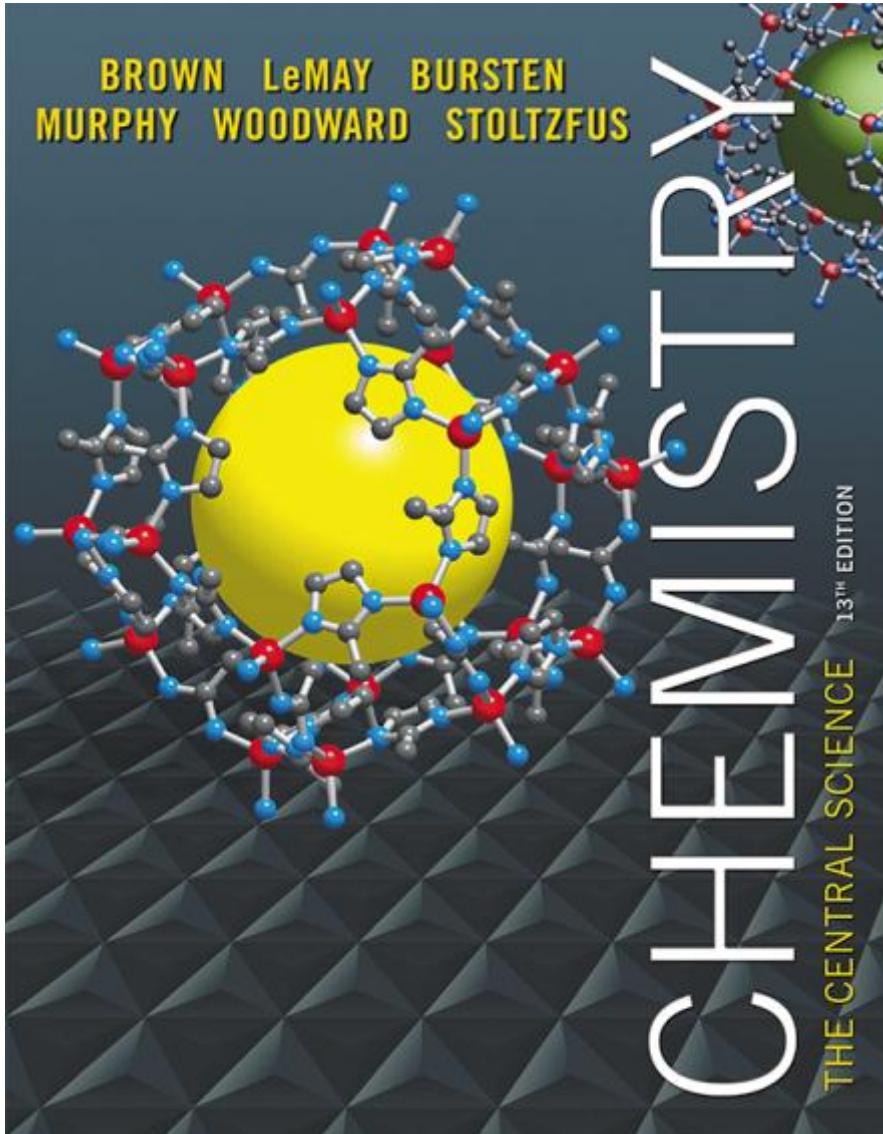


Review of chapter 6, chapter 7, and chapter 9

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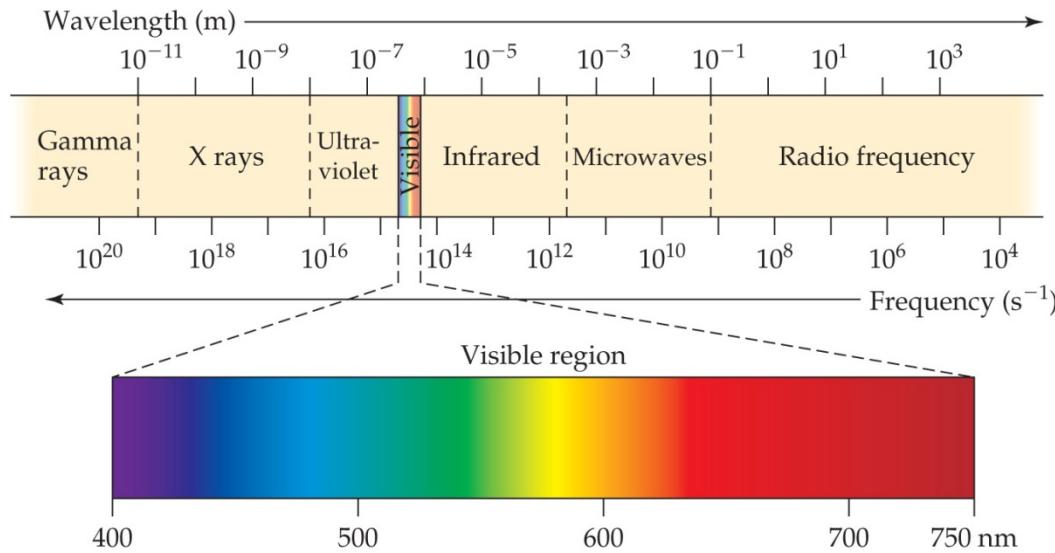
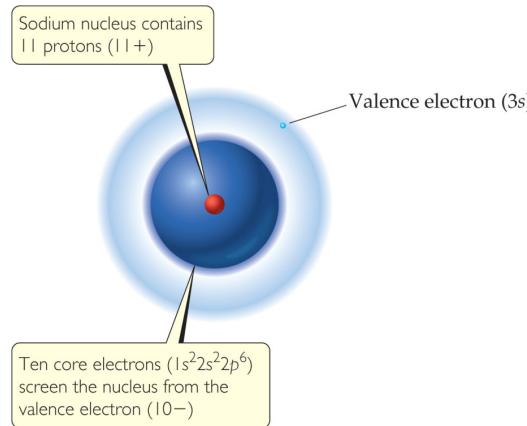
Lecture Presentation

Chapter 6

Electronic Structure of Atoms

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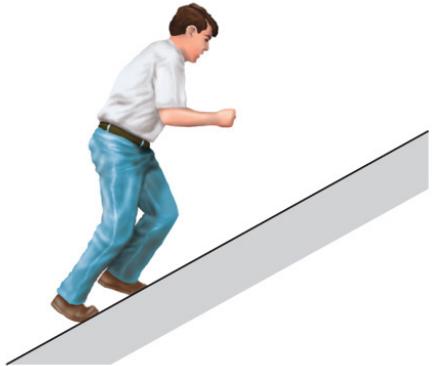
The electronic structure of an atom describes the **energies and arrangement of electrons around the atom**. Much of what is known about the electronic structure of atoms was obtained by **observing the interaction of light with matter**.



- All electromagnetic radiation travels at the same velocity: The speed of light (c) is 3.00×10^8 m/s.

$$c = \lambda \nu; E = h \nu = hc/\lambda$$

The Nature of Energy—Quanta

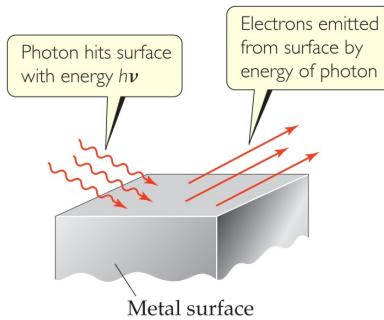


Potential energy of person walking up ramp increases in uniform, continuous manner



Potential energy of person walking up steps increases in stepwise, quantized manner

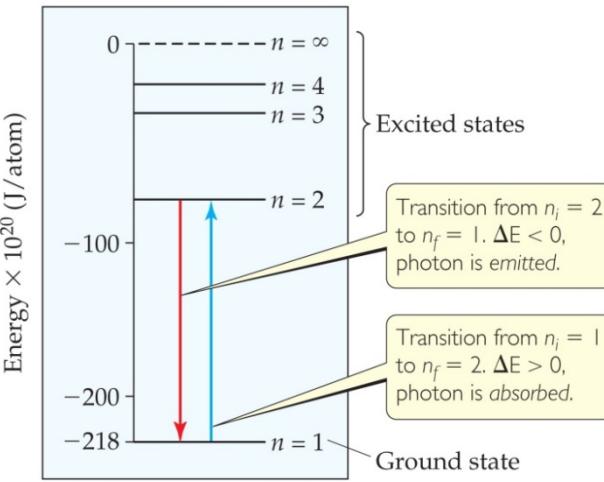
Max Planck explained it by assuming that energy comes in packets called **quanta** (singular: quantum).



He concluded that energy is proportional to frequency:

$$E = h\nu$$

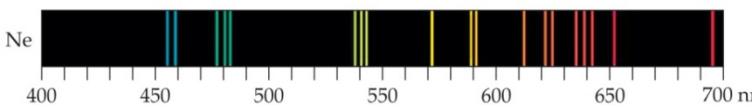
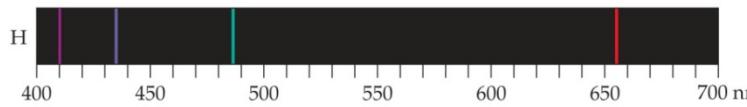
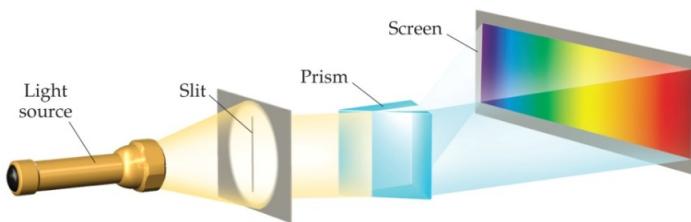
where h is Planck's constant, $6.626 \times 10^{-34} \text{ J}\cdot\text{s}$.



Principal quantum number: n

Ground state

Excited state



The Bohr Model

Niels Bohr adopted Planck's assumption and explained these phenomena

- (1) Electrons exist only in certain discrete energy levels.
- (2) Energy is involved in the transition of an electron from one level to another.

$$\frac{1}{\lambda} = (R_H) \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Let's see how to apply these concepts by considering a transition in which the electron moves from $n_i = 3$ to $n_f = 1$. From Equation 6.6 we have

$$\Delta E = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{1^2} - \frac{1}{3^2} \right) = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{8}{9} \right) = -1.94 \times 10^{-18} \text{ J}$$

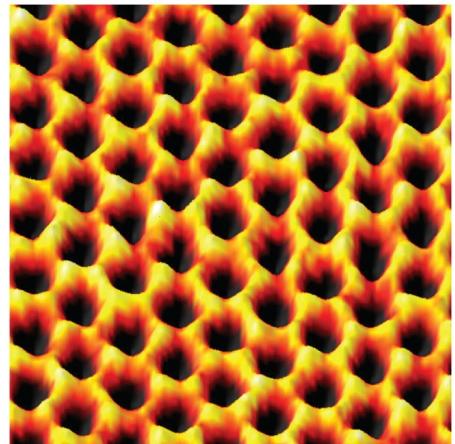
$$\lambda = \frac{c}{\nu} = \frac{hc}{E_{\text{photon}}} = \frac{hc}{-\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J-s})(2.998 \times 10^8 \text{ m/s})}{+1.94 \times 10^{-18} \text{ J}} = 1.02 \times 10^{-7} \text{ m}$$

Thus, a photon of wavelength $1.02 \times 10^{-7} \text{ m}$ (102 nm) is *emitted*.

$\Delta E > 0$ ($n_f > n_i$): Photon *absorbed* with $E_{\text{photon}} = h\nu = \Delta E$

$\Delta E < 0$ ($n_f < n_i$): Photon *emitted* with $E_{\text{photon}} = h\nu = -\Delta E$

The Wave Nature of Matter



- Louis de Broglie theorized that if light can have material properties, matter should exhibit wave properties.
- He demonstrated that the relationship between mass and wavelength was

$$\lambda = \frac{h}{mv}$$

What is the wavelength of an electron moving with a speed of 5.97×10^6 m/s? The mass of the electron is 9.11×10^{-31} kg.

$$h = 6.626 \times 10^{-34} \text{ J-s}$$

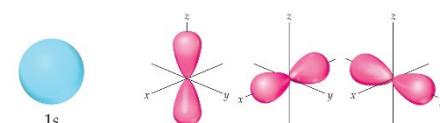
$$\begin{aligned}\lambda &= \frac{h}{mv} \\ &= \frac{(6.626 \times 10^{-34} \text{ J-s})}{(9.11 \times 10^{-31} \text{ kg})(5.97 \times 10^6 \text{ m/s})} \left(\frac{1 \text{ kg-m}^2/\text{s}^2}{1 \text{ J}} \right) \\ &= 1.22 \times 10^{-10} \text{ m} = 0.122 \text{ nm} = 1.22 \text{ \AA}\end{aligned}$$

Quantum Number

- The solution of Schrödinger's wave equation is designated with a lowercase Greek psi (ψ).
- The square of the wave equation, ψ^2 , gives the **electron density**, or probability of where an electron is likely to be at any given time.

