Chemistry Olympiad - Kolack

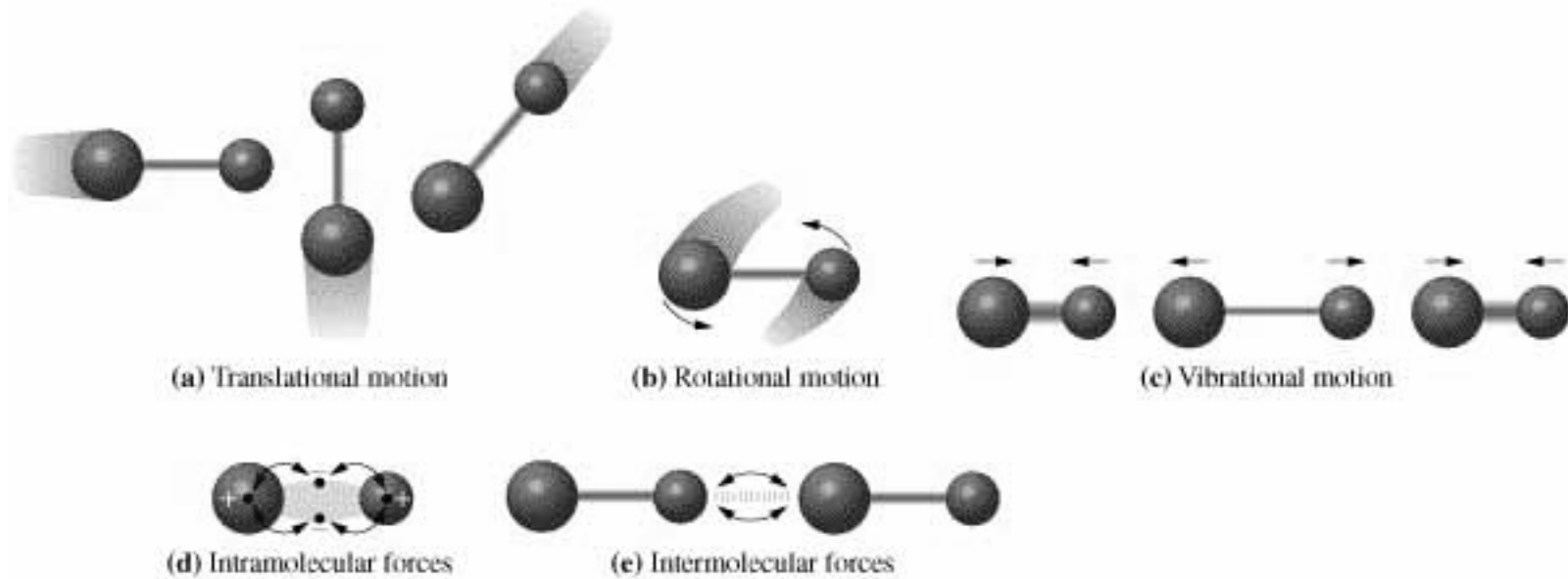## Thermochemistry, atomic structure, e^- config, periodic table, bonding

Thermochemistry

Energy

- The Universe is composed of matter and energy
- ENERGY is the capacity to do work
- POTENTIAL ENERGY is the energy of position (or composition)
- KINETIC ENERGY is the energy of an object in motion = $\frac{1}{2}\, mv^2$
- Units are kg (m/s)^2 = Joules
- Note that since work = force x distance, N x m = (kg m/s^2) x m = J

Kinetic energy

(a) Translational motion   (b) Rotational motion   (c) Vibrational motion

(d) Intramolecular forces   (e) Intermolecular forces

Definitions

- THERMOCHEMISTRY is the study of energy changes that occur during chemical reactions

- Something loses energy; something else gains it

- The SYSTEM is the part of the Universe we are studying

- The SURROUNDINGS are the rest of the Universe

Definitions (cont'd)

- An OPEN SYSTEM exchanges matter and energy with the surroundings
- A CLOSED SYSTEM exchanges energy only with the surroundings
- An ISOLATED system exchanges neither matter nor energy with the surroundings
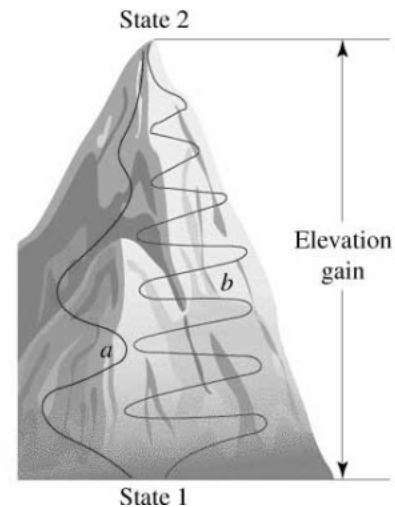
Definitions (cont'd)

- INTERNAL ENERGY (U) is the total energy of the system (PE + KE)
- HEAT (q) is an energy transfer between the system and surroundings
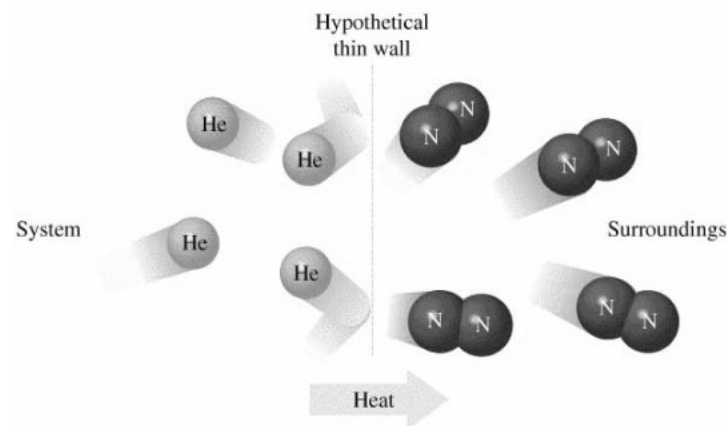
More on internal energy

- Can't be measured (too many variables)
- Can still be useful as a STATE FUNCTION
- Value depends only on current state, not path taken to get there
- q and w aren't state functions

Work

- Like heat, is an energy transfer between system and surroundings
- We only focus on PV work
  - (and electrical work later)
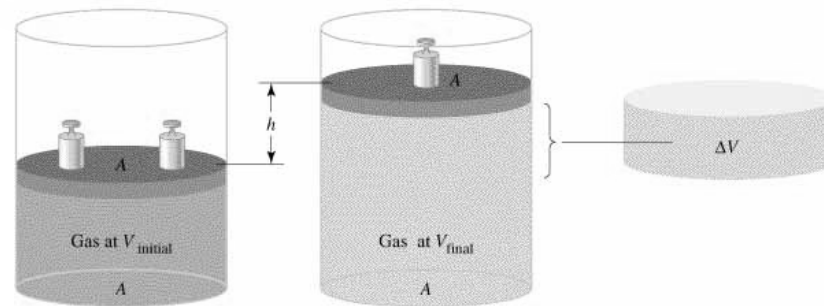
Laws

- Law of conservation of energy
  - Energy can be exchanged, but neither created nor destroyed
- First law of thermodynamics
  - $\Delta U = q + w$
    - Heat absorbed by system, $q > 0$
    - Work done on system $w > 0$
    - Heat given off by system $q < 0$
   - Work done by system $w < 0$

Heat of reaction

- In an EXOTHERMIC reaction, heat is given off by the system to the surroundings (q is negative)
- In an ENDOTHERMIC reaction, heat is absorbed by the system from the surroundings (q is positive)

Enthalpy (H)

- H = U + PV
- We will not derive it, but ΔH (enthalpy change) is the heat of reaction carried out at constant temperature and pressure with all work limited to PV work
- EXTENSIVE property – depends on how much is present
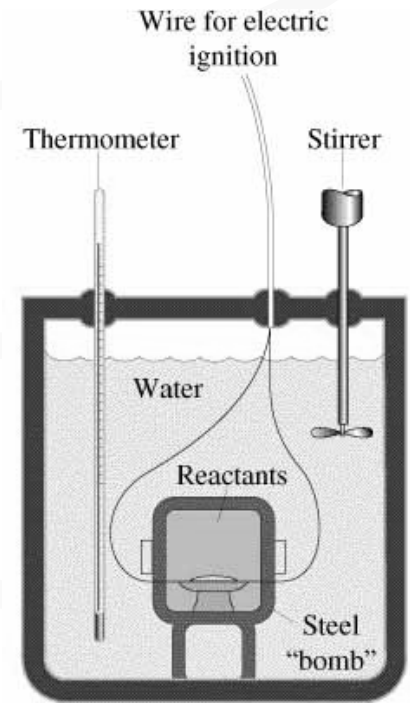- Is a state function

