Professor K

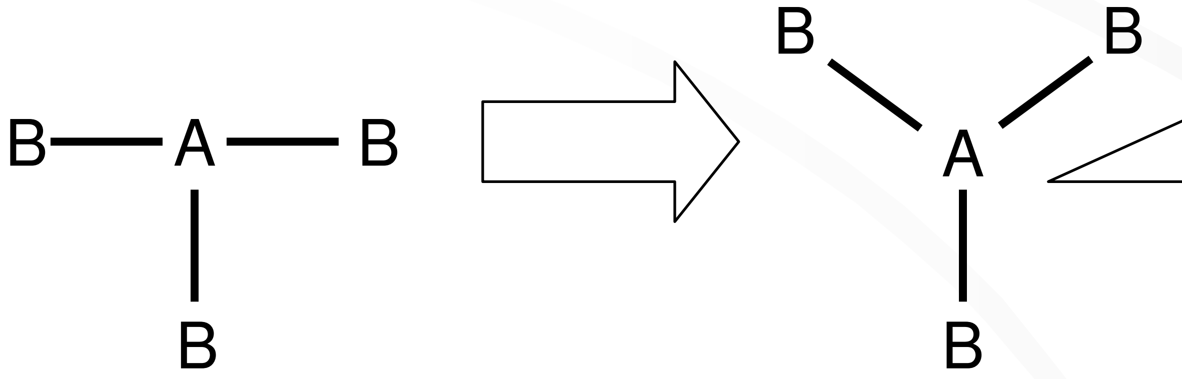
Bonding expanded-
Molecular shape

Flashback / flashforward

- We’ve learned how to write chemical formulas and line structures...
- We’ve learned how to show the locations of electrons in Lewis structures...
- How can we determine the actual shape of a molecule (and/or the *geometry* around atoms) from these things?

Valence-Shell Electron-Pair Repulsion theory (VSEPR theory)

- Electron pairs (bonded and lone pairs) will orient themselves so that they are as far apart from one another as possible (the four electrons in a double bond and the six in a triple bond are each considered one "group")
- A lone pair takes up more space around an atom than a bonded pair

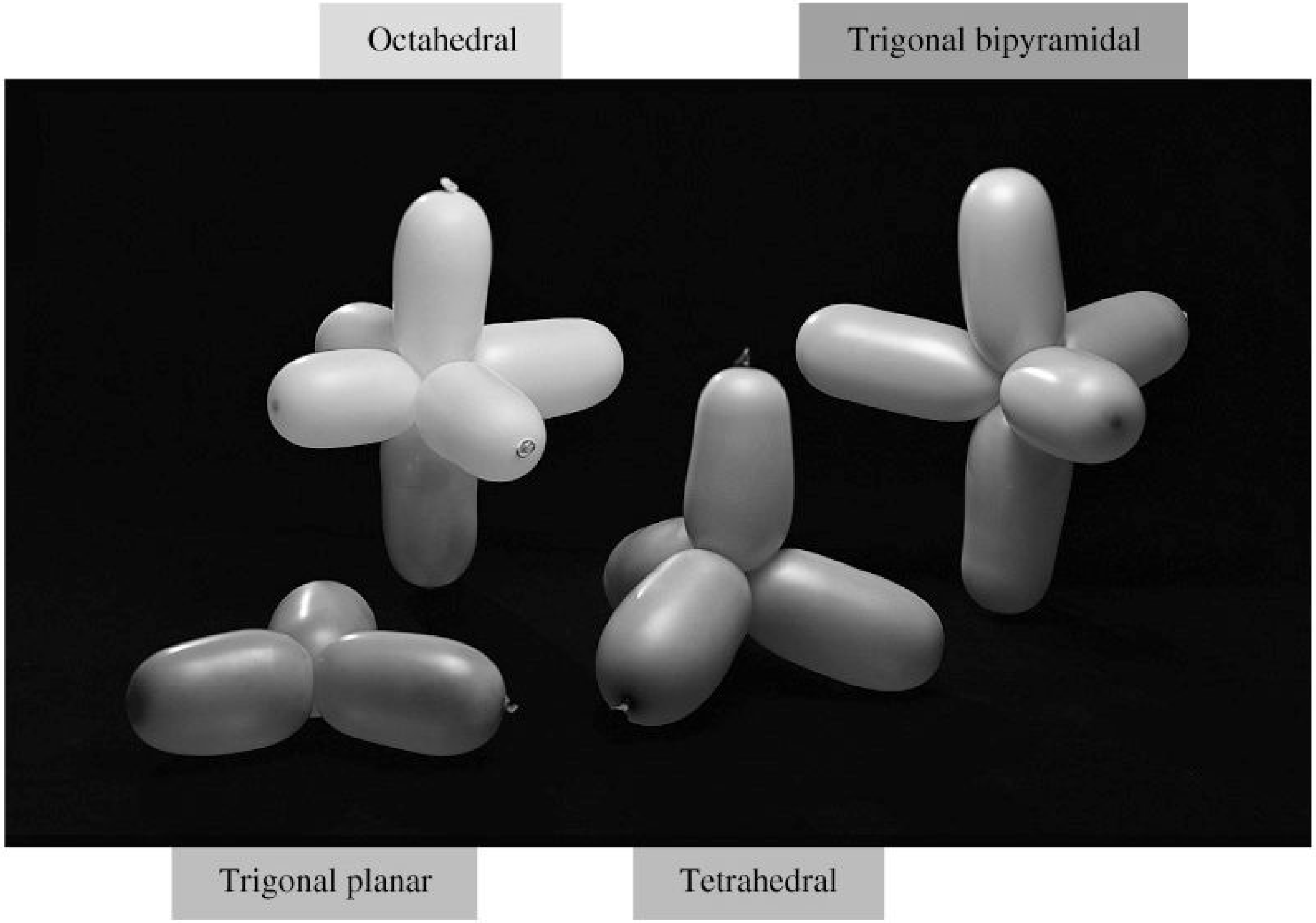


When the electron pairs (bonds) are as far apart as they can get, what will be the B-A-B angle?

Electron group geometry

- 2 electron pairs- linear
- 3 electron pairs- trigonal planar
- 4 electron pairs- tetrahedral
- 5 electron pairs- trigonal bipyramidal
- 6 electron pairs- octahedral

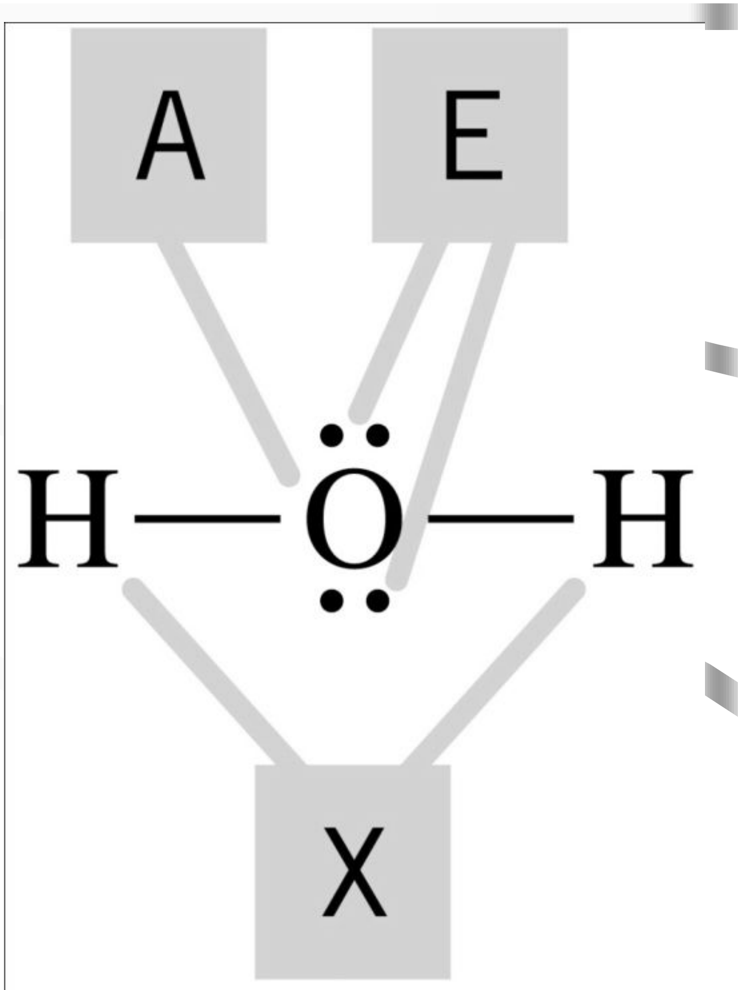
e^- group geometry (cont'd)



VSEPR notation

- central atoms are denoted "A"
- terminal atoms are denoted "X"
- lone pairs are denoted "E“

Thus, water is AX_2E_2



Molecular shape

- AX_2 - linear
- AX_3 - trigonal planar
- AX_4 - tetrahedral
- AX_5 - trigonal bipyramidal
- AX_6 - octahedral
- The AX_5 and AX_6 require an expanded valence shell and, therefore, the central atom must be a third-period or higher element.

Molecular shape vs.
electron group geometry…
MOST BOOKS ARE CONFUSING!

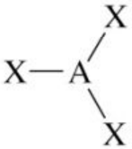
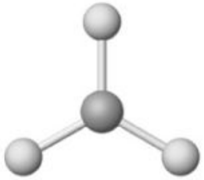
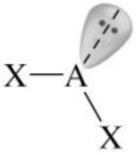
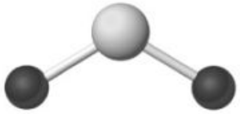
- For structures with no lone pairs on the central atom (AXn), the molecular ~~geometry~~ SHAPE is the same as the electron-group geometry.
- When there are lone pairs, the molecular ~~geometry~~ SHAPE is derived from the electron-group geometry.
- In either case, the electron-group geometry is the tool we use to obtain the molecular ~~geometry~~ SHAPE.

Molecular shape vs. electron group geometry

- The presence of lone pairs affects ONLY the SHAPE of the molecule (which is described in terms of locations of atoms), NOT the electron group geometry (sometimes referred to as the *molecular geometry*) (which takes into account lone pairs)
- AX_2E vs AX_3
- AX_3E vs AX_4
- AX_2E_2 vs AX_4
- AX_4E vs AX_5
- AX_3E_2 vs AX_5
- AX_2E_3 vs AX_5
- AX_5E vs AX_6
- AX_4E_2 vs AX_6

Shape and geometry

Table 10.1 (Part 1) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
2	Linear	0	AX_2	 Linear	180°	$BeCl_2$	
3	Trigonal planar	0	AX_3	 Trigonal planar	120°	BF_3	
3	Trigonal planar	1	AX_2E	 Angular	120°	SO_2	

Shape and geometry (cont'd)

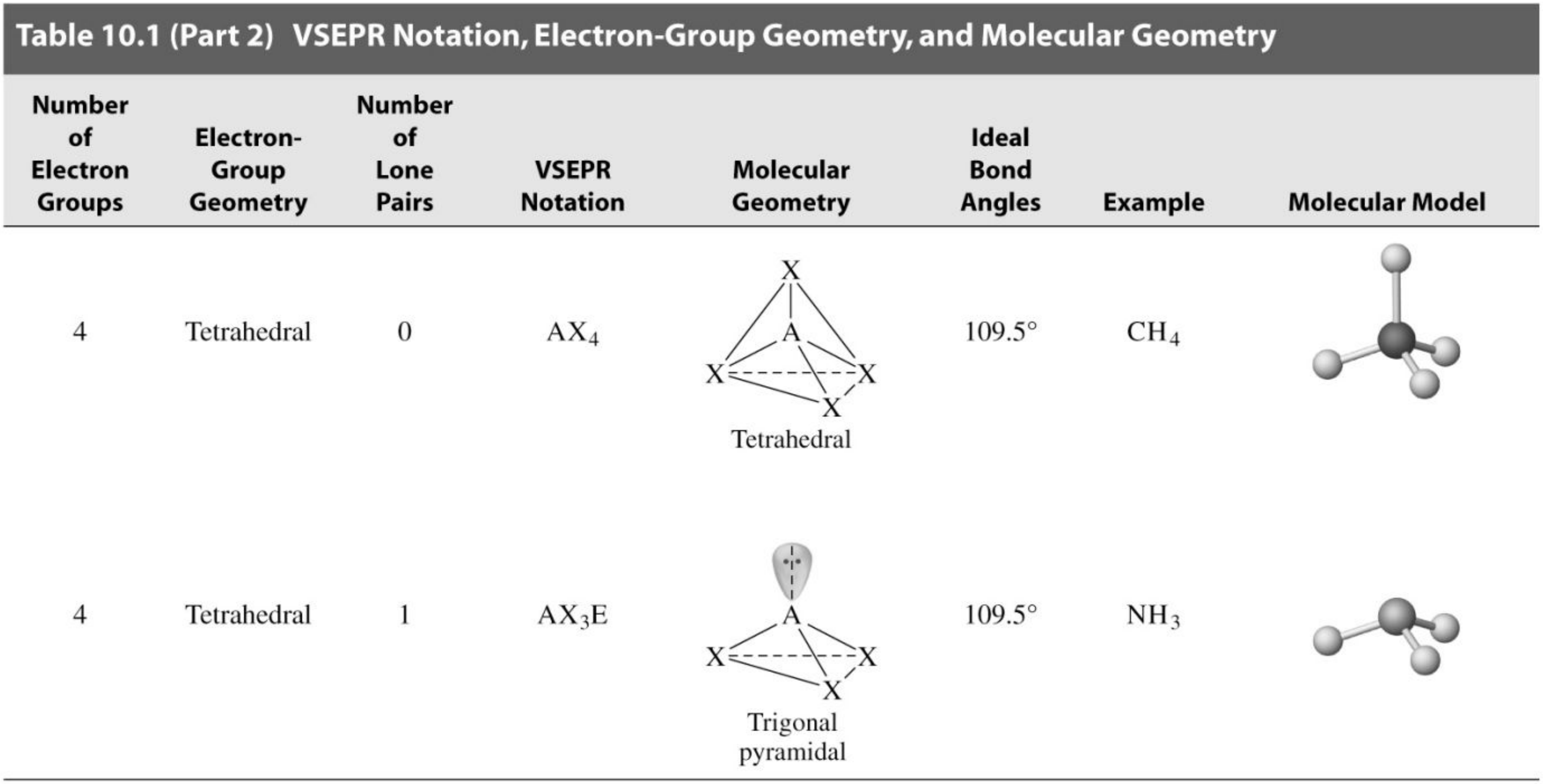
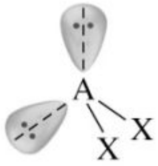
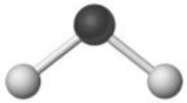
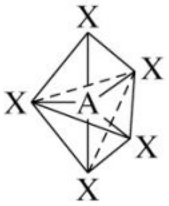
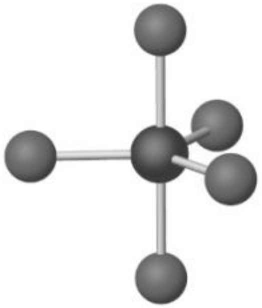


