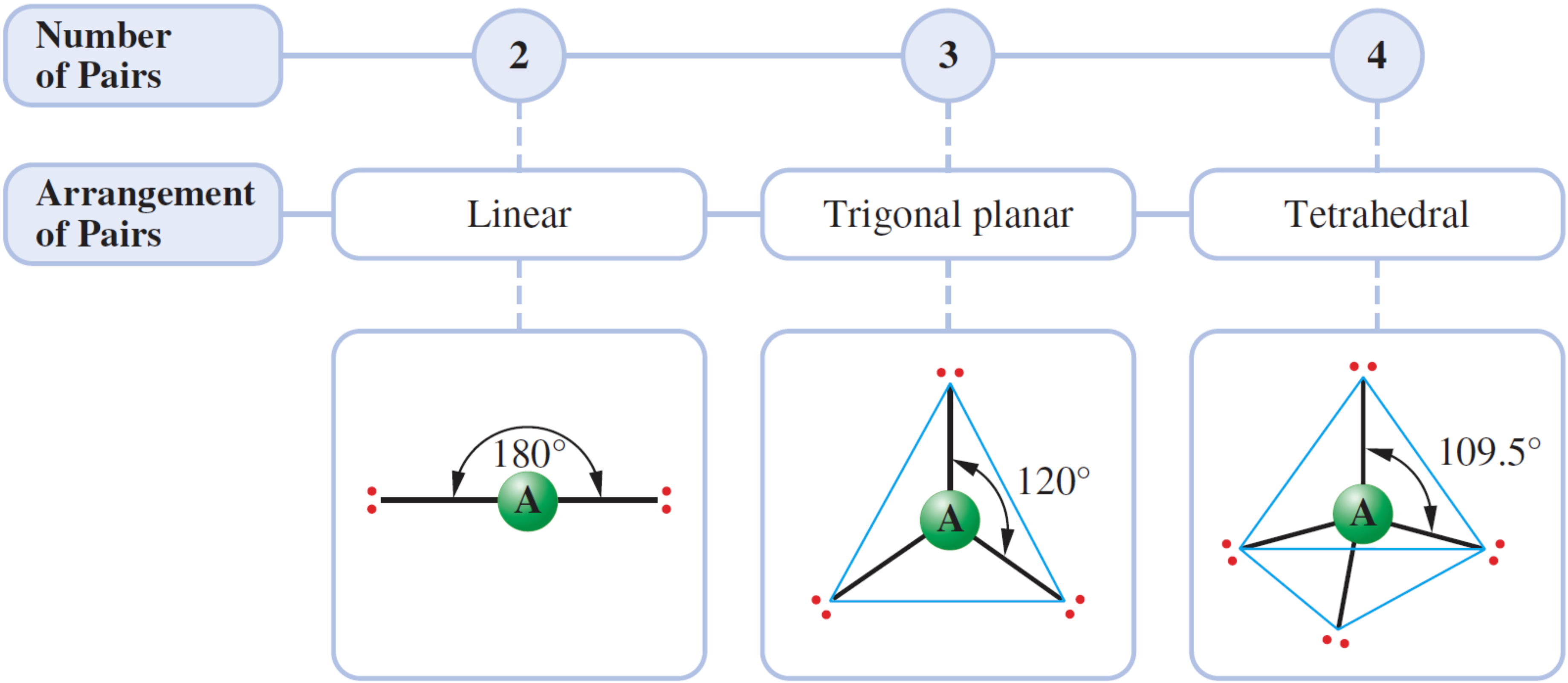
Molecular geometry: the general shape of a molecule, as determined by the relative positions of the atomic nuclei.

10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- valence-shell electron-pair repulsion (VSEPR) model: predicts the shapes of molecules and ions by assuming that the valence-shell electron pairs are arranged about each atom so that electron pairs are kept as far away from one another as possible, thus minimizing electron-pair repulsions.

10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- VSEPR model



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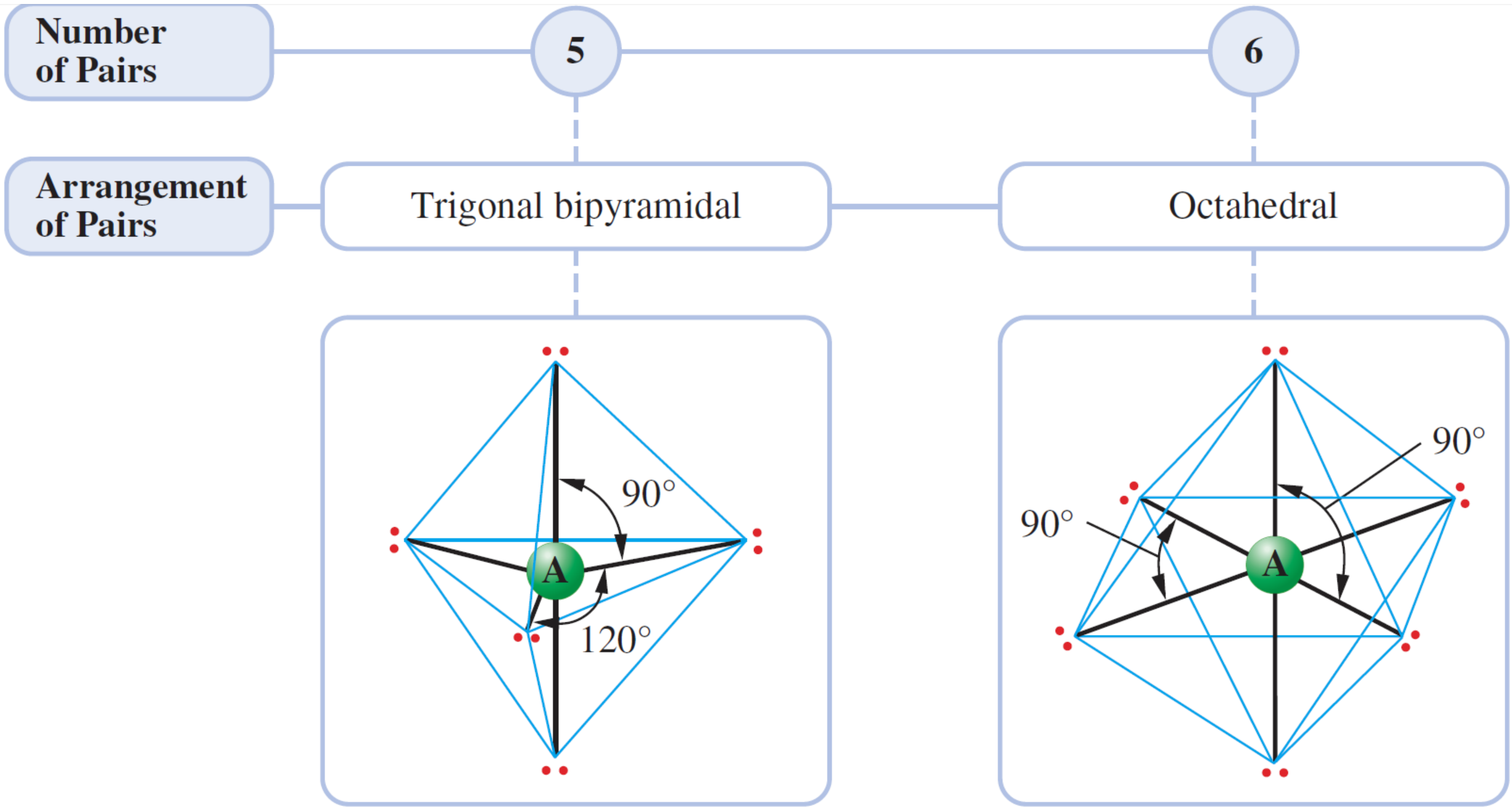
- VSEPR model



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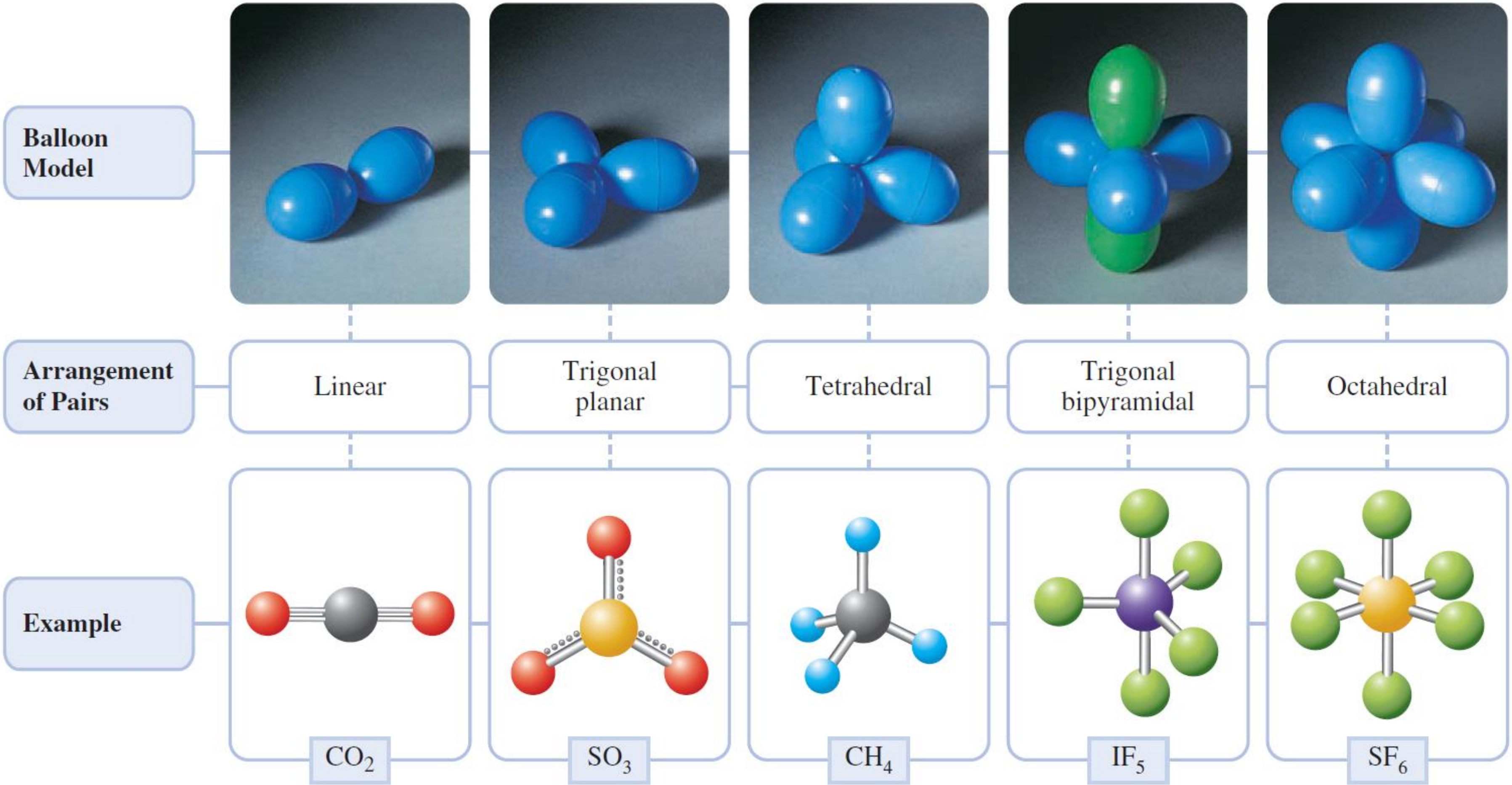
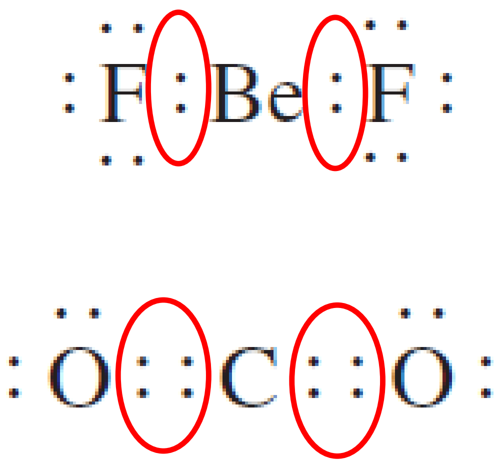
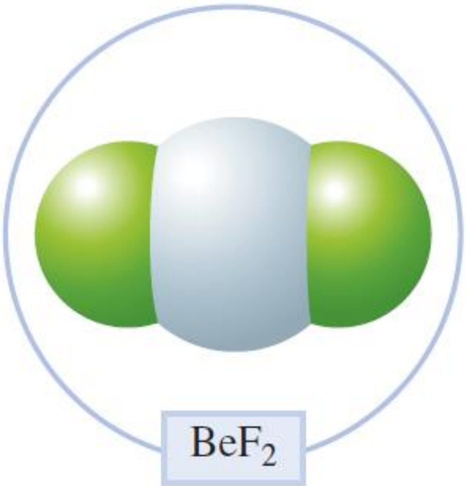
- VSEPR model

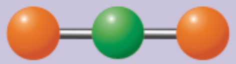


10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- Two Electron Pairs (Linear Arrangement)

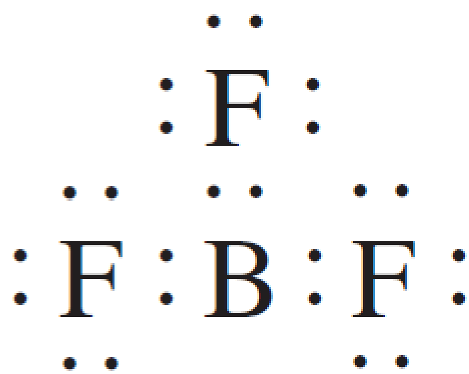


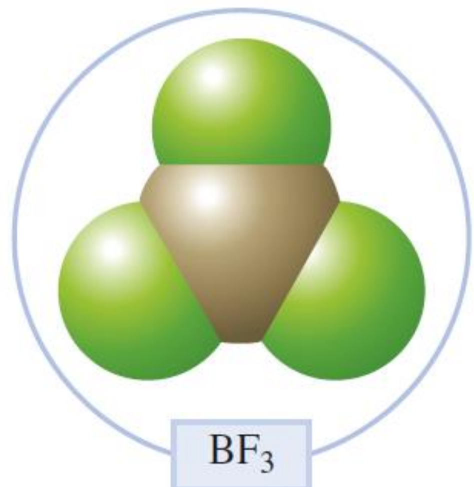


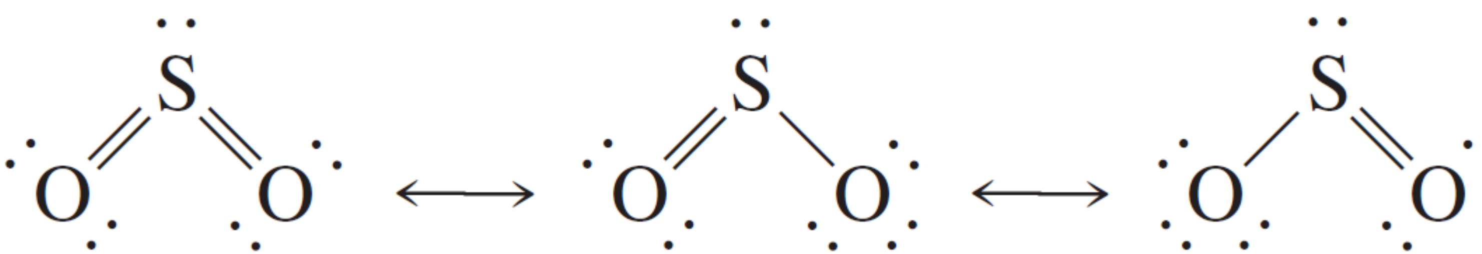
Electron Pairs			Arrangement of Pairs	Molecular Geometry		Example	
Total	Bonding	Lone					
2	2	0	Linear	Linear AX_2		BeF_2	**F—Be—F**

10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- Three Electron Pairs (Trigonal Planar Arrangement)