Principal Quantum Number (n)

Angular Momentum Quantum Number (l)
s,p,d,f



Magnetic Quantum Number (m_l)

n, l, m_l

$l: 0 \text{ to } n - 1$

$m_l: -l \leq m_l \leq l$

A) 2, 0, 0

B) 2, 1, -1

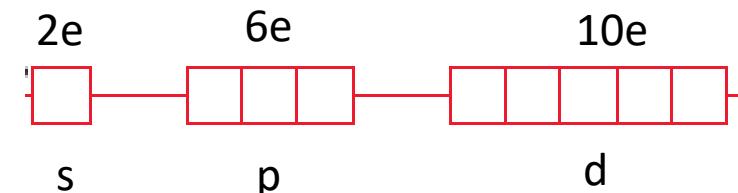
C) 3, 1, -1

D) 1, 1, 1

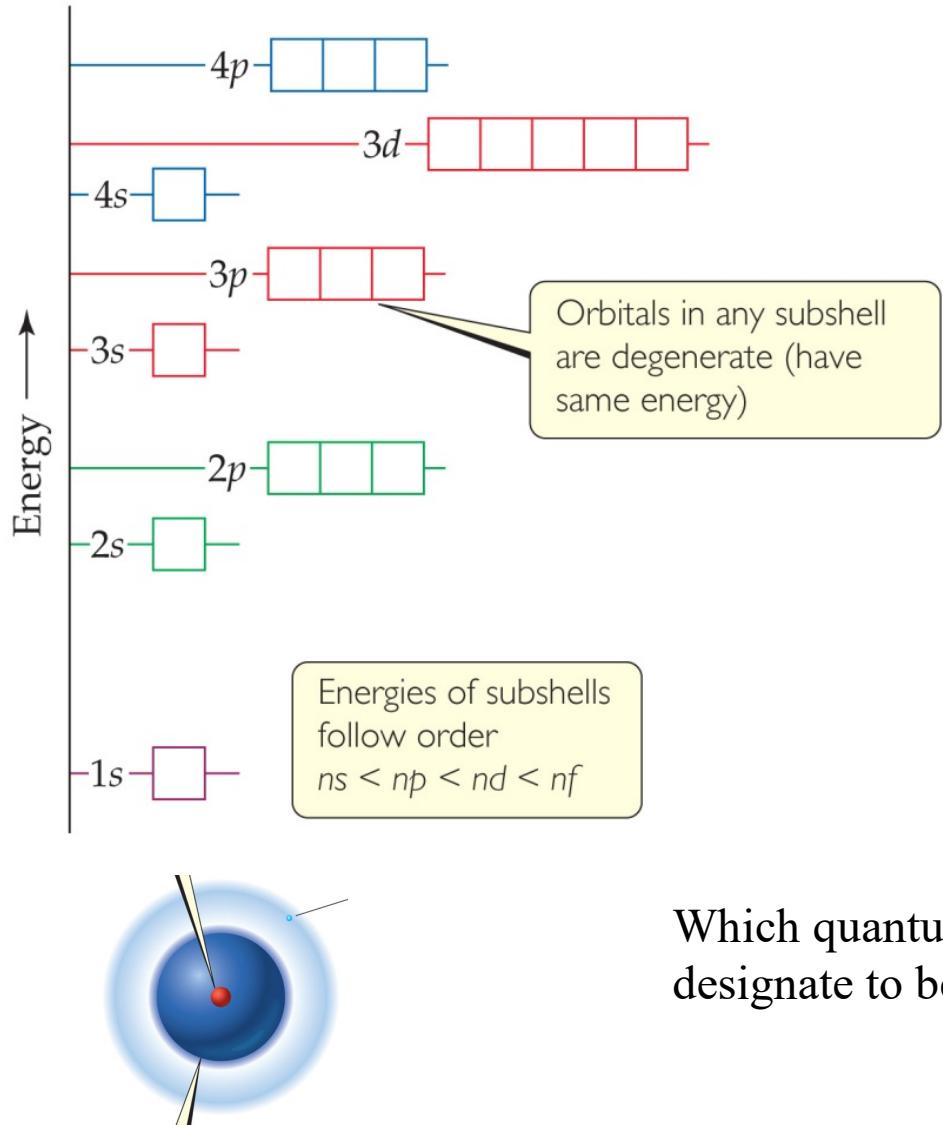
E) 3, 2, 1

Table 6.2 Relationship among Values of n , l , and m_l through $n = 4$

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	
	1	2p	1, 0, -1	3	4
3	0	3s	0	1	
	1	3p	1, 0, -1	3	
	2	3d	2, 1, 0, -1, -2	5	9
4	0	4s	0	1	
	1	4p	1, 0, -1	3	
	2	4d	2, 1, 0, -1, -2	5	
	3	4f	3, 2, 1, 0, -1, -2, -3	7	16



Energies of Orbitals—Many-electron Atoms



- As the number of electrons increases, so does the repulsion between them.
- Therefore, in atoms with more than one electron, not all orbitals on the same energy level are degenerate.
- Orbital sets in the same sublevel are still degenerate.
- Energy levels start to overlap in energy (e.g., 4s is lower in energy than 3d.)

Which quantum numbers must be the same for the orbitals that they designate to be degenerate in a multiple-electron system?

Hund's Rule

Table 6.3 Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram	Electron Configuration
		1s 2s 2p 3s	
Li	3		$1s^2 2s^1$
Be	4		$1s^2 2s^2$
B	5		$1s^2 2s^2 2p^1$
C	6		$1s^2 2s^2 2p^2$
N	7		$1s^2 2s^2 2p^3$
Ne	10		$1s^2 2s^2 2p^6$
Na	11		$1s^2 2s^2 2p^6 3s^1$

Condensed Electron Configurations

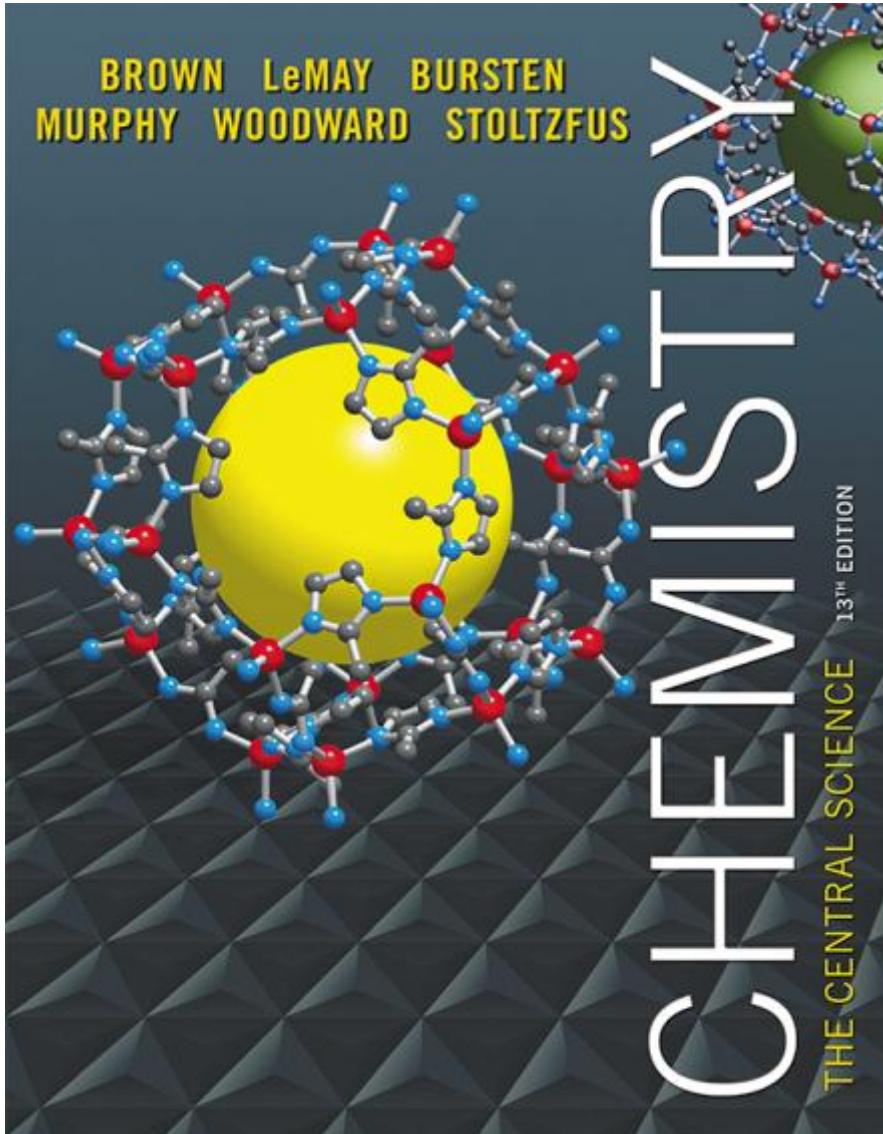
F: $1s^2 2s^2 2p^5$ He: $1s^2$ F: [He] $2s^2 2p^5$

Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$ Ne: $1s^2 2s^2 2p^6$

“For degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.”

- This means that, for a set of orbitals in the same sublevel, there must be *one* electron in each orbital before pairing and the electrons have the *same* spin, as much as possible.

C	[He] $2s^2 2p^2$	$1s^2 2s^2 2p^6 3s^1$
N	[He] $2s^2 2p^3$	$1s^2 2s^2 2p^6 3s^2$
O	[He] $2s^2 2p^4$	$1s^2 2s^2 2p^6 3s^2 3p^1$
F	[He] $2s^2 2p^5$	$1s^2 2s^2 2p^6 3s^2 3p^4$
Ne	[He] $2s^2 2p^6$	$1s^2 2s^2 2p^6 3s^2 3p^5$



Lecture Presentation

Chapter 7

Periodic Properties of the Elements

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Period, group

		Periodic Table of Elements																		
		1A		Period														8A		
		1	2	2s							2p							1	2	
1s		n=1	1 H	2 Be														18 He		
1s 2s2p		n=2	3 Li	4 Be														10 Ne		
1s 2s2p 3s3p3d		n=3	11 Na	12 Mg	3B 3	4B 4	5B 5	6B 6	7B 7	8B			1B 8	2B 9	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
			19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
			37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
			55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
			87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cp	113 Fl	114 Lv	115 At	116 Rn	117 Fr	118 Og

Metals
Metalloids
Nonmetals

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Down a group

Lithium	[He]2s ¹
Sodium	[Ne]3s ¹
Potassium	[Ar]4s ¹
Rubidium	[Kr]5s ¹
Cesium	[Xe]6s ¹

Beryllium	[He]2s ²
Magnesium	[Ne]3s ²
Calcium	[Ar]4s ²
Strontium	[Kr]5s ²
Barium	[Xe]6s ²

Oxygen	[He]2s ² 2p ⁴
Sulfur	[Ne]3s ² 3p ⁴
Selenium	[Ar]3d ¹⁰ 4s ² 4p ⁴
Tellurium	[Kr]4d ¹⁰ 5s ² 5p ⁴
Polonium	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴

Fluorine	[He]2s ² 2p ⁵
Chlorine	[Ne]3s ² 3p ⁵
Bromine	[Ar]4s ² 3d ¹⁰ 4p ⁵
Iodine	[Kr]5s ² 4d ¹⁰ 5p ⁵

1A

2A

6A

7A

Effective Nuclear Charge

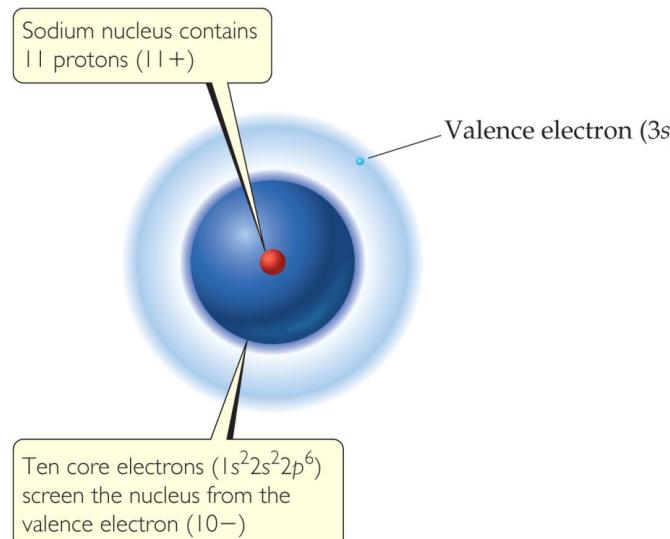
➤ The effective nuclear charge, Z_{eff} , is found this way:

$$Z_{\text{eff}} = Z - S$$

where Z is the atomic number and S is a screening constant, usually close to the number of inner electrons.

➤ Effective nuclear charge is a periodic property:

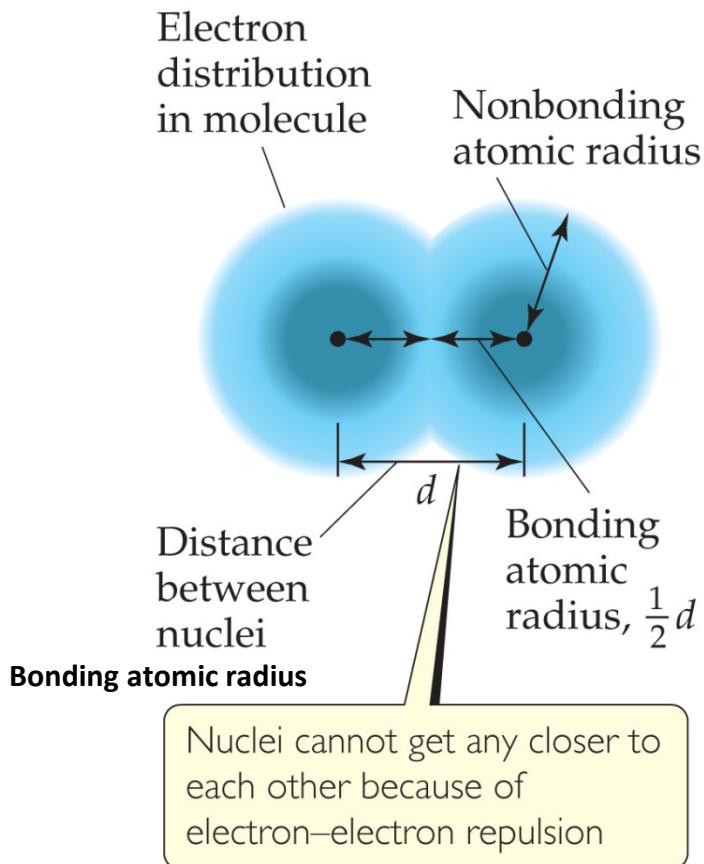
- It increases across a period.
- It increases down a group.



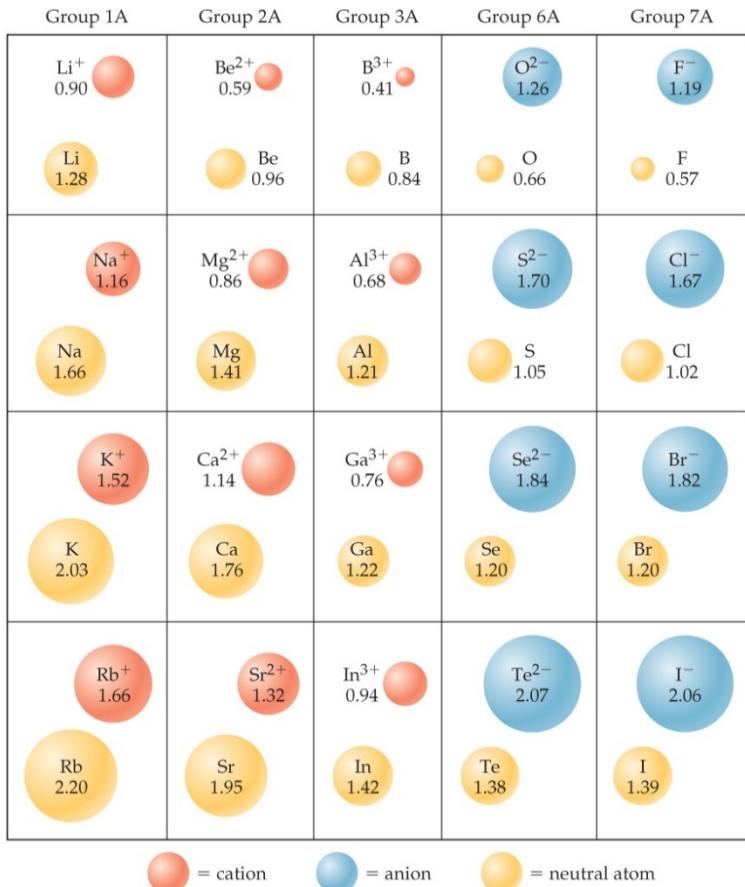
Effective nuclear charge, which is the portion of the nuclear charge that an outer electron experiences after **screening by inner electrons**.