Table 10.1 (Part 2) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
4	Tetrahedral	0	AX_4	Tetrahedral	109.5°	CH_4	
4	Tetrahedral	1	AX_3E	Trigonal pyramidal	109.5°	NH_3	

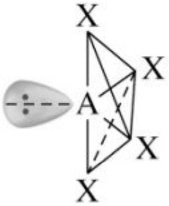
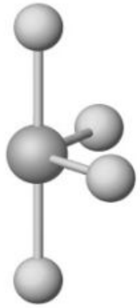
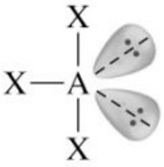
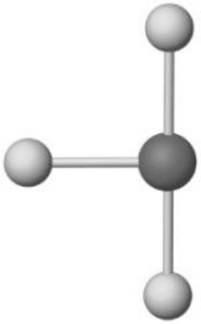
Shape and geometry (cont'd)

Table 10.1 (Part 3) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
4	Tetrahedral	2	AX_2E_2	 Angular	109.5°	OH_2	
5	Trigonal bipyramidal	0	AX_5	 Trigonal bipyramidal	90°, 120°, 180°	PCl_5	

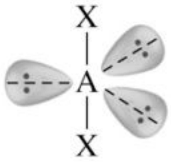
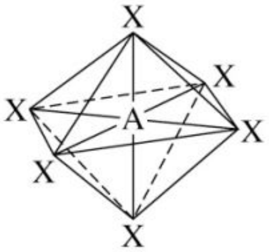
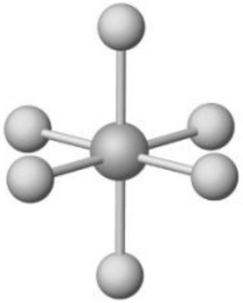
Shape and geometry (cont'd)

Table 10.1 (Part 4) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
5	Trigonal bipyramidal	1	AX_4E	 Seesaw	90°, 120°, 180°	SF_4	
5	Trigonal bipyramidal	2	AX_3E_2	 T-shaped	90°, 180°	ClF_3	

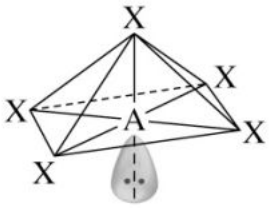
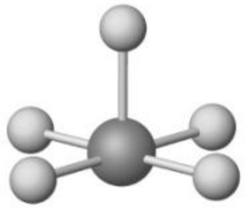
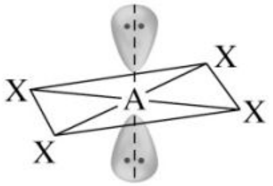
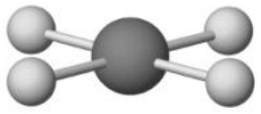
Shape and geometry (cont'd)

Table 10.1 (Part 5) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
5	Trigonal bipyramidal	3	AX_2E_3	 Linear	180°	XeF_2	
6	Octahedral	0	AX_6	 Octahedral	90°, 180°	SF_6	

Shape and geometry (cont'd)

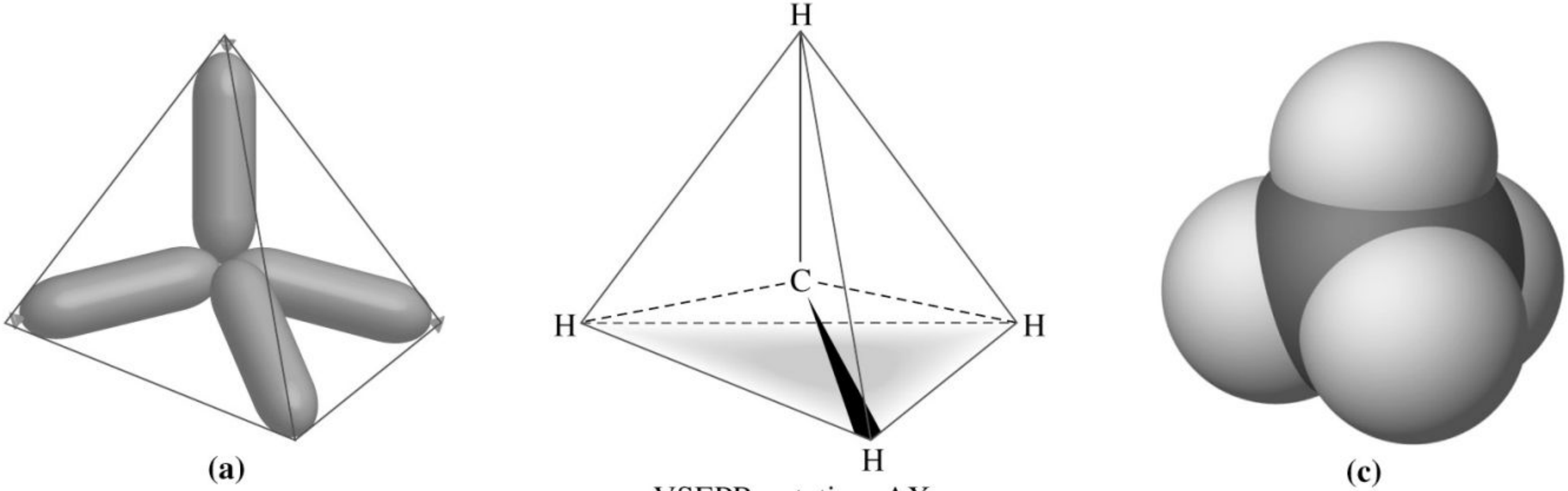
Table 10.1 (Part 6) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
6	Octahedral	1	AX_5E	 Square pyramidal	90°	BrF_5	
6	Octahedral	2	AX_4E_2	 Square planar	90°	XeF_4	

Example

- Use the VSEPR method to predict the shape of the nitrate ion.

Shape of methane



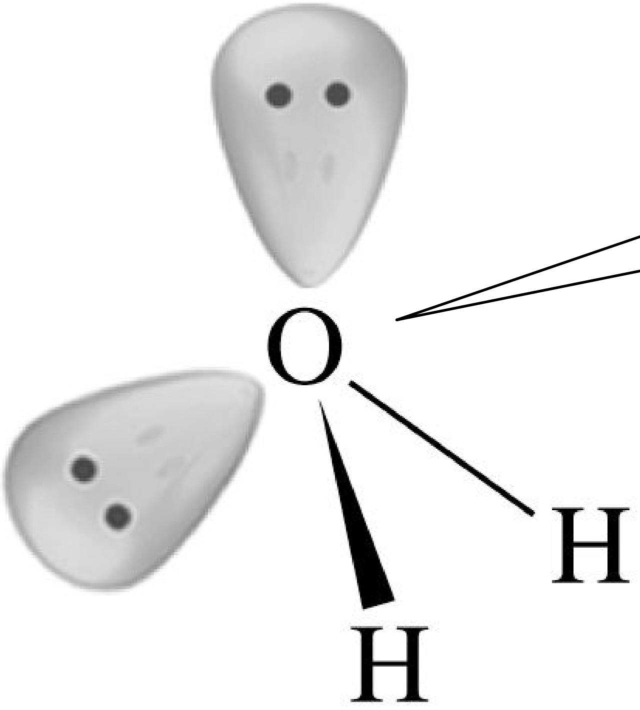
(a)

VSEPR notation: AX_4

(b)

(c)

Molecular shape of water



Is the water molecule tetrahedral?

No; its electron groups are tetrahedrally arranged. The *molecule* is ________.

VSEPR notation: AX_2E_2

Complex molecules

- For molecules with more than one central atom, the geometry and resulting shape around each atom must be evaluated

Electronegativity revisited-polarity and dipole moment

- Molecular dipoles
- Molecular shape and dipoles

Polar molecules and dipole moments

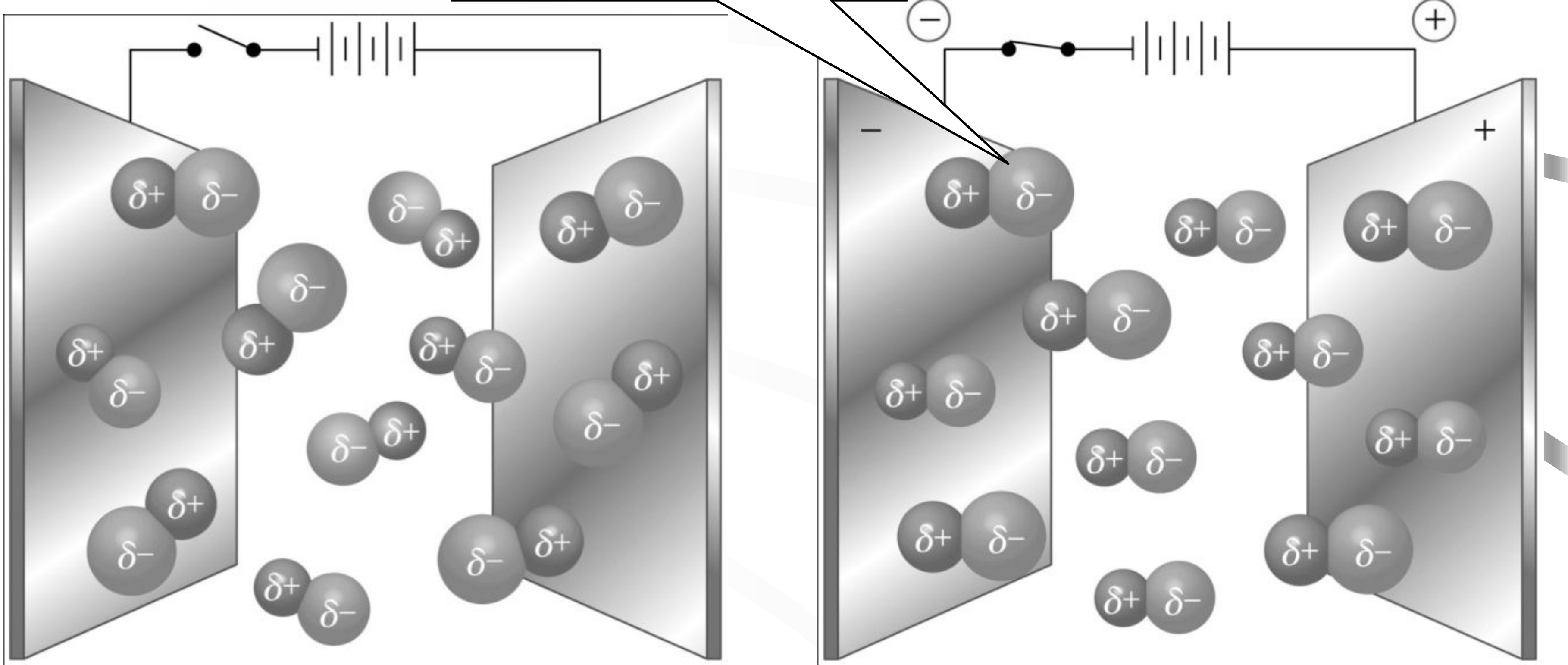
- A ***polar bond*** (Chapter 9) has separate centers of positive and negative charge.
- A ***molecule*** with separate centers of positive and negative charge is a ***polar molecule.***
- The ***dipole moment*** *(μ)* of a molecule is the product of the magnitude of the charge (δ) and the distance (*d*) that separates the centers of positive and negative charge.

$$\mu = \delta d$$

- A unit of dipole moment is the D***ebye (D)***.
- One debye (D) is equal to 3.34 x 10^{-30} C m.

Polar molecules in an electric field

An electric field causes polar molecules to align with the field.



(a)

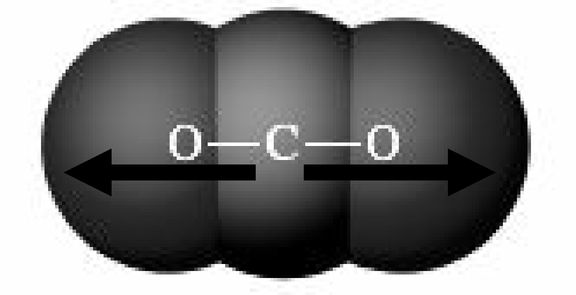
(b)

Bond dipoles and molecular dipoles

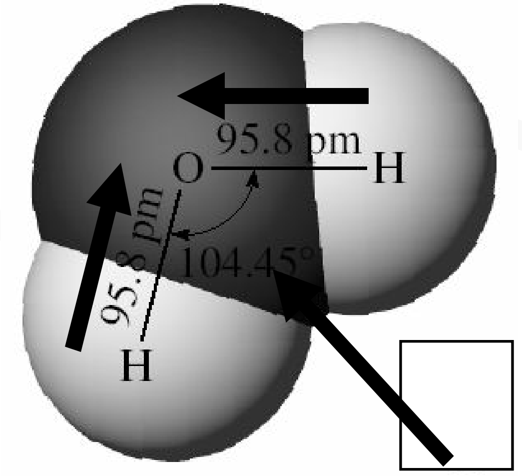
- A polar covalent bond has a ***bond dipole***; a separation of positive and negative charge centers in an individual bond.
- Bond dipoles have both a ***magnitude*** and a ***direction*** (they are ***vector*** quantities).
- Ordinarily, a polar molecule must have polar bonds, *BUT …* polar bonds are not sufficient.
- A molecule may have polar bonds and be a ***nonpolar*** molecule – *IF* the bond dipoles cancel.