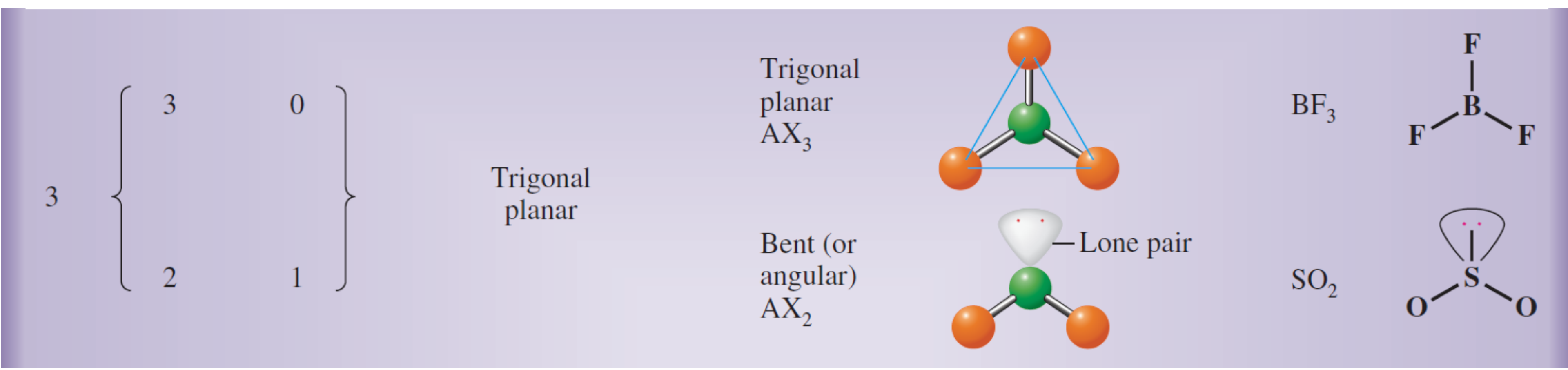
bent, or angular

10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- Three Electron Pairs (Trigonal Planar Arrangement)

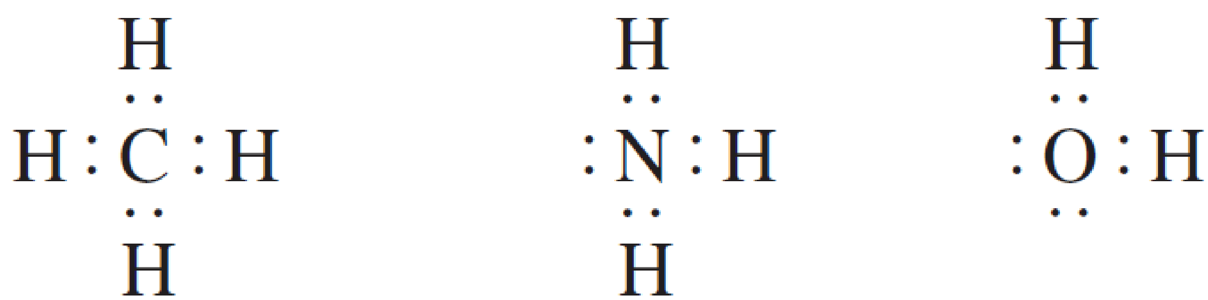
arrangement of electron pairs

molecular geometry



10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

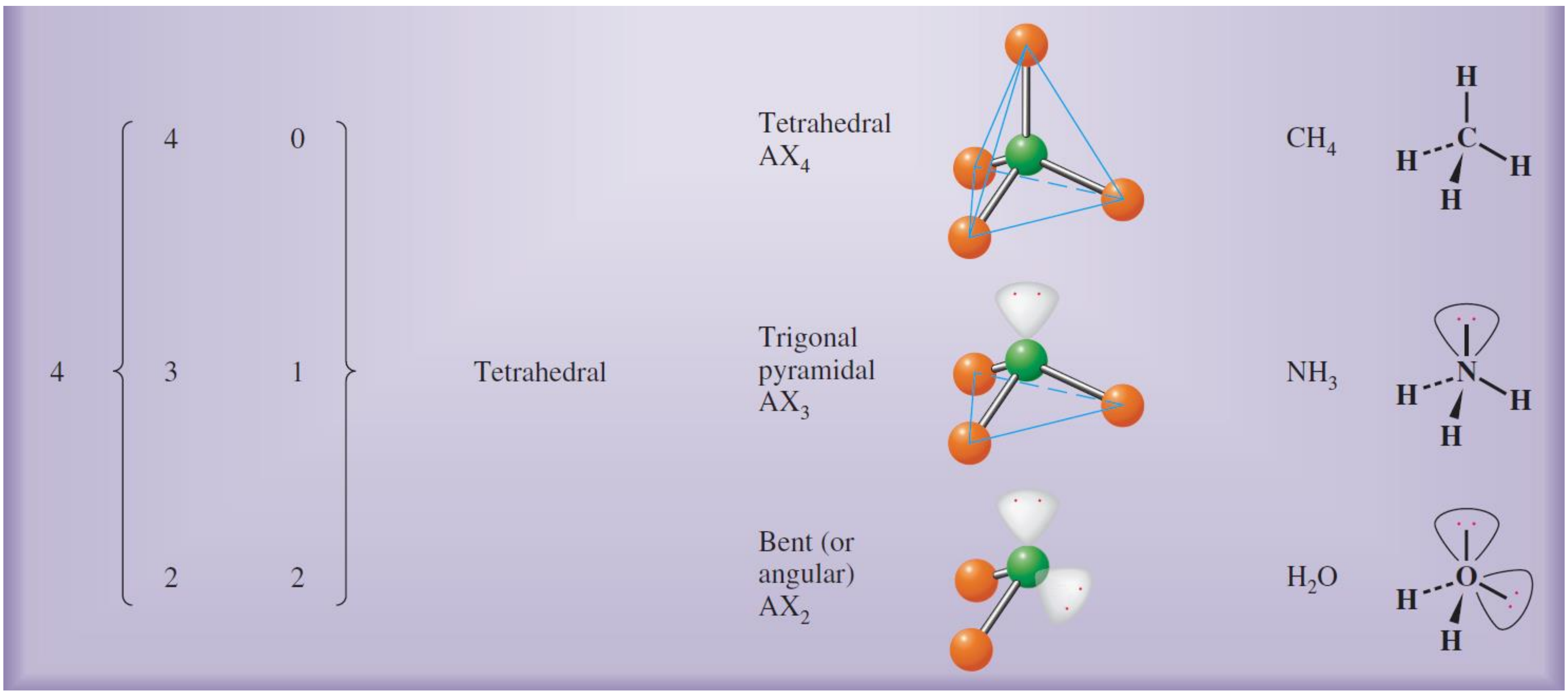
- Four Electron Pairs (Tetrahedral Arrangement)



	CH_4	NH_3	H_2O
Molecular geometry:	tetrahedral	trigonal pyramidal	bent

10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- Four Electron Pairs (Tetrahedral Arrangement)



10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- Steps in the Prediction of Geometry by the VSEPR Model

1. Write the electron-dot formula from the molecular formula
2. Determine the number of electron pairs around the central atom

10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

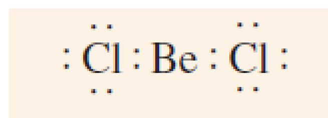
- Steps in the Prediction of Geometry by the VSEPR Model

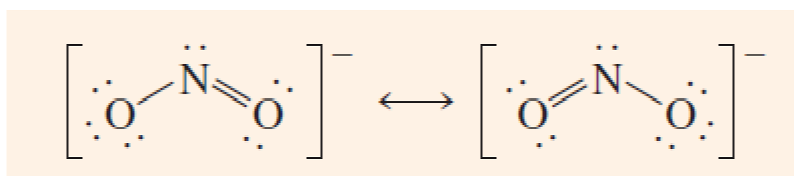
3. Determine the arrangement of these electron pairs about the central atom
4. Obtain the molecular geometry from the directions of the bonding pairs for this arrangement

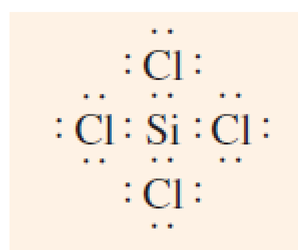
P379 Example 10.1

Predict the geometry of the following molecules or ions, using the VSEPR method: a. $BeCl_2$; b. NO_2^-; c. $SiCl_4$.

linear bent tetrahedral



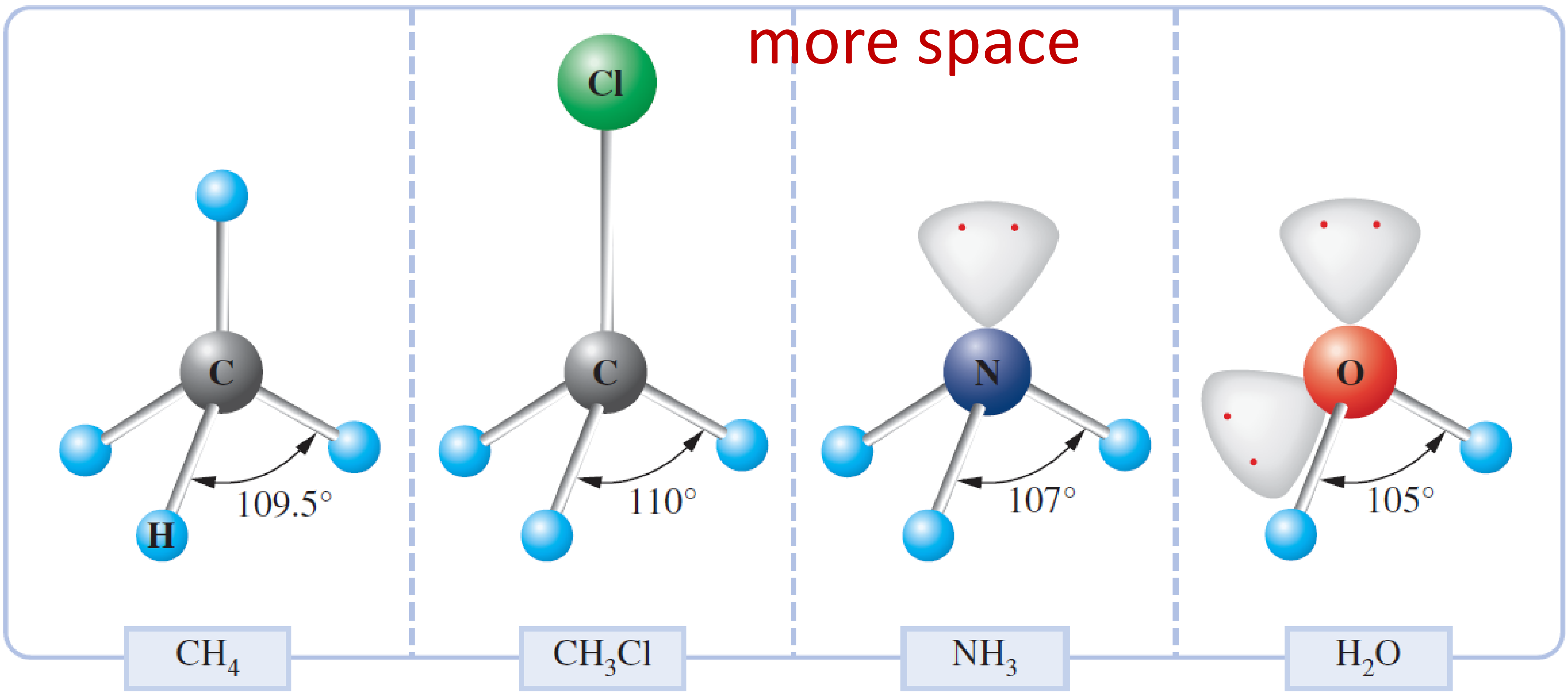




10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- Bond Angles and the Effect of Lone Pairs

A lone pair tends to require more space

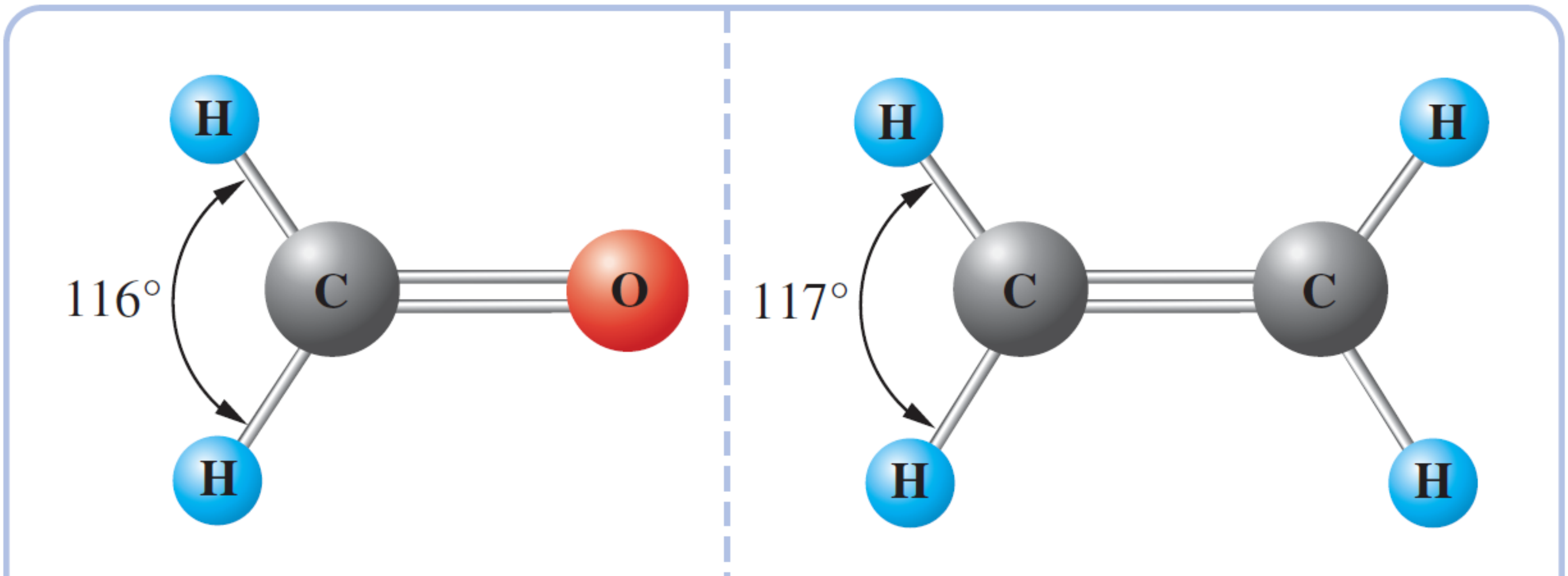


10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- Bond Angles and the Effect of Lone Pairs

Multiple bonds require more space than single bonds because of the greater number of electrons