What Is the Size of an Atom?

The **nonbonding atomic radius** or **van der Waals radius** is half of the shortest distance separating two nuclei during a collision of atoms.



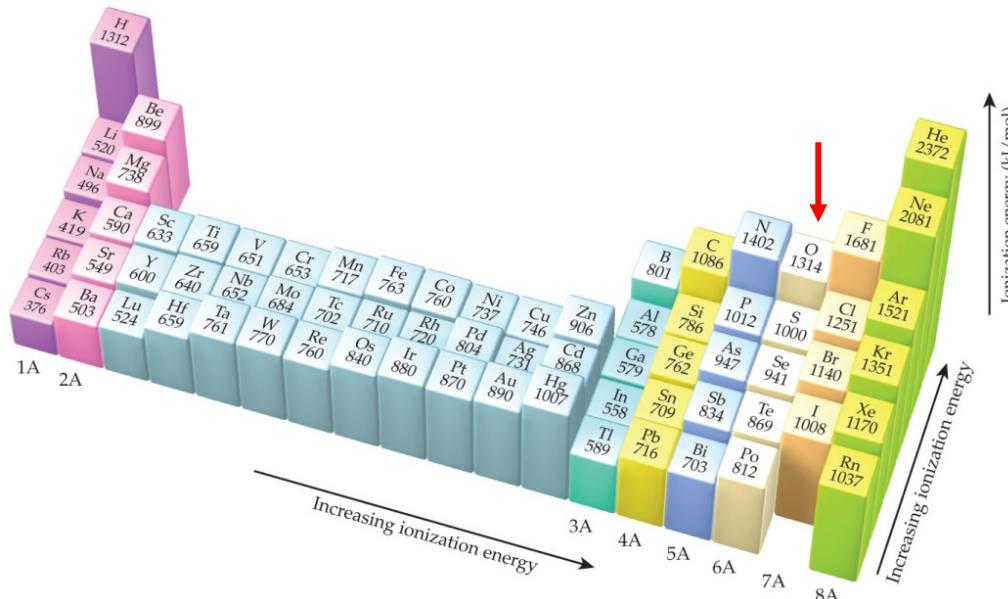
Sizes of Ions



- Determined by interatomic distances in ionic compounds
- Ionic size depends on
 - the nuclear charge.
 - the number of electrons.
 - the orbitals in which electrons reside.

Factors that Influence Ionization Energy

- Smaller atoms have higher Z_{eff} values.
 - Z_{eff} values depend on **effective nuclear charge** and **average distance** of the electron from the nucleus.



Electron Configurations of Ions

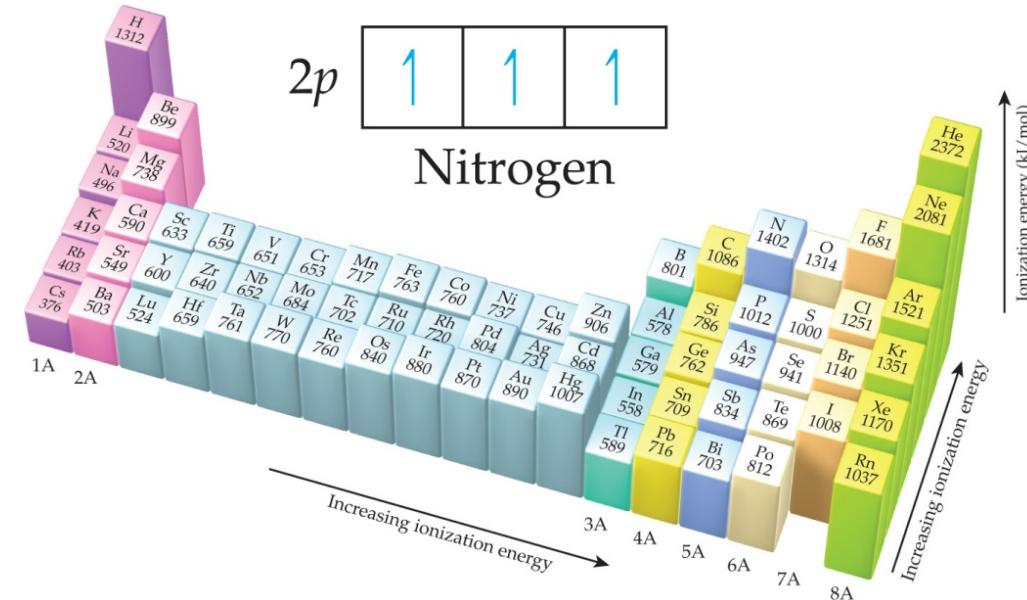
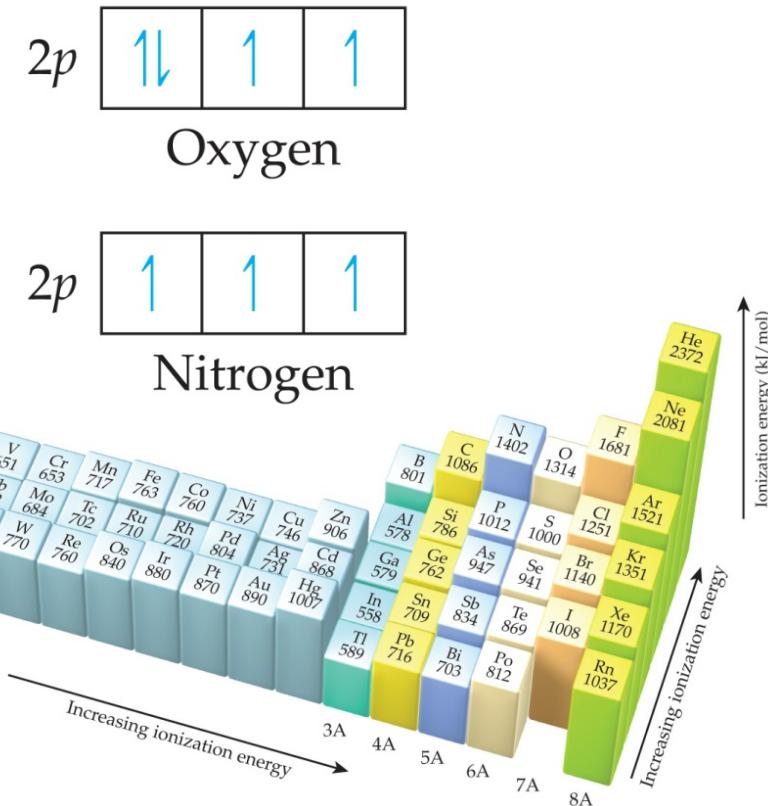
- Cations: The electrons are lost from the *highest* energy level (n value).
 - Li⁺ is $1s^2$ (losing a 2s electron).
 - Fe²⁺ (number 26) is $1s^22s^22p^63s^23p^63d^6$ (losing two 4s electrons).
- Anions: The electron configurations are filled to ns^2np^6 ; e.g., F⁻ is $1s^22s^22p^6$ (gaining one electron in 2p).

Ionization Energy

- It requires more energy to remove each successive electron.
- When all valence electrons have been removed, it takes a great deal more energy to remove the next electron.

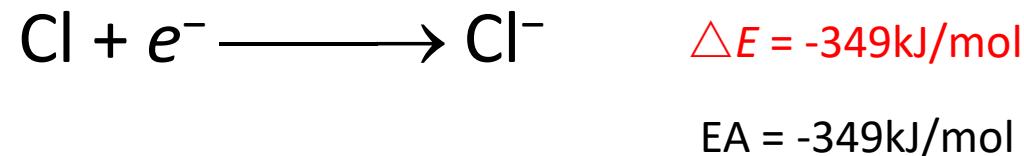
- 1) I_1 generally increases across a period.
- 2) I_1 generally decreases down a group.

- Smaller atoms have higher I values.
- I values depend on effective nuclear charge and average distance of the electron from the nucleus.



Electron Affinity

- **Electron affinity** is the energy change accompanying the addition of an electron to a gaseous atom:



- It is typically *exothermic*, so, for most elements, it is negative!

A negative electron affinity means that energy is released when the electron is added; hence, when the electron affinity is negative the anion is stable.

By contrast, a positive electron affinity means that the anion is not stable relative to the separated atom and electron, in which case its exact value cannot be measured.

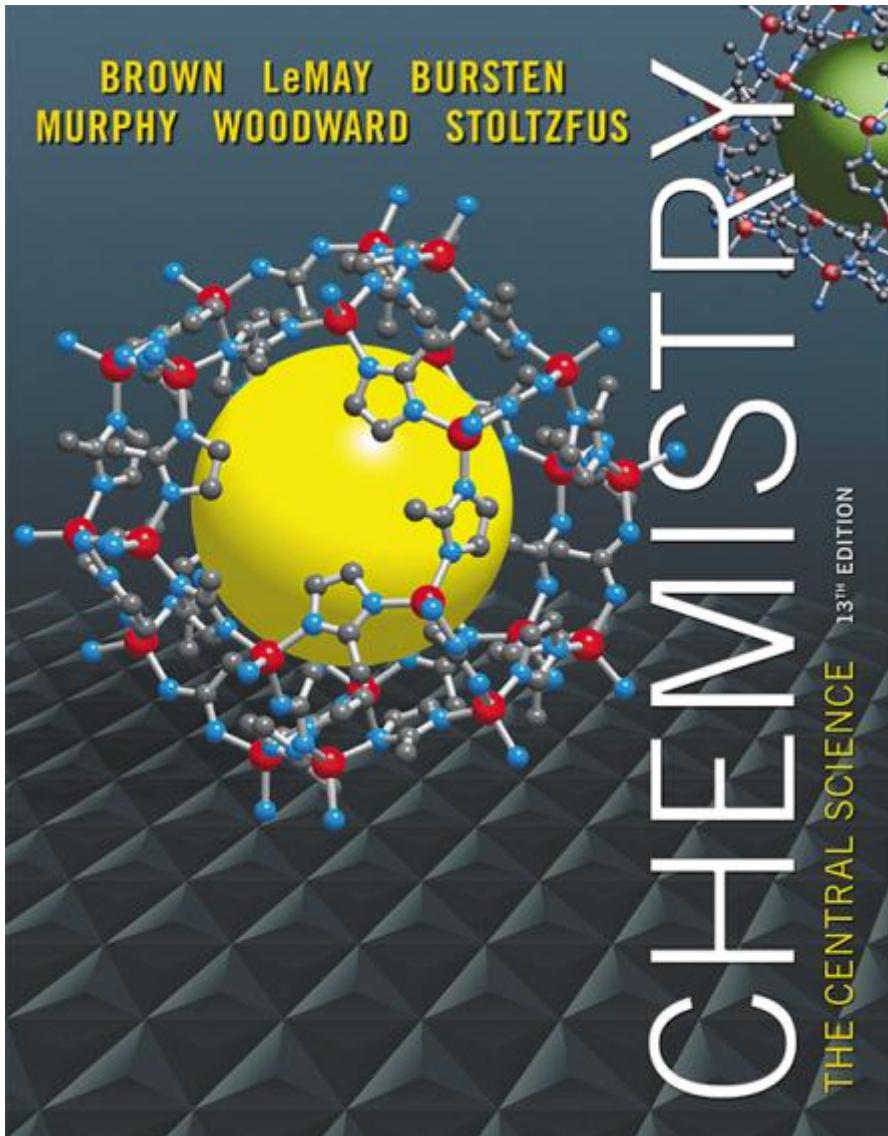
General Trend in Electron Affinity

- Not much change in a group.
 - Across a period, it generally increases. *Three* notable exceptions include the following:

- 1) Group 2A: s sublevel is full!
 - 2) Group 5A: p sublevel is half-full!
 - 3) Group 8A: p sublevel is full!

Note: the electron affinity for many of these elements is *positive* (X^- is unstable).

1A						8A	
H	2A	3A	4A	5A	6A	7A	He
-73	Be -> 0	B -27	C -122	N -> 0	O -141	F -328	Ne -> 0
Li -60	Mg -> 0	Al -43	Si -134	P -72	S -200	Cl -349	Ar -> 0
Na -53	Ca -2	Ga -30	Ge -119	As -78	Se -195	Br -325	Kr -> 0
K -48	Rb -47	In -30	Sn -107	Sb -103	Te -190	I -295	Xe -> 0
	Sr -5						



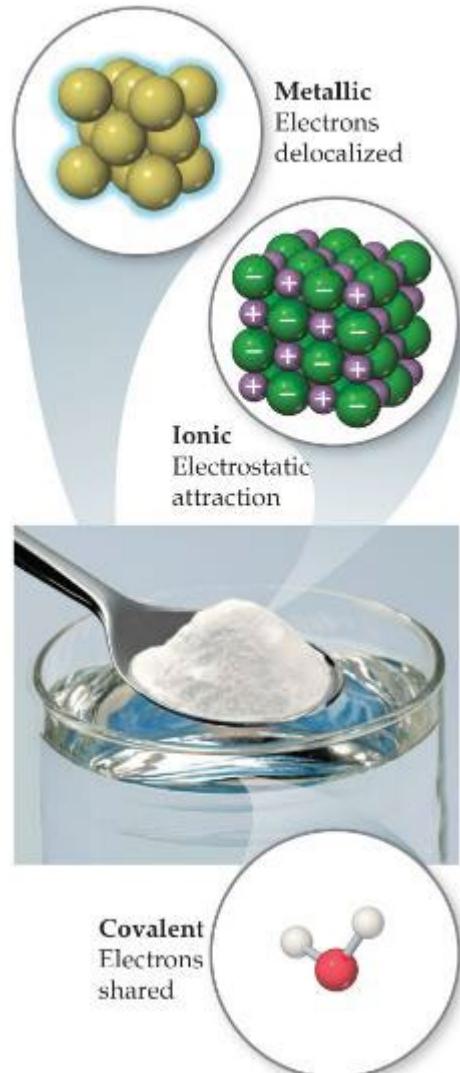
Lecture Presentation

Chapter 8

Basic Concepts of Chemical Bonding

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Chemical Bonds



- Three basic types of bonds
 - Ionic
 - Electrostatic attraction between ions.
 - Covalent
 - Sharing of electrons by two atoms.
 - Metallic
 - Metal atoms bonded to several other atoms.