Bond dipoles and molecular dipoles (cont'd)

- CO_2 has polar bonds, but is a linear molecule; the bond dipoles cancel and it has no net dipole moment (μ = 0 D).
- The water molecule has polar bonds also, but is an ***angular*** molecule.
- The bond dipoles do ***not*** cancel (μ = 1.84 D), so water is a ***polar*** molecule.



No net dipole



Net dipole

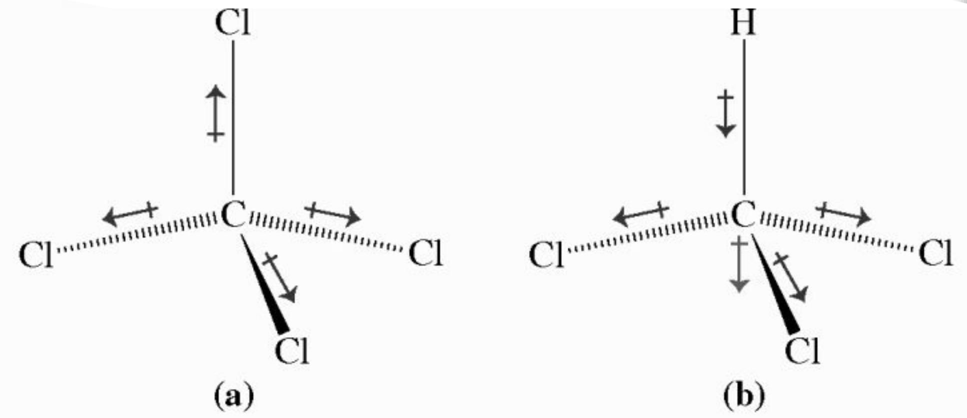
Molecular shapes and dipole moments

- To predict molecular polarity:
  1. Use electronegativity values to predict bond dipoles.
  2. Use the VSEPR method to predict the molecular shape.
  3. From the molecular shape, determine whether bond dipoles cancel to give a nonpolar molecule, or combine to produce a resultant dipole moment for the molecule. (Can you cut the molecule in half twice?)
- Note: Lone-pair electrons can also make a contribution to dipole moments.

Example

- Explain whether you expect the following molecules to be polar or nonpolar:
  (a) $CHCl_3$
  (b) CCl_4

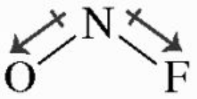
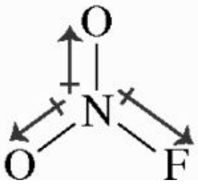
The distribution of bond dipoles in CCl_4 is shown in Figure 10.9a. The resultant dipole in the downward direction produced by the three bond dipoles directed down and away from the center of the structure is just matched by the straight upward bond dipole at the top. Thus all the bond dipoles cancel, so there is no molecular dipole, and CCl_4 is a nonpolar molecule.



▲ FIGURE 10.9 Molecular geometry and molecular dipoles
The bond dipoles are represented by black cross-based arrows ⟵⟶
(a) The individual bond dipoles cancel, and there is no molecular dipole.
(b) All the bond dipoles point downward and combine to form a molecular dipole (red arrow).

Example

- Of the two compounds NOF and NO_2F, one has μ = 1.81 D and the other has μ = 0.47 D. Which dipole moment do you predict for each compound? Explain.

Electron groups around central atom	3	3
Electron-group geometry	Trigonal planar	Trigonal planar
VSEPR notation	AX_2E	AX_3
Molecular ~~geometry~~	Angular	Trigonal planar
Bond dipoles (electronegativities F > O > N)		

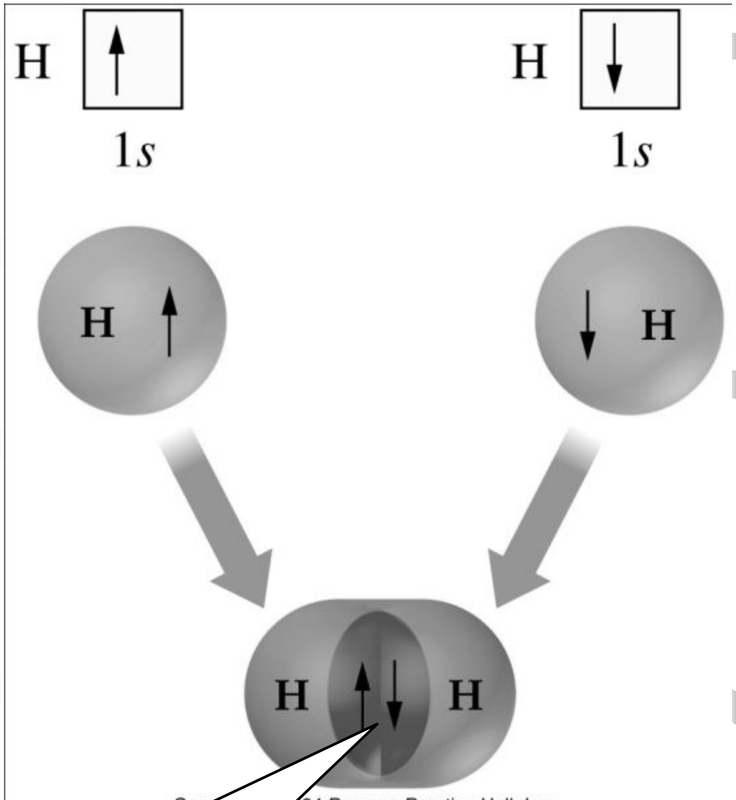
In NOF, there are two bond dipoles and both point downward, leading to a net downward molecular dipole. In NO_2F, the upward-pointing N—O bond dipole opposes the other two, and consequently we expect a smaller molecular dipole. Our prediction is therefore NOF, μ = 1.81 D, and NO_2F, μ = 0.47 D.

BIG POINT

- Bonds are formed by the overlap of orbitals

Atomic orbital (AO) overlap

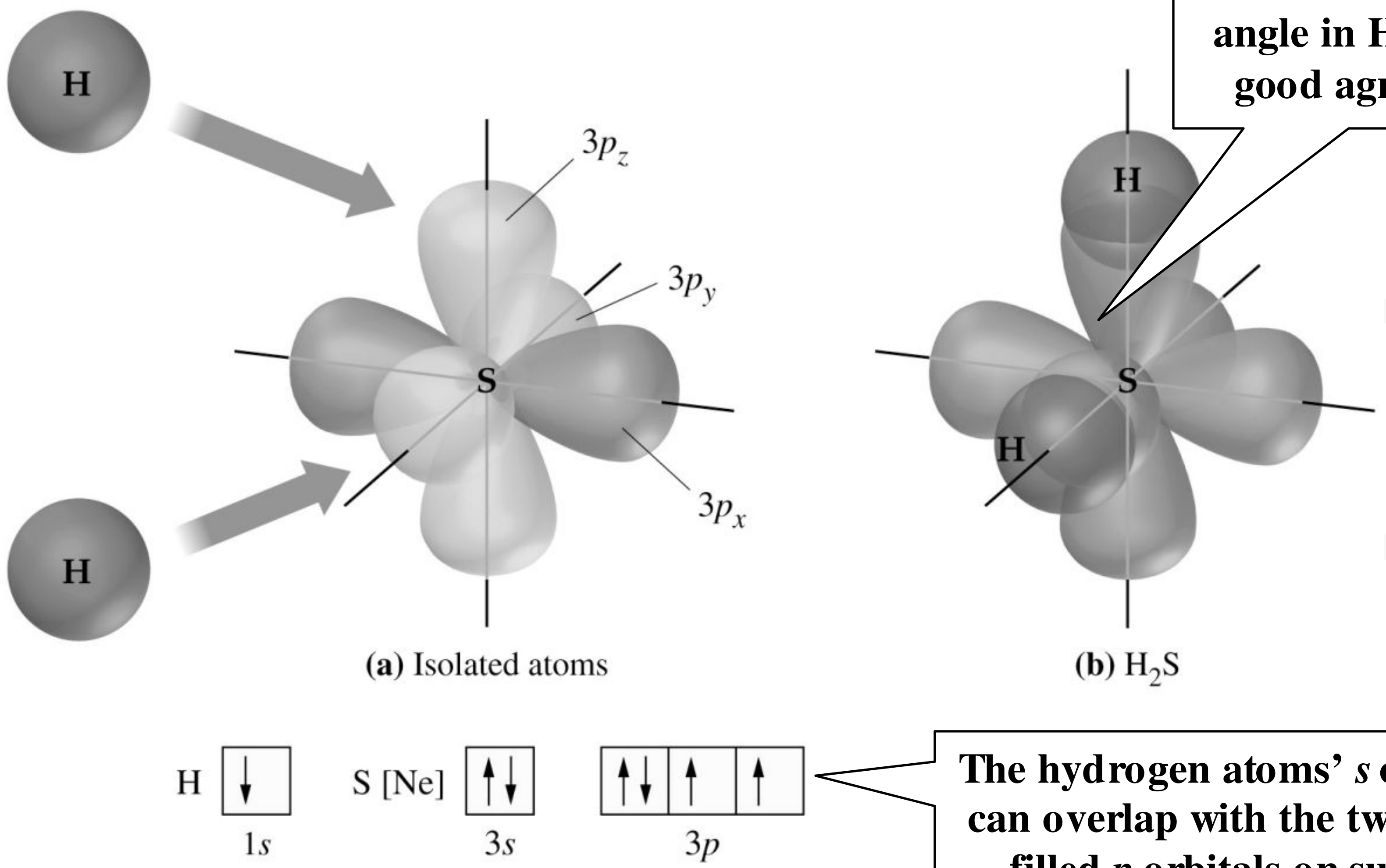
- ***Valence Bond** (**VB**)* theory states that a covalent bond is formed when atomic orbitals (AOs) overlap.
- In the overlap region, electrons with opposing spins produce a high electron charge density.
- In general, the more extensive the overlap between two orbitals, the stronger is the bond between two atoms.



Overlap region between nuclei has high electron density

Bonding in H_2S

The measured bond angle in H_2S is 92°; good agreement.



(a) Isolated atoms

(b) H_2S

The hydrogen atoms' *s* orbitals can overlap with the two half-filled *p* orbitals on sulfur.

Hybridization of atomic orbitals

- Often, the number of equivalent bonds around a central atom cannot be adequately explained using "conventional orbitals"
- sp^3 orbitals
- sp^2 orbitals
- sp orbitals
- d hybrids

Important points of VB theory

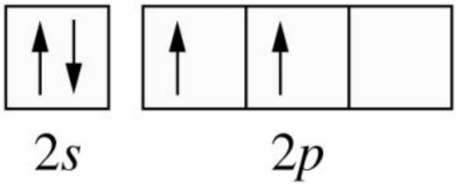
- Most of the electrons in a molecule remain in the same orbital locations that they occupied in the separated atoms.
- Bonding electrons are ***localized*** in the region of AO overlap.
- For AOs with directional lobes (such as *p* orbitals), maximum overlap occurs when the AOs overlap ***end to end***.
- VB theory is not without its problems …

Hybridization of atomic orbitals

VB theory: carbon should have just ***two*** bonds, and they should be about 90° apart.

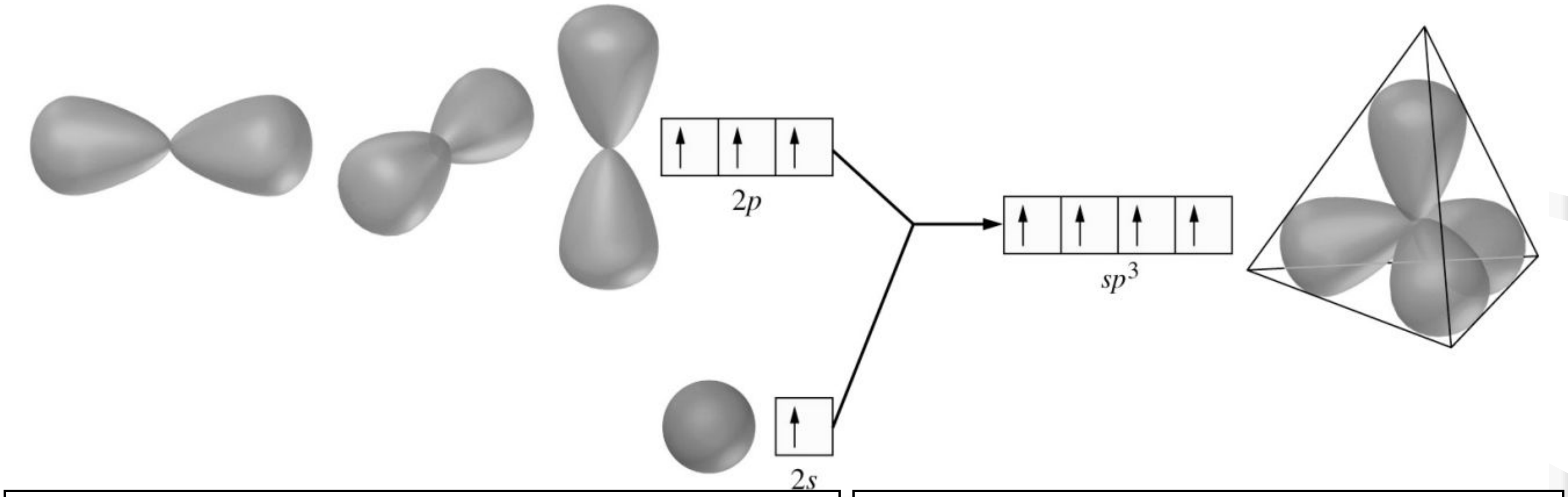
But CH_4 has *four* C—H bonds, 109° apart.

Ground-state electron configuration of C: [He]



- We can ***hybridize*** the four orbitals holding valence electrons; mathematically combine the wave functions for the 2*s* orbital and the three 2*p* orbitals on carbon.
- The four AOs combine to form 4 new sp^3 ***hybrid*** AOs.
- The four hybrid AOs are degenerate (same energy) and each has a single electron (Hund's rule).