< 120°

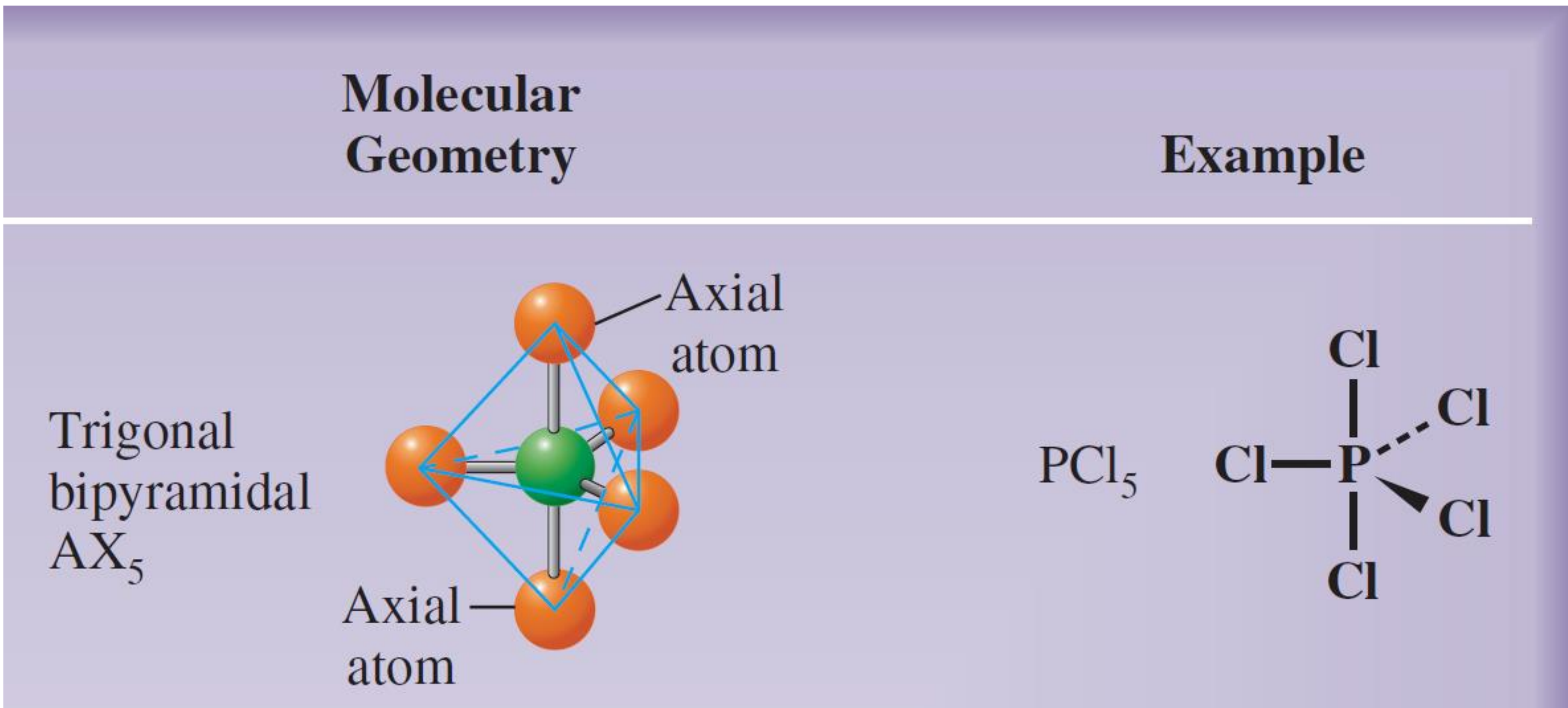


CH_2O

CH_2CH_2

10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- Five Electron Pairs (Trigonal Bipyramidal Arrangement)



10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

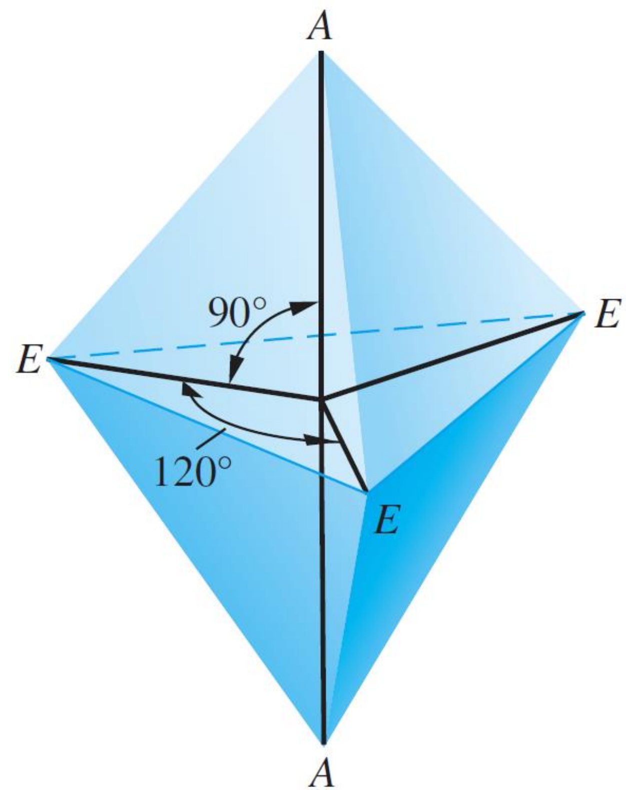
- Five Electron Pairs (Trigonal Bipyramidal Arrangement)

axial directions

Five vertexes

Bond angles not the same

equatorial directions



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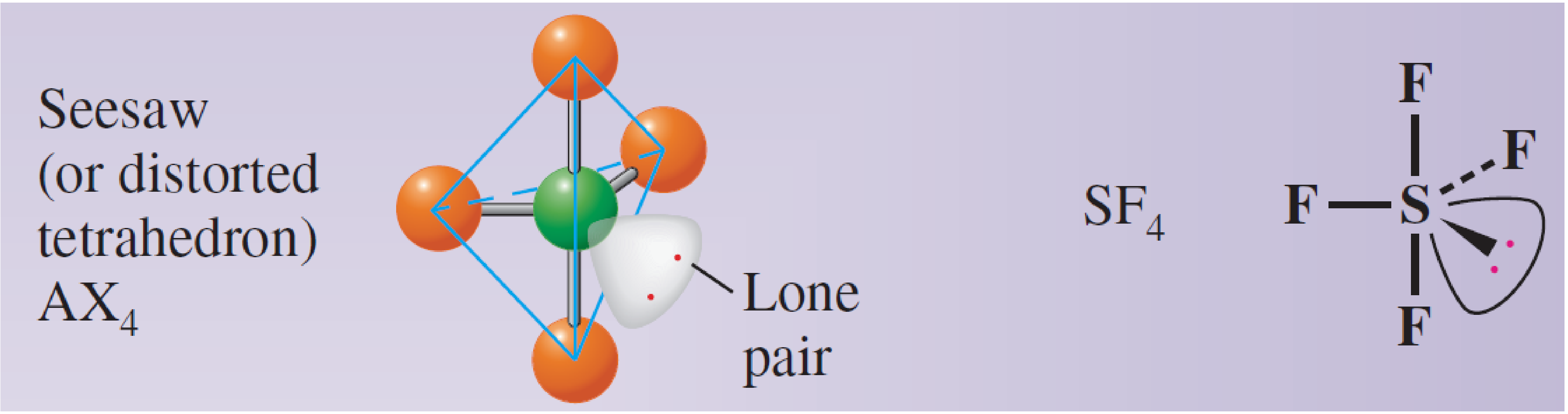

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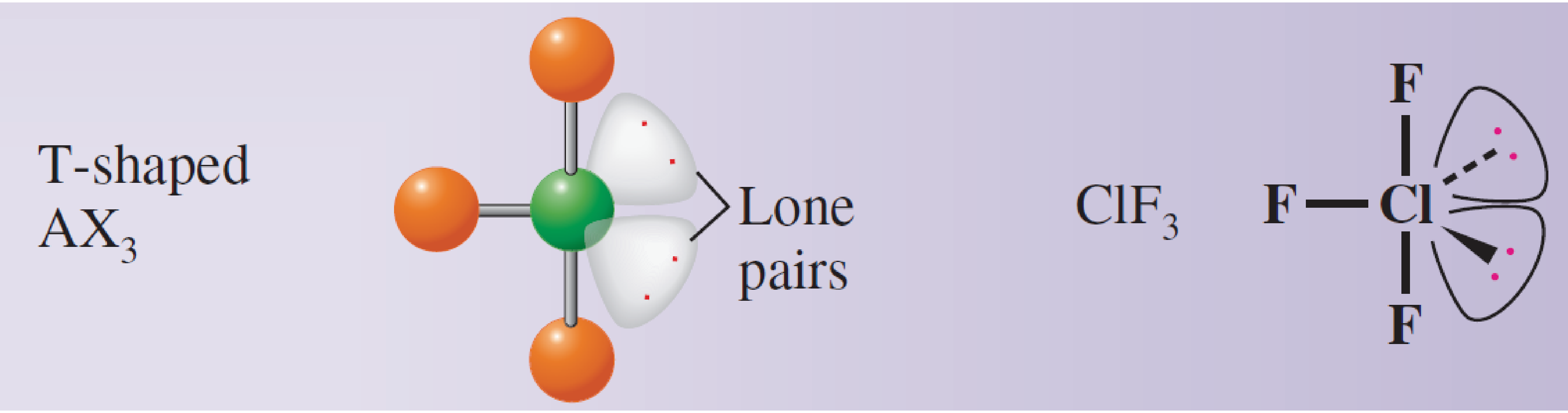

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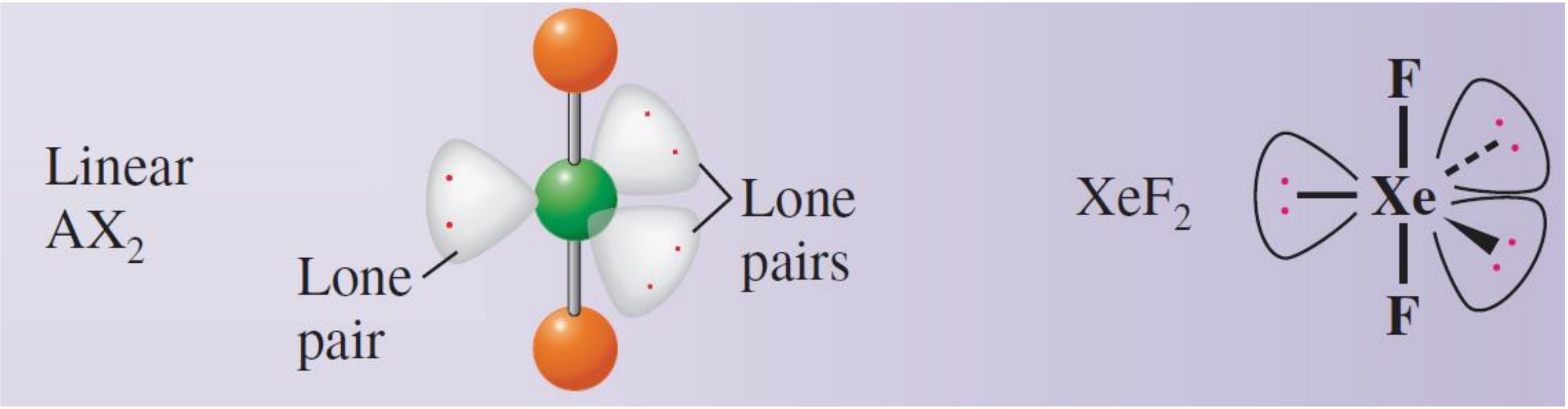
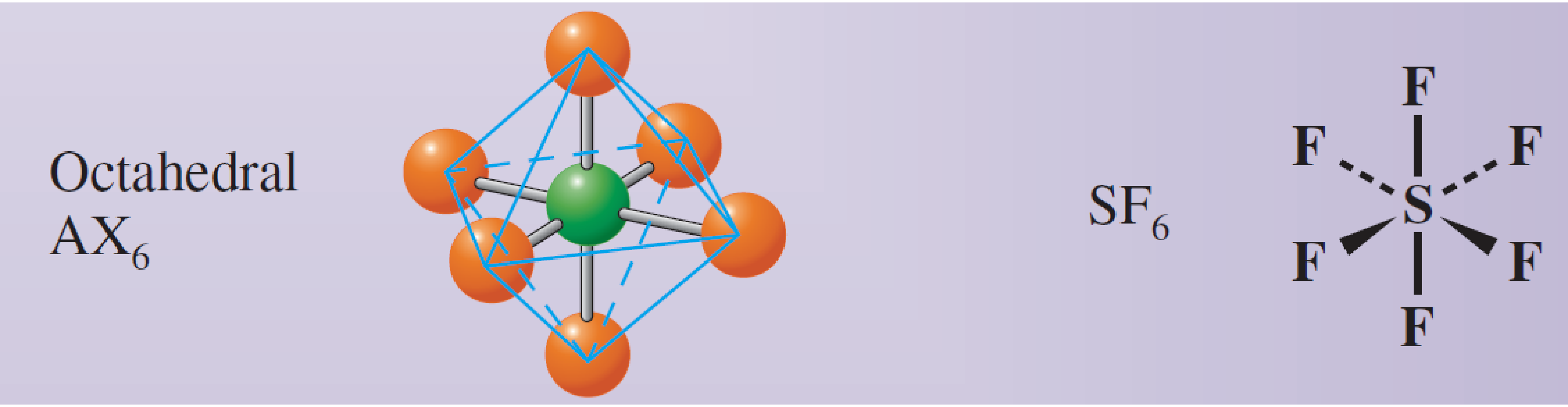


10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- Six Electron Pairs (Octahedral Arrangement)



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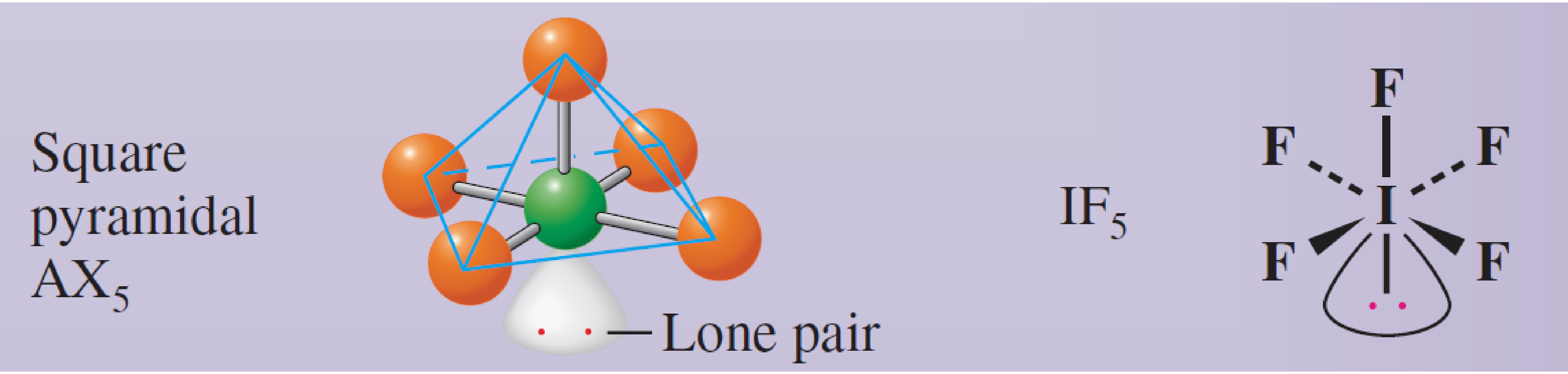

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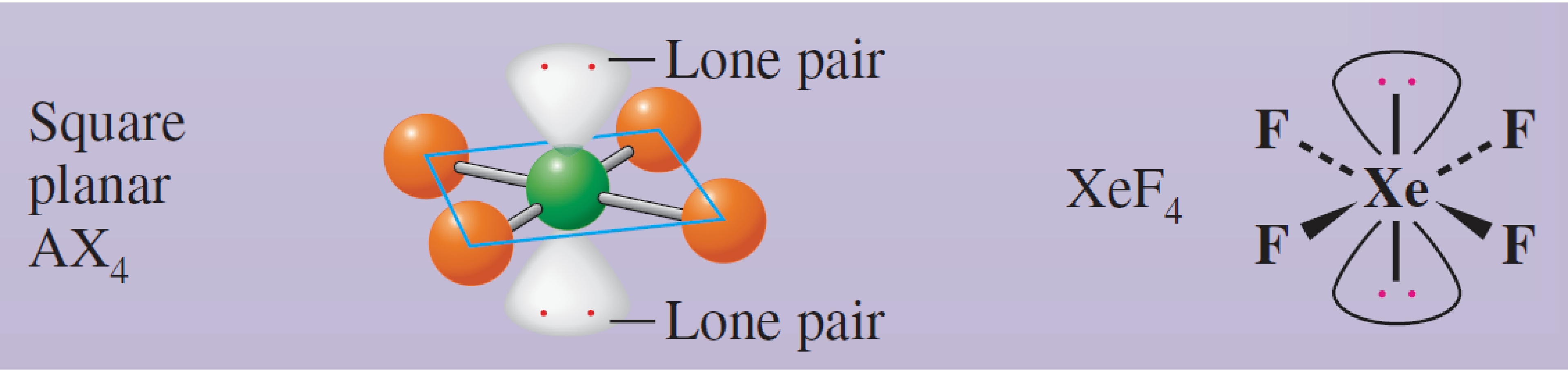
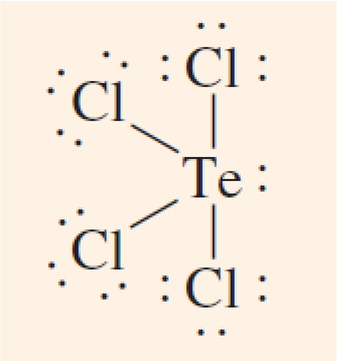


P383 Example 10.2

What do you expect for the geometry of tellurium tetrachloride, $TeCl_4$? seesaw



10.2 Dipole Moment and Molecular Geometry

- dipole moment: a quantitative measure of the degree of charge separation in a molecule

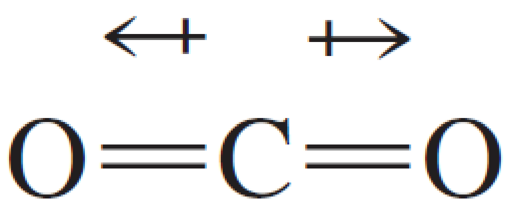
$$\overset{\delta^{+}}{\mathrm{H}}-\overset{\delta^{-}}{\mathrm{Cl}}$$

- polar molecules: molecules having a dipole moment

10.2 Dipole Moment and Molecular Geometry

- relate the presence or absence of a dipole moment in a molecule to its molecular geometry

$$\overset{\delta^-}{O}=\overset{2\delta^+}{C}=\overset{\delta^-}{O}$$



Dipole is a vector quantity. It has both magnitude and direction.