The formation of bonds involves interactions of the outermost electrons of atoms, their valence electrons.



Give It Some Thought

Are all these Lewis symbols for Cl correct?



Table 8.1 Lewis Symbols

Group	Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
1A	Li	[He] $2s^1$	Li \cdot	Na	[Ne] $3s^1$	Na \cdot
2A	Be	[He] $2s^2$	$\cdot\text{Be}\cdot$	Mg	[Ne] $3s^2$	$\cdot\text{Mg}\cdot$
3A	B	[He] $2s^22p^1$	$\cdot\dot{\text{B}}\cdot$	Al	[Ne] $3s^23p^1$	$\cdot\dot{\text{Al}}\cdot$
4A	C	[He] $2s^22p^2$	$\cdot\dot{\text{C}}\cdot$	Si	[Ne] $3s^23p^2$	$\cdot\dot{\text{Si}}\cdot$
5A	N	[He] $2s^22p^3$	$\cdot\dot{\text{N}}:$	P	[Ne] $3s^23p^3$	$\cdot\ddot{\text{P}}:$
6A	O	[He] $2s^22p^4$	$:\ddot{\text{O}}:$	S	[Ne] $3s^23p^4$	$:\ddot{\text{S}}:$
7A	F	[He] $2s^22p^5$	$:\ddot{\text{F}}:$	Cl	[Ne] $3s^23p^5$	$:\ddot{\text{Cl}}:$
8A	Ne	[He] $2s^22p^6$	$:\ddot{\text{Ne}}:$	Ar	[Ne] $3s^23p^6$	$:\ddot{\text{Ar}}:$

octet rule: Atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons

Ionic Bonding

- Atoms tend to lose (metals) or gain (nonmetals) electrons to make them isoelectronic to the noble gases (stable form 2e, 8e, 18e).

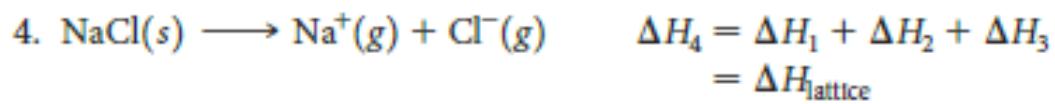
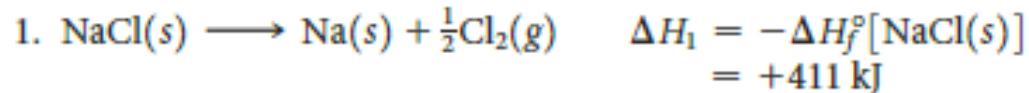


The stability of ionic compounds result from the attraction between ions of opposite charge. The strength of the attraction of these interactions is represented by lattice energy.

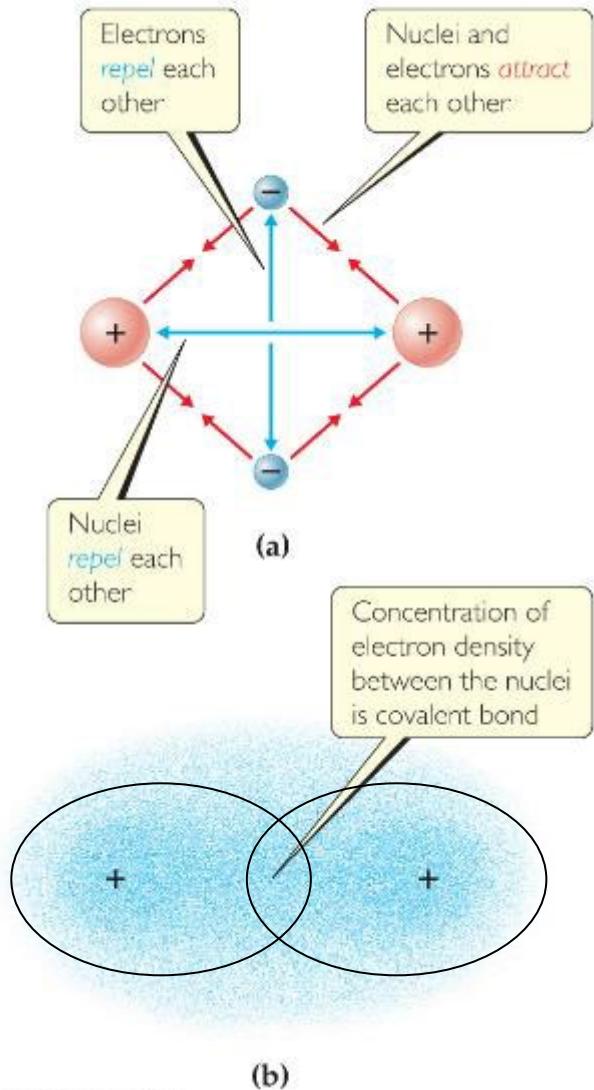
- Lattice energy increases with:
 - increasing charge on the ions
 - decreasing size of ions

$$E_{\text{el}} = \kappa \frac{Q_1 Q_2}{d}$$

Born-Haber Cycle

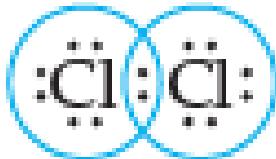


Covalent Bonding



- In covalent bonds, atoms share electrons.
- There are several electrostatic interactions in these bonds:
 - attractions between electrons and nuclei,
 - repulsions between electrons, and
 - repulsions between nuclei.
- For a bond to form, the attractions must be greater than the repulsions.

Electrons on Lewis Structures



- Lone pairs: electrons located on *only one* atom in a Lewis structure
- Bonding pairs: shared electrons in a Lewis structure; they can be represented by two dots or one line

Multiple Bonds

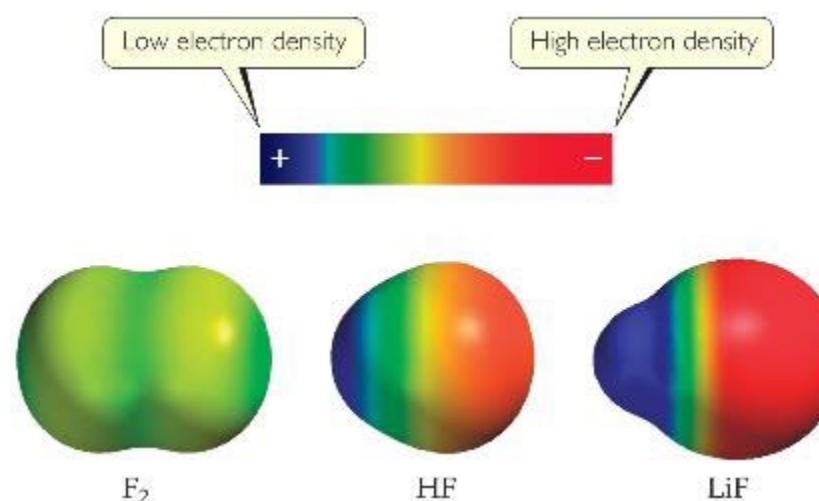
- Some atoms share only one pair of electrons. These bonds are called **single bonds**.
- Sometimes, two pairs need to be shared. These are called **double bonds**.
- There are even cases where three bonds are shared between two atoms. These are called **triple bonds**.



Bond length: single bond > double bond > triple bond

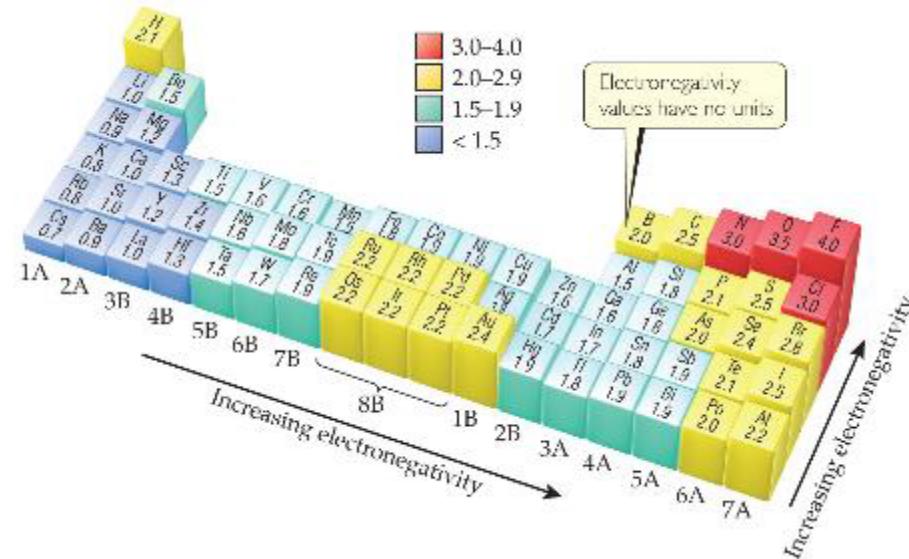
Polar Covalent Bonds

- The electrons in a covalent bond are not always shared equally.
- Fluorine pulls harder on the electrons it shares with hydrogen than hydrogen does.
- Therefore, the fluorine end of the molecule has more electron density than the hydrogen end.



Electronegativity

- Electronegativity is the ability of an atom in a molecule to attract electrons to itself.
- On the periodic table, electronegativity generally increases as you go
 - from left to right across a period.
 - from the bottom to the top of a group.



Dipoles

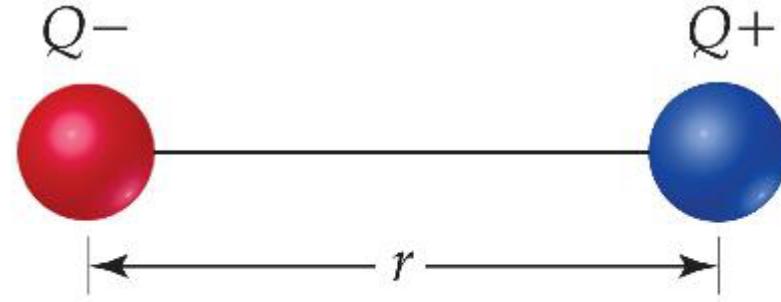
Table 8.3 Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

- When two equal, but opposite, charges are separated by a distance, a **dipole** forms.
- A **dipole moment**, μ , produced by two equal but opposite charges separated by a distance, r , is calculated:

$$\mu = Qr$$

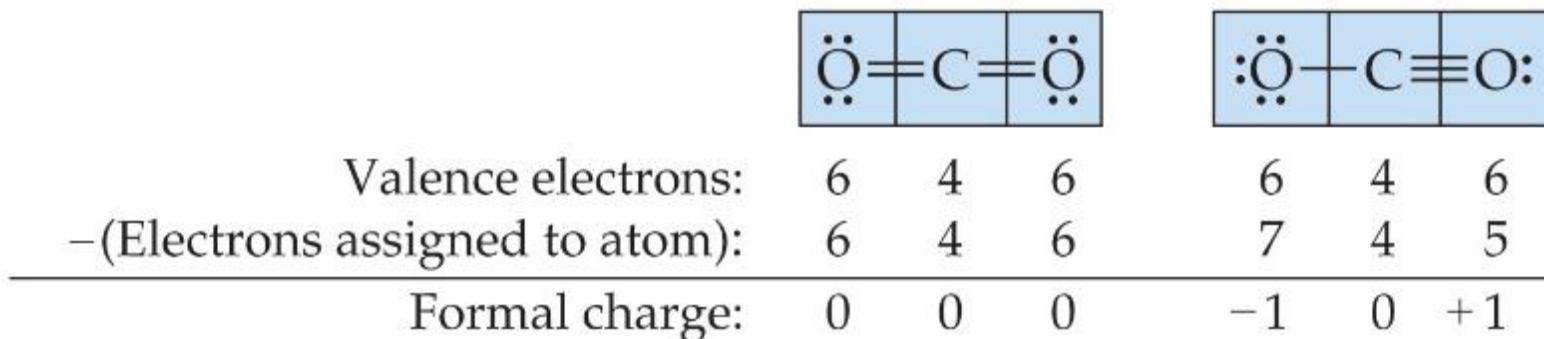
- It is measured in debyes (D).



$$\text{Dipole moment } \mu = Qr$$

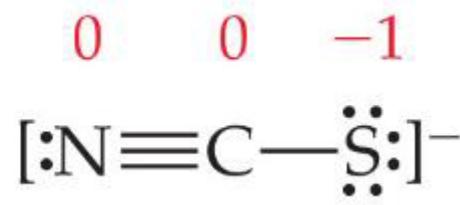
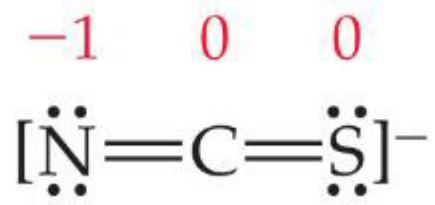
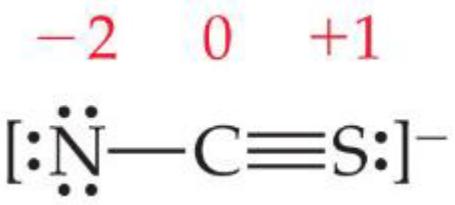
Writing Lewis Structures

- Then assign formal charges.
- **Formal charge** is the charge an atom would have if all of the electrons in a covalent bond were shared equally.
- Formal charge = valence electrons – $\frac{1}{2}$ (bonding electrons) – *all* nonbonding electrons



Writing Lewis Structures

- The dominant Lewis structure
 - is the one in which atoms have formal charges closest to zero.
 - puts a negative formal charge on the most electronegative atom.