Enthalpy (cont'd)
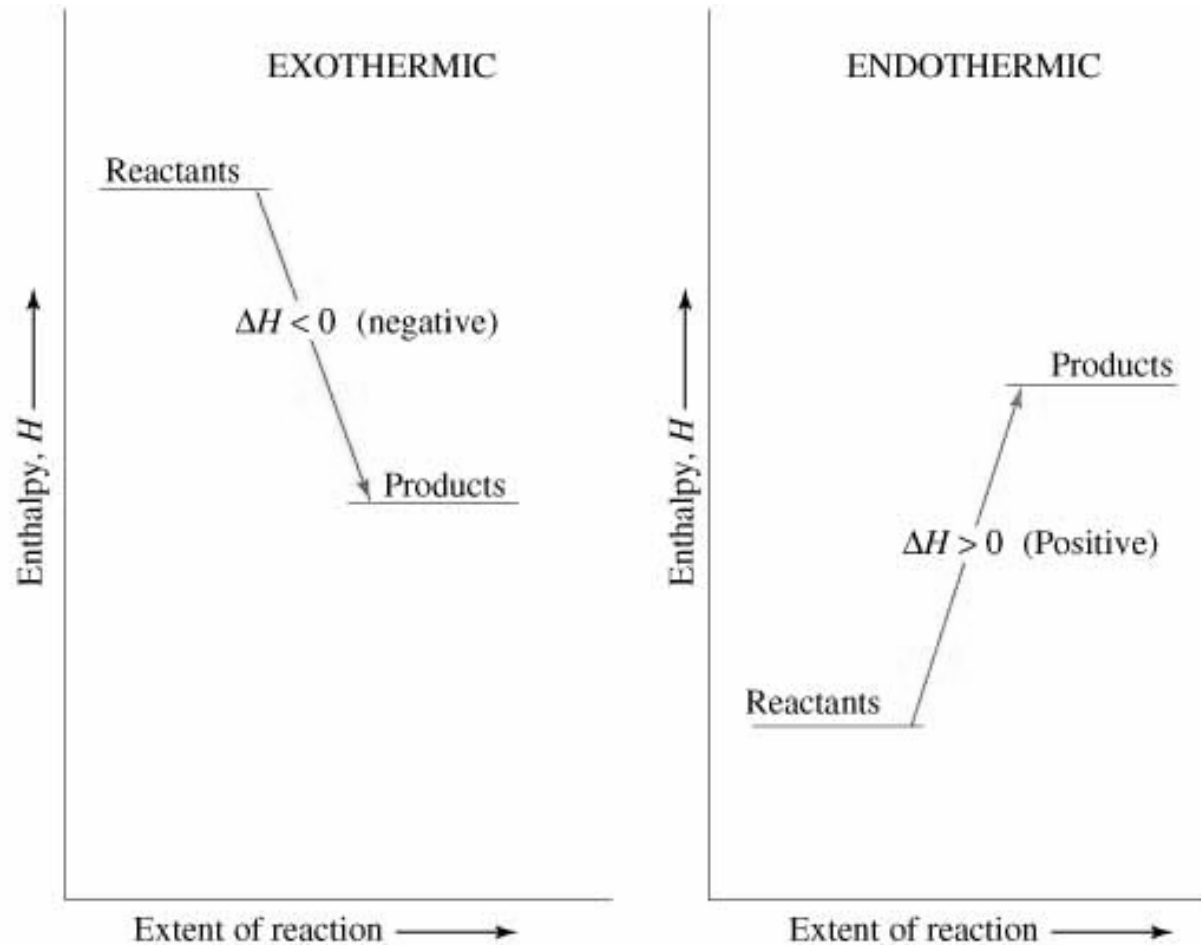
Problem-solving

- How much heat is given off or absorbed when 5.67 mol HCl (g) is formed in the following reaction?
  H_2 (g) + Cl_2 (g) → 2HCl (g) ΔH = -184.6 kJ

- 5.67 mol HCl x (-184.6 kJ/2mol HCl)
- = -523kJ
- (exothermic)

Calorimetry

- The measurement of heat is called CALORIMETRY ("calorie measurement")
- 1 cal = 4.184 J
- 1 Cal = 1000 cal
- Lab expts make assumptions

Heat capacity

- The HEAT CAPACITY of a system is the quantity of heat required to change the temperature of the system by 1°C (or 1K)

- Units are either J/^{o}C or J/K

- MOLAR HEAT CAPACITY is the heat capacity of one mole of a substance

- SPECIFIC HEAT is the heat capacity of a 1g sample

Hess' Law

- HESS' LAW OF HEAT SUMMATION says that the heat of a reaction is constant, whether the reaction is one step or many steps

- Example:
  given $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$ ΔH=-283.0kJ
  and C (graphite) $+ O_2(g) \rightarrow CO_2(g)$ ΔH=-393.5kJ
  what is ΔH for $C(graphite) + \frac{1}{2} O_2(g) \rightarrow CO$ (g)?

- Reversing the first equation and adding it to the second gives us the equation we're looking for:
  $CO_2(g) \rightarrow CO(g) + \frac{1}{2} O_2(g)$
  C (graphite) $+ O_2(g) \rightarrow CO_2(g)$

- Doing the same to the heats of reaction gives us the heat of reaction we're looking for: -(-283.0kJ) + (-393.5kJ) = -110.5kJ

Hess' Law (cont'd)
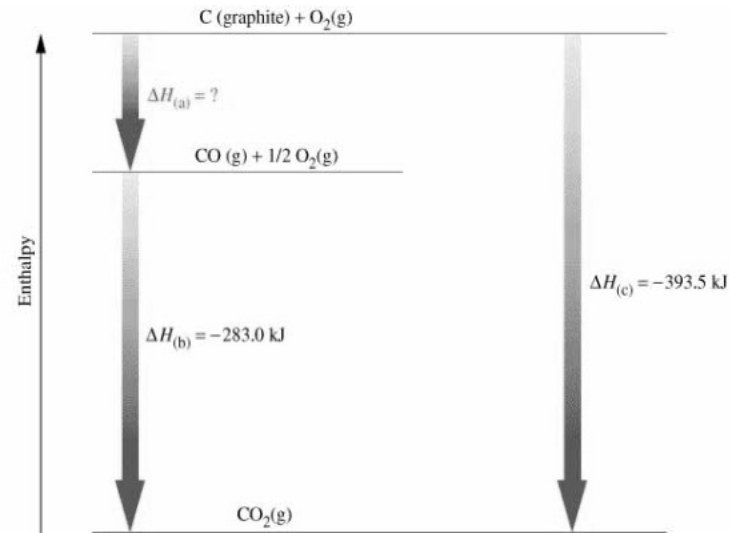
- Reverse the eq., reverse the ΔH
- Multiply the equation, multiply the ΔH

Standard enthalpy

- STANDARD STATE of a liquid or solid or gas is the substance at 1atm and the T of interest
- Just like altitude is given relative to sea level, STANDARD ENTHALPY OF FORMATION ΔH_f^o is the enthalpy change that occurs in the formation of 1 mol of the substance from its elements in their standard states
- STANDARD ENTHALPY OF REACTION (ΔH^o) is the enthalpy change when the reactants in their standard states form products in their standard states

    $= \Delta H_f^o$ (products) - ΔH_f^o (reactants)

end of section

Review

- Reaction- the formation and breaking of chemical bonds
- Bond- a transfer or sharing of electrons

Electrons

- Abbreviated e⁻
- What are they?
- How were they discovered?

Early experiments

- William Crookes used an evacuated tube hooked up to a source of electricity (in 1879) and saw a fluorescent beam

- JJ Thomson (in 1897) determined the particles causing this fluorescence were negatively charged, based on their behavior in the presence of a magnetic field
- Thomson found the fluorescence was independent of the identity of the residual gas in the tube....the particles must therefore be a property of all matter

Cathode rays

Cathode rays deflected downward by magnet

Cathode

Anode
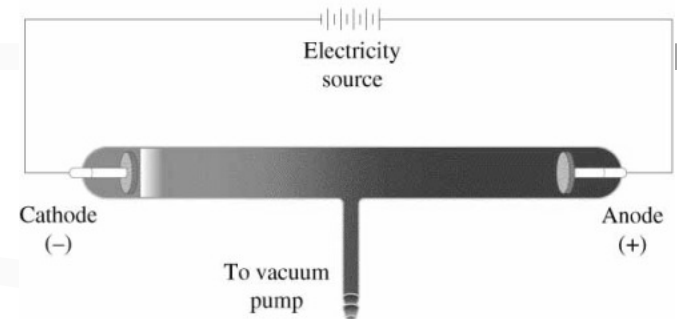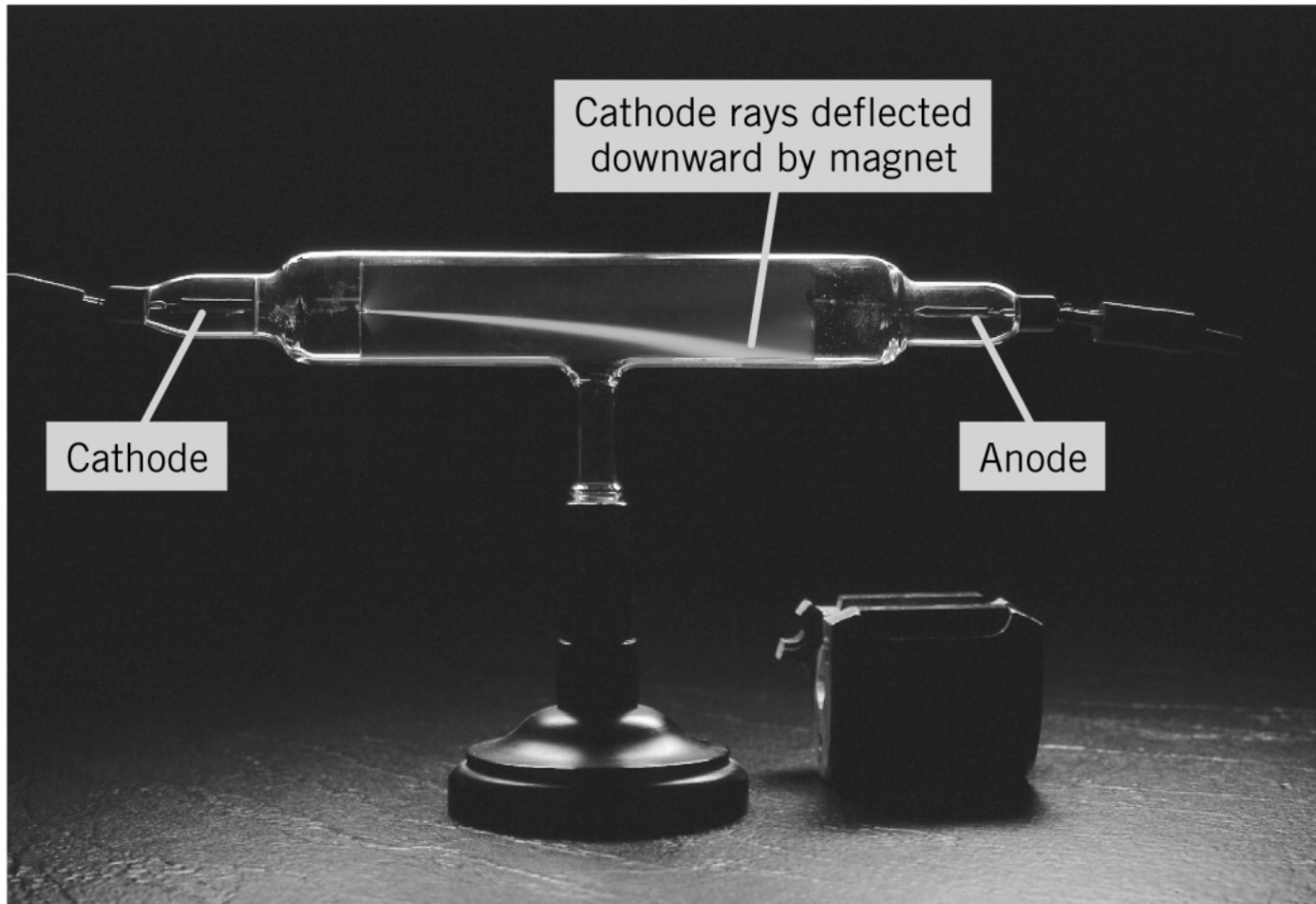
More on Thomson