10.2 Dipole Moment and Molecular Geometry

Table 10.1 Relationship Between Molecular Geometry and Dipole Moment

Formula	Molecular Geometry	Dipole Moment*
AX	Linear	Can be nonzero
AX_2	Linear	Zero
	Bent	Can be nonzero
AX_3	Trigonal planar	Zero
	Trigonal pyramidal	Can be nonzero
	T-shaped	Can be nonzero
AX_4	Tetrahedral	Zero
	Square planar	Zero
	Seesaw	Can be nonzero
AX_5	Trigonal bipyramidal	Zero
	Square pyramidal	Can be nonzero
AX_6	Octahedral	Zero

*All X atoms are assumed to be identical.

P387 Example 10.3

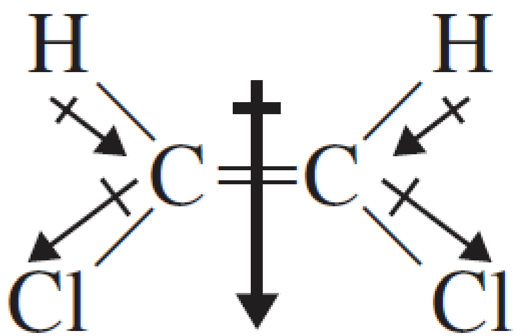
Each of the following molecules has a nonzero dipole moment. Select the molecular geometry that is consistent with this information. Explain your reasoning.

a. SO_2 linear, bent

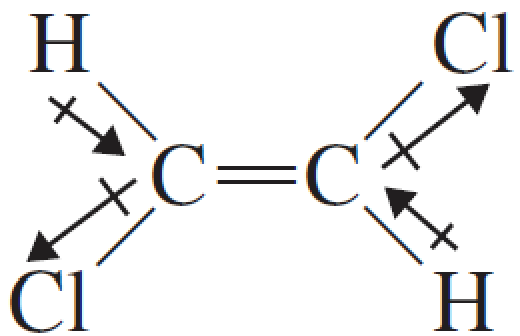
b. PH_3 trigonal planar, trigonal pyramidal

10.2 Dipole Moment and Molecular Geometry

- Effect of Polarity on Molecular Properties



cis-1,2-Dichloroethene



trans-1,2-Dichloroethene

	cis	*trans*
Boiling point	60 °C	48 °C
Polarity	polar	non-polar

10.3 Valence Bond Theory

- Basic Theory

a bond forms between two atoms when：

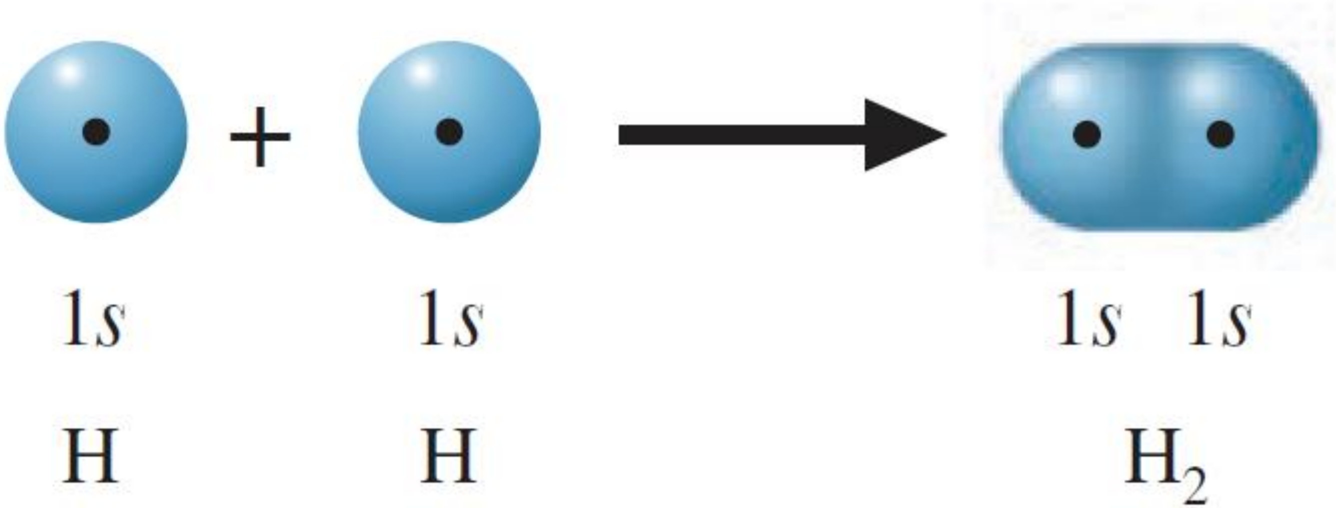
(1) Two orbitals overlap;

the greater the overlap, the greater the bond strength

(2) The total number of electrons in both orbitals is no more than two.

10.3 Valence Bond Theory

- Basic Theory

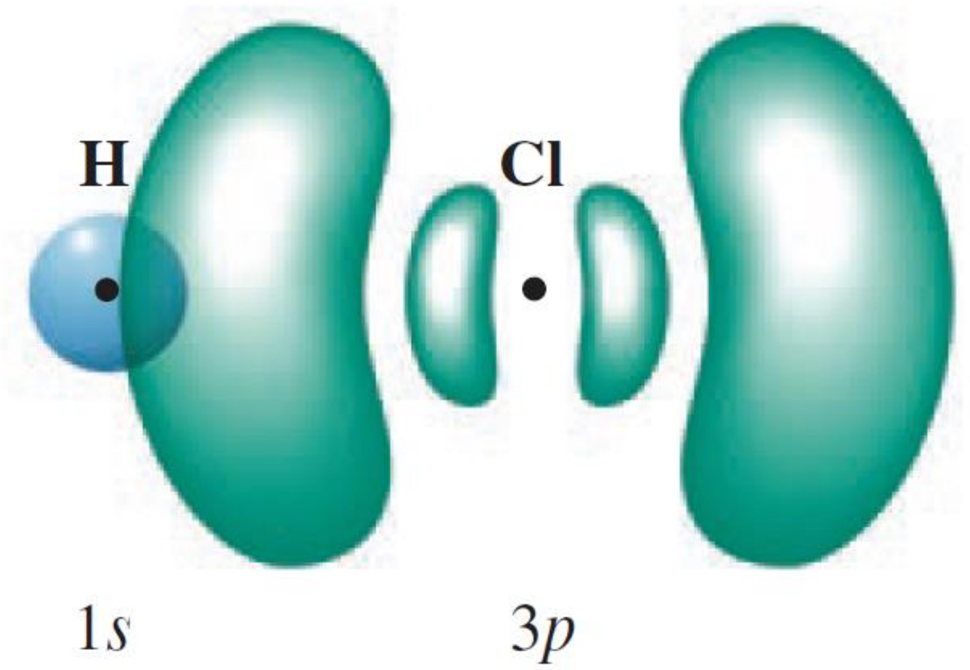


He_2 ✗

10.3 Valence Bond Theory

- Basic Theory

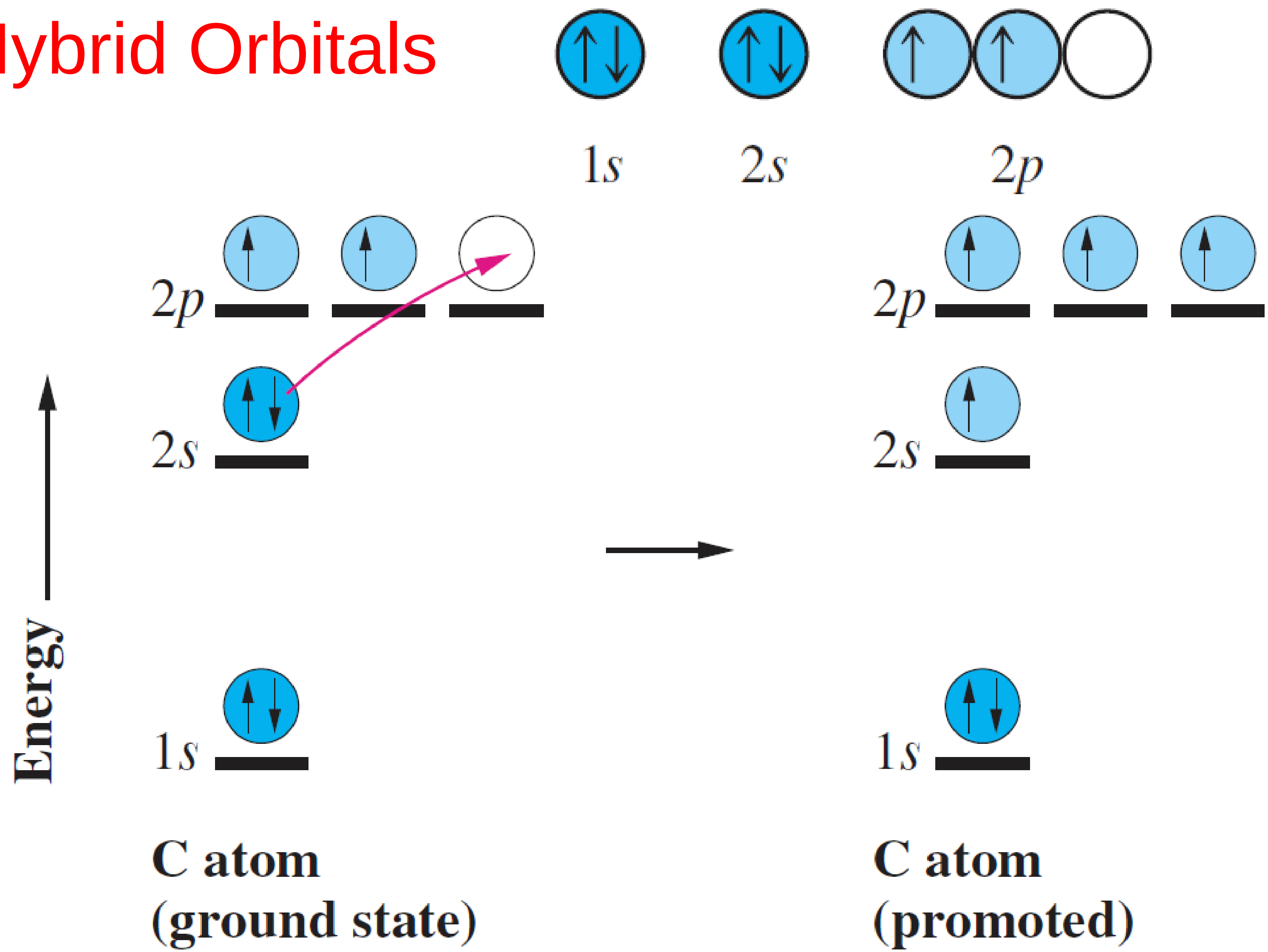
Orbitals bond in the directions in which they protrude or point, to obtain maximum overlap.



Along bond axis

10.3 Valence Bond Theory

- Hybrid Orbitals

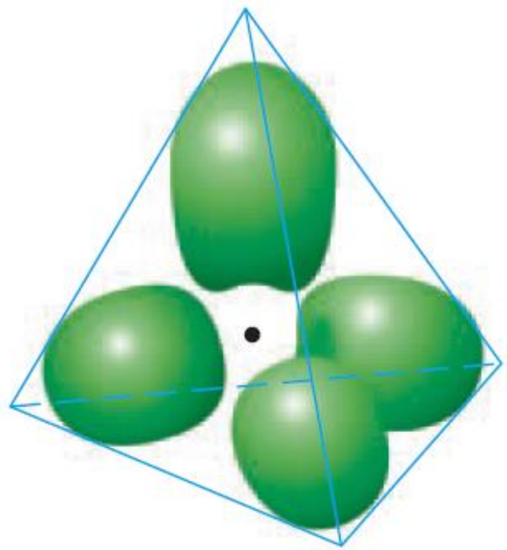


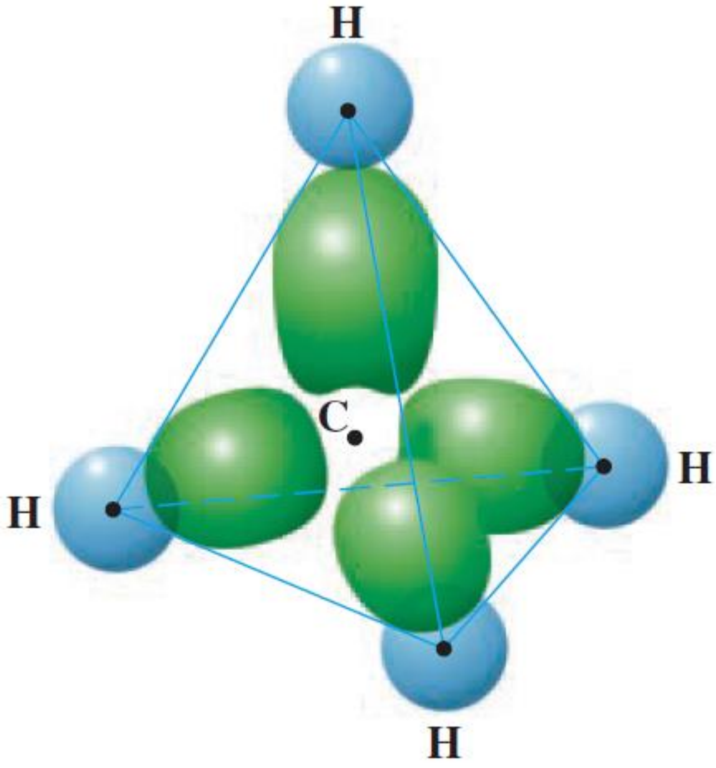
10.3 Valence Bond Theory

- Hybrid Orbitals: orbitals used to describe bonding that are obtained by taking combinations of atomic orbitals of the isolated atoms