Practice excise:

The sulfate ion, SO_4^{2-} , can be drawn in many ways. If you minimize formal charge on the sulfur, how many S=O double bonds should you draw in the lewis structure

A:0

B:1

C:2

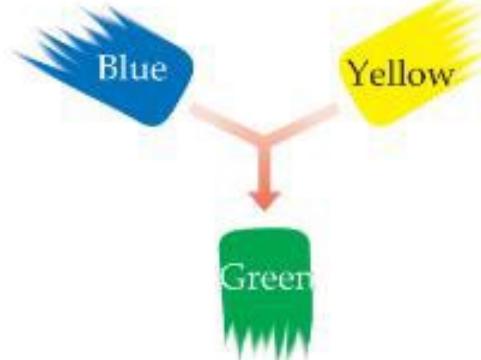
D:3

E:4

Resonance

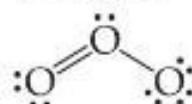
- One Lewis structure cannot accurately depict a molecule like ozone.
- We use multiple structures, **resonance structures**, to describe the molecule.

Primary color Primary color

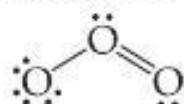


(a)

Resonance structure

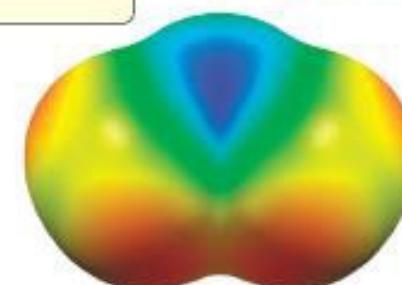


Resonance structure



Position of electron distribution is different

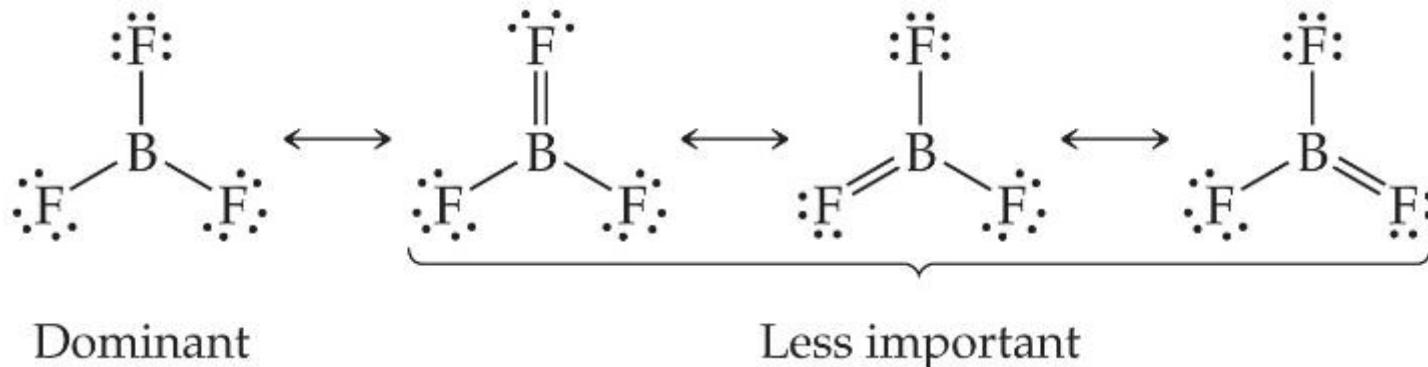
Notice that the electron density distributed symmetrically across the molecule.



Ozone molecule
(b)

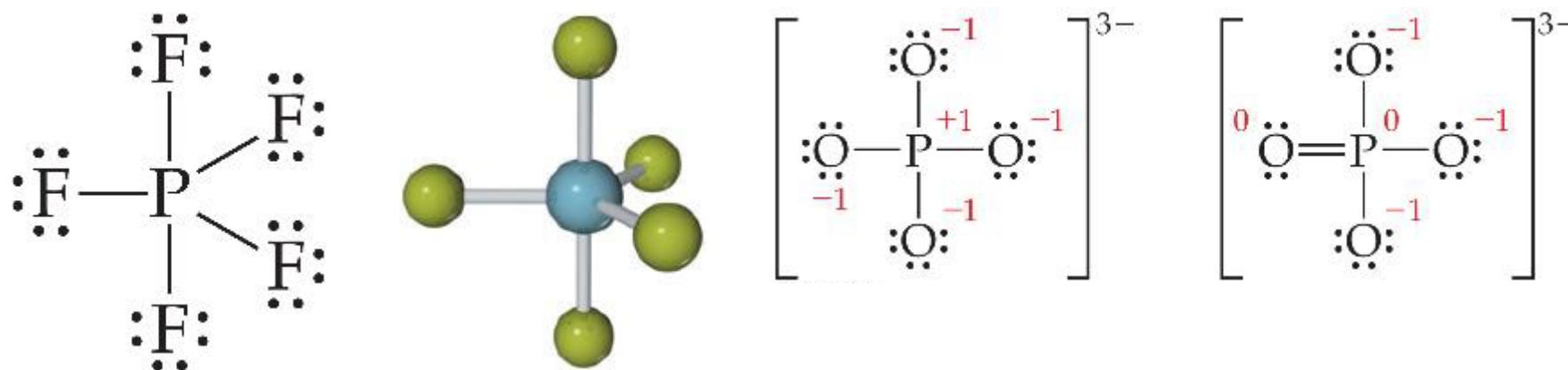
Fewer Than Eight Electrons

- Elements in the second period *before* carbon can make stable compounds with fewer than eight electrons.
- Consider BF_3 :
 - Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine.
 - This would not be an accurate picture of the distribution of electrons in BF_3 .



More Than Eight Electrons

- When an element is in period 3 or below in the periodic table (e.g., periods 3, 4, 5, etc.), it can use *d*-orbitals to make *more* than four bonds.
- Examples: PF_5 and phosphate below
(Note: Phosphate will actually have four resonance structures with five bonds on the P atom!)

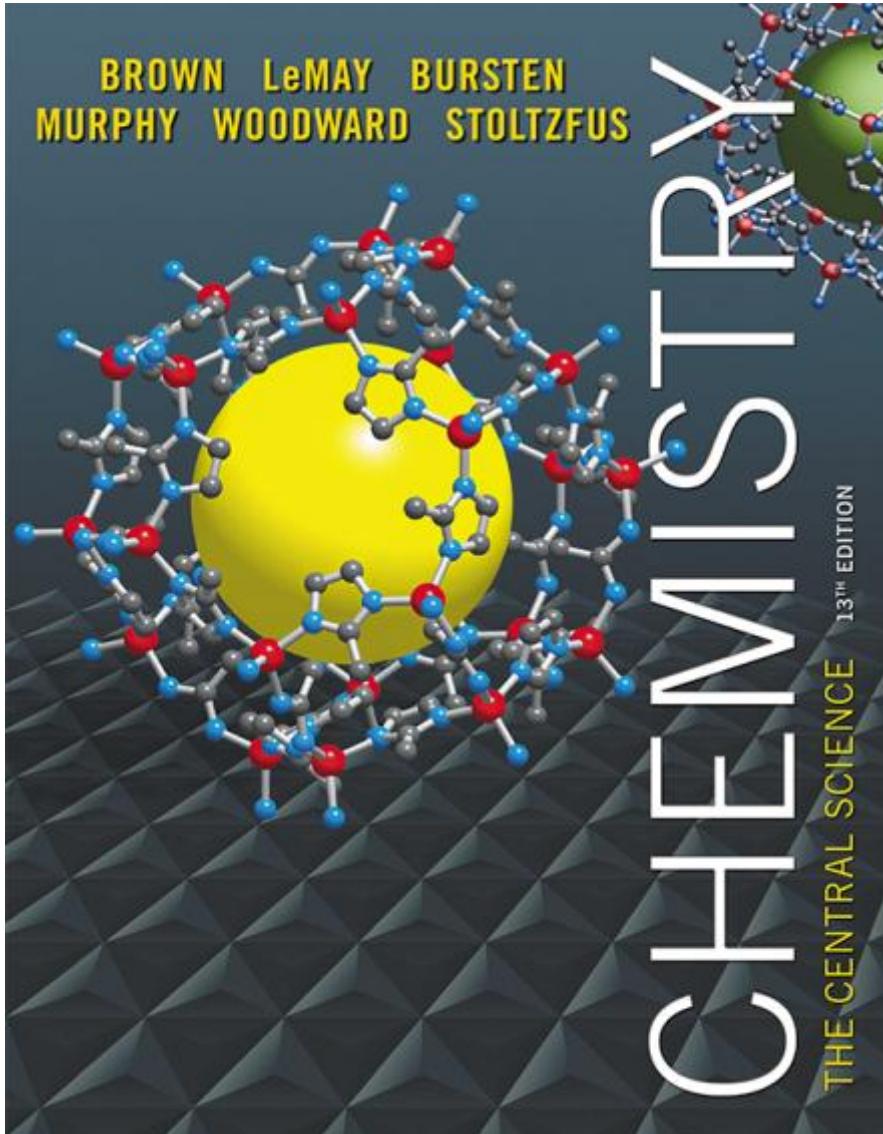


Bond Enthalpy and Bond Length

- We can also measure an average bond length for different bond types.
- As the number of bonds between two atoms increases, the bond length decreases.

Table 8.5 Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		



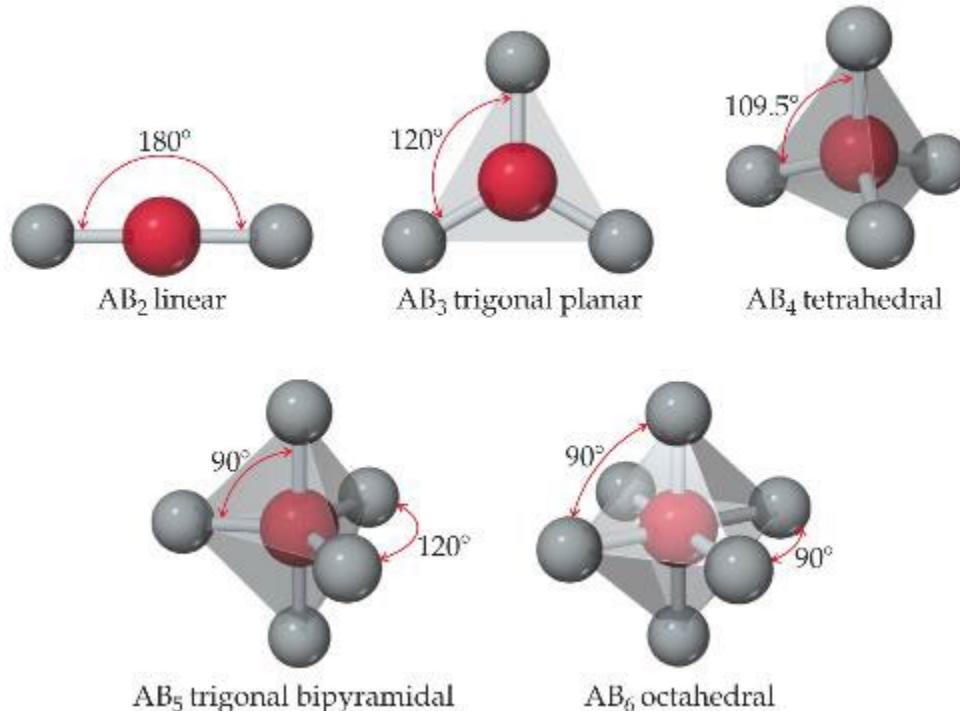
Lecture Presentation

Chapter 9

Molecular Geometry and Bonding Theories

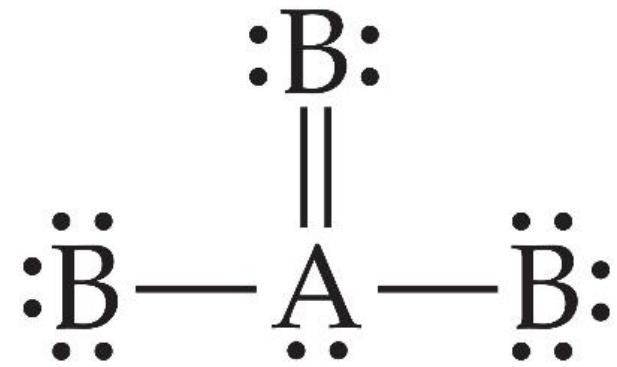
What Determines the Shape of a Molecule?

- Simply put, electron pairs, whether they be bonding or nonbonding, repel each other.
- By assuming the electron pairs are placed as far as possible from each other, we can predict the shape of the molecule.



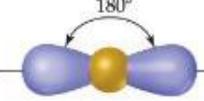
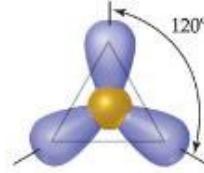
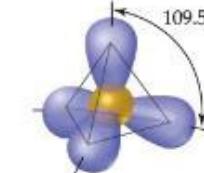
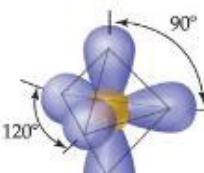
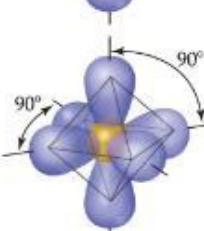
- This is the Valence-Shell Electron-Pair Repulsion (VSEPR) model.

Electron Domains



- We can refer to the directions to which electrons point as **electron domains**. This is true whether there is one or more electron pairs pointing in that direction.
- The central atom in this molecule, A, has four electron domains.

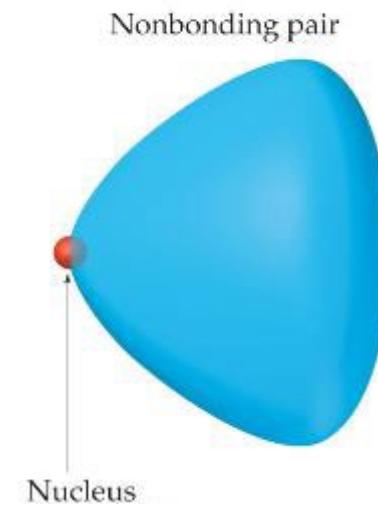
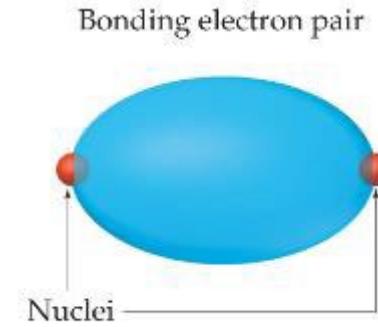
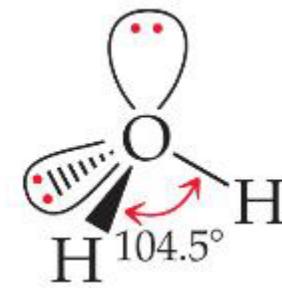
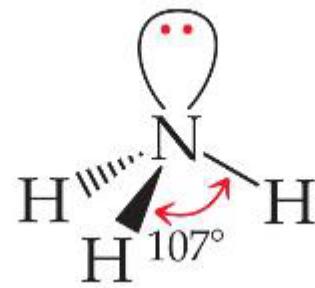
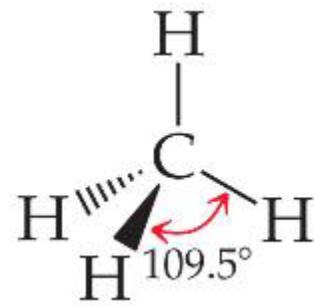
Table 9.1 Electron-Domain Geometries as a Function of Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

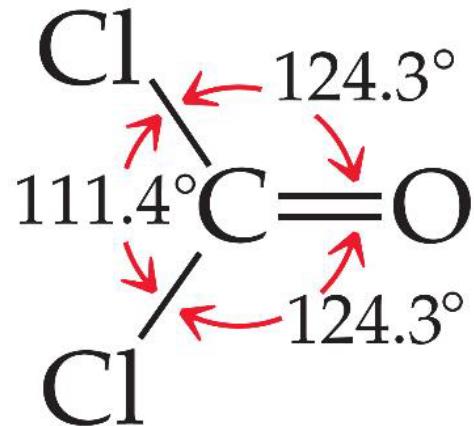
The **electron domain** and **molecular geometry** of BrO_2^- ?