- Thomson determined the mass to charge ratio (m_e/e = -5.686x10^{-12} kg/C) and decided (based on previous knowledge with H$^+$) he had one of three situations:
  - If the charge were similar to H$^+$, then mathematically the mass of the particle must be much less than that of H$^+$
  - If the mass were similar to H$^+$, then mathematically the charge must be much greater than that on H$^+$
  - Something in between the two extremes
- He suspected the first case to be true, but could not prove it

Electricity source

Cathode   Anode

Magnet

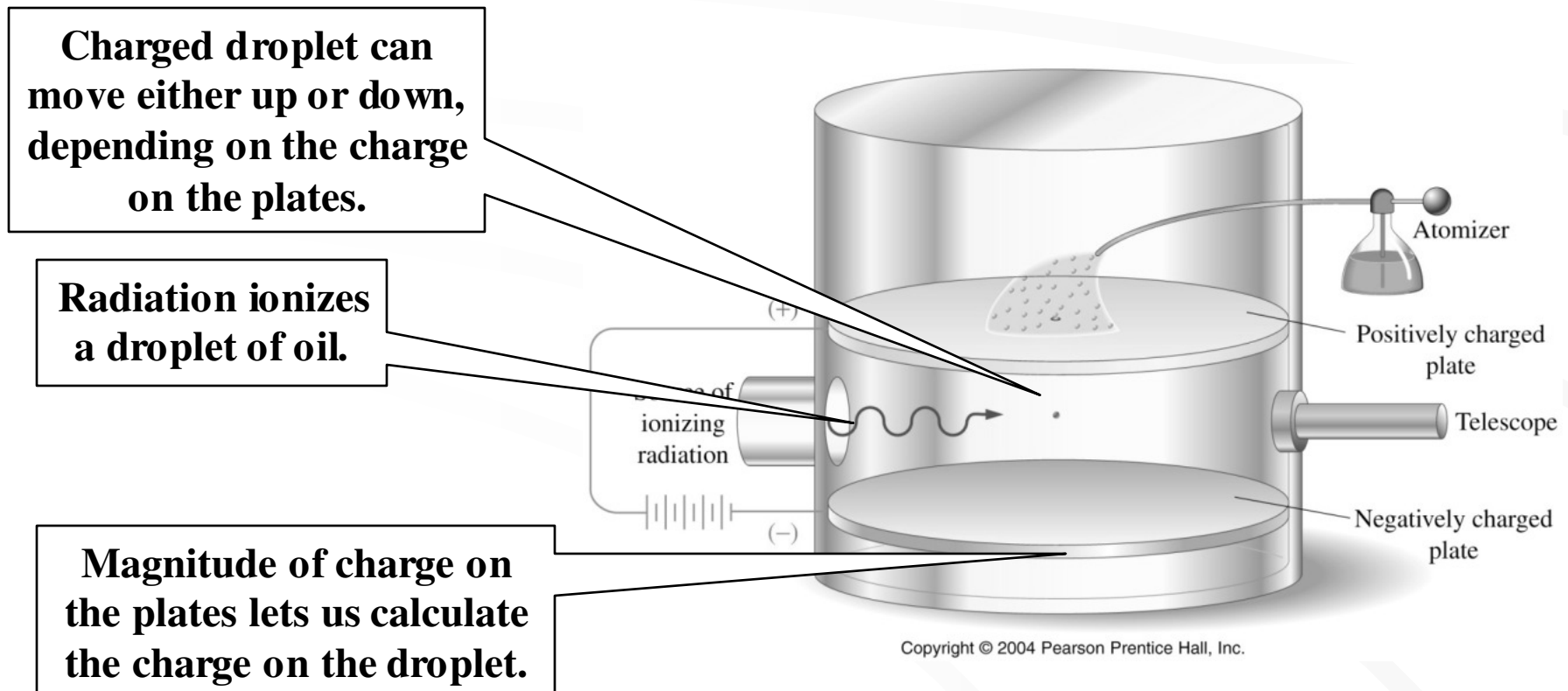Electrical condenser plates

Measuring scale
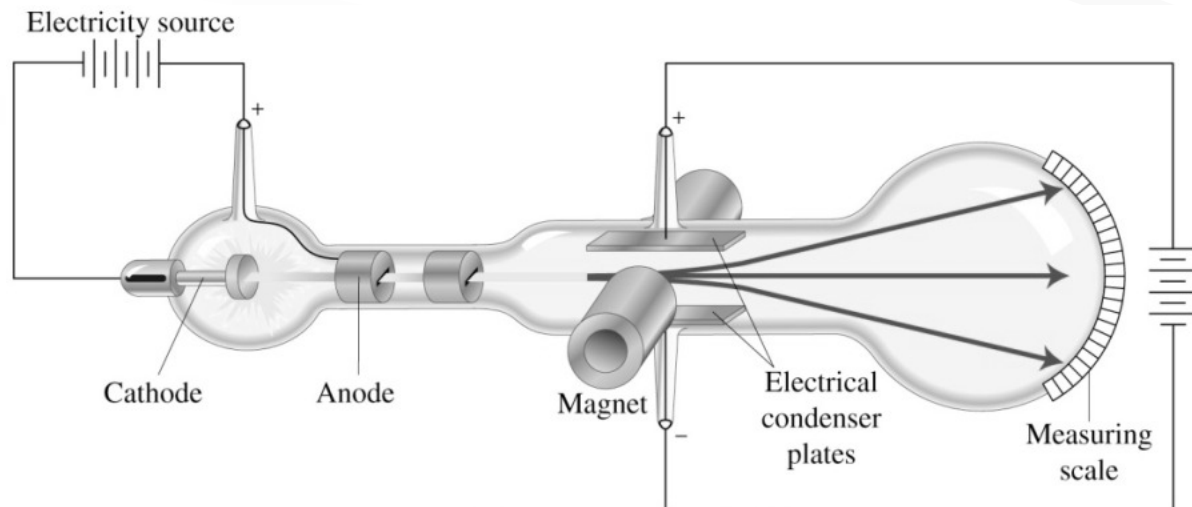
Explanations

- 1909 Millikan's oil drop experiment (next slide) showed that the rate of fall (velocity) of a charged oil drop could be varied in the presence of an electric field such that the charge could only in multiples of a fundamental unit (e=-1.602x10^{-19})

- Thomson knew the e$^-$ had to be neutralized by + charges, but was unsure of the arrangement and devised the "raisin pudding" model (2 slides ahead)

- Ernest Rutherford (a student of Thomson's) studied *radioactivity*, a phenomenon of unstable heavy atoms giving off radiation during disintegration

- Rutherford bombarded metal foils with alpha particles (He^{2+})...most went through, but some were scattered at odd angles...not explained by the Thomson model of the atom...

- Can be explained with a *nuclear* model (three slides ahead)

Millikan's Oil Drop Experiment

- George Stoney: names the cathode-ray particle the **electron.**
- Robert Millikan: determines a value for the electron's charge:

$$e = -1.602 \times 10^{-19} \text{ C}$$

Charged droplet can move either up or down, depending on the charge on the plates.

Radiation ionizes a droplet of oil.

Magnitude of charge on the plates lets us calculate the charge on the droplet.

Atomizer

Positively charged plate

ionizing radiation

Telescope
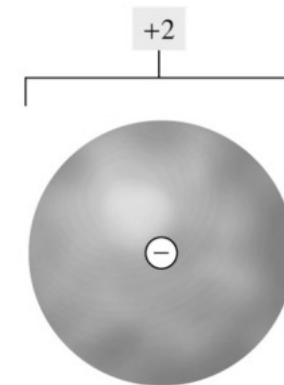
Negatively charged plate

(+)

(−)

J. J. Thomson's Model of the Atom

- Thomson proposed an atom with a positively charged sphere containing equally spaced electrons inside.

- He applied this model to atoms with up to 100 electrons.
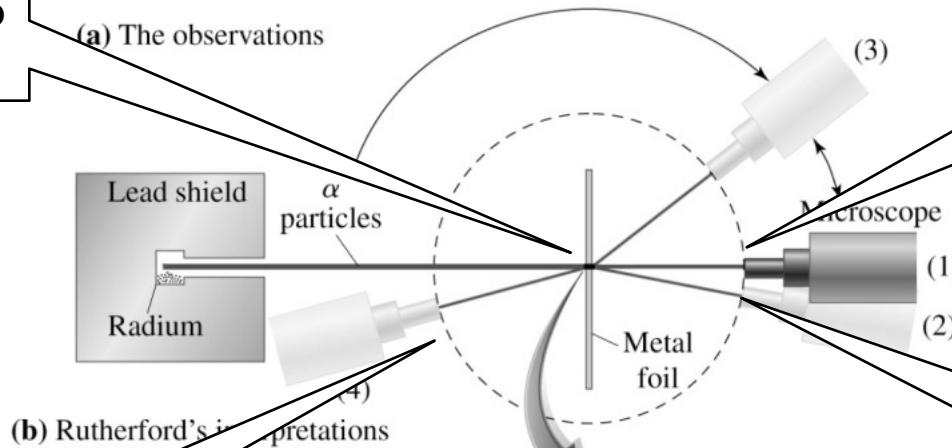
Uniformly distributed positive charge

+2

Helium atom, He

+2

Helium ion, He⁺

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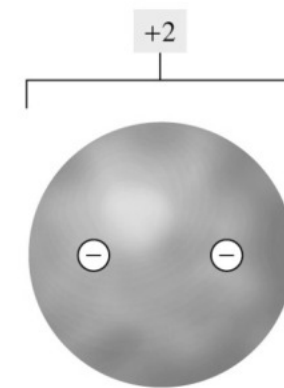
Alpha Scattering "Gold Foil Expt": Rutherford's observations

Alpha particles were "shot" into thin metal foil.