10.3 Valence Bond Theory

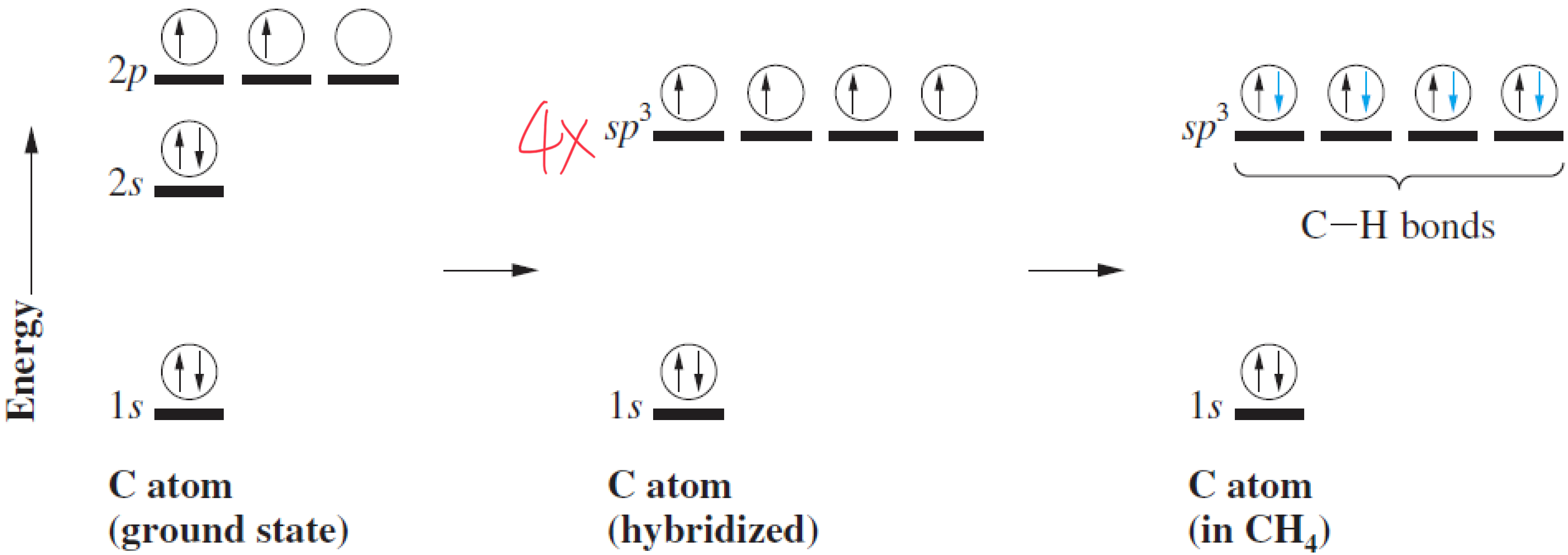
- *sp*^{3} Hybrid Orbitals





10.3 Valence Bond Theory

- Hybrid Orbitals



10.3 Valence Bond Theory

- Hybrid Orbitals sp^n 1+n个轨道

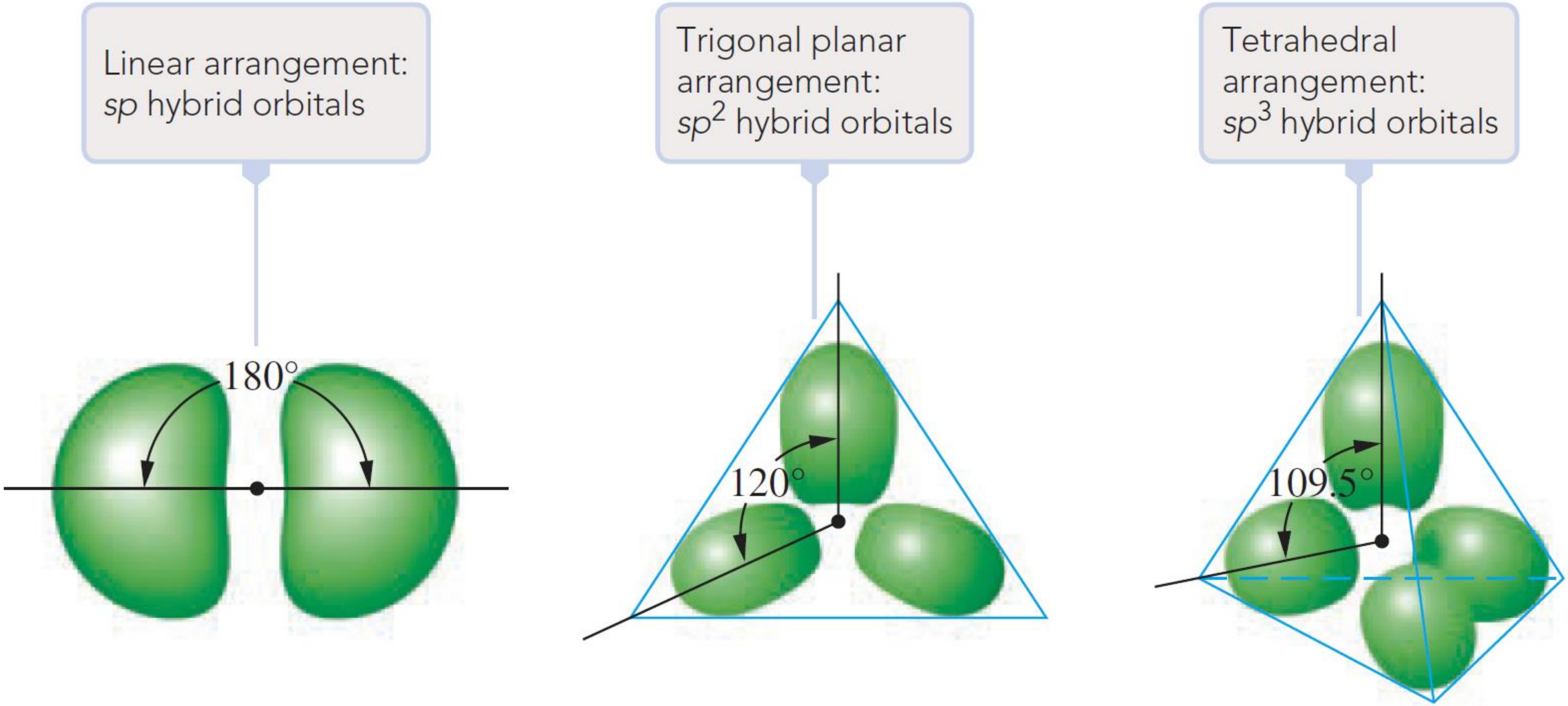
The number of hybrid orbitals formed always equals the number of atomic orbitals used.

Table 10.2 Kinds of Hybrid Orbitals

Hybrid Orbitals	Geometric Arrangement	Number of Orbitals	Example
sp	Linear	2	Be in BeF_2
sp^2	Trigonal planar	3	B in BF_3
sp^3	Tetrahedral	4	C in CH_4

10.3 Valence Bond Theory

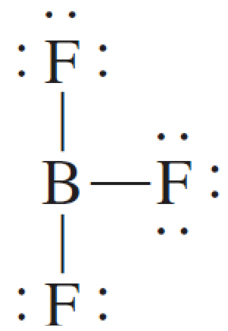
- Hybrid Orbitals

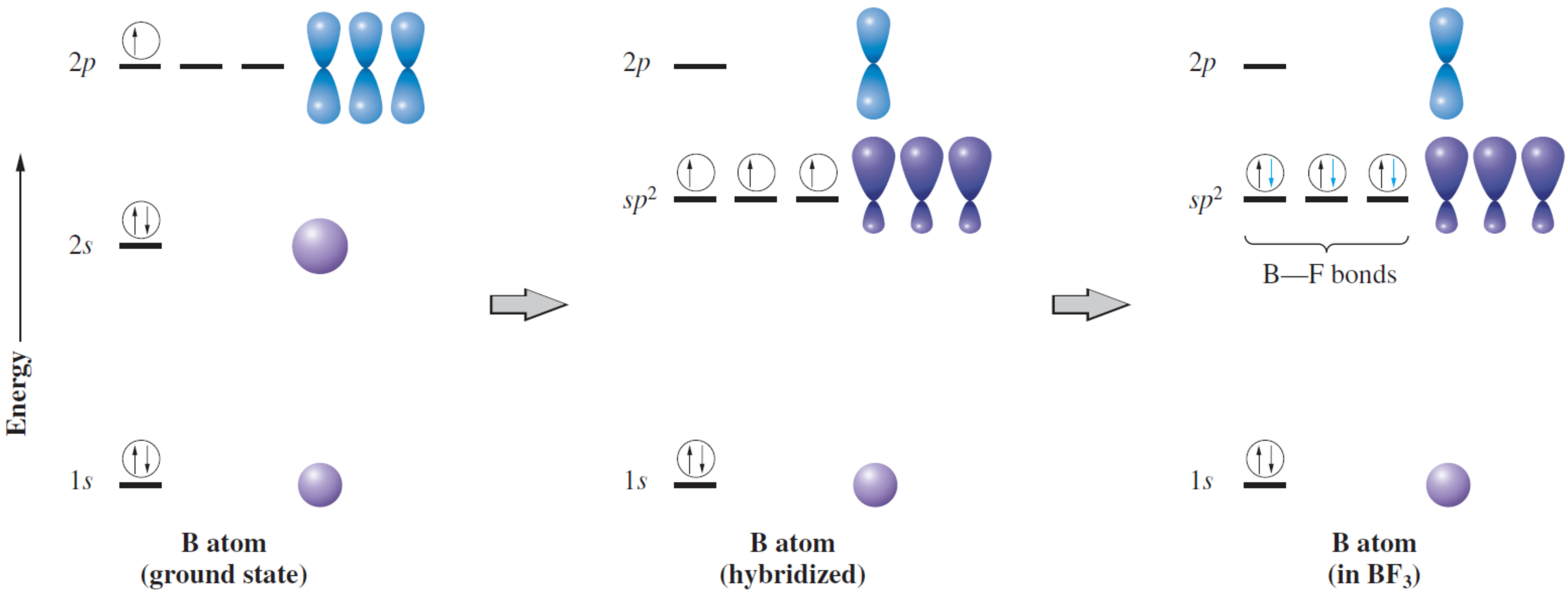


10.3 Valence Bond Theory

- Hybrid Orbitals

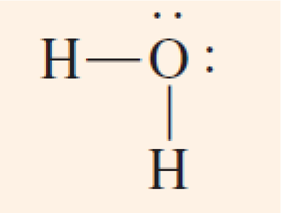
  Example:

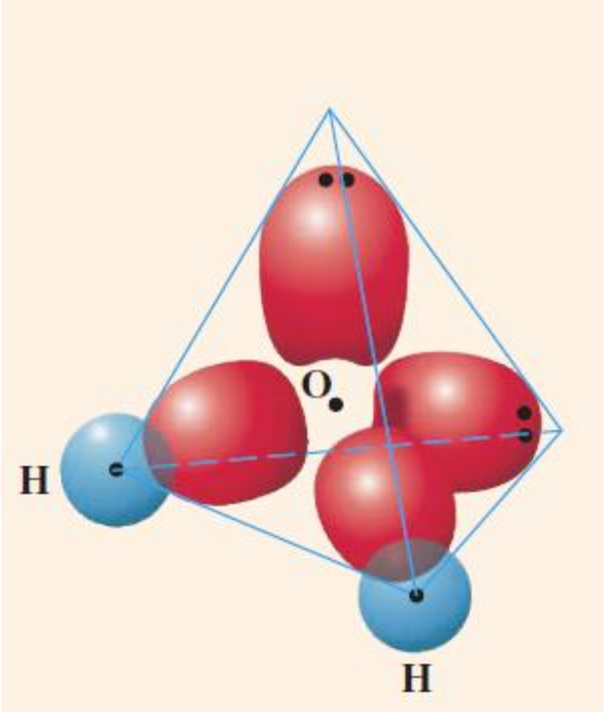




P393 Example 10.4

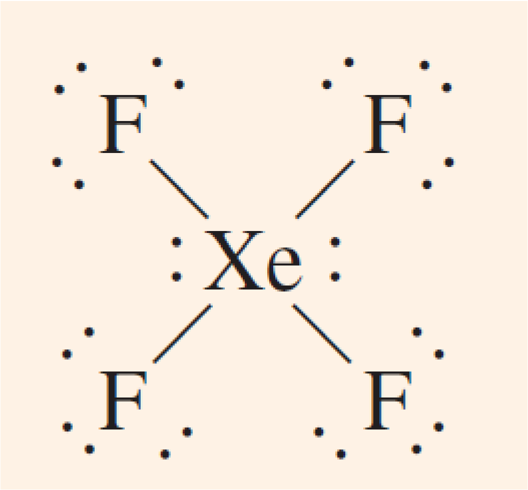
Describe the bonding in H_2O according to valence bond theory. Assume that the molecular geometry is the same as given by the VSEPR model.





P393 Example 10.5

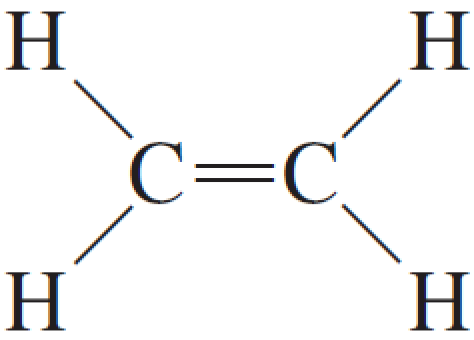
Describe the bonding in XeF_4 using hybrid orbitals.

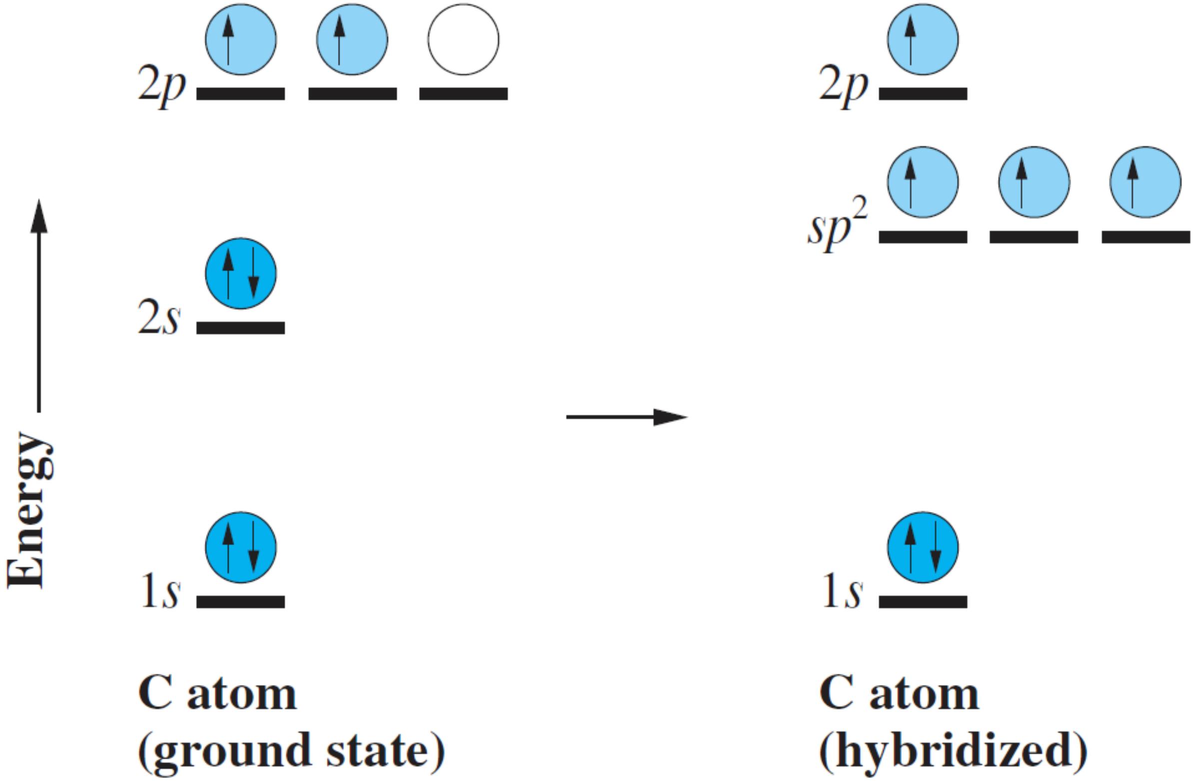


sp^3d^2 hybrid orbitals

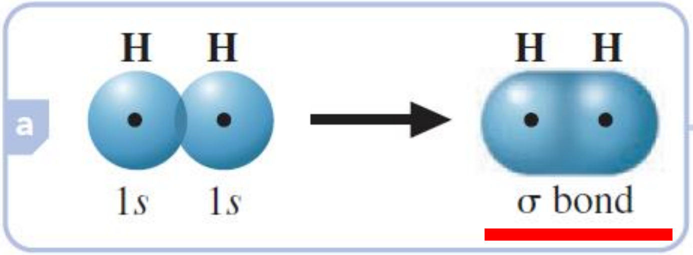
10.4 Description of Multiple Bonding

- One hybrid orbital is needed for each bond (whether a single or a multiple bond) and for each lone pair.