Nonbonding Pairs and Bond Angle

- Nonbonding pairs are physically larger than bonding pairs.
- Therefore, their repulsions are greater; this tends to compress bond angles.



Multiple Bonds and Bond Angles

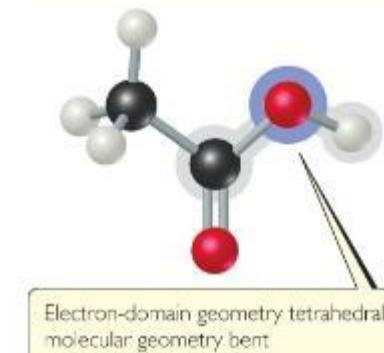
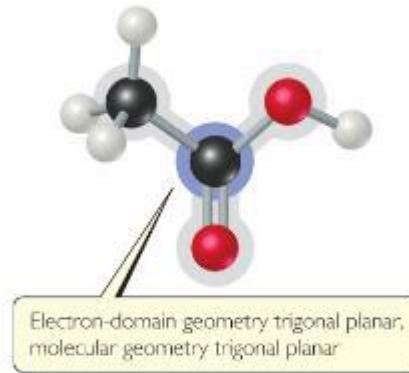
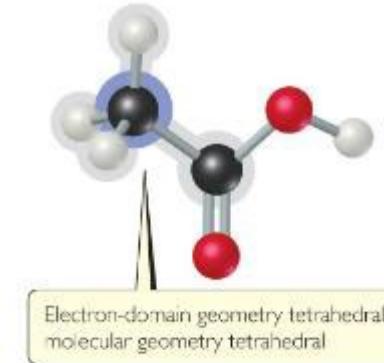
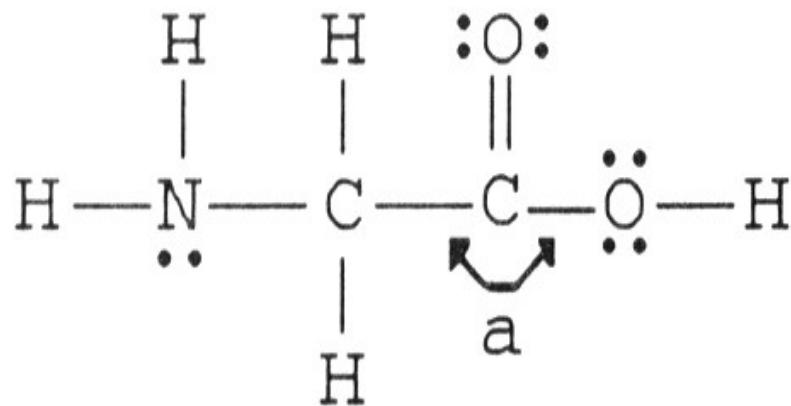


- Double and triple bonds have larger electron domains than single bonds.
- They exert a greater repulsive force than single bonds, making their bond angles greater.



Shapes of Larger Molecules

For larger molecules, look at the geometry about each atom rather than the molecule as a whole.



Polarity of Molecules

Ask yourself:

COVALENT or IONIC? If COVALENT:

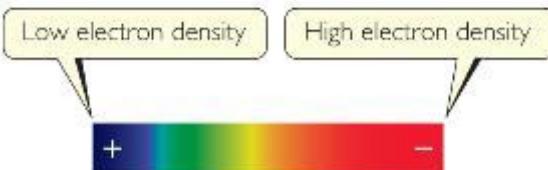
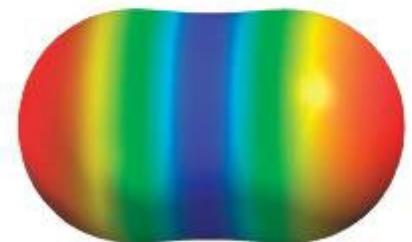
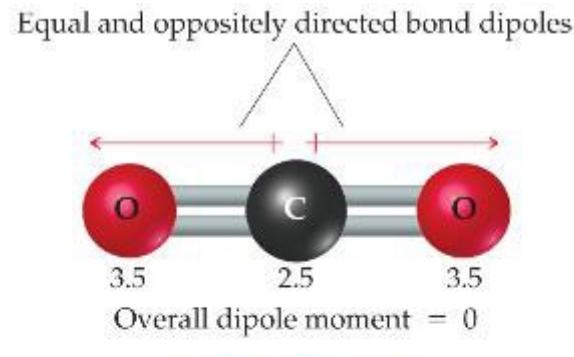
Are the BONDS polar?

- a. NO: The molecule is NONPOLAR!
- b. YES: Continue—Do the AVERAGE position of $\delta+$ and $\delta-$ coincide?
 - 1) YES: The molecule is NONPOLAR.
 - 2) NO: The molecule is POLAR.

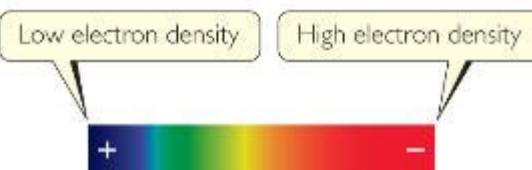
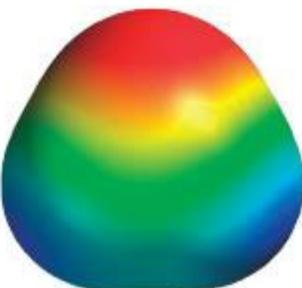
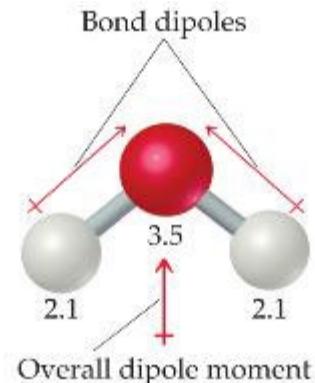
NOTE: Different atoms attached to the central atom have different polarity of bonds.

Comparison of the Polarity of Two Molecules

A NONPOLAR molecule



A POLAR molecule



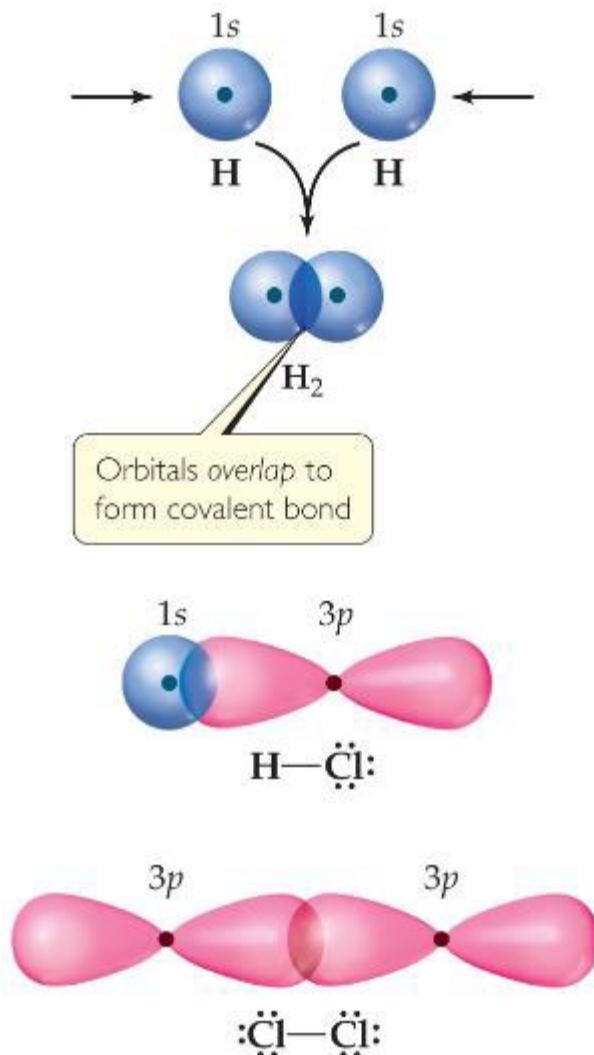
CCl₄

CH₄

SF₄

SiCl₄

Valence-Bond Theory



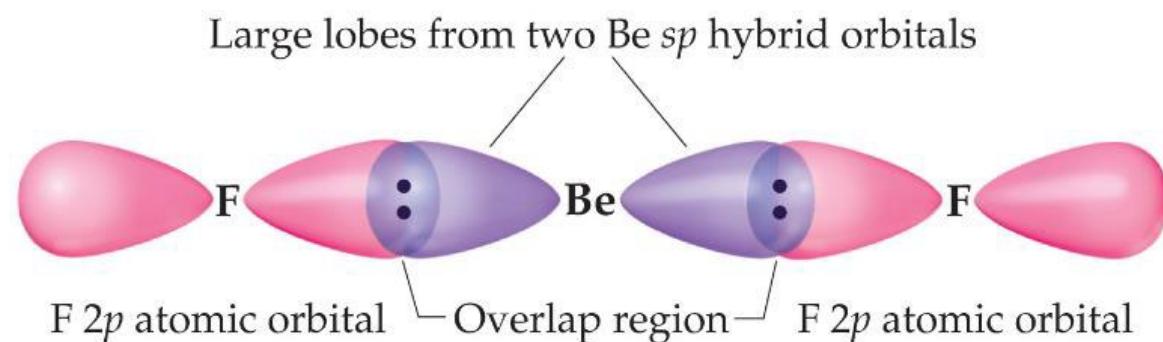
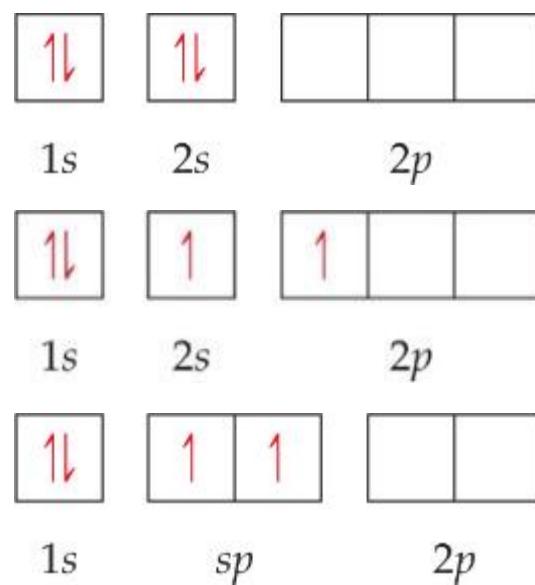
- In Valence-Bond Theory, electrons of two atoms begin to occupy the same space.
- This is called “overlap” of orbitals.
- The sharing of space between two electrons of opposite spin results in a covalent bond.

VSEPR and Hybrid Orbitals

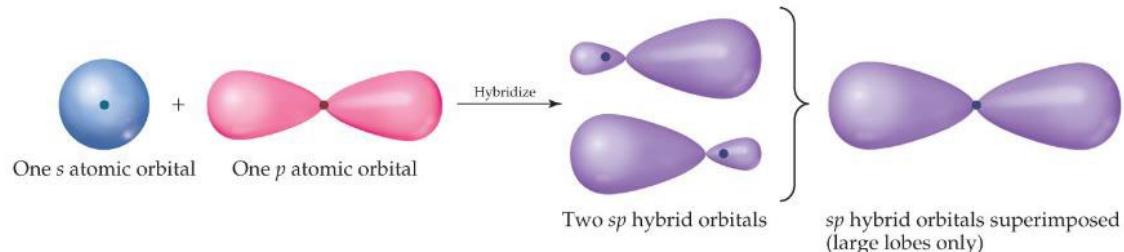
- VSEPR predicts shapes of molecules very well.
- How does that fit with orbitals?
- Let's use H₂O as an example:
- If we draw the best Lewis structure to assign VSEPR, it becomes bent.
- If we look at oxygen, its electron configuration is 1s²2s²2p⁴. If it shares two electrons to fill its valence shell, they should be in 2p.
- Wouldn't that make the angle 90° ?
- Why is it 104.5° ?

Hybrid Orbitals

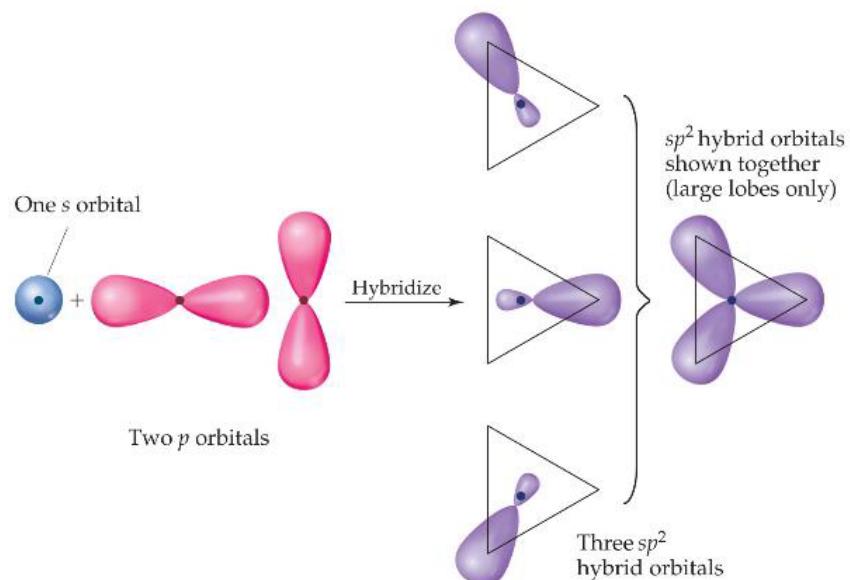
- **Hybrid orbitals** form by “mixing” of atomic orbitals to create new orbitals of equal energy, called degenerate orbitals.
- When two orbitals “mix” they create two orbitals; when three orbitals mix, they create three orbitals; etc.