Most of the alpha particles passed *through* the foil.

A few particles were *deflected slightly* by the foil.

A *very* few "bounced back" to the source!

(a) The observations

Lead shield

Radium

α particles

(3)

Microscope

(1)

(2)

Metal foil

(b) Rutherford's interpretations

(1)
(1)
(1)
(1)
(3)
(4)
(1)
(1)
(2)
(1)
(1)

Alpha particles

Gold atom

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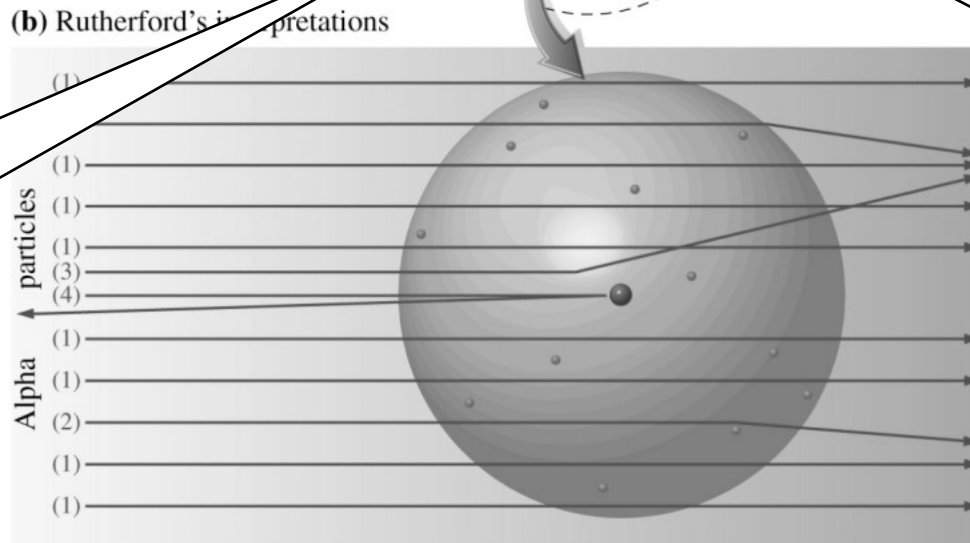
Alpha Scattering Experiment:

Rutherford's conclusions

If Thomson's model of the atom was correct, most of the alpha particles should have been deflected a little, like bullets passing through a cardboard target.
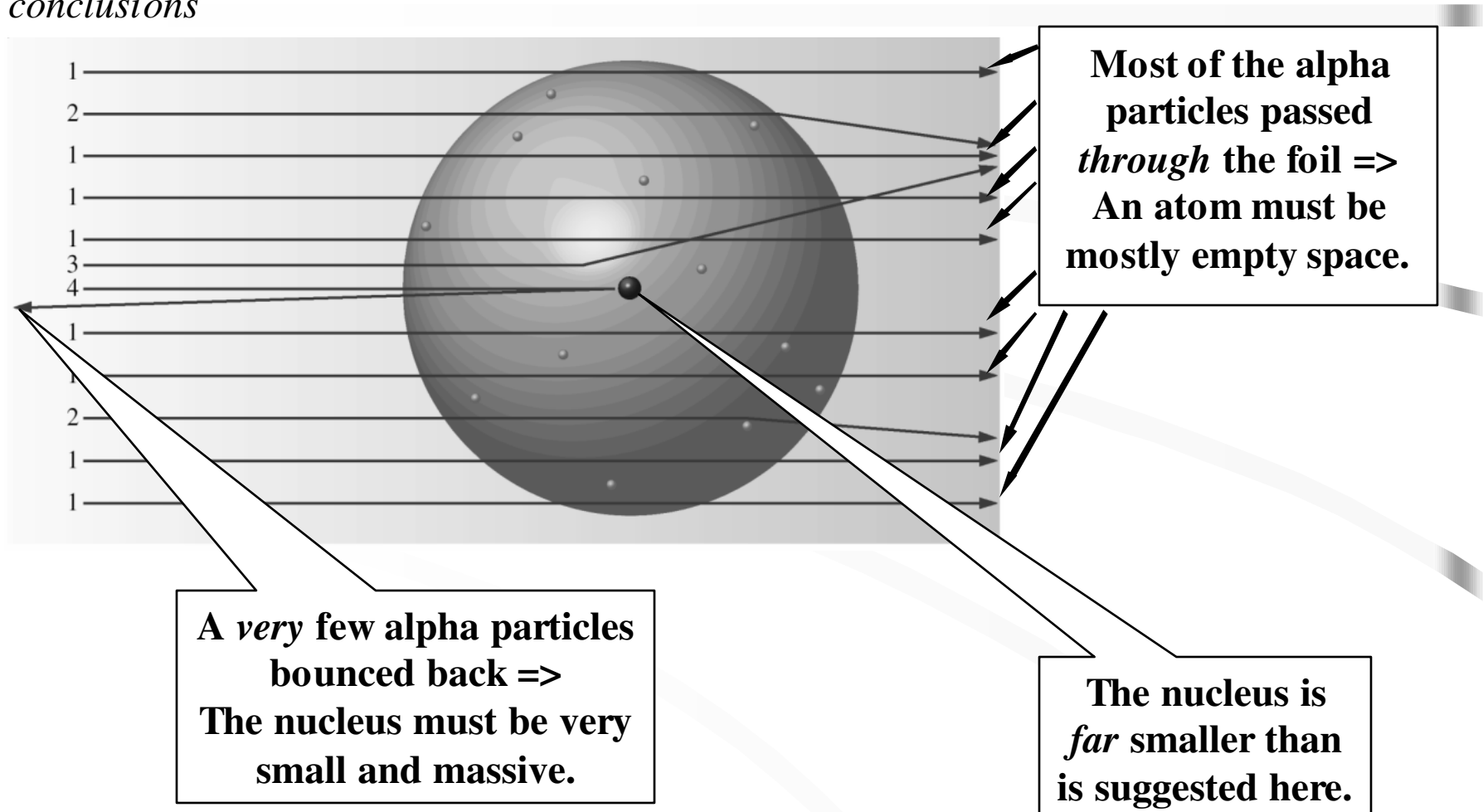
Most of the alpha particles passed *through* the foil => An atom must be mostly empty space.

A *very* few alpha particles bounced back => The nucleus must be very small and massive.

The nucleus is *far* smaller than is suggested here.

Rearranging the periodic table

- Prior to 1914, atomic numbers were given out simply by arranging the elements in order of mass...
- Now that the number of protons and electrons could be determined and the mass of them calculated, there was some additional mass to be explained.
- A neutral particle was postulated, the existence of which was proven in **1932** by Chadwick

Proof

- A Crookes tube can also be constructed to detect positive ions drawn to the cathode (negative pole) (or deflected away from the anode (positive pole).
- These experiments ARE matter dependent.
- A mass analyzer (mass spectrometer) is based on this concept.

196 198 200 202 204

Photographic plate

Mass spectrum of mercury vapor

Stream of positive ions
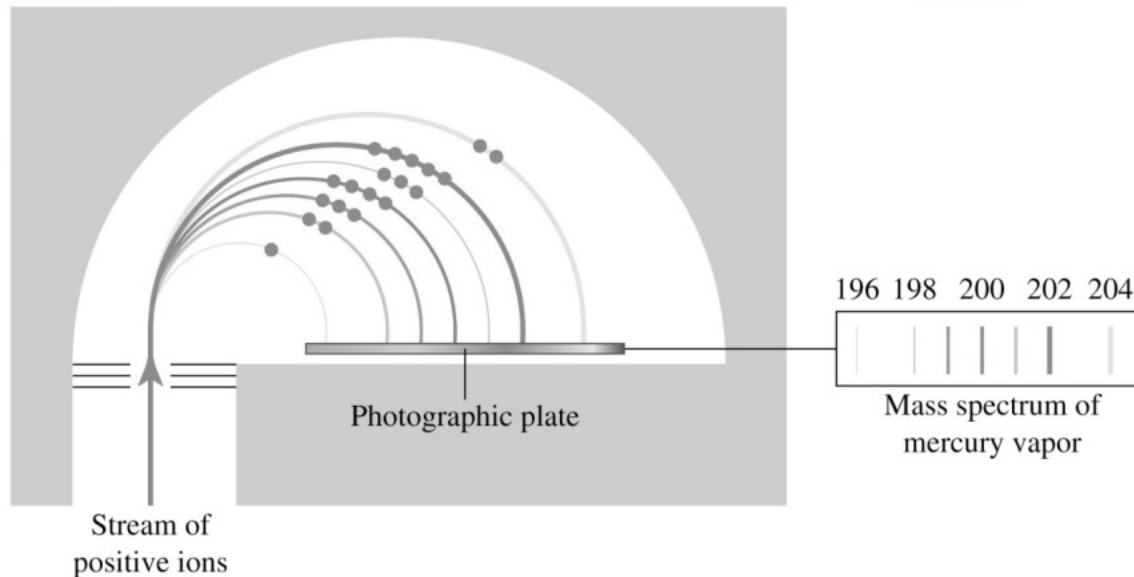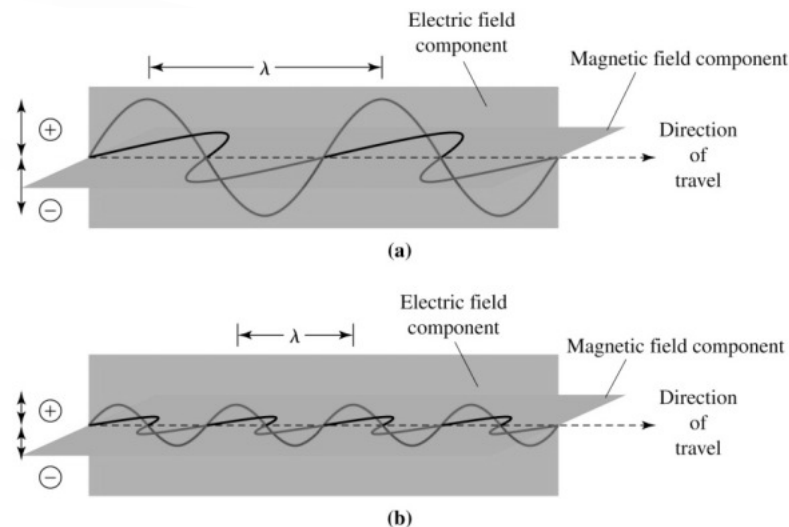
A mass spectrum for mercury

Mass spectrum of an *element* shows the abundance of its isotopes. What are the three most abundant isotopes of mercury?