The sp^3 *hybridization scheme*

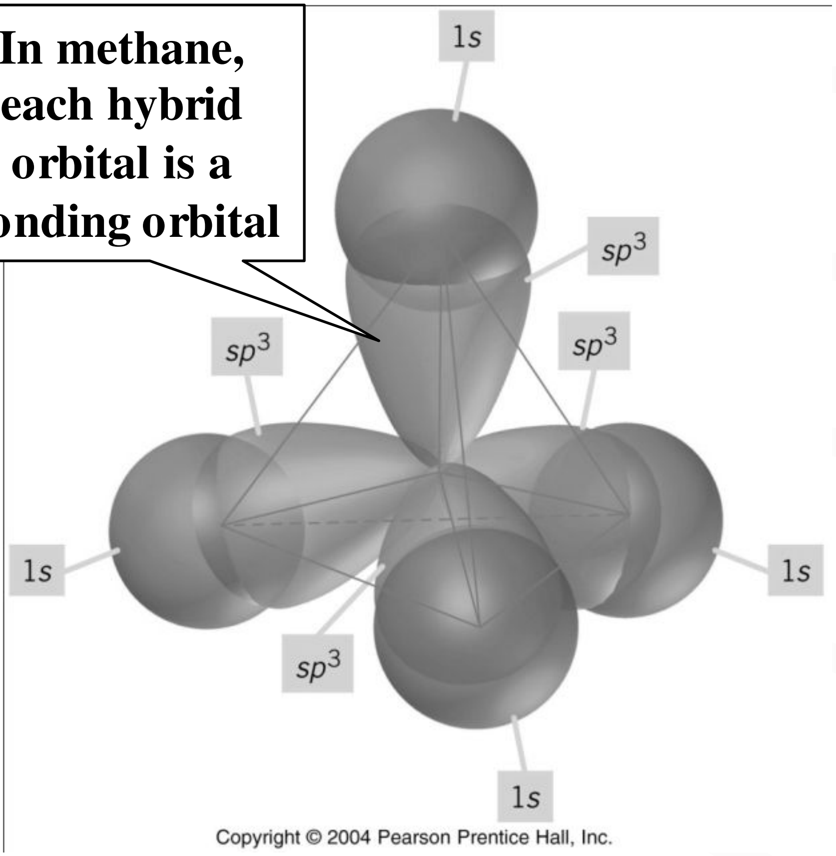


Four AOs …

… form four new hybrid AOs.

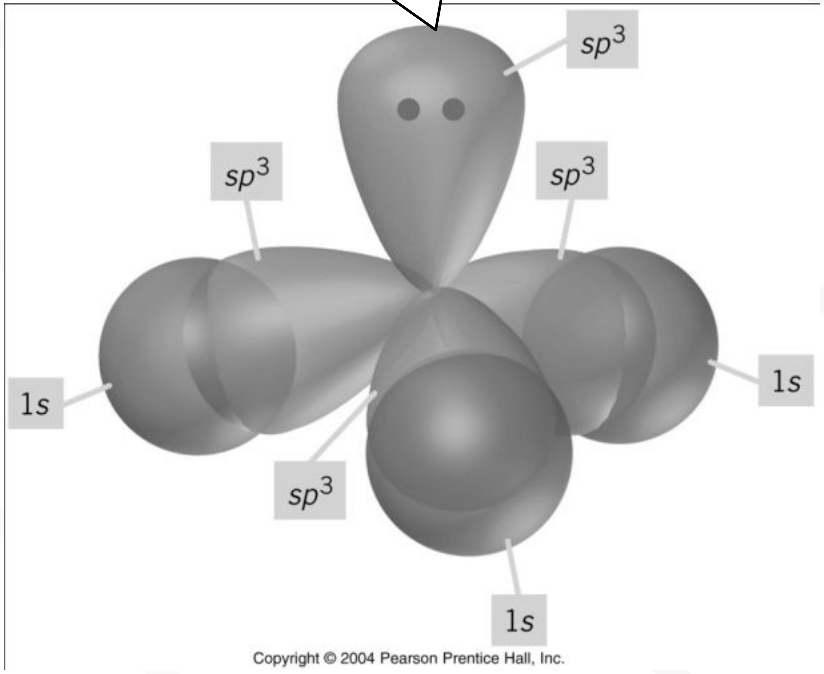
Methane and ammonia

In methane, each hybrid orbital is a bonding orbital



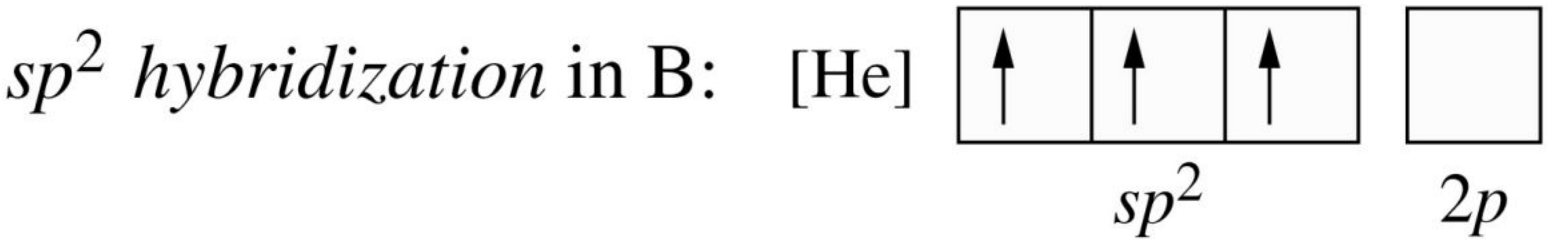
Four *sp*³ hybrid orbitals: tetrahedral
Four electron groups: tetrahedral
Coincidence? Hardly.

In ammonia, one of the hybrid orbitals contains the lone pair that is on the nitrogen atom

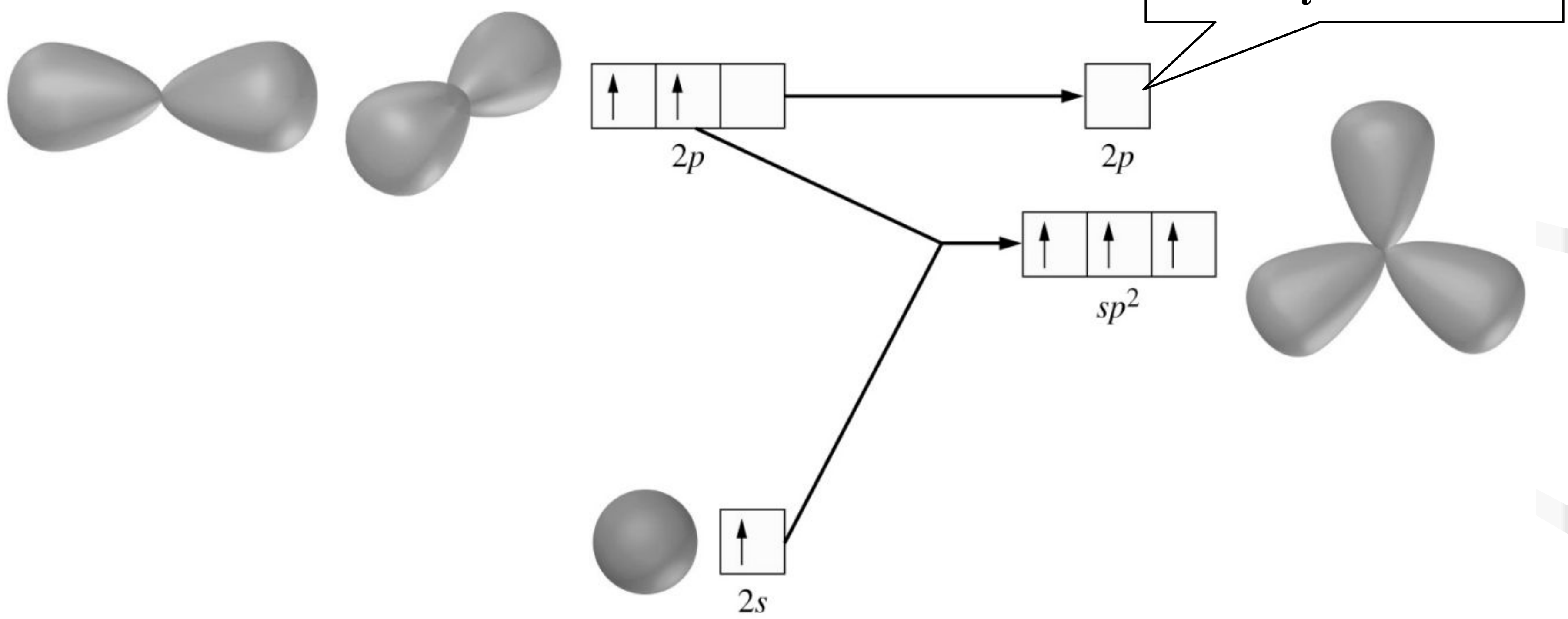


sp^2 *hybridization*

- Three ***sp^2*** hybrid orbitals are formed from an *s* orbital and two *p* orbitals.
- The empty *p* orbital remains unhybridized. It may be used in a multiple bond.
- The *sp^2* hybrid orbitals are in a plane, 120° apart.
- This distribution gives a ***trigonal planar*** molecular geometry, as predicted by VSEPR.



The sp^2 *hybridization scheme in boron*



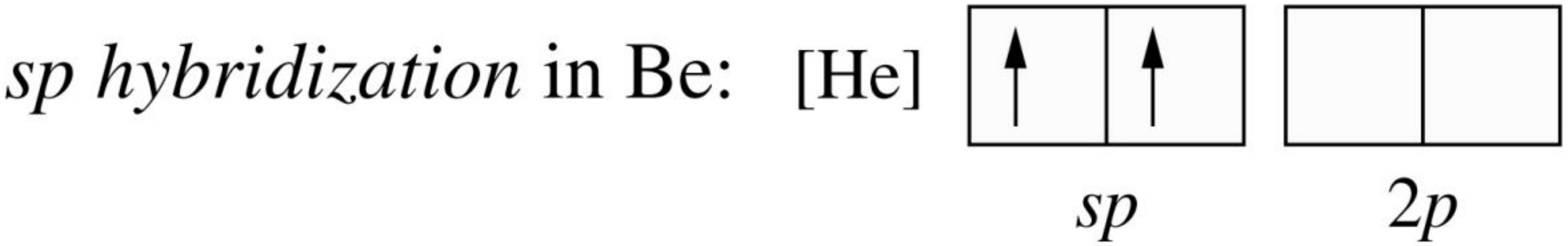
A 2*p* orbital remains unhybridized.

Three AOs combine to form …

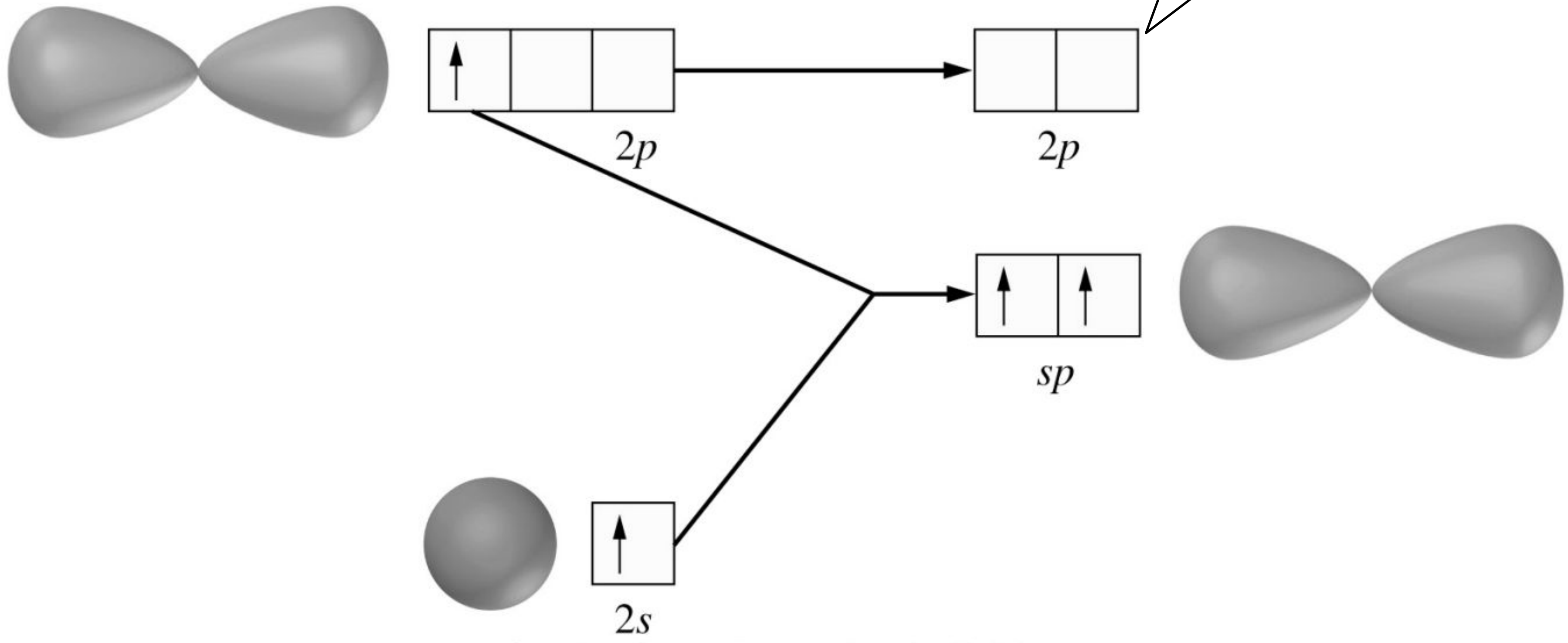
… three hybrid AOs.

sp *hybridization*

- Two ***sp*** hybrid orbitals are formed from an *s* orbital and a *p* orbital.
- Two empty *p* orbitals remains unhybridized; the *p* orbitals may be used in a multiple bond.
- The *sp* hybrid orbitals are 180° apart.
- The geometry around the hybridized atom is ***linear***, as predicted by VSEPR.



sp *hybridization in Be*



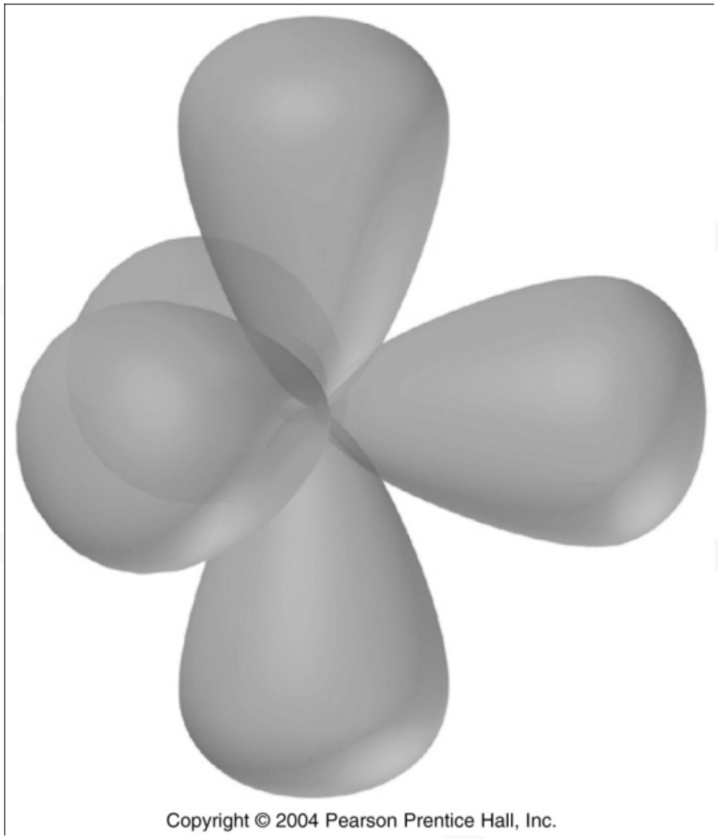
… with two unused *p* orbitals.