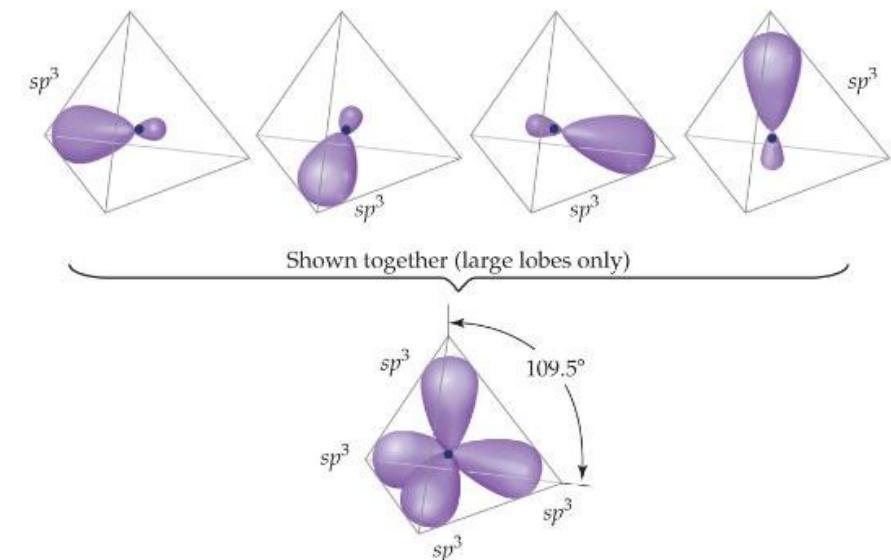
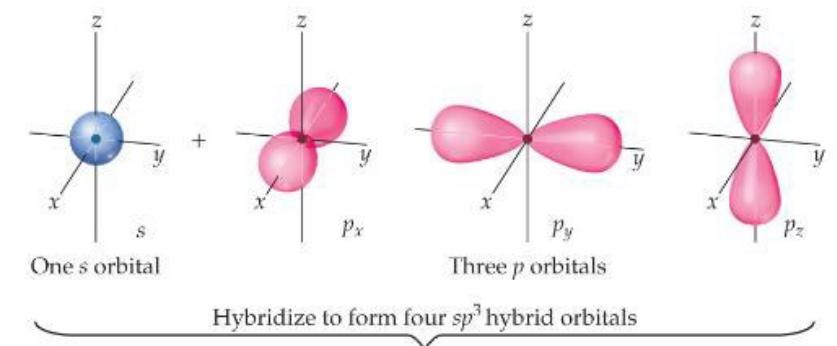
sp Orbitals



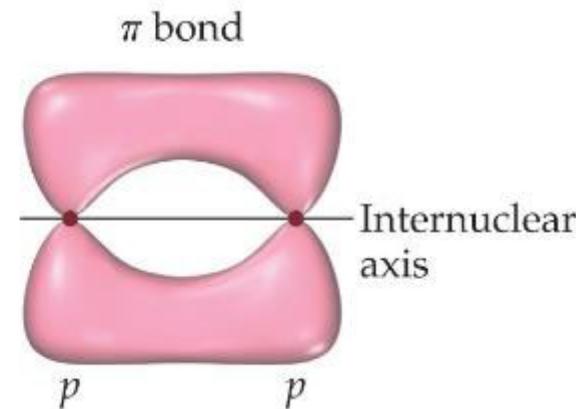
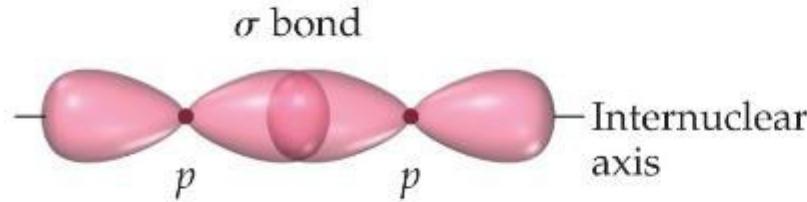
*sp*² Hybridization



Carbon: *sp*³ Hybridization



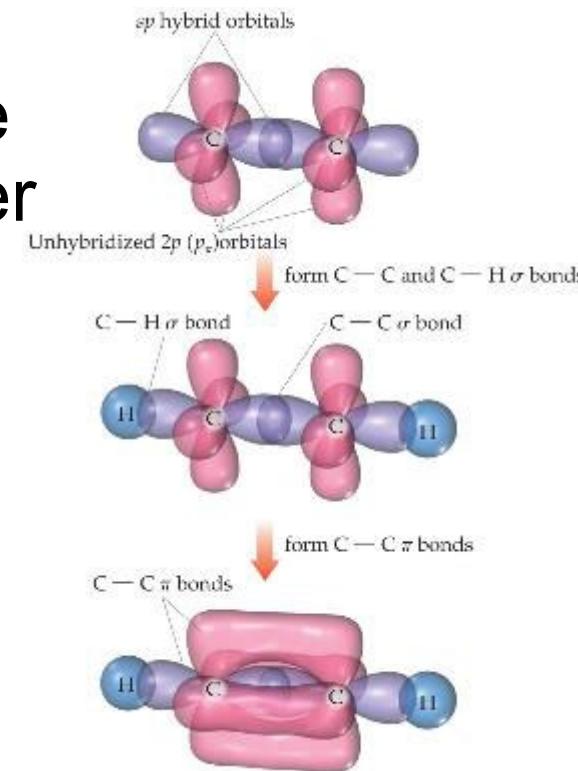
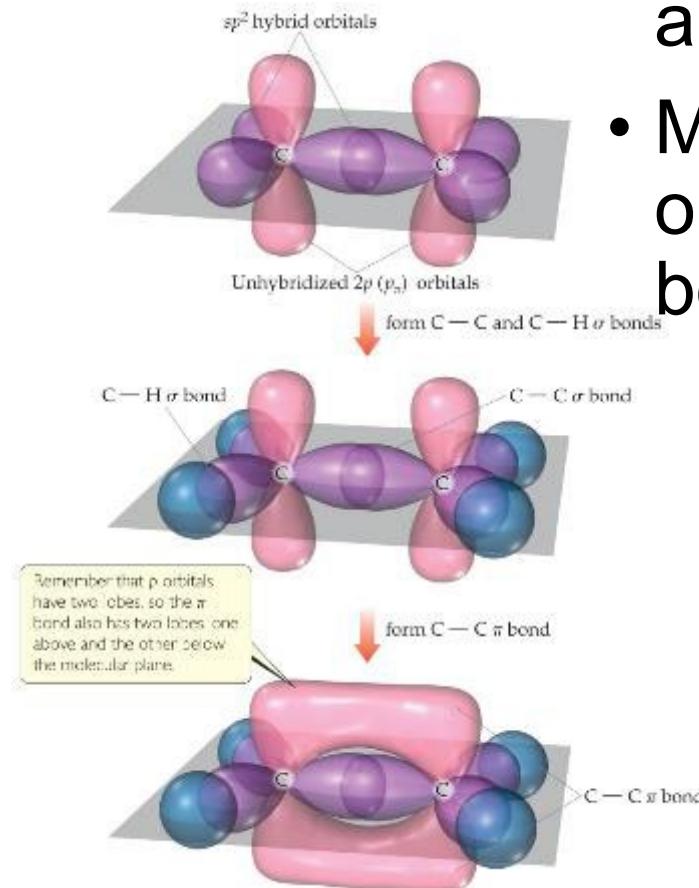
Sigma (σ) and Pi (π) Bonds



- Sigma bonds are characterized by
 - head-to-head overlap.
 - cylindrical symmetry of electron density about the internuclear axis.
- Pi bonds are characterized by
 - side-to-side overlap.
 - electron density above and below the internuclear axis.

Bonding in Molecules

- Single bonds are always σ -bonds.
- Multiple bonds have one σ -bond, all other bonds are π -bonds.



Molecular Orbital (MO) Theory

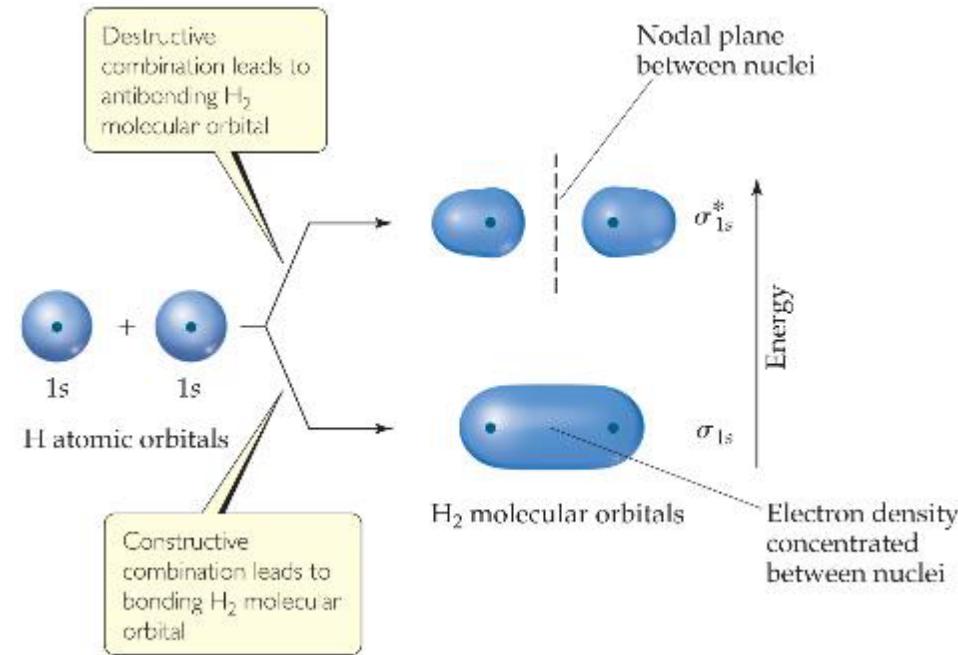
- Wave properties are used to describe the energy of the electrons in a molecule.
- **Molecular orbitals** have many characteristics like atomic orbitals:
 - maximum of two electrons per orbital
 - Electrons in the same orbital have opposite spin.
 - Definite energy of orbital
 - Can visualize electron density by a contour diagram

More on MO Theory

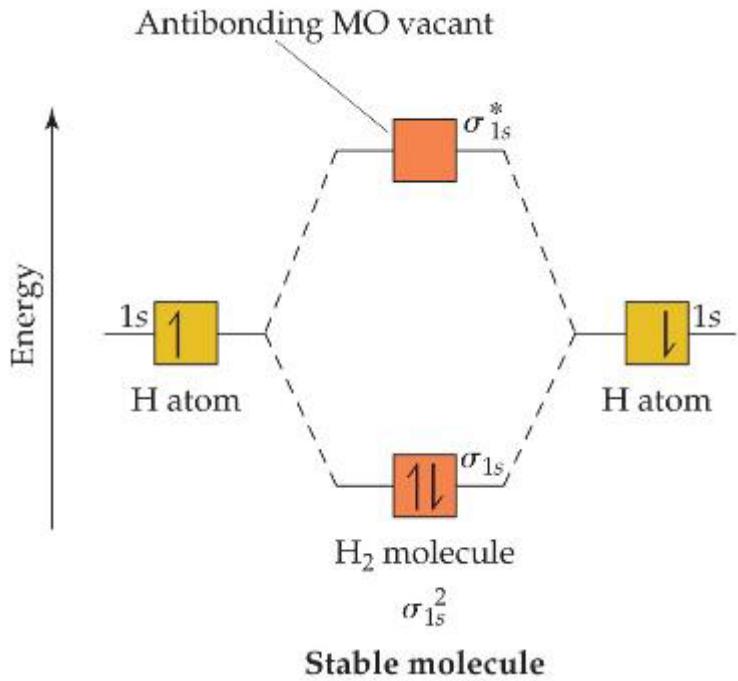
- They differ from atomic orbitals because they represent the entire molecule, not a single atom.
- Whenever two atomic orbitals overlap, two molecular orbitals are formed: one bonding, one antibonding.
- **Bonding orbitals** are constructive combinations of atomic orbitals.
- **Antibonding orbitals** are destructive combinations of atomic orbitals. They have a new feature unseen before: A **nodal plane** occurs where electron density equals zero.

Molecular Orbital (MO) Theory

Whenever there is direct overlap of orbitals, forming a bonding and an antibonding orbital, they are called **sigma (σ) molecular orbitals**. The antibonding orbital is distinguished with an asterisk as σ^* . Here is an example for the formation of a hydrogen molecule from two atoms.