Mass spectrum of a *compound* can give information about the structure of the compound.

Relative number of atoms

Mass-to-charge ratio

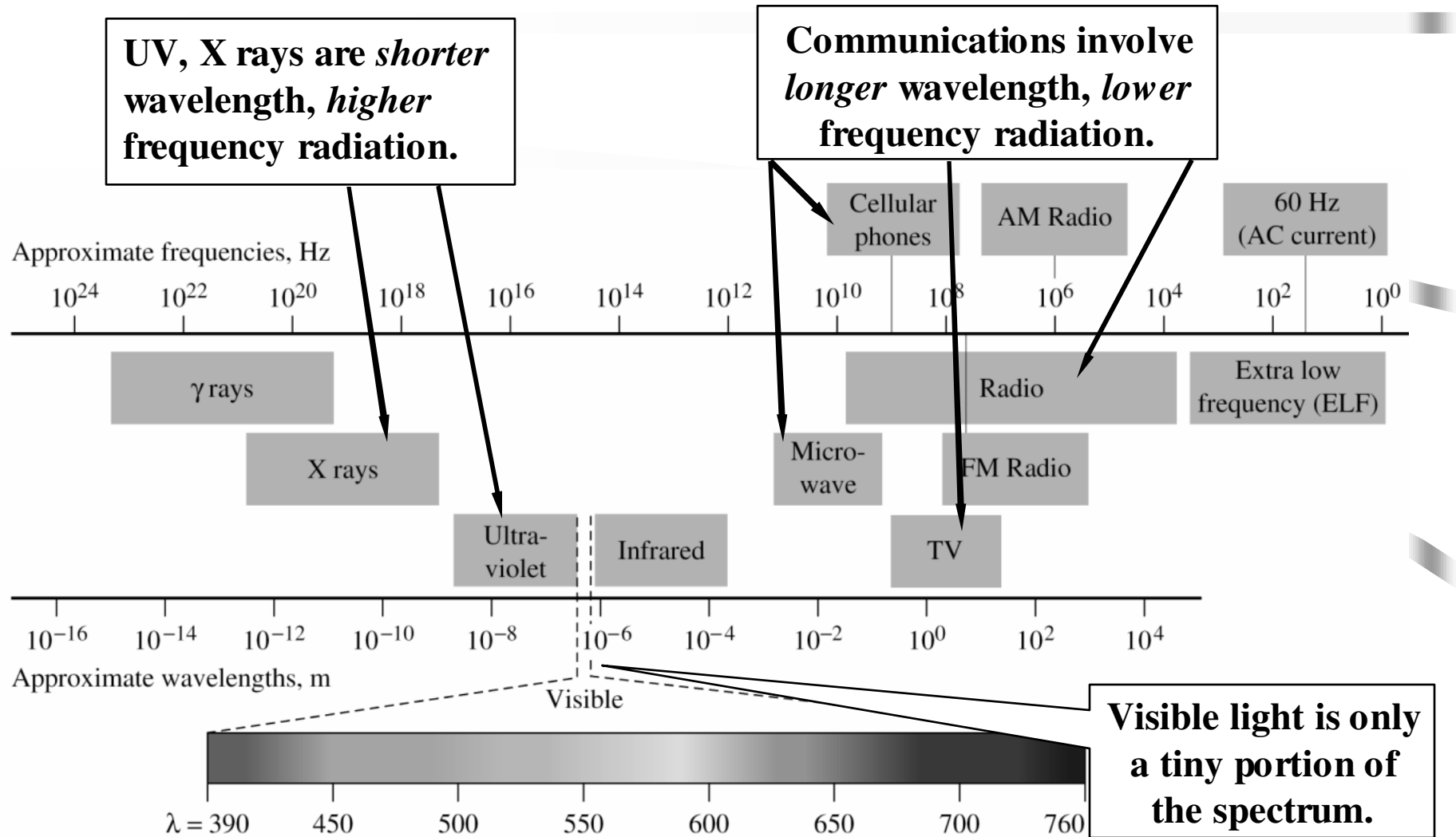Copyright © 2004 Pearson Prentice Hall, Inc.
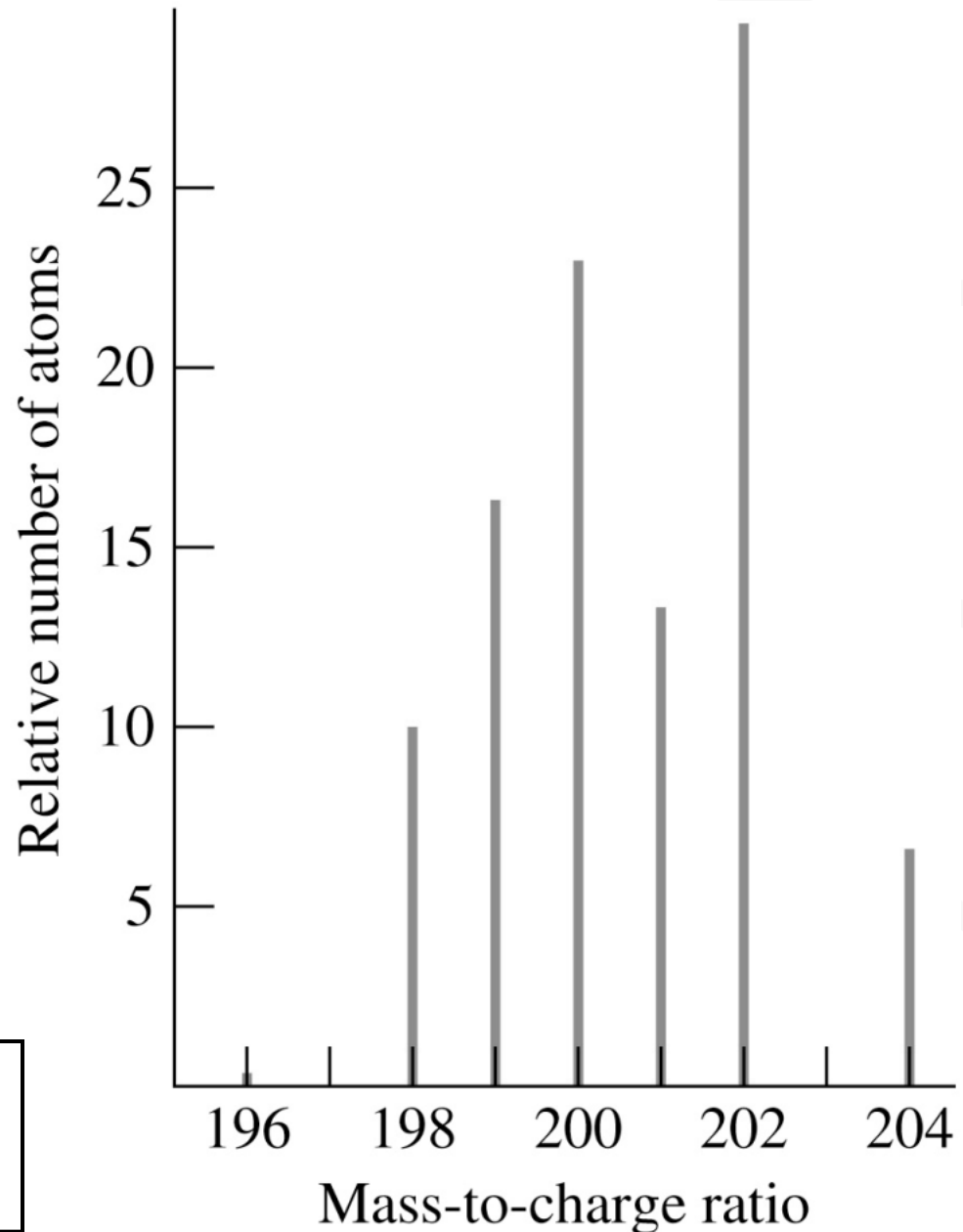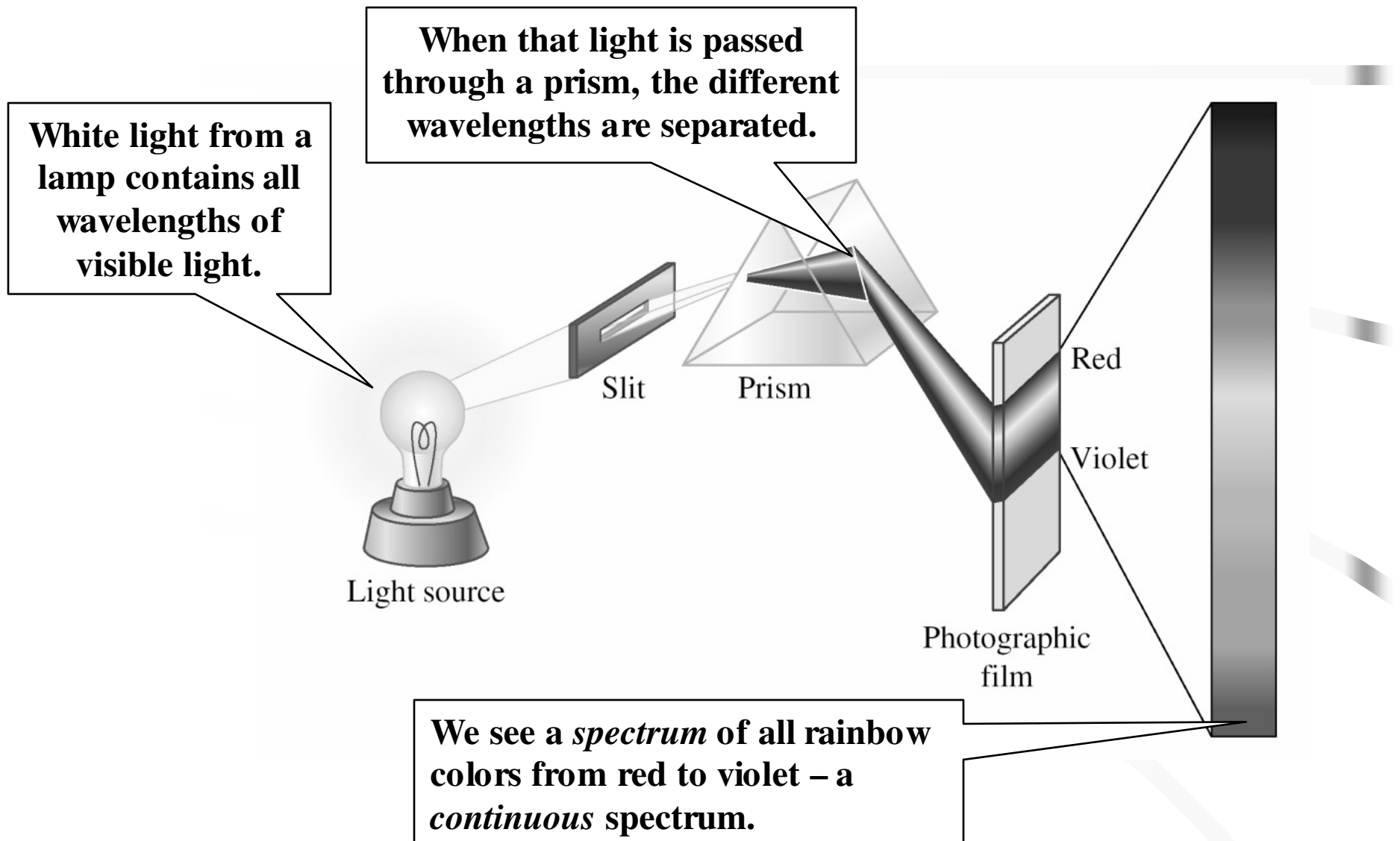
Electromagnetic (EM) radiation