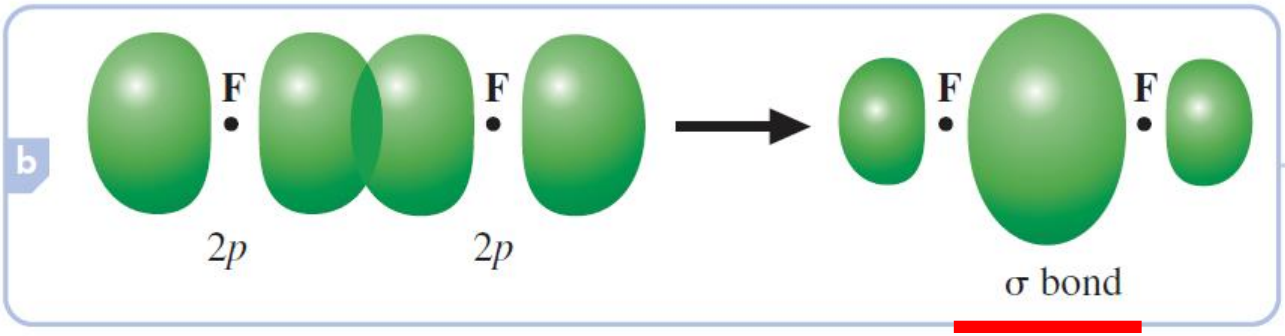


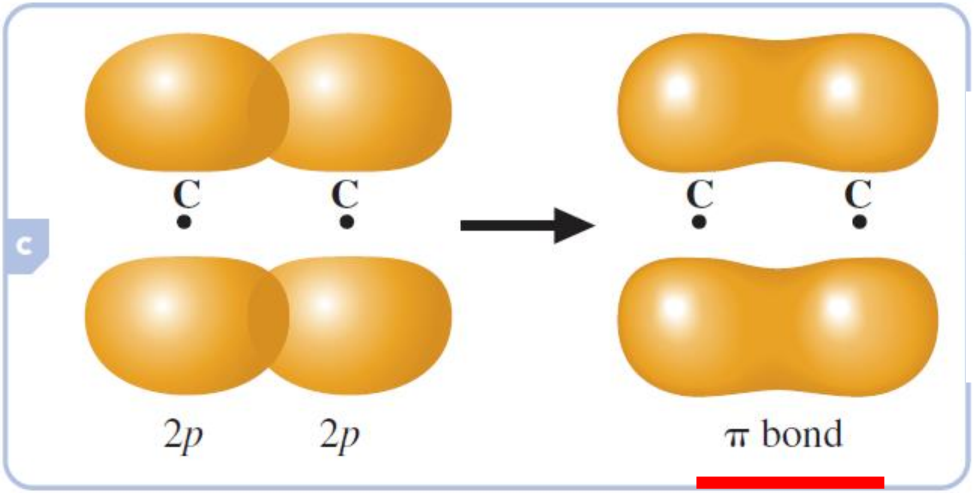


10.4 Description of Multiple Bonding



has a cylindrical shape about the bond axis

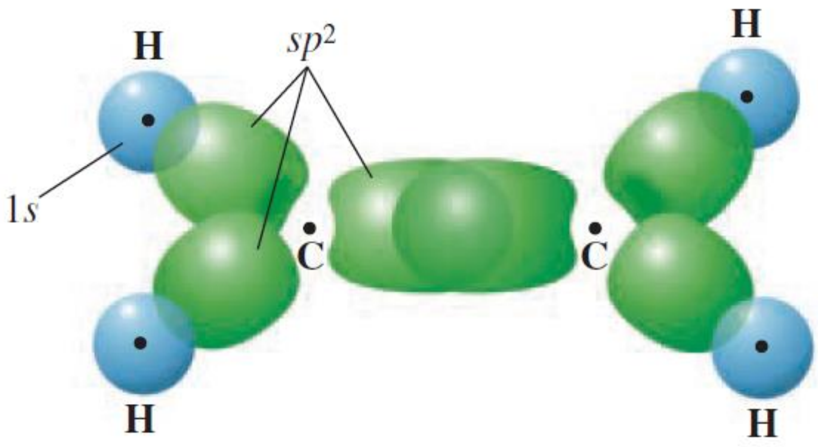


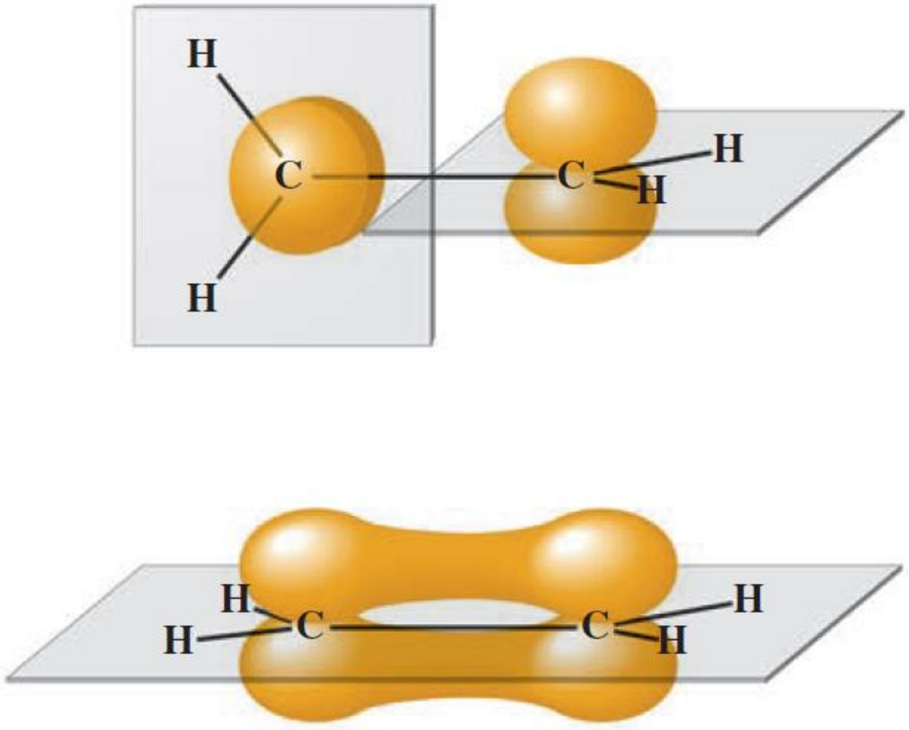


has an electron distribution above and below the bond axis

10.4 Description of Multiple Bonding

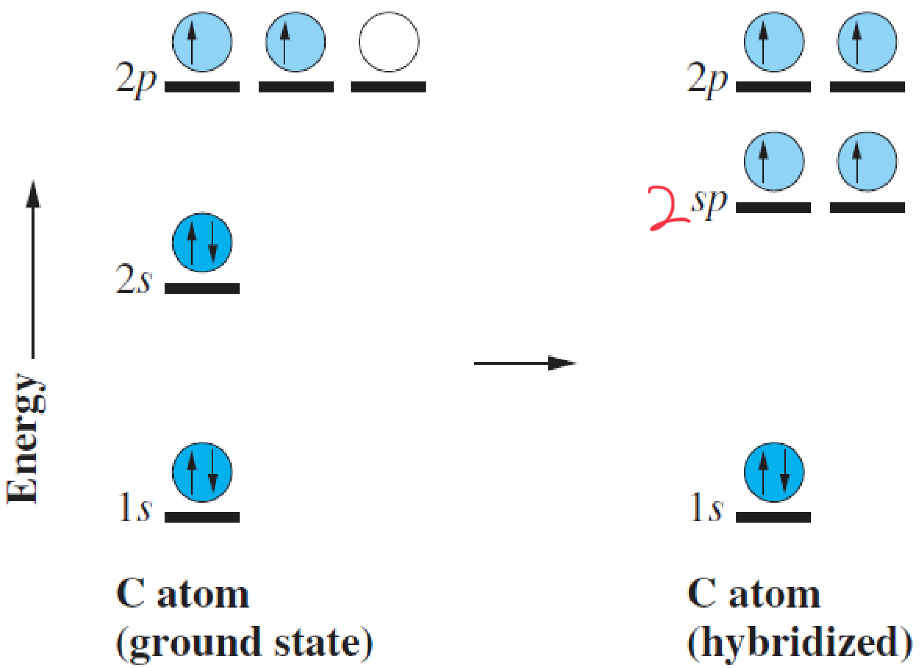
- Bonding in ethylene

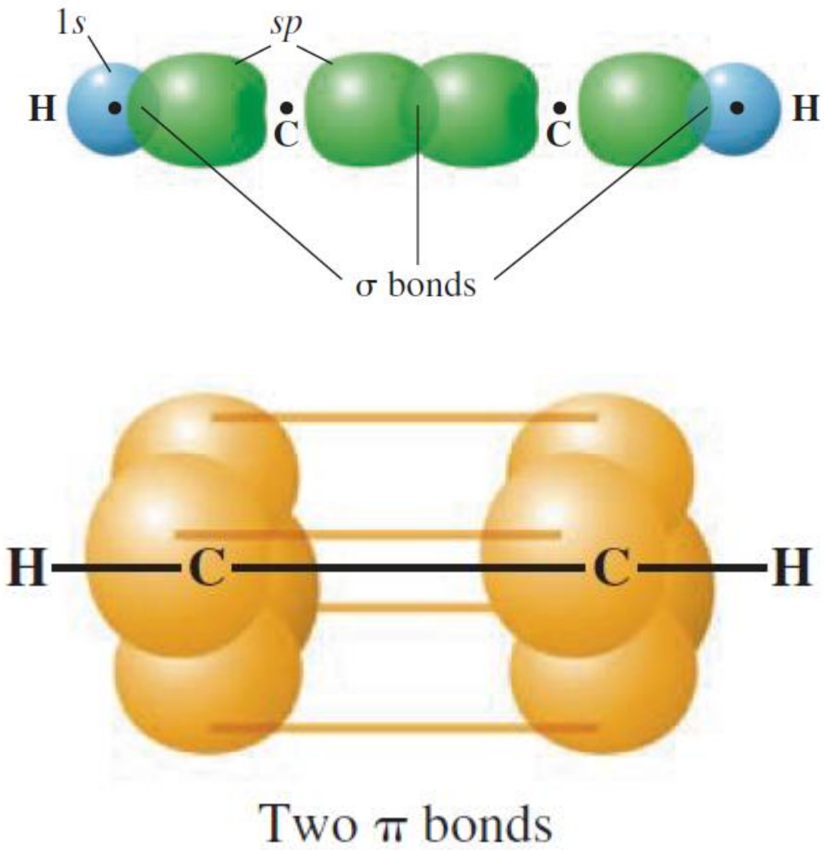




10.4 Description of Multiple Bonding

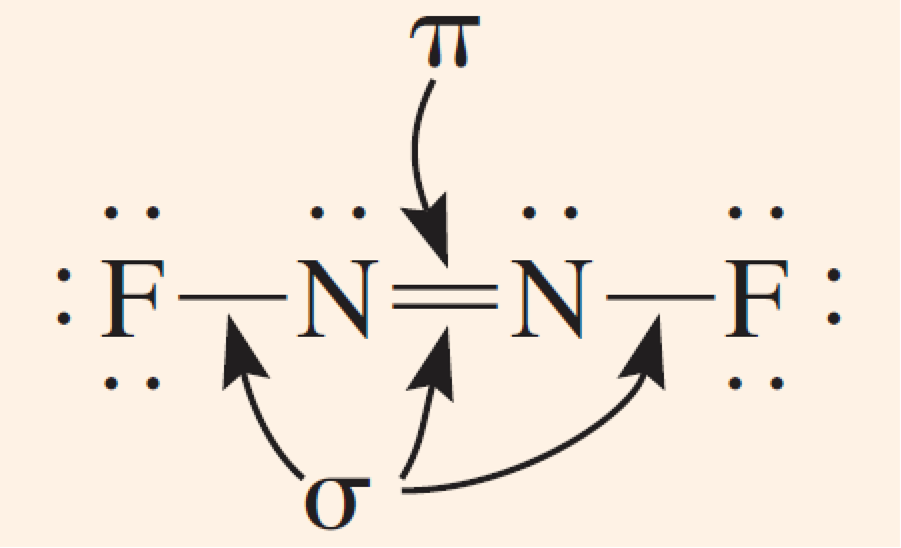
- Bonding in acetylene





P397 Example 10.6

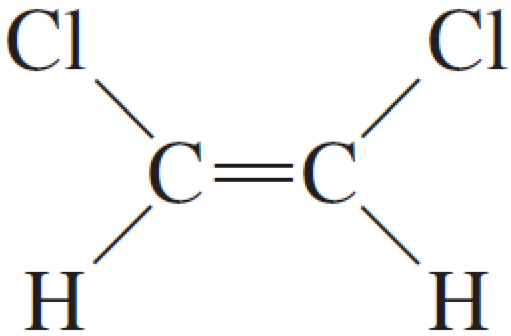
Describe the bonding on a given N atom in dinitrogen difluoride, N_2F_2, using valence bond theory.