Two AOs combine to form …

… two hybrid AOs …

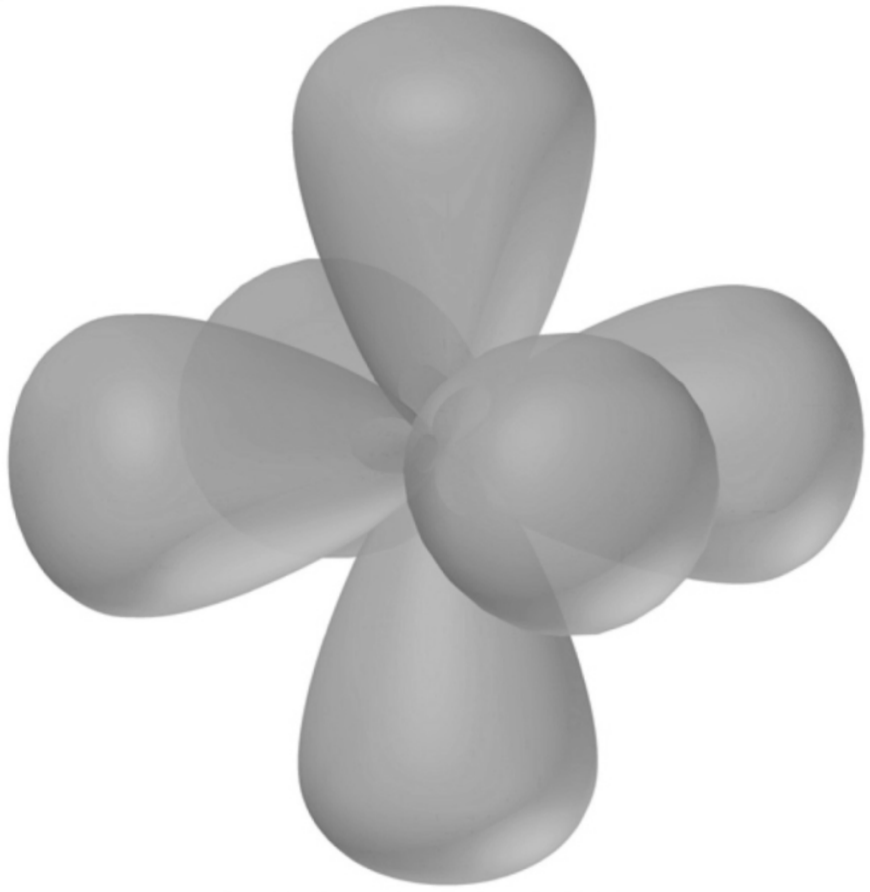
Hybrid orbitals involving d *subshells*

- This hybridization allows for ***expanded valence shell*** compounds.
- By hybridizing one *s*, three *p*, and one *d* orbital, we get five ***sp^3d*** hybrid orbitals.
- This hybridization scheme gives trigonal bipyramidal electron-group geometry.



Hybrid orbitals involving d *subshells (cont'd)*

- By hybridizing one *s*, three *p*, and two *d* orbitals, we get six ***sp^3d^2*** hybrid orbitals.
- This hybridization scheme gives octahedral geometry.

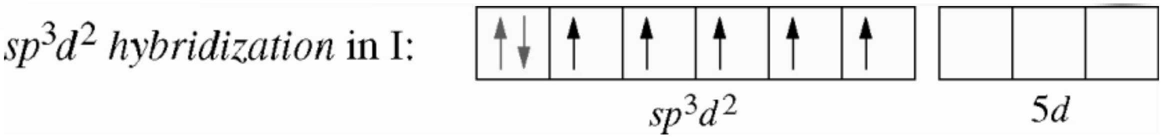


Predicting hybridization schemes

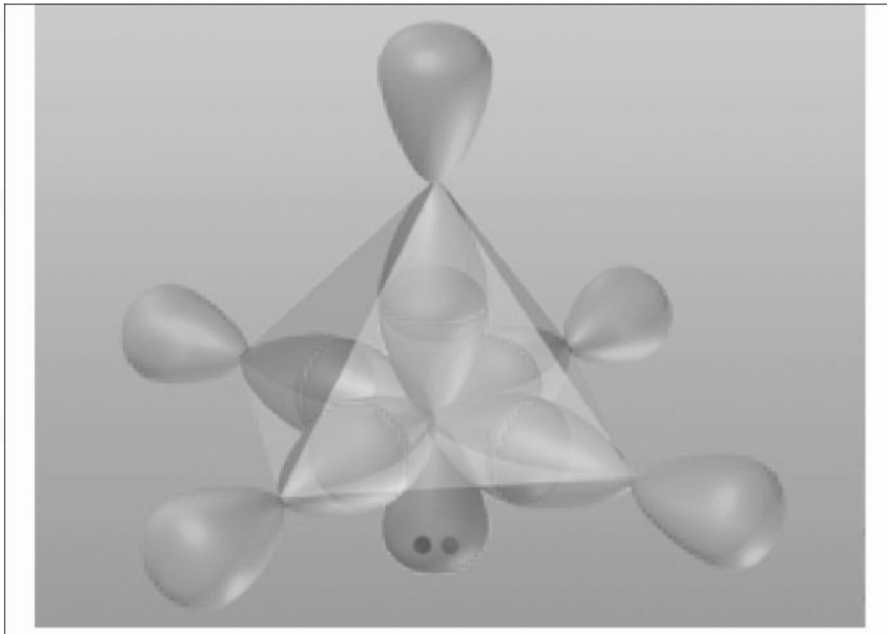
In the absence of experimental evidence, probable hybridization schemes can be predicted:

1. Write a plausible Lewis structure for the molecule or ion.
2. Use the VSEPR method to predict the electron-group geometry of the central atom.
3. Select the hybridization scheme that corresponds to the VSEPR prediction.
4. Describe the orbital overlap and molecular shape.

Example



- Iodine pentafluoride, IF_5, is used commercially as a fluorinating agent– a substance that, via a chemical reaction, introduces fluorine into other compounds. Describe a hybridization scheme for the central atom, and sketch the molecular geometry of the IF_5 molecule.



▲ **FIGURE 10.19 Bonding scheme for iodine pentafluoride, IF_5**

The orbitals around the central I atom are six sp^3d^2 hybrid orbitals. One of them (red) is occupied by the LP electrons. The other five are the bonding orbitals. Each bond involves the overlap of an I sp^3d^2 hybrid orbital with a $2p$ atomic orbital of a terminal F atom. Because of repulsions between the LP electrons and the bonding pairs, the (imaginary) plane at the base of the molecule is raised slightly above the I atom.

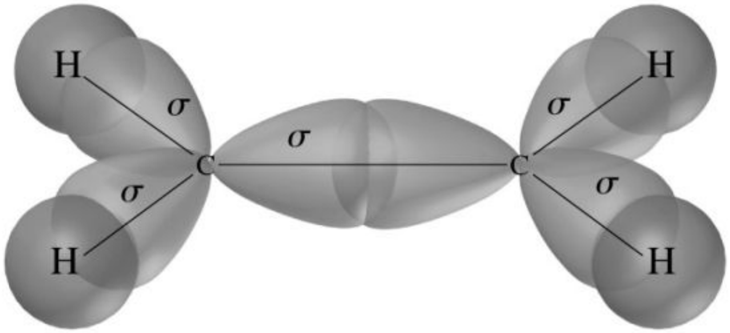
Hybrid orbitals and multiple bonds

- More than 2 orbitals cannot overlap the same region of space
- Double and triple bonds result from the overlap of multiple sets of orbitals in different regions of space

Hybrid orbitals and multiple covalent bonds

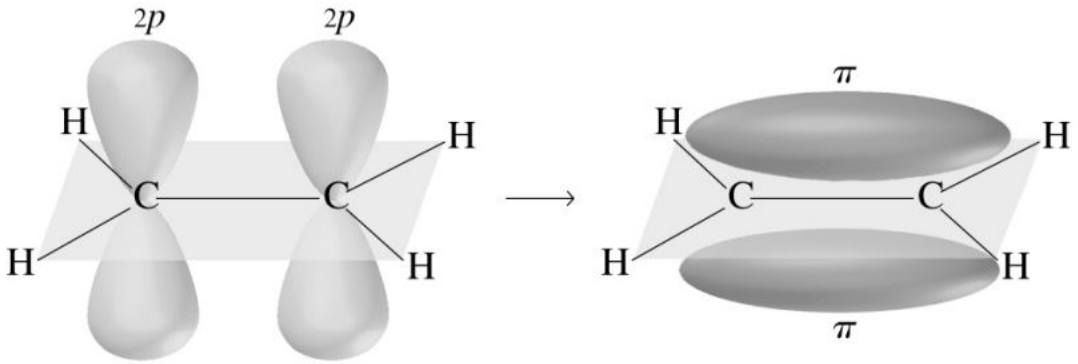
- Covalent bonds formed by the end-to-end overlap of orbitals are called ***sigma** (σ)* ***bonds***.
- All single bonds are sigma bonds.
- A bond formed by parallel, or side-by-side, orbital overlap is called a ***pi** (π)* ***bond***.
- A double bond is made up of ***one*** sigma bond and ***one*** pi bond.
- A triple bond is made up of ***one*** sigma bond and ***two*** pi bonds.

VB theory for ethylene, C_2H_4



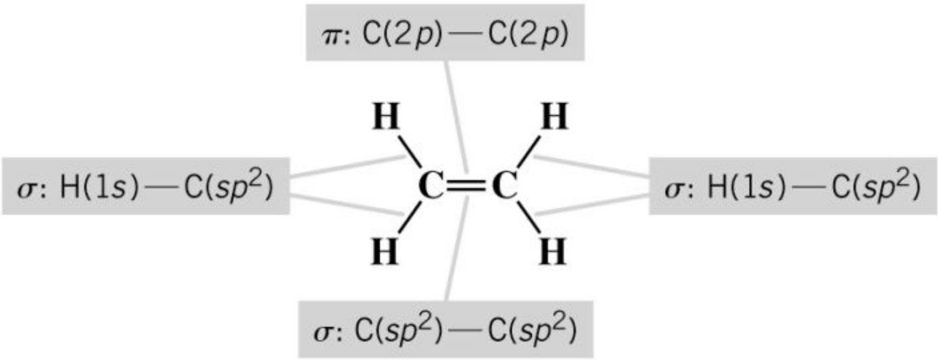
(a) The σ-bond framework

π-bond has *two* lobes (above and below plane), but is *one* bond. Side overlap of 2*p*–2*p*.



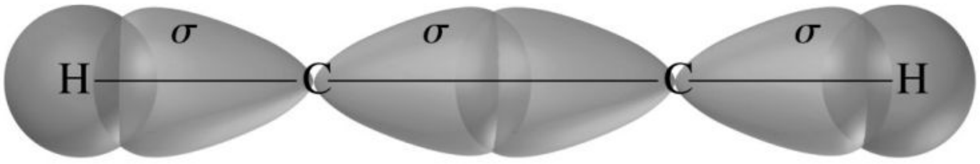
(b) The formation of a π-bond by the overlap of the half-filled 2*p* orbitals

The hybridization and bonding scheme is described by listing each bond and its overlap.