- Composed of perpendicular electric and magnetic field waves (something that repeats as it progresses through space)
- The region of the full spectrum which WE call light is only a small portion (next slide)
- Wavelength (λ) is the distance between equivalent wave points on adjacent peaks, expressed in meters

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Electromagnetic (EM) radiation

UV, X rays are *shorter* wavelength, *higher* frequency radiation.

Communications involve *longer* wavelength, *lower* frequency radiation.

Cellular phones

AM Radio

60 Hz (AC current)

Approximate frequencies, Hz

10^{24} 10^{22} 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4} 10^{2} 10^{0}

γ rays

X rays

Ultra-violet

Infrared

Micro-wave

Radio

FM Radio

TV

Extra low frequency (ELF)

10^{-16} 10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4}

Approximate wavelengths, m

Visible

Visible light is only a tiny portion of the spectrum.

$\lambda = 390$ 450   500   550   600   650   700   760

A continuous *spectrum*

When that light is passed through a prism, the different wavelengths are separated.

White light from a lamp contains all wavelengths of visible light.

We see a *spectrum* of all rainbow colors from red to violet – a *continuous* spectrum.
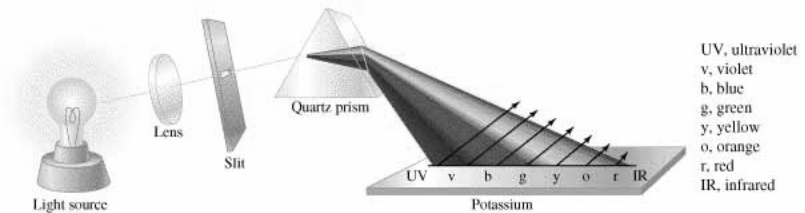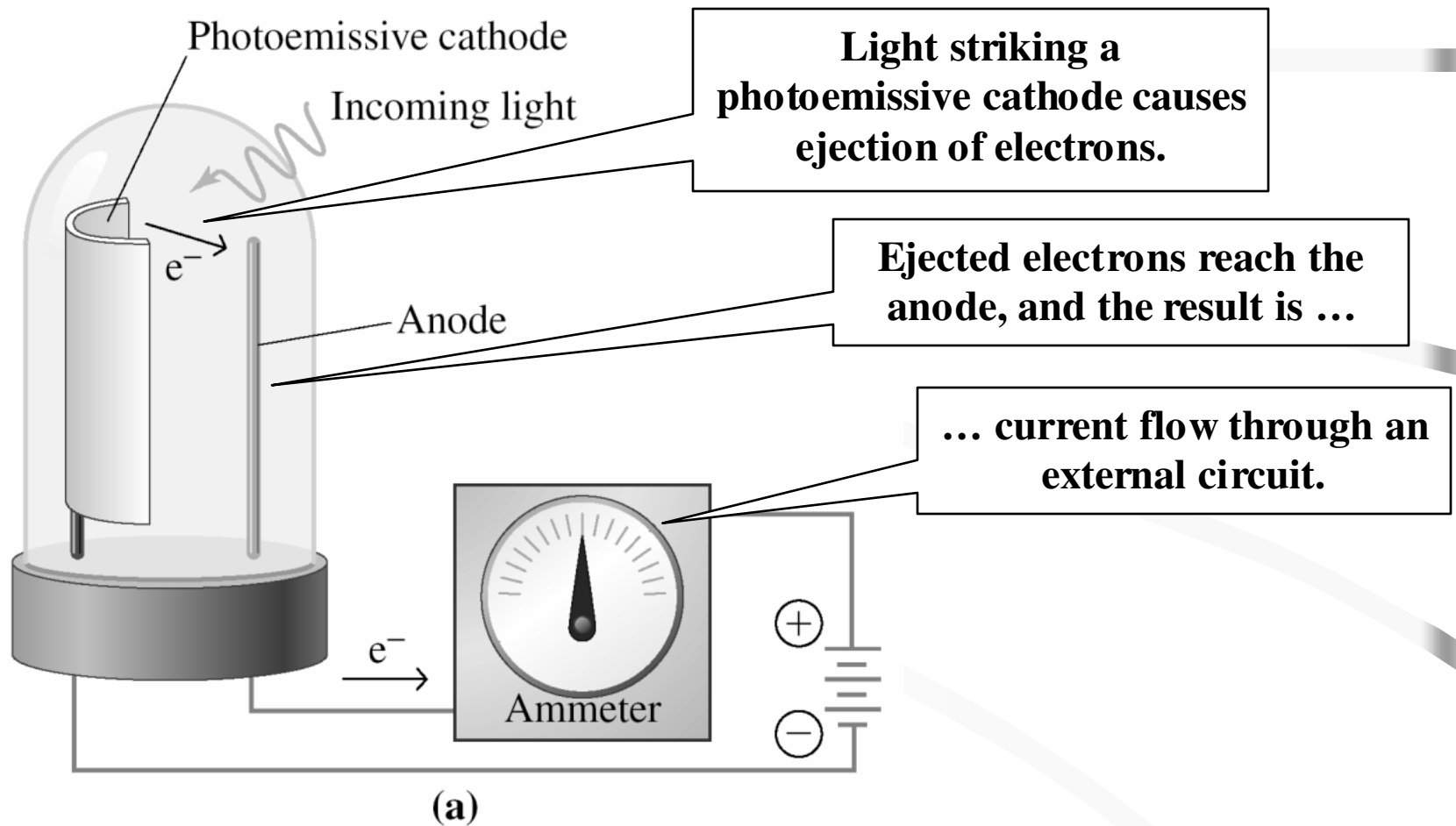
Slit

Prism

Light source

Red

Violet

Photographic film

Frequency

- Frequency (ν) is how many waves pass a fixed point per unit time, expressed in hertz (Hz, s-1)
- Frequency times wavelength = speed, c= 2.99792458×10^8 m/s (or just 3×10^8 m/s)
- In 1900, Max Planck explained the behavior of both high and low frequency radiation by equating energy with frequency and a constant, E=hν, where h is Planck's constant = 6.626×10^{-34} (think how small this number is)
- Planck's equation demonstrates that light comes only in discrete "packets" called quanta (singular = "quantum")

Einstein

- In 1905, Einstein used Planck's theories to explain how electrons can result from bombarding a sample with light...

- This plus the observation of line spectra when elements were heated lead to...

The Photoelectric Effect

Photoemissive cathode

Incoming light

e⁻

Anode

e⁻

Ammeter

(+)

(−)

Light striking a photoemissive cathode causes ejection of electrons.

Ejected electrons reach the anode, and the result is …

… current flow through an external circuit.

(a)

But not "any old" light will cause ejection of electrons …

A Line *Spectrum*

Light from an electrical discharge through a gaseous element (e.g., neon light, hydrogen lamp) does *not* contain all wavelengths.
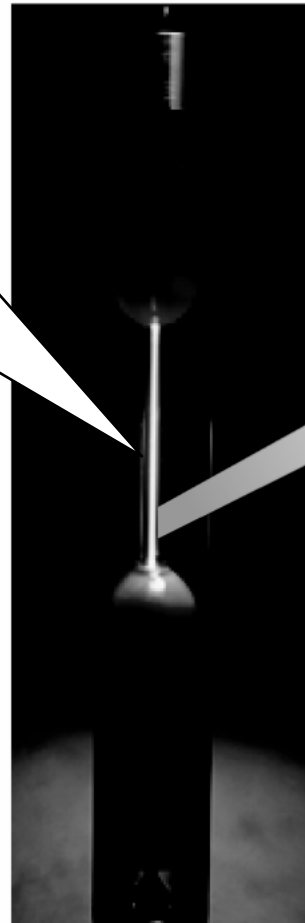
The spectrum is *discontinuous*; there are big gaps.

We see a pattern of lines, multiple images of the slit. This pattern is called a *line spectrum*. (duh!)

Slit   Prism

Photographic film

Hydrogen lamp

The Bohr model of the atom

- Combined classical physics and quantum theory
- Different energy levels of electrons correspond to orbits of different distances from the nuclei of atoms
- The lowest energy level (that nearest the nucleus) is level 1, the next is level 2, and so on
- The electron energy levels $E_n = -B/n^2$, where n is the energy level (an integer) and B is a constant related to Planck's and the mass and charge of an electron (negative energy for an attractive force)

The Bohr Model of hydrogen

When excited, the electron is in a *higher* energy level.

Emission: The atom gives off energy—as a photon.

Upon emission, the electron drops to a *lower* energy level.

Excitation: The atom absorbs energy that is exactly equal to the *difference* between two energy levels.