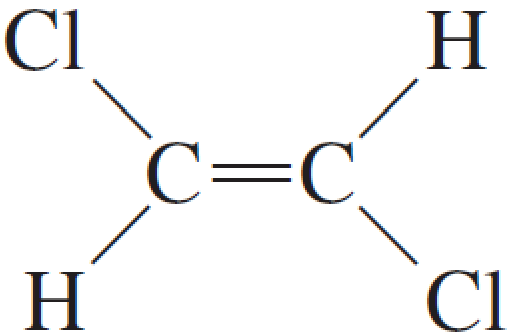
sp^2 hybridization

10.4 Description of Multiple Bonding

- geometric, or *cis–trans*, isomers



cis-1,2-Dichloroethene

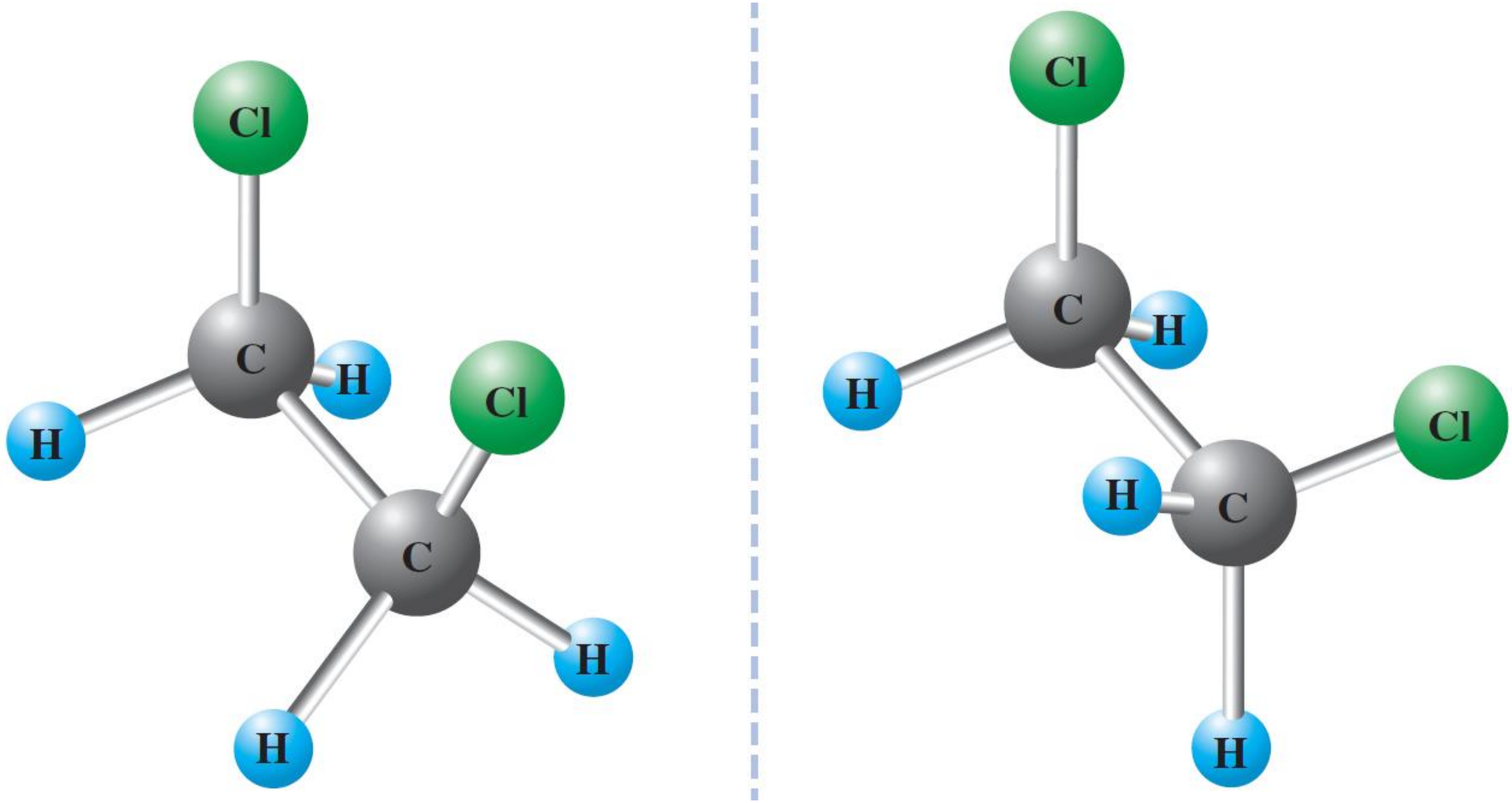


trans-1,2-Dichloroethene

not easily interconverted

10.4 Description of Multiple Bonding

In comparison: one compound

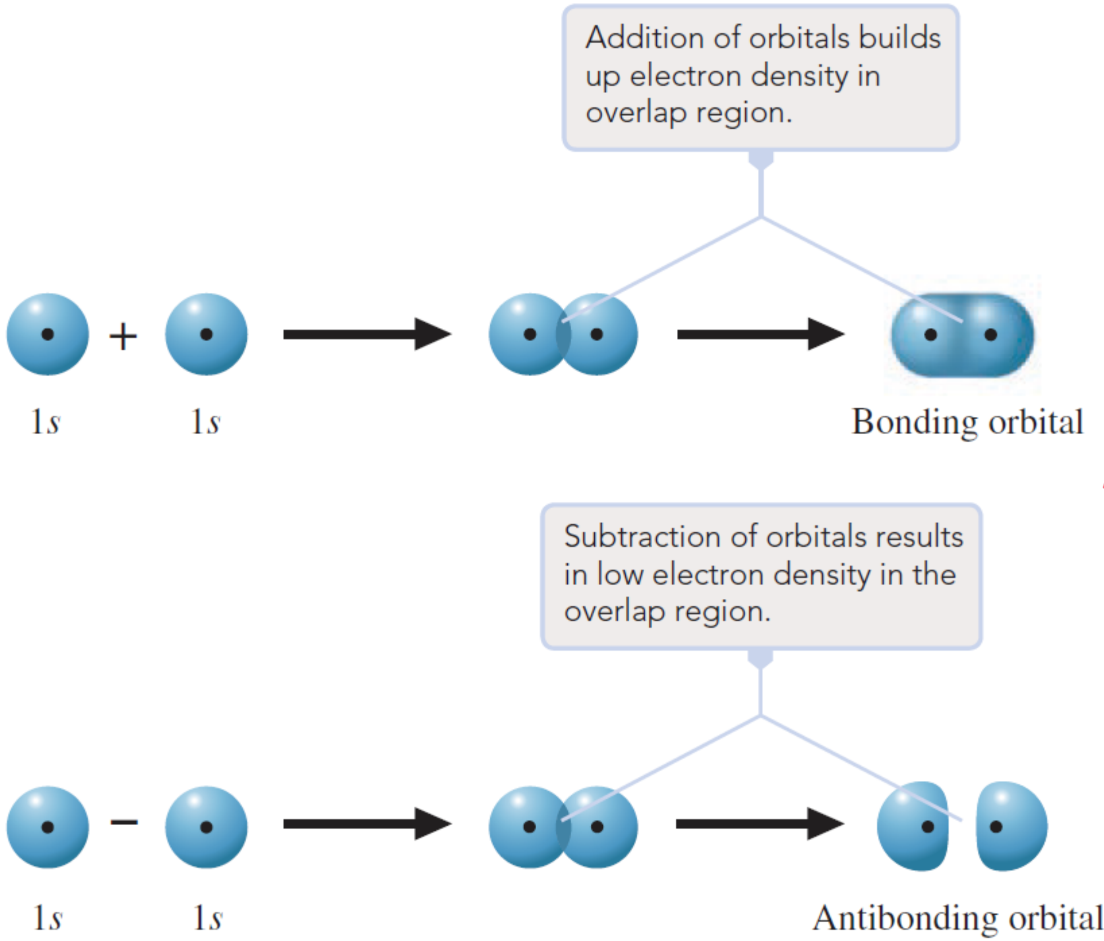


10.5 Principles of Molecular Orbital Theory

- Molecular orbital theory: a theory of the electronic structure of molecules in terms of molecular orbitals, which may spread over several atoms or the entire molecule

10.5 Principles of Molecular Orbital Theory

- Bonding and Antibonding Orbitals



σ_{1s}

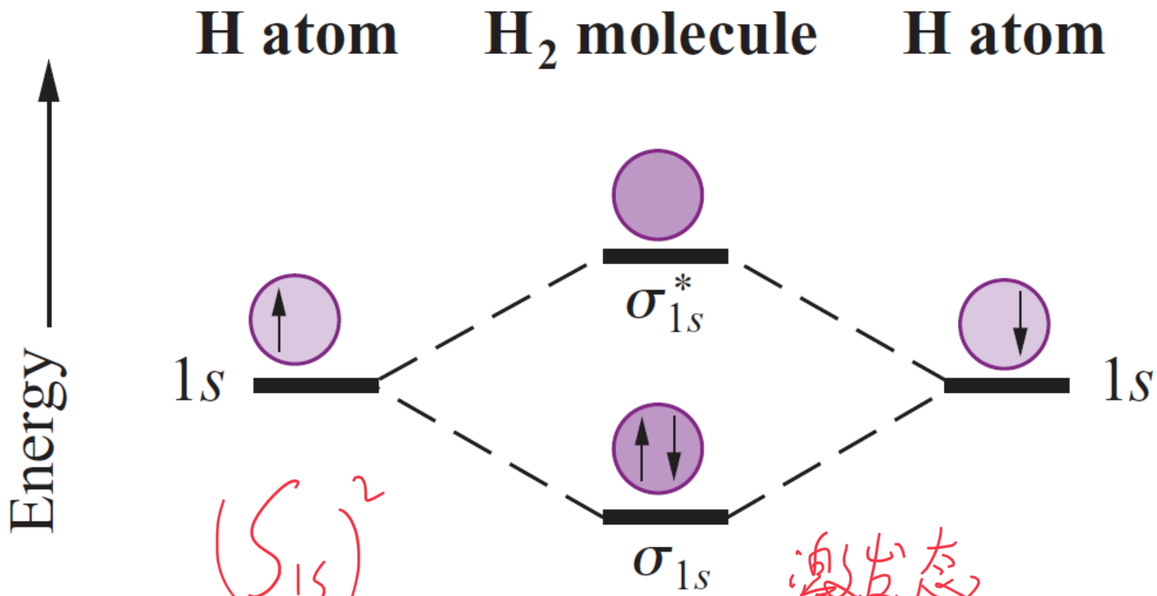
成键轨道

σ^*_{1s}

反键轨道

10.5 Principles of Molecular Orbital Theory

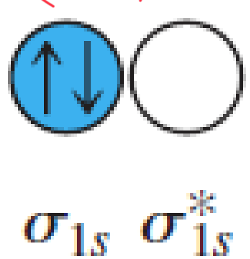
- Bonding and Antibonding Orbitals



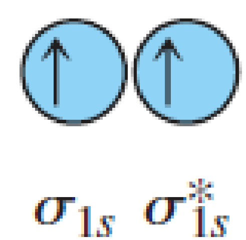
$(\sigma_{1s})^2$

激发态

Ground state



Excited state



10.5 Principles of Molecular Orbital Theory

键级

- Bond Order: the number of bonds that exist between two atoms 原子间有几个化学键

$$\text{Bond order} = \frac{1}{2}(n_{\text{b}} - n_{\text{a}})$$

反键轨道电子数

成键轨道电子数

For H_2

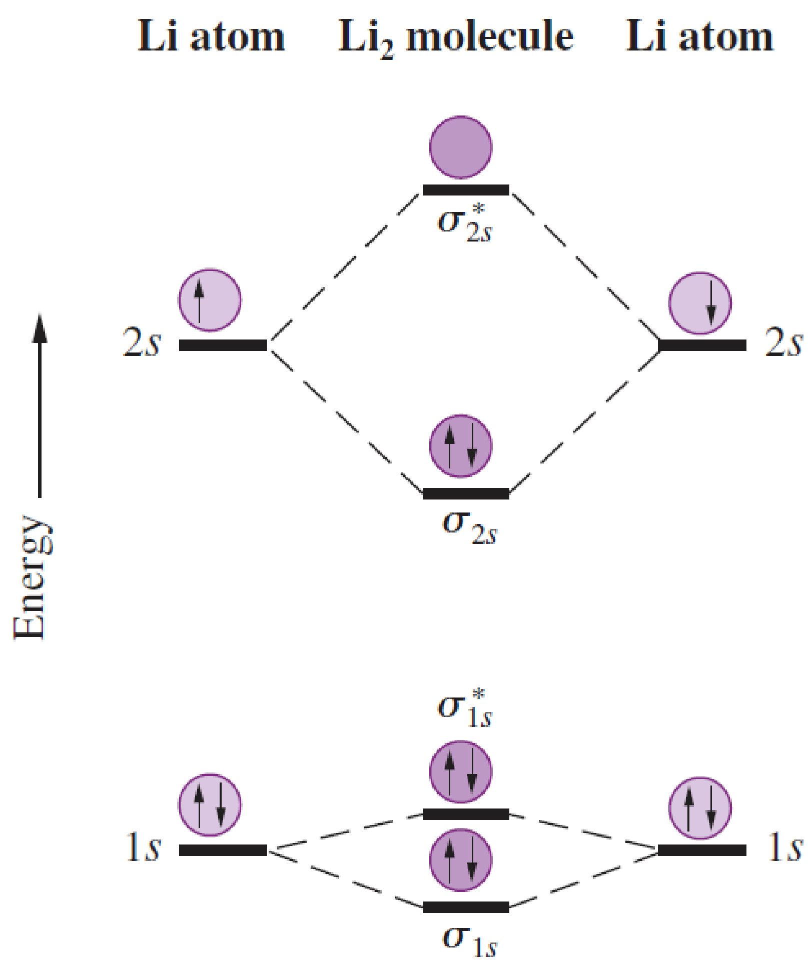
$$\text{Bond order} = \frac{1}{2}(2 - 0) = 1$$

10.5 Principles of Molecular Orbital Theory

- Factors That Determine Orbital Interaction
- For the interaction to be strong, the energies of the two orbitals must be approximately equal and the overlap must be large.

10.5 Principles of Molecular Orbital Theory

- Factors That Determine Orbital Interaction



$Li_2 \quad (\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2$

$Li_2 \quad KK(\sigma_{2s})^2$

10.6 Electron Configurations of Diatomic Molecules of the Second-Period Elements

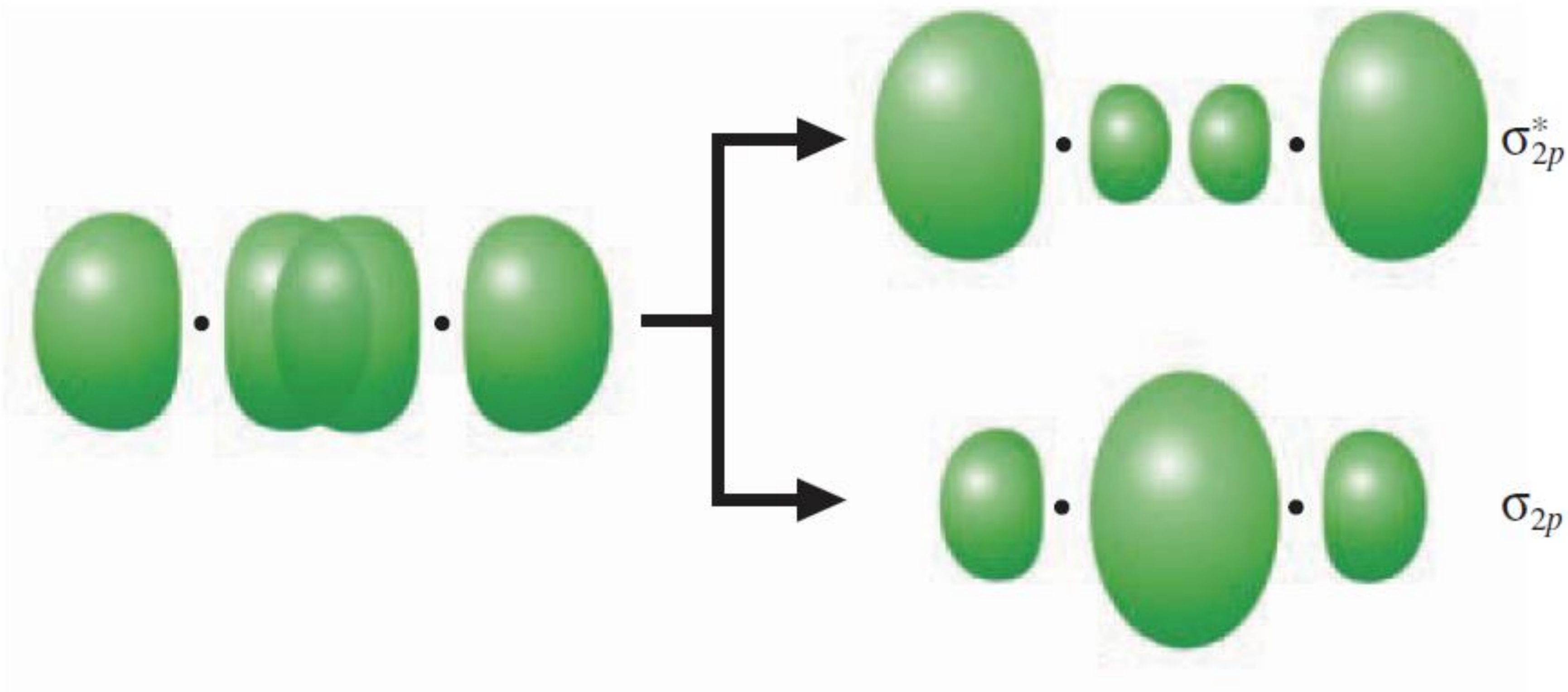
homonuclear diatomic molecules
e.g., H_2, O_2