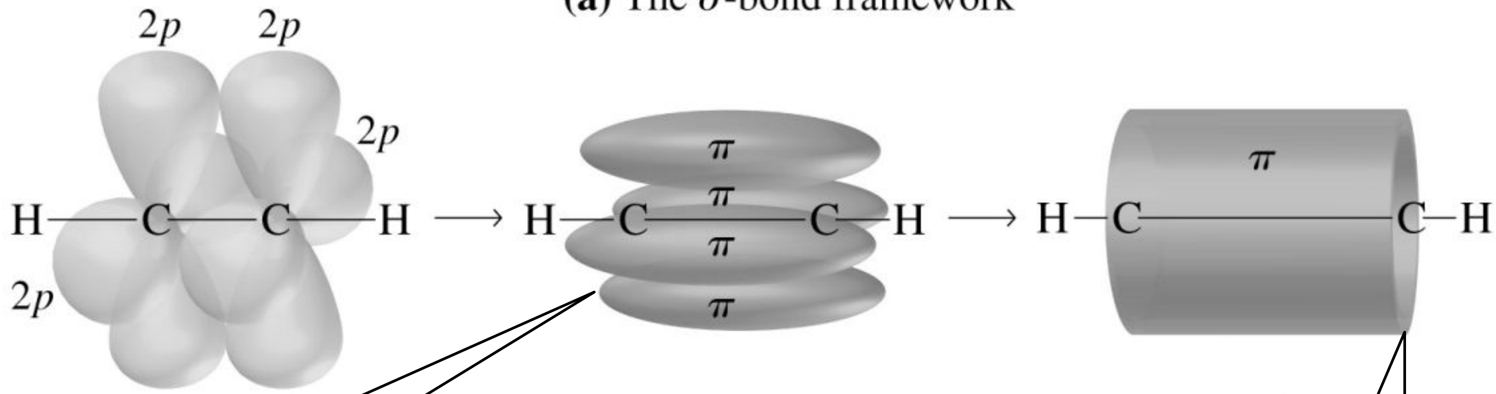


(c) Hybridization and bonding scheme

VB theory for acetylene, C_2H_2

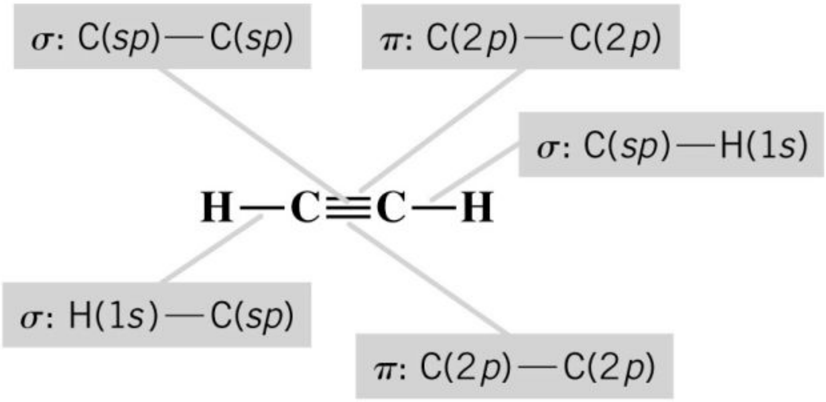


(a) The σ-bond framework



(b) Formation of π-bonds by the overlap of half-filled 2p orbitals

Two π-bonds (above and below, and front and back) from 2*p*–2*p* overlap …



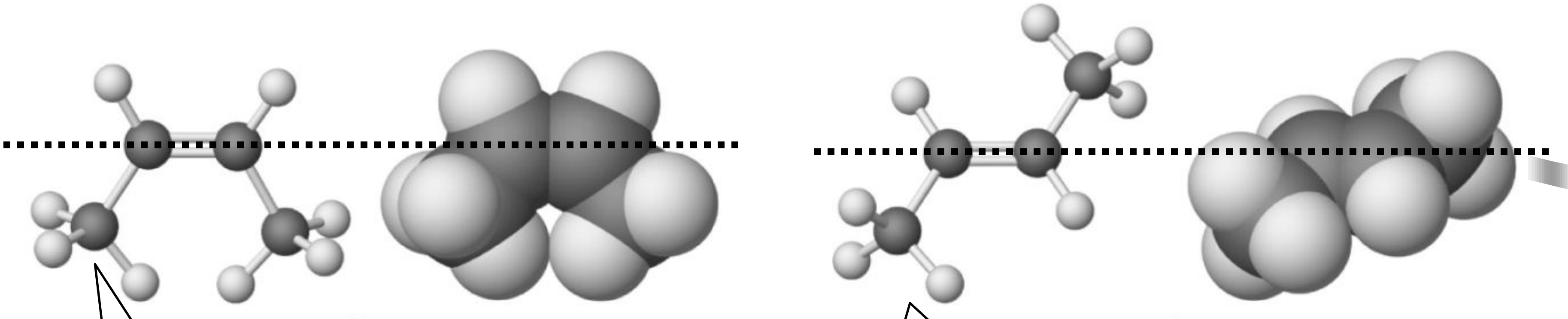
… form a cylinder of π-electron density around the two carbon atoms.

(c) Hybridization and bonding scheme

Geometric isomers

- Same formula, different arrangement in space
- ***Geometric isomers*** are isomers that differ only in the geometric arrangement of certain substituent groups.
- Two types of geometric isomers include:
  - ***cis***: substituent groups are on the same side
  - ***trans***: substituent groups are on opposite sides
- *cis*- and *trans*- compounds are distinctly different in both physical and chemical properties.
- Usually formed across double bonds and in square planar compounds.

Geometric isomerism in 2-butene



cis isomer
(a)

trans isomer
(b)

Groups are on the *same side* of the double bond: *cis*-isomer

Groups are on *opposite* sides of double bond: *trans*-isomer

***n-Butane* does not have these isomers; why not??**

Example

- Is it possible to write a unique structural formula for 1,2-dichloroethene if we are told that the molecule is nonpolar?

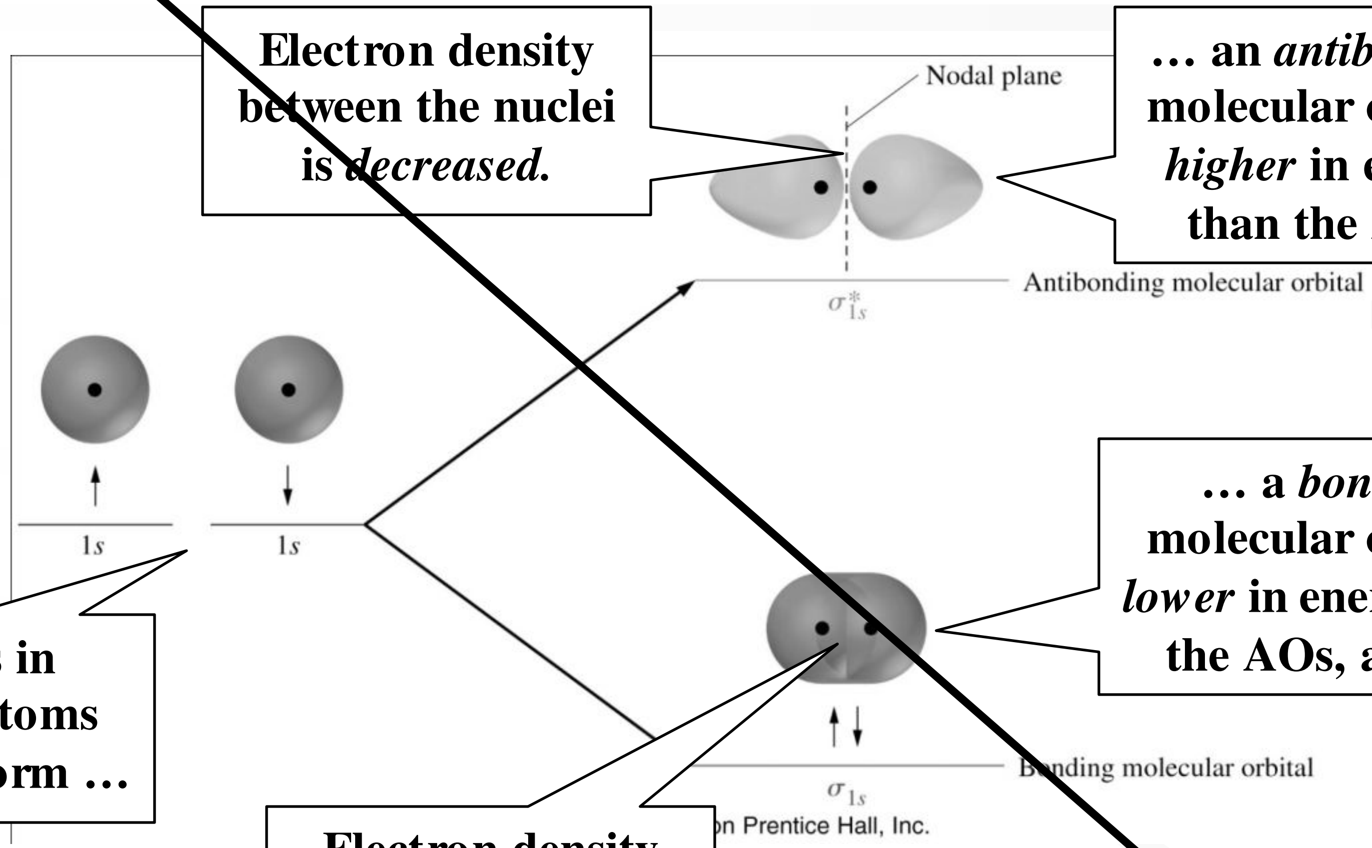
Molecular orbital theory (MO theory)

- An alternative scheme to VB theory uses molecular orbitals.
- A ***molecular orbital*** (***MO***) is a mathematical description of the region in a ***molecule*** where there is a high probability of finding electrons.
- In MO theory, molecular orbitals are formed by the combination of atomic orbitals.

Characteristics of MOs

- Two atomic orbitals combine => two molecular orbitals result.
- Of each pair of molecular orbitals, one is a ***bonding*** molecular orbital.
  - The bonding orbital is at a ***lower*** energy than the separate atomic orbitals.
  - Electrons in a bonding orbital ***increase*** the stability of the molecule.
- The second orbital is an ***antibonding*** orbital.
  - The antibonding orbital is at a ***higher*** energy than the AOs.
  - Electrons in an antibonding orbital ***decrease*** the stability of the molecule.
- There are *nonbonding* orbitals which we will not discuss.

Types of MOs



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Electron density between the nuclei is *decreased.*

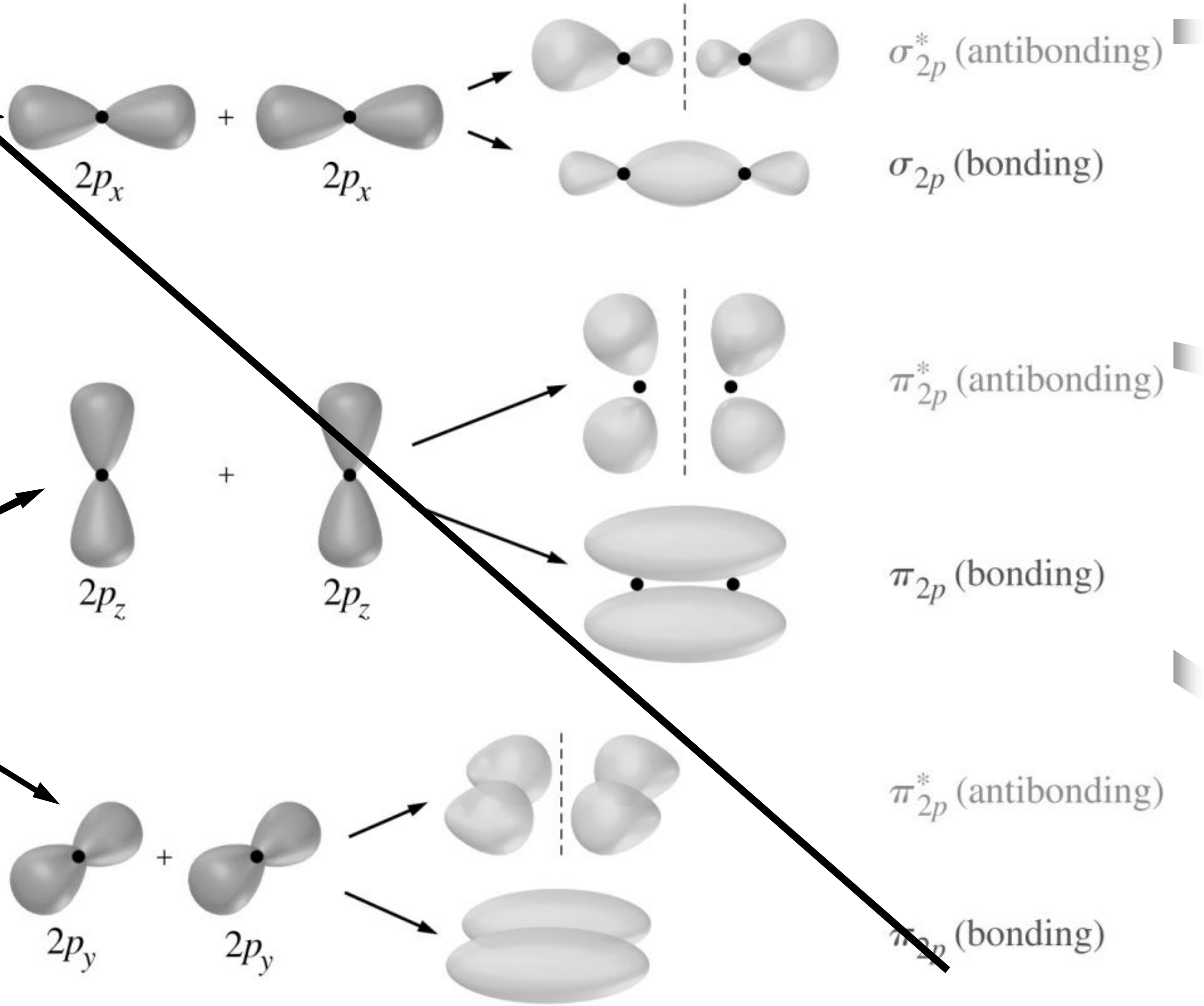
… an *antibonding* molecular orbital, *higher* in energy than the AOs.