Electron excitation

Light emission

Each circle represents an allowed energy level for the electron. The electron may be thought of as orbiting at a fixed distance from the nucleus.

$n = 1$

$n = 2$ $n = 3$ $n = 4$ $n = 5$

(a)

Experimental

- Bohr then explained line spectra as being due to the energy difference between 2 levels

$$E_f = \frac{-B}{n_f^2} \quad and \quad E_i = \frac{-B}{n_i^2} \quad so \quad \Delta E = B\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

- (That should be n_i-n_f)

Atoms

- When an atom has all its electrons in their lowest possible energy levels, the atom is in its GROUND STATE

- If energy has been supplied sufficient to promote an electron to a higher level, the atom is in an EXCITED STATE

Energy levels and spectral lines for hydrogen

Shell

$n = \infty$

$n = 5$

$n = 4$

$n = 3$

Balmer
series

$n = 2$

Ionization

Lyman
series

$n = 1$

Energy

$E_\infty = 0$

$E_5 = -B/5^2$

$E_4 = -B/4^2$

Paschen
series

$E_3 = -B/3^2$

$\Delta E = E_2 - E_3$

$E_2 = -B/2^2$

$E_1 = -B/1^2$
$= -2.179 \times 10^{-18} \text{J}$

What is the (transition that produces the) longest-wavelength line in the Balmer series? In the Lyman series? In the Paschen series?
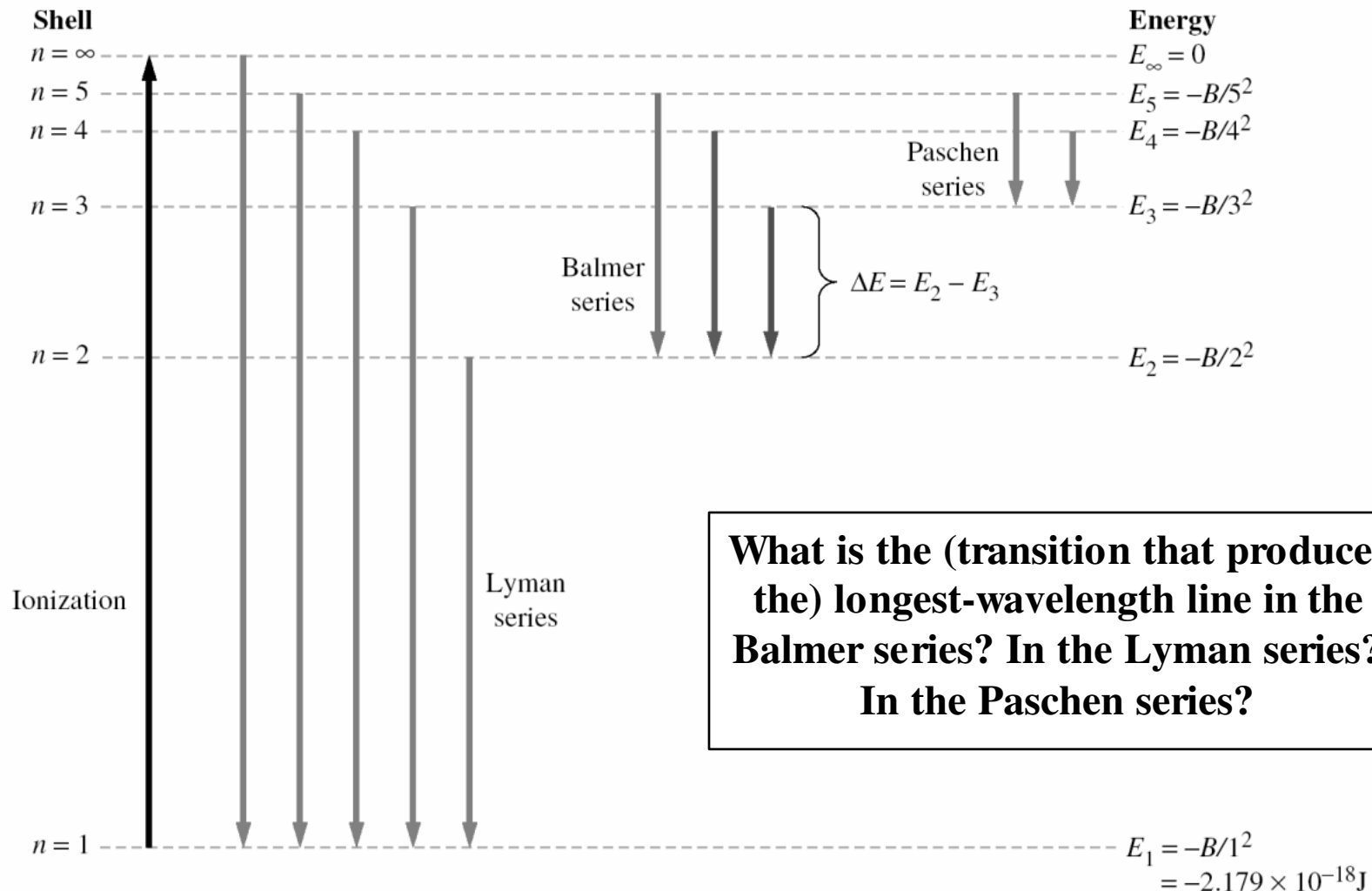
Wave-particle duality

- If light can act like particles of matter, can particles act like waves?
- According to DeBroglie's theories, yes!

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

Particles as waves

- The Bohr model is mostly classical, but if the particles are treated as waves, *quantum* or *wave mechanics* are needed

- In 1926 Erwin Schrodinger developed a mathematical equation to describe the hydrogen atom (a *wave equation*, the solution to which is called a *wave function*

- According to Max Born, the square of the wave function (ψ^2) gives the probability of finding an electron in a particular volume of space in an atom

Particles as waves (cont'd)

- According to Werner Heisenberg, in fact, we *cannot* know both the *exact* position and motion of a tiny particle like an electron *simultaneously*... think of it this way- the act of measuring its position changes its motion, and vice versa

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Microscope

Photon

Electron

(a)

Photon

Electron

(b)
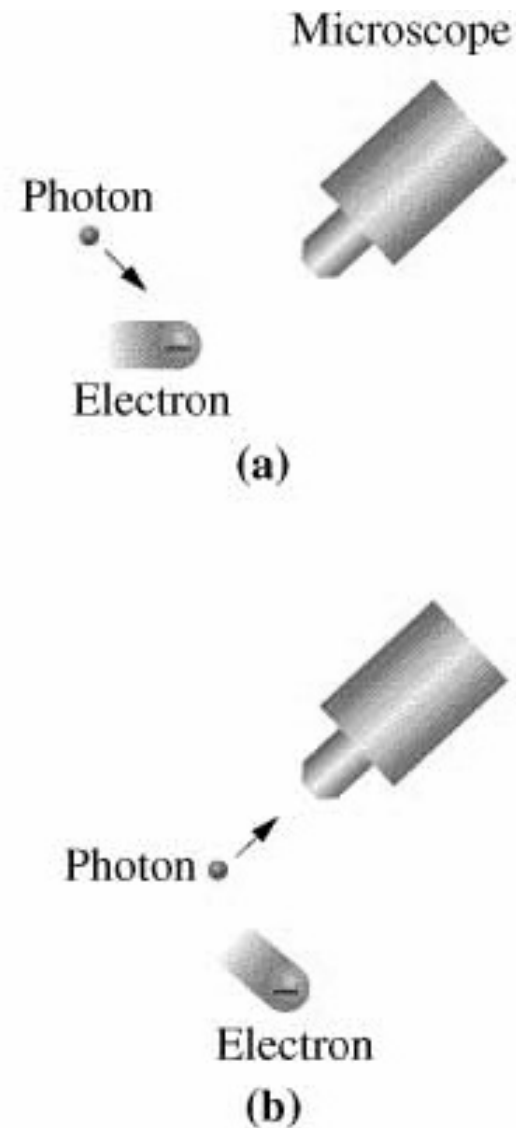
Quantum numbers

- Integral value parameters from the wave function of the hydrogen atom...
- A set of these three wave function quantum numbers (there is a fourth) is called an *atomic orbital*, a mathematical expression which allows us to visualize a 3D region in an atom where there is a significant *probability* of finding an electron

Quantum numbers (cont'd)

- Principal quantum number (n)
  - energy level
  - 1,2,3,4,5,....
- Orbital angular momentum (azimuthal) quantum number (l)
  - shape
  - 0,1,2,3,...(n-1) (s,p,d,f)
- Magnetic quantum number (m_l)
  - direction
  - 0, +/-1, +/-2,...+/-l
- Spin quantum number (m_s)
  - + ½, - ½

Quantum Numbers: n

The **principal quantum number (n)**:

- Is independent of the other two quantum numbers.
- Can only be a positive integer ($n = 1, 2, 3, 4, \ldots$)
- The **size** of an orbital and its electron energy depend on the value of n.
- Orbitals with the same value of n are said to be in the same **principal shell**.

Quantum numbers: 1

The **orbital angular momentum quantum number (l)**:

- Determines the **shape** of the orbital.
- Can have positive integral values from $0,1,2...(n-1)$
- Orbitals having the same values of n and of l are said to be in the same **subshell**.

Value of l	0	1	2	3
Subshell	s	p	d	f

- Each orbital designation represents a different region of space and a different shape.

Quantum numbers: m_l

The **magnetic quantum number (m_l)**:

- Determines the **orientation** in space of the orbitals of any given type in a subshell.

- Can be any integer from $-l$ to $+l$

- The number of possible values for m_l is $(2l + 1)$, and this determines the number of orbitals in a subshell.