heteronuclear diatomic molecules
e.g., NO, CO

10.6 Electron Configurations of Diatomic Molecules of the Second-Period Elements

- Different ways in which 2*p* orbitals can interact

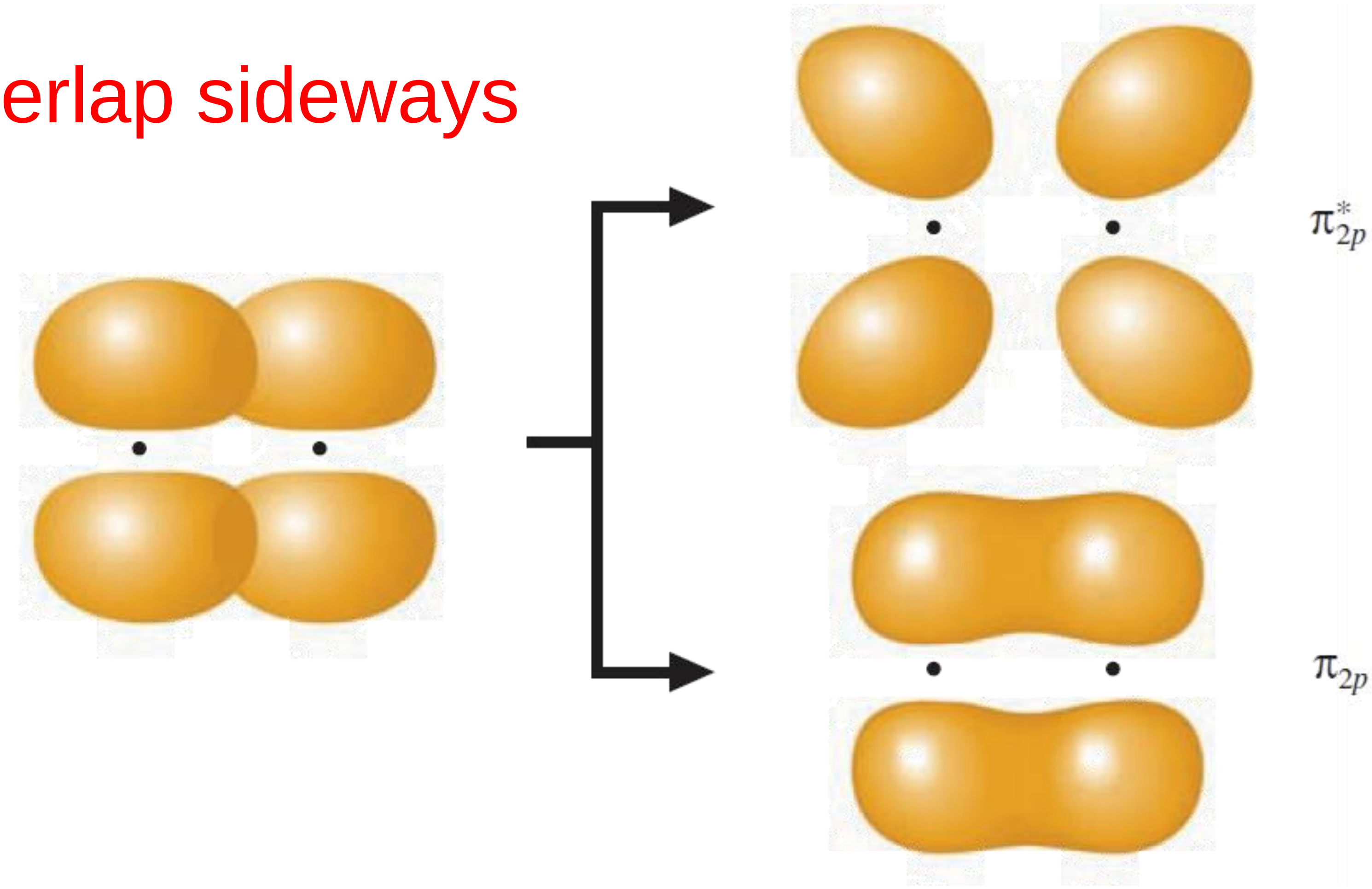
overlap along their axes



10.6 Electron Configurations of Diatomic Molecules of the Second-Period Elements

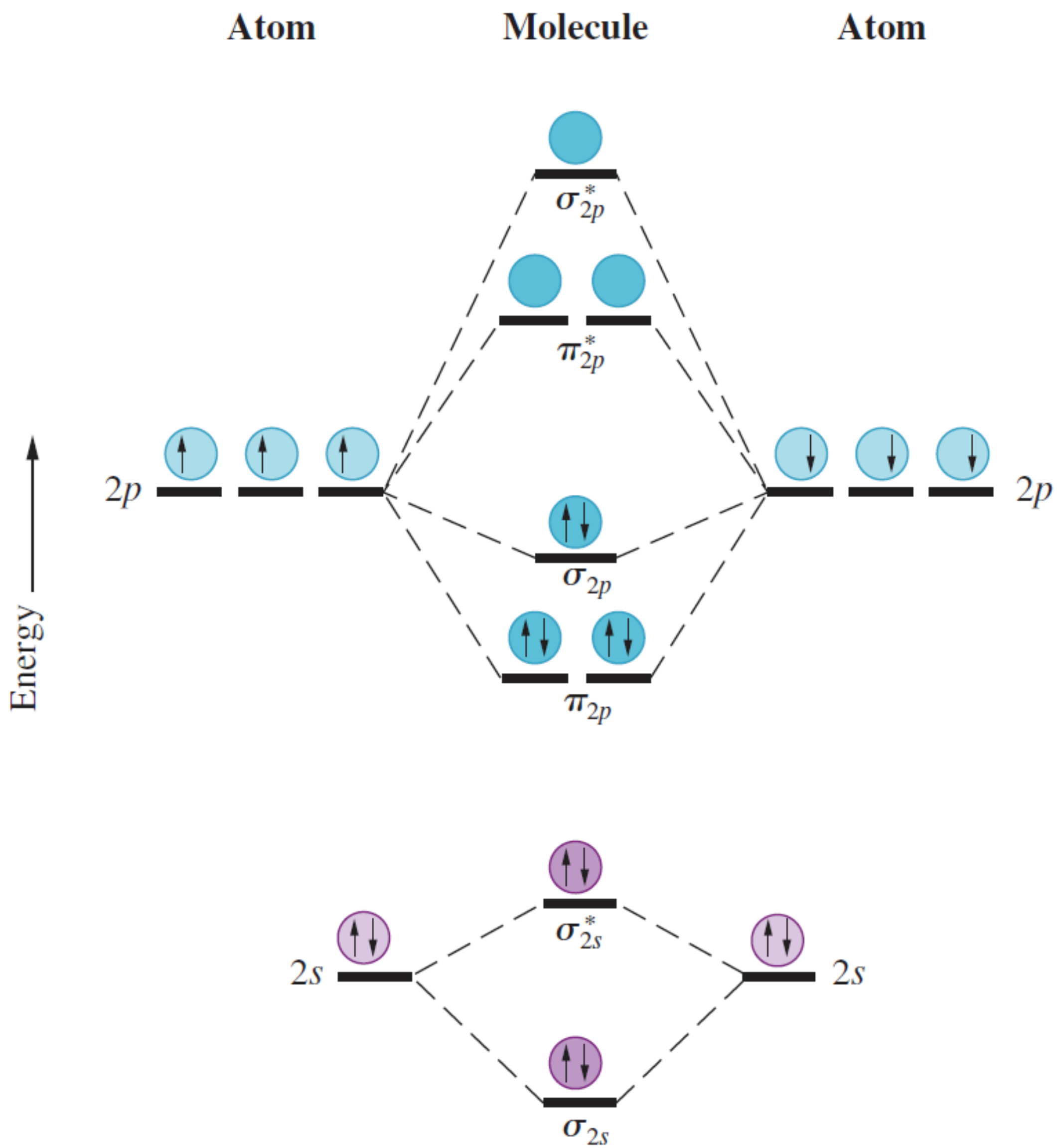
- Different ways in which 2*p* orbitals can interact

overlap sideways



10.6 Electron Configurations of Diatomic Molecules of the Second-Period Elements

- N_2



P404 Example 10.7

Give the orbital diagram of the O_2 molecule. Is the molecular substance diamagnetic or paramagnetic? What is the electron configuration? What is the bond order of O_2?

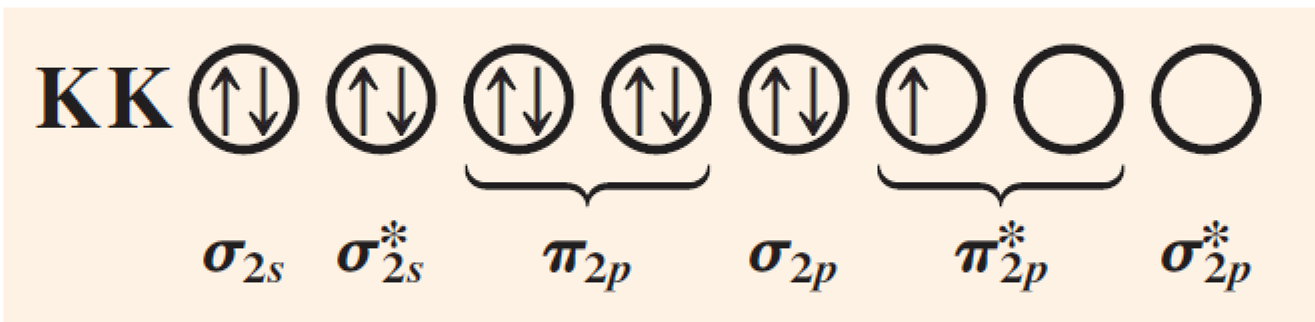
$$\mathrm{KK}\ \underset{\sigma_{2s}}{(\uparrow\downarrow)}\ \underset{\sigma^*_{2s}}{(\uparrow\downarrow)}\ \underbrace{(\uparrow\downarrow)(\uparrow\downarrow)}_{\pi_{2p}}\ \underset{\sigma_{2p}}{(\uparrow\downarrow)}\ \underbrace{(\uparrow\ )(\uparrow\ )}_{\pi^*_{2p}}\ \underset{\sigma^*_{2p}}{(\ \ )}$$

$$\mathbf{KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2(\pi^*_{2p})^2}$$

$$\text{Bond order} = \tfrac{1}{2}(8 - 4) = \mathbf{2}$$

P405 Example 10.8

Write the orbital diagram for nitrogen monoxide (nitric oxide), NO. What is the bond order of NO?



$$\text{Bond order} = \frac{1}{2}(8 - 3) = \mathbf{\frac{5}{2}}$$

10.6 Electron Configurations of Diatomic Molecules of the Second-Period Elements

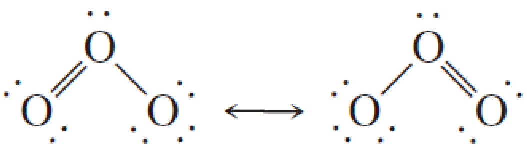
TABLE 10.3 **Theoretical Bond Orders and Experimental Data for the Second-Period Homonuclear Diatomic Molecules**

Molecule	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Magnetic Character
Li_2	1	267	110	Diamagnetic
Be_2	0	*	*	*
B_2	1	159	290	Paramagnetic
C_2	2	124	602	Diamagnetic
N_2	3	110	942	Diamagnetic
O_2	2	121	494	Paramagnetic
F_2	1	142	155	Diamagnetic
Ne_2	0	*	*	*

The symbol * means that no stable molecule has been observed.

10.7 Molecular Orbitals and Delocalized Bonding

- Molecular orbital theory describes the bonding in terms of a single electron configuration.



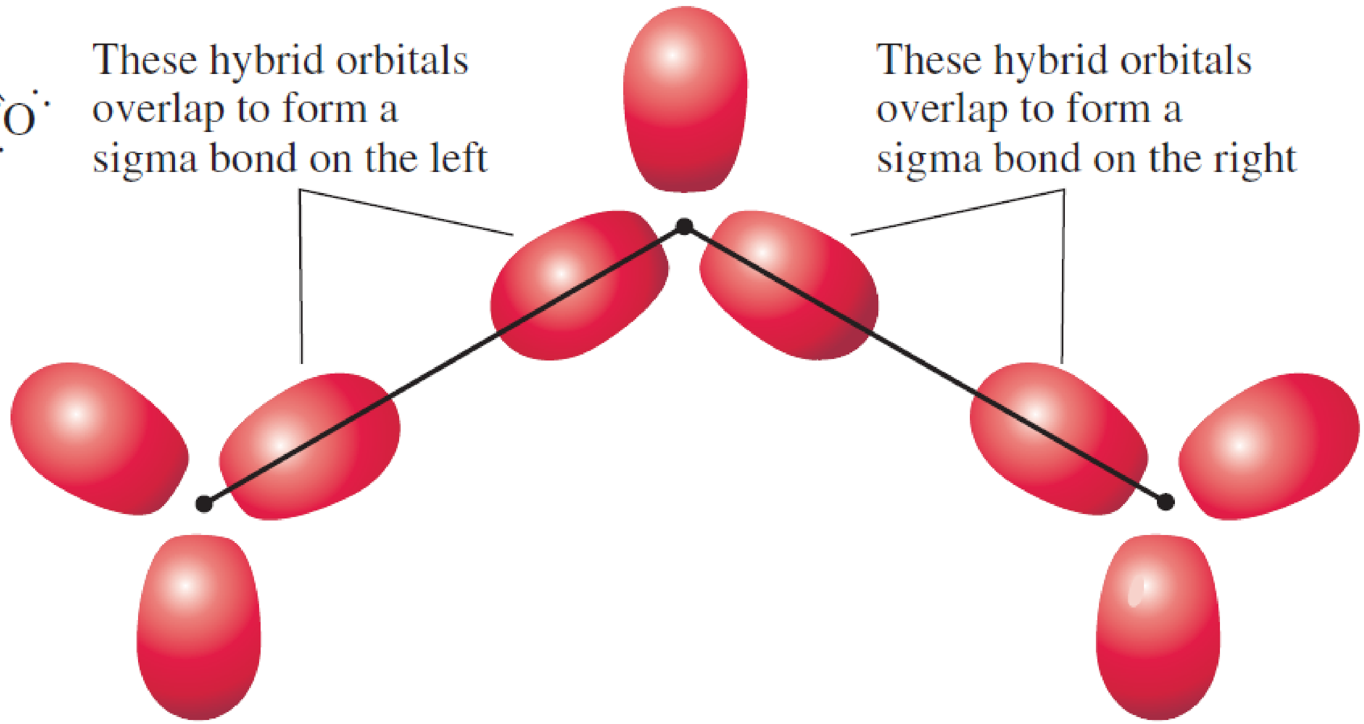
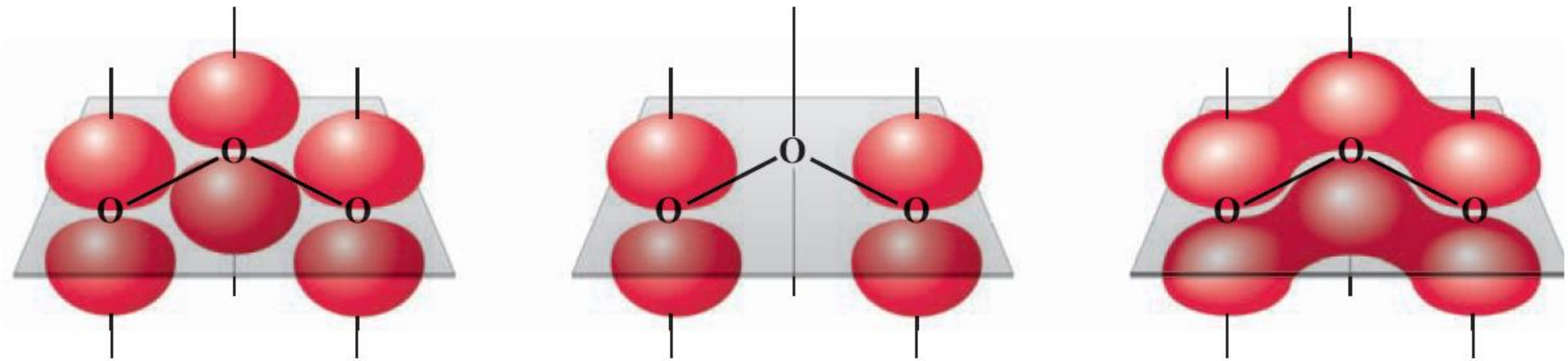


FIGURE 10.36

Hybrid orbitals on oxygen atoms of ozone, O_3

10.7 Molecular Orbitals and Delocalized Bonding

- Molecular orbital theory describes the bonding in terms of a single electron configuration.



Antibonding π orbital Nonbonding π orbital Bonding π orbital