Two AOs in hydrogen atoms combine to form …

… a *bonding* molecular orbital, *lower* in energy than the AOs, and …

Electron density between the nuclei is *increased.*

Homonuclear diatomic molecules of the second period elements



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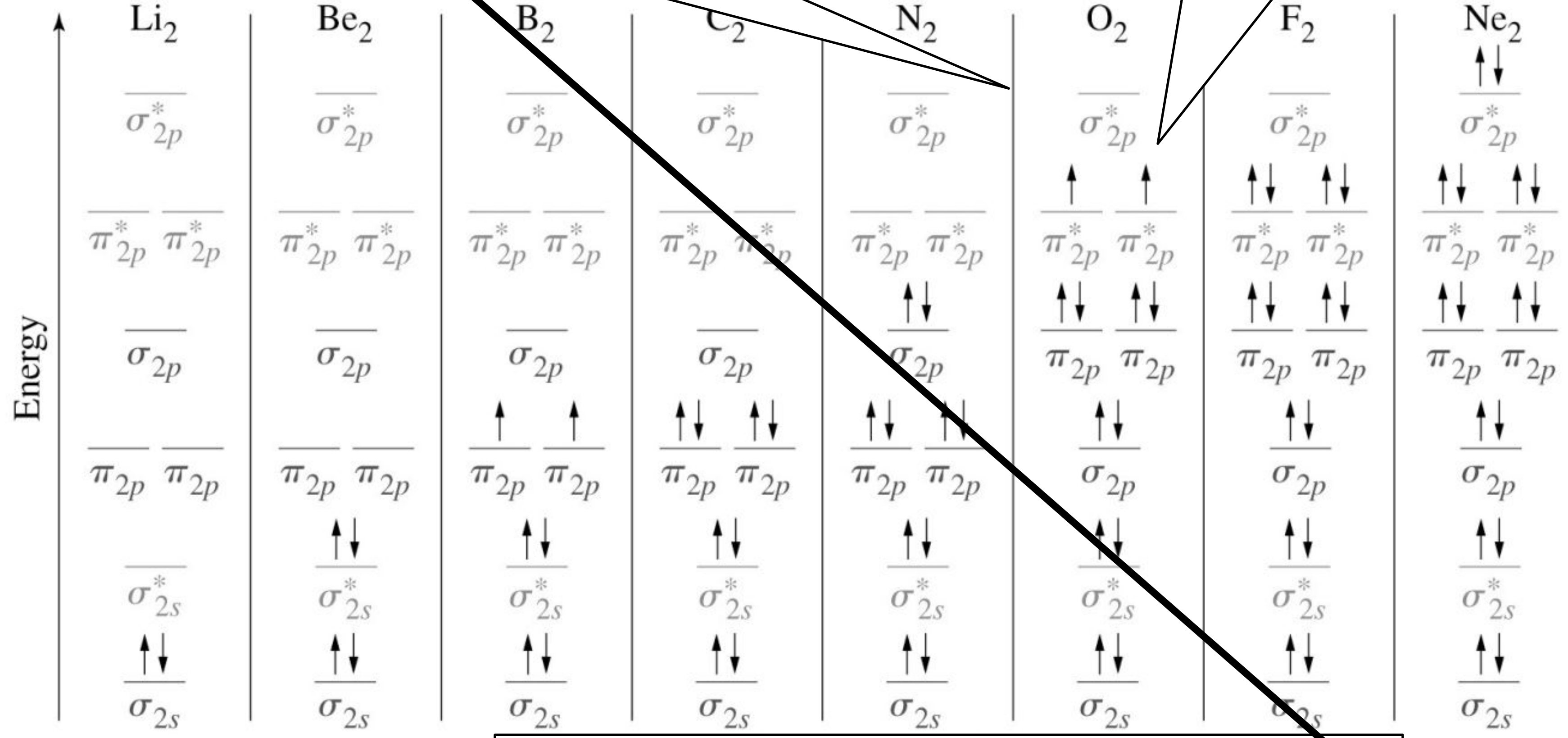
The two p_x orbitals combine to form *sigma* bonding and antibonding MOs.

The two p_y orbitals and the two p_z orbitals give *pi* bonding and antibonding MOs.

MO diagrams of diatomic molecules of the second period elements

Just like AOs: there are some irregularities in the filling order …

Remember how O_2 was paramagnetic?



Electrons fill MOs in the same way that AOs are filled – lowest energy to highest energy.

Jargon

- The Highest Occupied Molecular Orbital is called the HOMO
- The Lowest Unoccupied Molecular Orbital is called the LUMO

Example

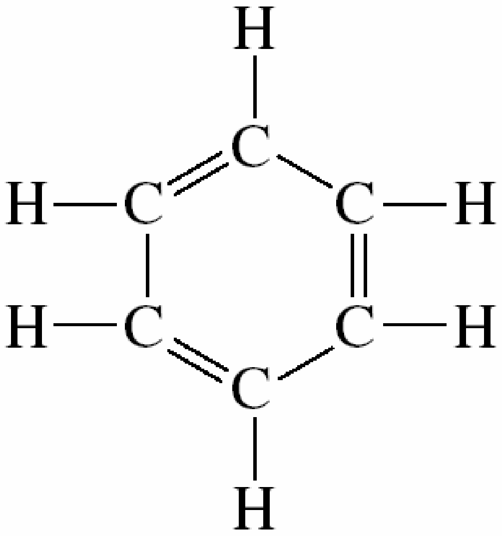
- When an electron is removed from a N_2 molecule, forming an N_2^+ ion, the bond between the N atoms is weakened. When an O_2 molecule is ionized to O_2^+, the bond between the O atoms is strengthened. Explain this difference.

Aromatic compounds

- Touched on briefly earlier…
- Many of the first benzene-like compounds discovered had pleasant odors, hence the name ***aromatic*** was applied to the compounds.
- Today an ***aromatic compound*** is one that has a ring structure and bonding characteristics related to those of benzene (more in Chapter 23).
- All organic compounds that are not aromatic are called ***aliphatic compounds***.

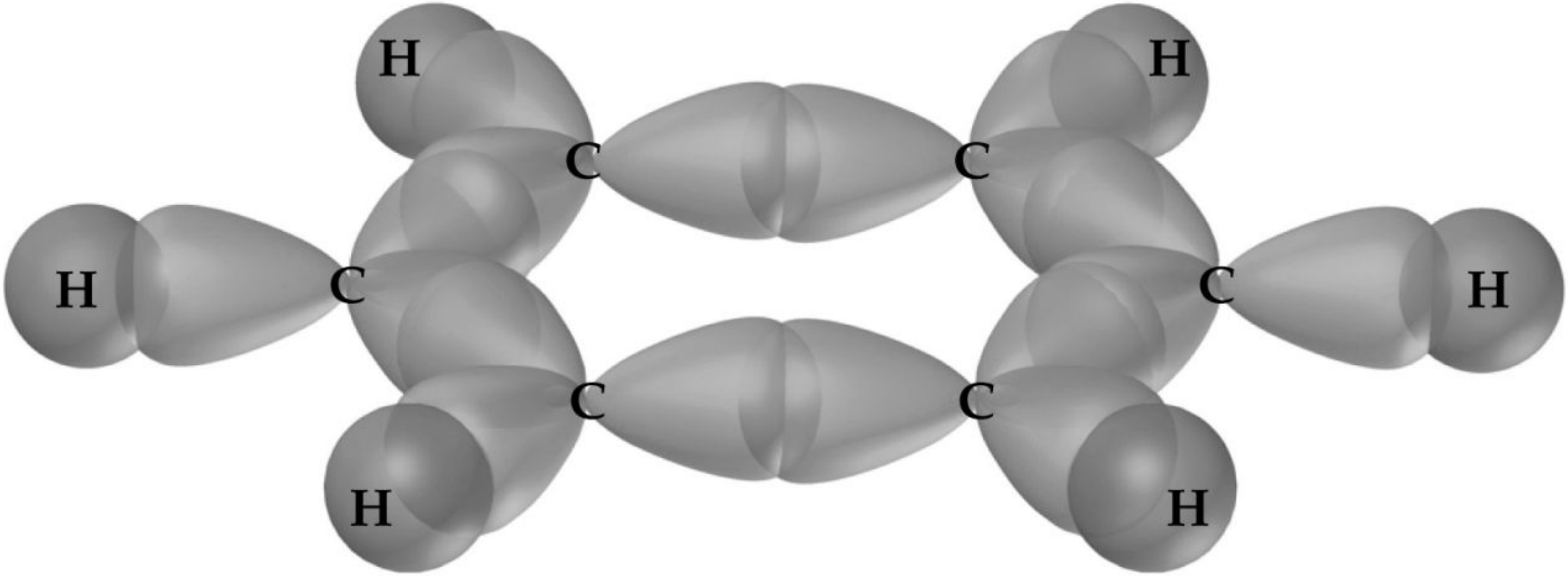
Aromatics – benzene

- In 1865, Kekulé proposed that benzene (C_6H_6) has a *cyclic* structure, with a hydrogen atom attached to each carbon atom. Alternating single and double bonds join the carbon atoms.

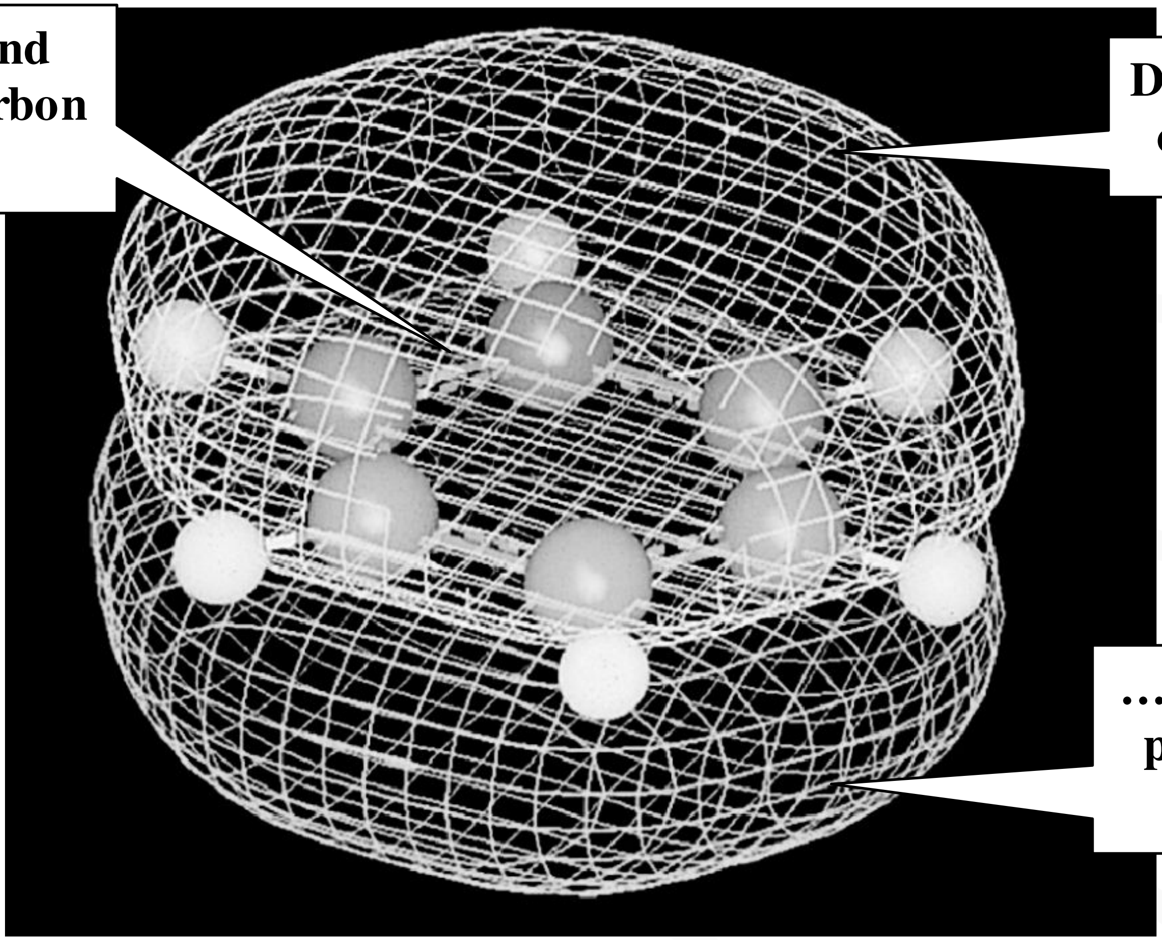


- Modern view: there are two resonance hybrids of benzene.
- The pi-electrons are not localized between any particular carbon atoms, but are ***delocalized*** among all six carbon atoms.

The σ-bonding framework in benzene



The π-bonding framework in benzene

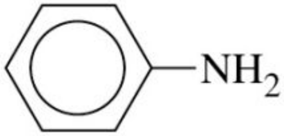
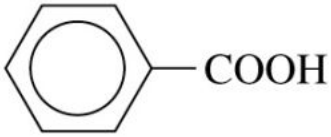
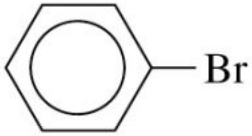
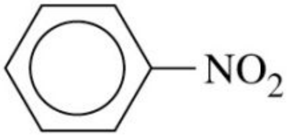
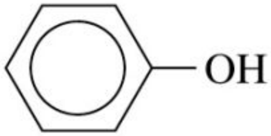
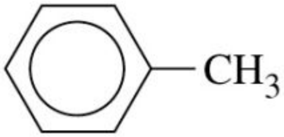


Sigma bond between carbon atoms

Donut-shaped pi-cloud above …

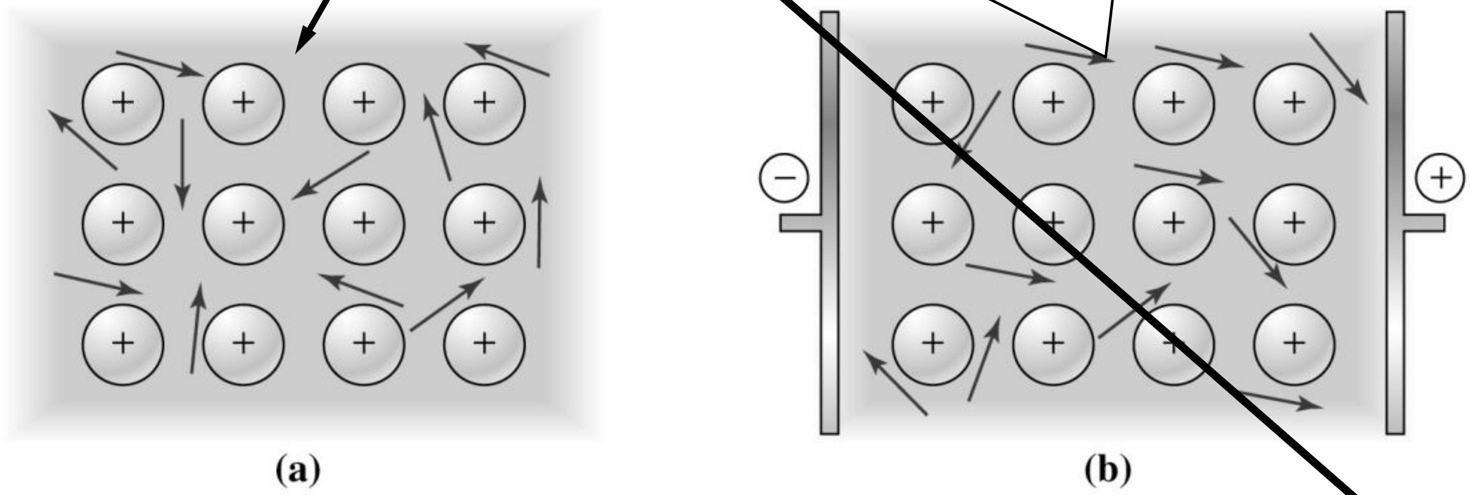
… and below the plane of sigma bonds.