MO Diagram

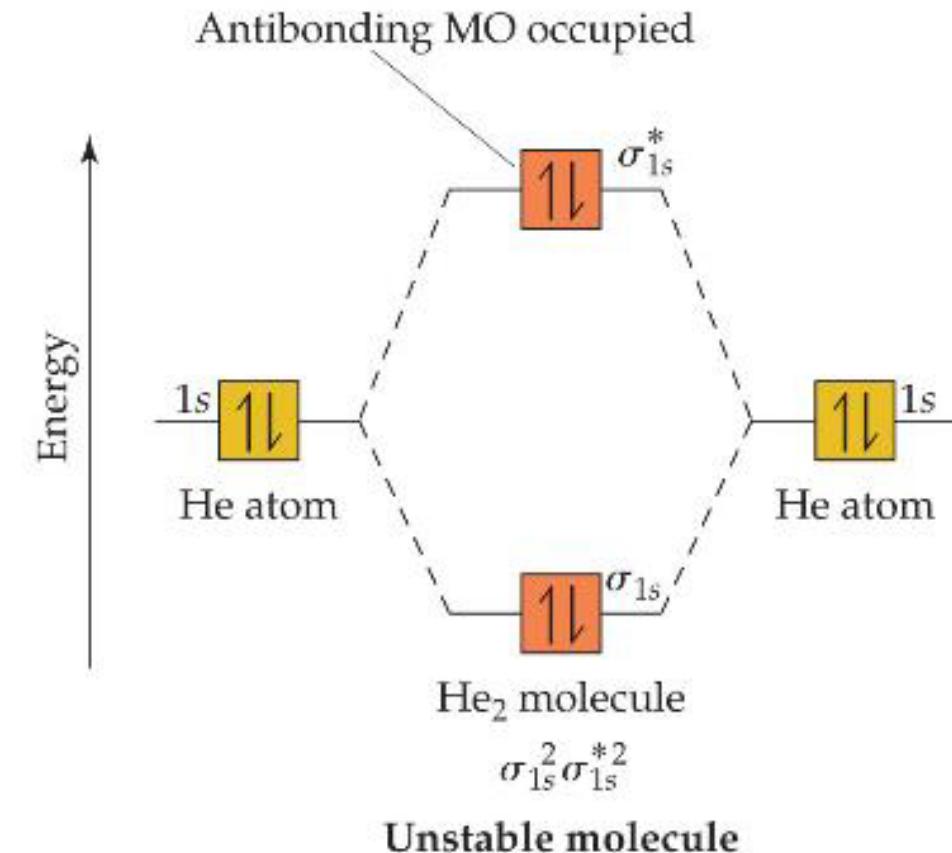


- An **energy-level diagram**, or **MO diagram** shows how orbitals from atoms combine to give the molecule.
- In H_2 the two electrons go into the bonding molecular orbital (lower in energy).
- **Bond order** = $\frac{1}{2}(\# \text{ of bonding electrons} - \# \text{ of antibonding electrons}) = \frac{1}{2}(2 - 0) = 1 \text{ bond}$

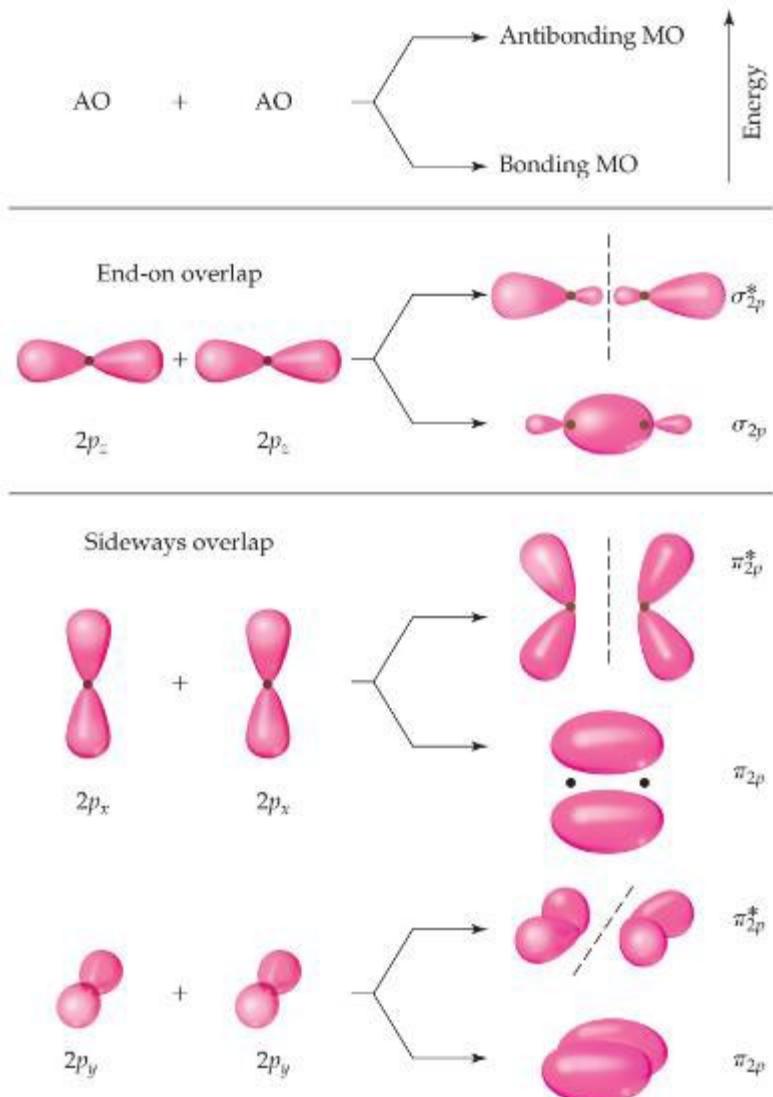
Can He₂ Form? Use MO Diagram and Bond Order to Decide!

- Bond Order = $\frac{1}{2}(2 - 2) = 0$ bonds
- Therefore, He₂ does *not* exist.

How about He₂⁺ ?



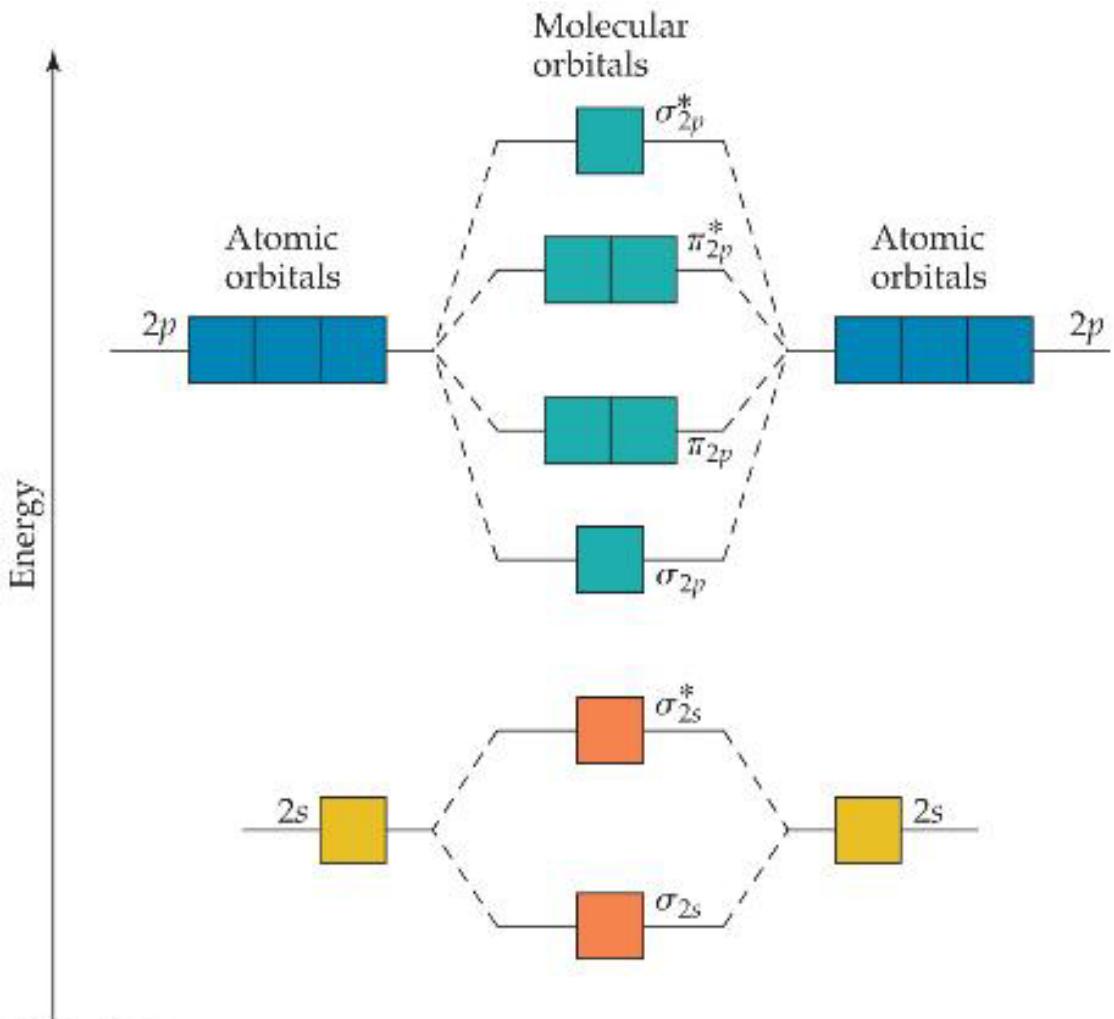
s and p Orbitals Can Interact



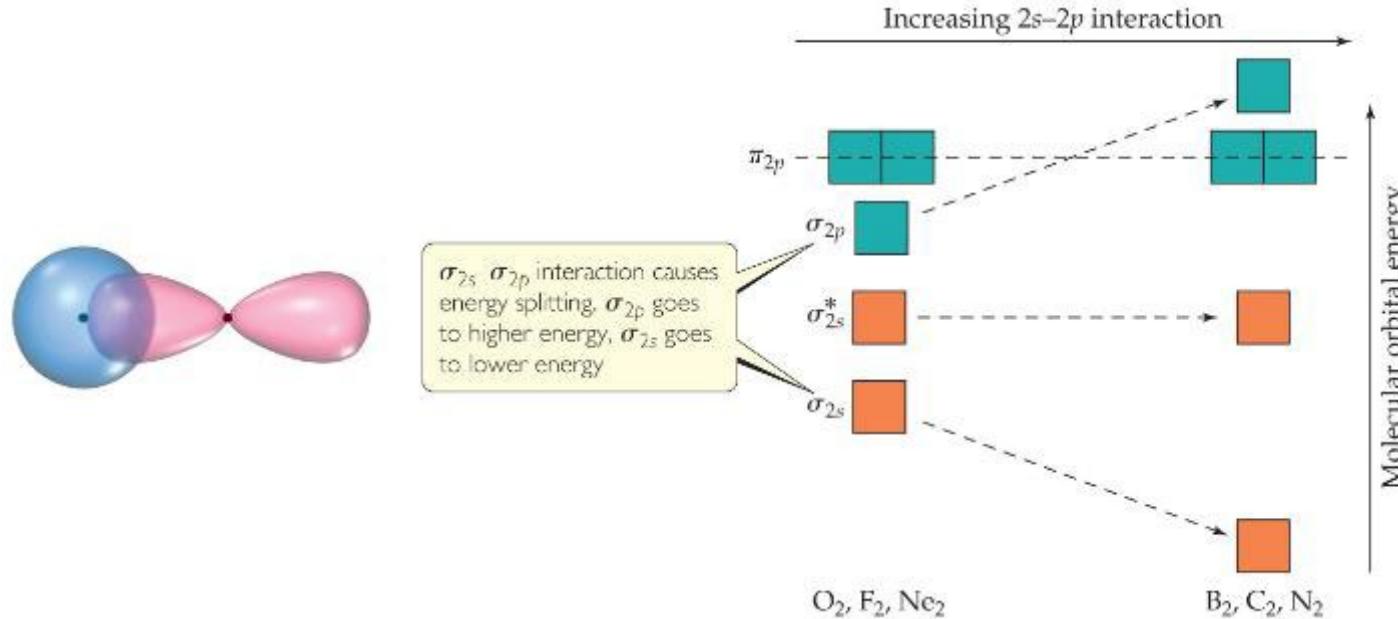
- For atoms with both s and p orbitals, there are two types of interactions:
 - The s and the p orbitals that face each other overlap in σ fashion.
 - The other two sets of p orbitals overlap in π fashion.
 - These are, again, direct and “side-ways” overlap of orbitals.

MO Theory

- The resulting MO diagram:
 - There are σ and σ^* orbitals from s and p atomic orbitals.
 - There are π and π^* orbitals from p atomic orbitals.
 - Since direct overlap is stronger, the effect of raising and lowering energy is greater for σ and σ^* .



s and *p* Orbital Interactions



- In some cases, *s* orbitals can interact with the p_z orbitals more than the p_x and p_y orbitals.
- It raises the energy of the p_z orbital and lowers the energy of the *s* orbital.
- The p_x and p_y orbitals are degenerate orbitals.

MO Diagrams for Diatomic Molecules of 2nd Period Elements

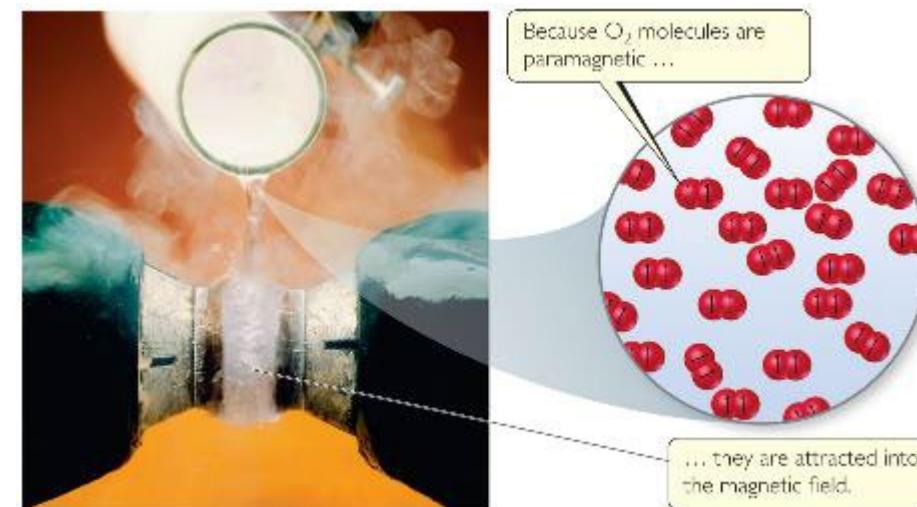
Large 2s-2p interaction			Small 2s-2p interaction		
B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ_{2p}^*					
π_{2p}^*					
σ_{2p}					
π_{2p}					
σ_{2s}^*					
σ_{2s}					
Bond order	1	2	3	2	1
Bond enthalpy (kJ/mol)	290	620	941	495	155
Bond length (Å)	1.59	1.31	1.10	1.21	1.43
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic

MO Diagrams and Magnetism

- **Diamagnetism** is the result of all electrons in every orbital being spin paired. These substances are weakly repelled by a magnetic field.
- **Paramagnetism** is the result of the presence of one or more unpaired electrons in an orbital.
- Is oxygen (O_2) paramagnetic or diamagnetic? Look back at the MO diagram! It is paramagnetic.

Paramagnetism of Oxygen

- Lewis structures would *not* predict that O_2 is paramagnetic.
- The MO diagram clearly shows that O_2 is paramagnetic.
- Both show a double bond (bond order = 2).



Heteronuclear Diatomic Molecules

- Diatomic molecules can consist of atoms from different elements.
- How does a MO diagram reflect differences?
- The atomic orbitals have different energy, so the interactions change slightly.
- The more electronegative atom has orbitals lower in energy, so the bonding orbitals will more resemble them in energy.