TABLE 10.3 Some Representative Aromatic Compounds

Name	**Structure**	**Typical Use(s)**
Aniline		Starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
Benzoic acid		Food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
Bromobenzene		Starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
Nitrobenzene		Starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
Phenol		Disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
Toluene		Solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

Band theory

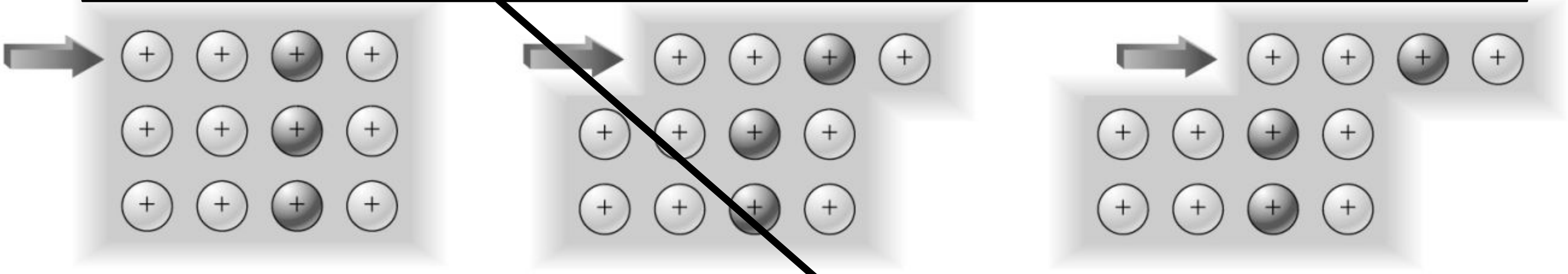
- In the ***free-electron model***, a metal consists of more-or-less immobile metal ions in a crystal lattice, surrounded by a “gas” of the valence electrons.



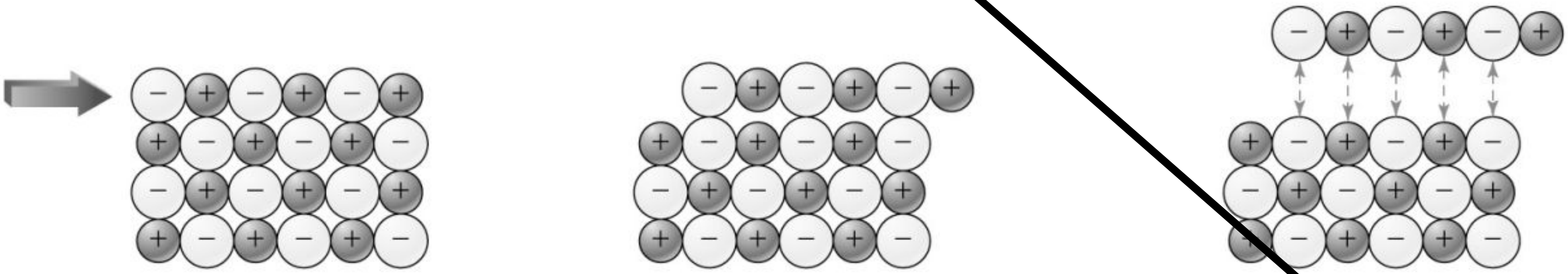
An applied electric potential causes the free-moving electrons to travel from (–) to (+).

~~*Deformation of a metal compared to an ionic solid*~~

~~In the free-electron model, deformation merely moves the positive ions relative to one another. Metals are therefore malleable and ductile.~~



(a) Metal



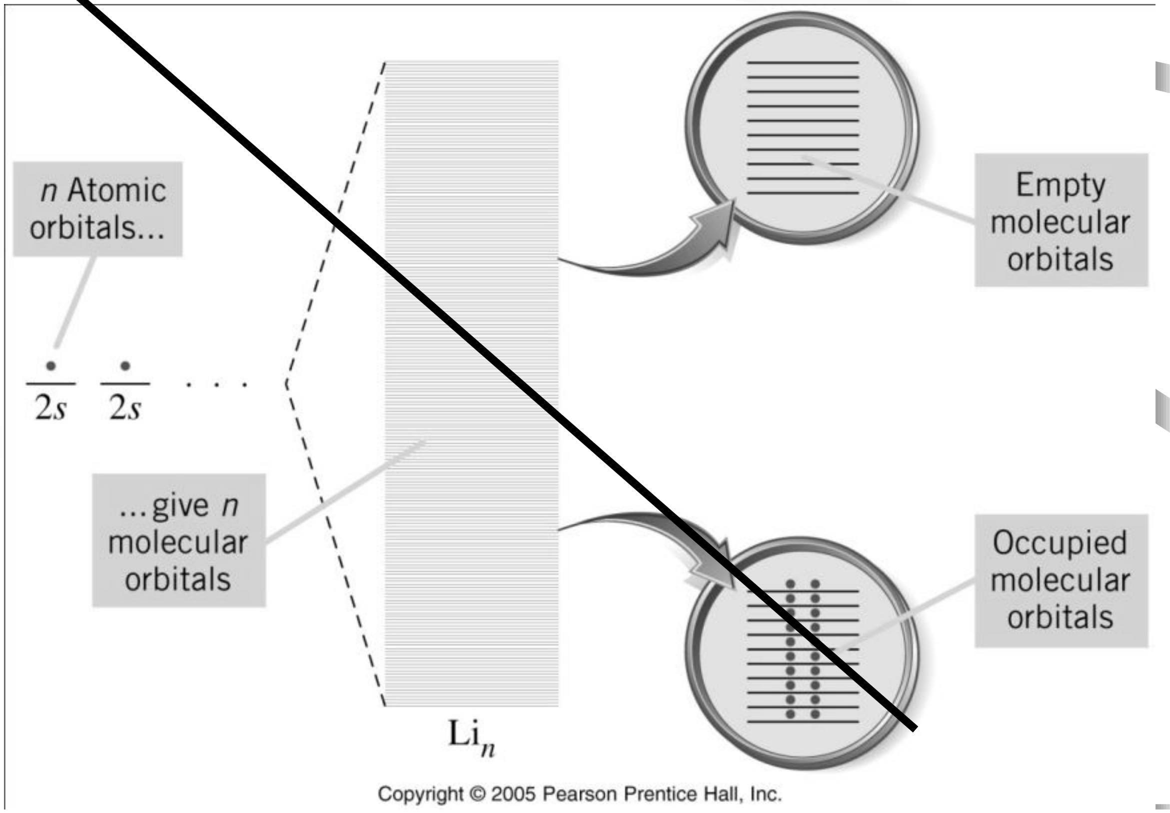
(b) Ionic crystal

~~In contrast, deformation of an ionic solid brings like-charged ions into proximity; the crystal is brittle and shatters or cleaves.~~

Explanation- band theory

- The free-electron model is a *classical* theory, which is less satisfactory in many ways than a *quantum-mechanical* treatment of bonding in metals.
- ***Band theory*** is a quantum-mechanical model.

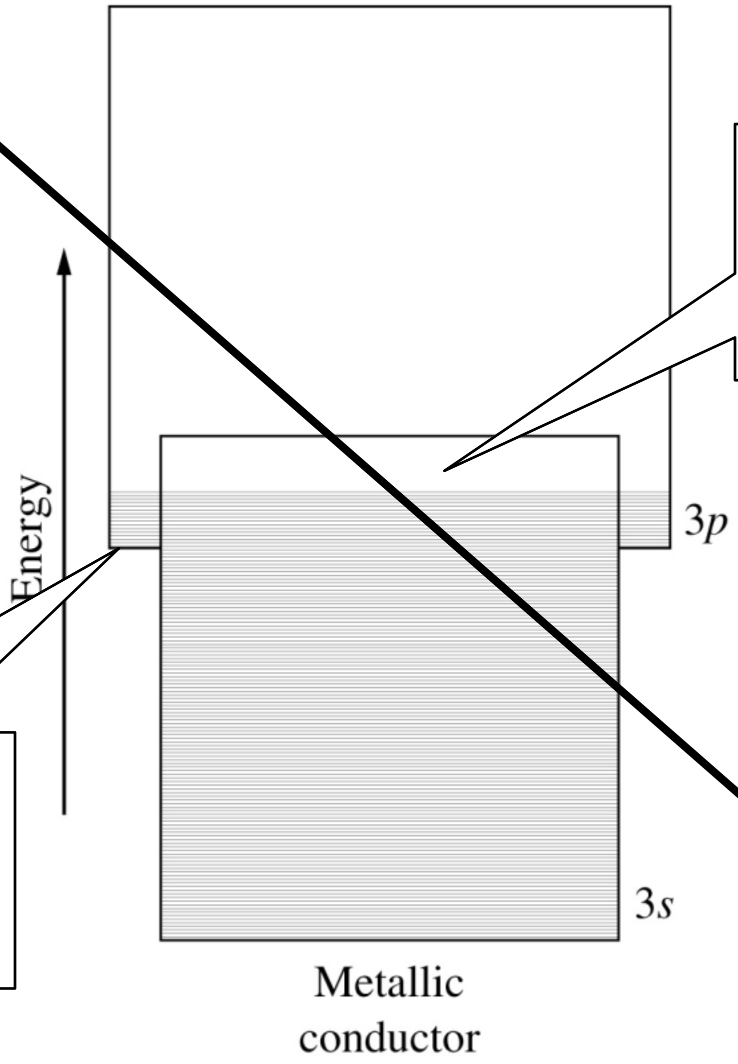
The spacing between electron energy levels is so minute in metals that the levels essentially merge into a *band*.



Band theory (cont'd)

- When the band is occupied by valence electrons, it is called a *valence band*. (Akin to the HOMO)
- In band theory, the presence of a *conduction band*—a partially filled band of energy levels—is required for conductivity.
- Because the energy levels in bands are so closely spaced, there are electronic transitions in a partially filled band that match in energy every component of visible light.
- Metals therefore absorb the light that falls on them and are opaque.
- At the same time electrons that have absorbed energy from incident light are very effective in radiating light of the same frequency—metals are highly reflective.

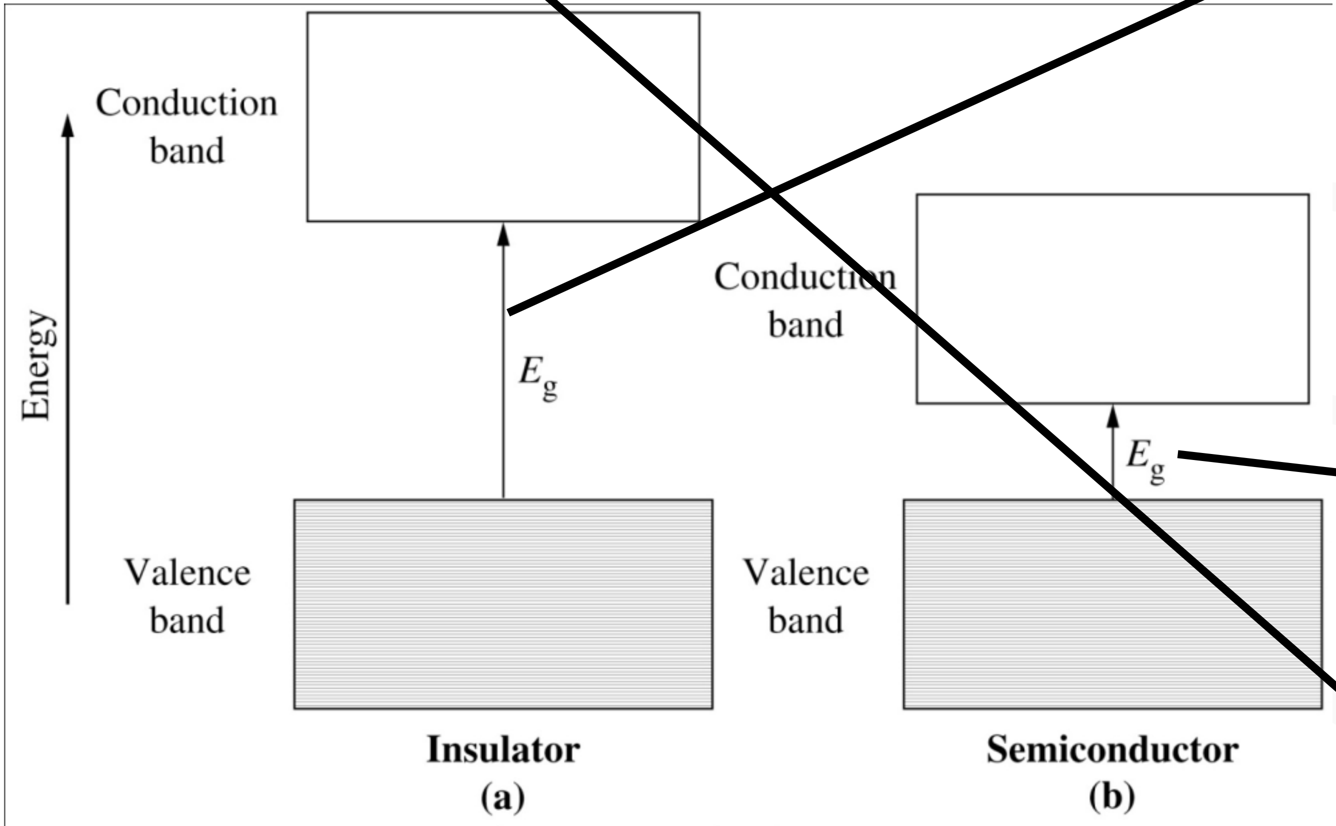
Band overlap in magnesium



The partially-filled band fulfills the requirement for electrical conductivity.

The 3*s* band is only partially filled because of overlap with the 3*p* band.

Semiconductors



In an insulator, the energy gap between conduction and valence band is large.
(“Band gap” like a large HOMO – LUMO gap.)

When the energy gap is small, some electrons can jump the gap; then it is a *semiconductor*.