Electron spin: m$_s$

- The **electron spin quantum number (m$_s$)** explains some of the finer features of atomic emission spectra.
- The number can have two values: $+\frac{1}{2}$ and $-\frac{1}{2}$.
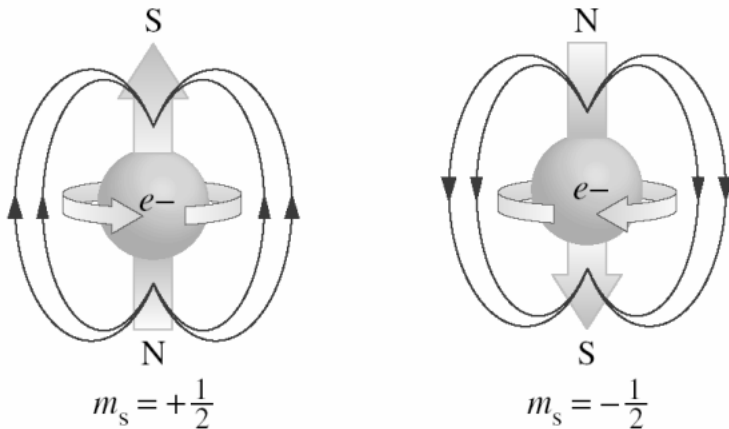
- The spin refers to a magnetic field induced by the moving electric charge of the electron as it spins.
- The magnetic fields of two electrons with opposite spins cancel one another; there is no net magnetic field for the pair.

The 1s orbital

- The 1s orbital ($n = 1$, $l = 0$, $m_l = 0$) has *spherical* symmetry.
- An electron in this orbital spends most of its time near the nucleus.

(a)

(b)

ψ^2

$r \longrightarrow$

(c)

$4\pi r^2 \psi_r^2$

$r \longrightarrow$

(d)
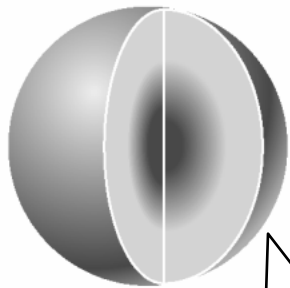
Spherical symmetry; probability of finding the electron is the same in each direction.
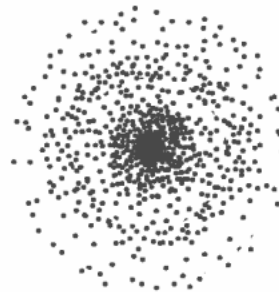
The electron cloud doesn't "end" here …
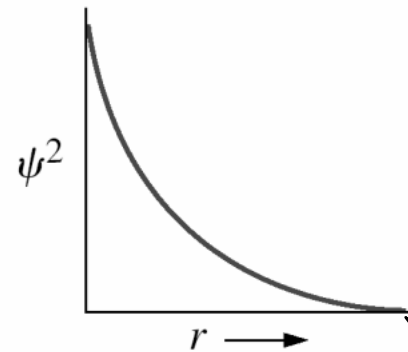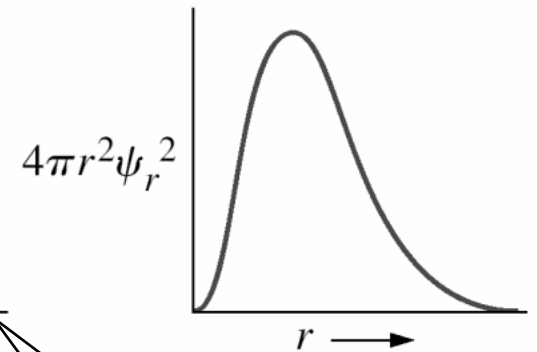
… the electron just spends very little time farther out.

Analogy to the 1s orbital

Highest "electron density" near the center …

10
20
30
40
50

… but the electron density never drops to zero; it just decreases with distance.
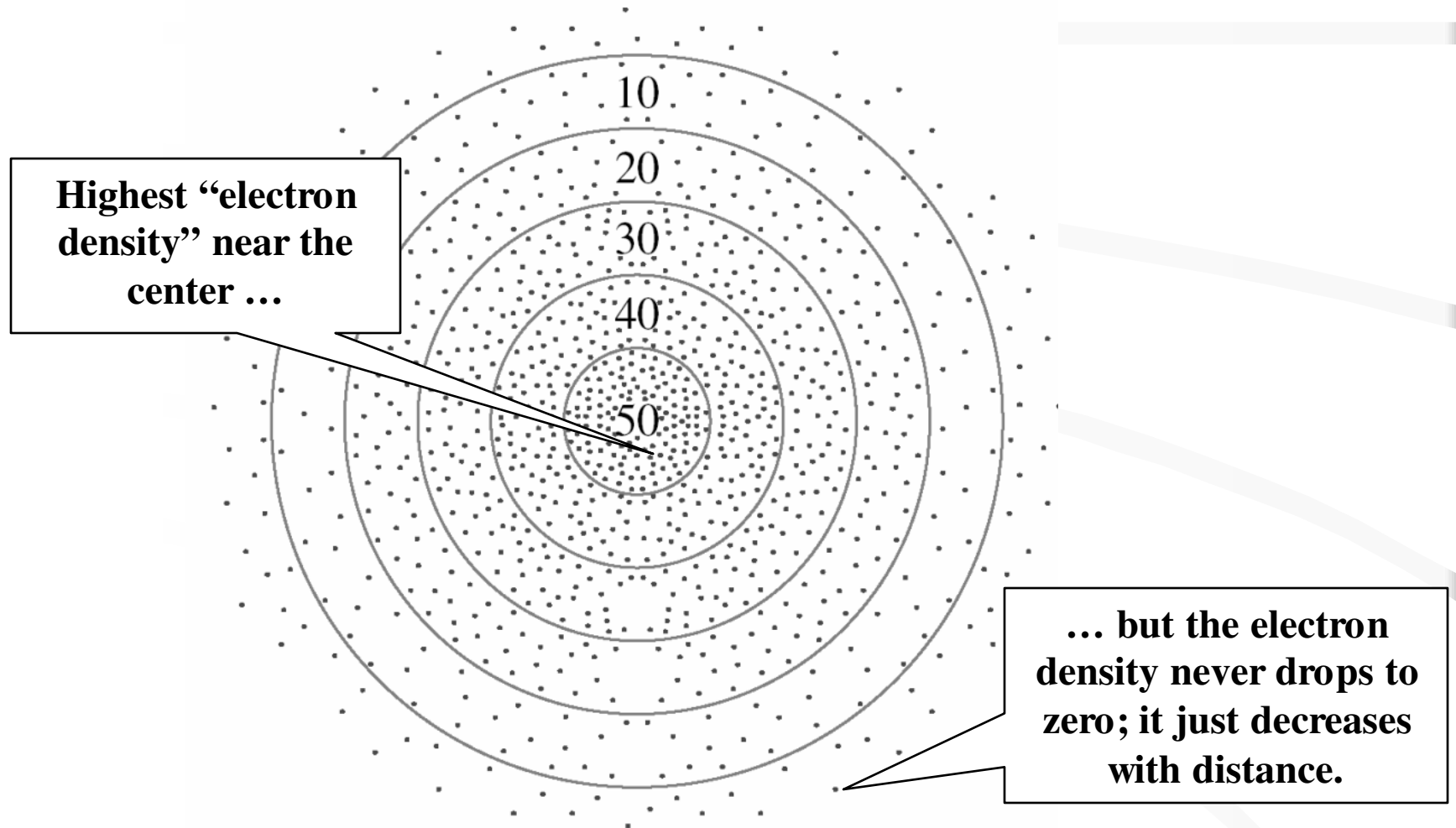
The 2s orbital

- The 2*s* orbital has two concentric, spherical regions of high electron probability.

- The region near the nucleus is separated from the outer region by a **node**—a region (a spherical shell in this case) in which the electron probability is zero.
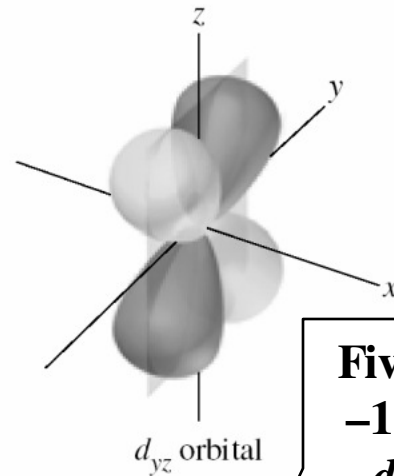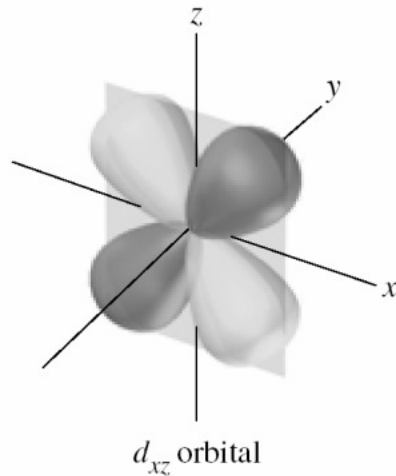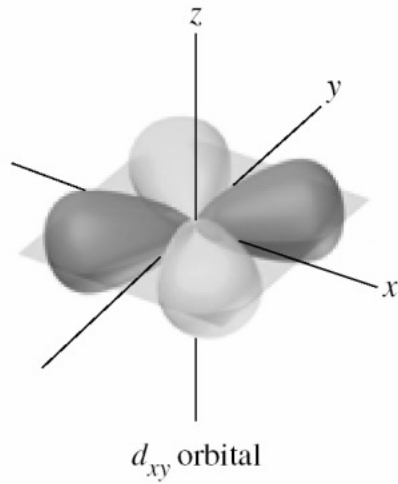

Node

ψ^2

$4\pi r^2 \psi_r^2$

$r \longrightarrow$

$r \longrightarrow$

(a)   (b)   (c)   (d)

The three p orbitals
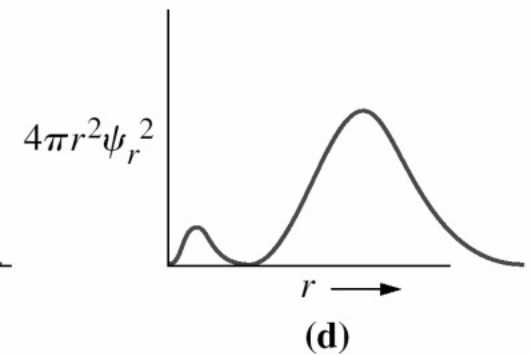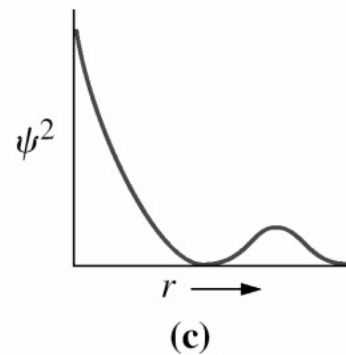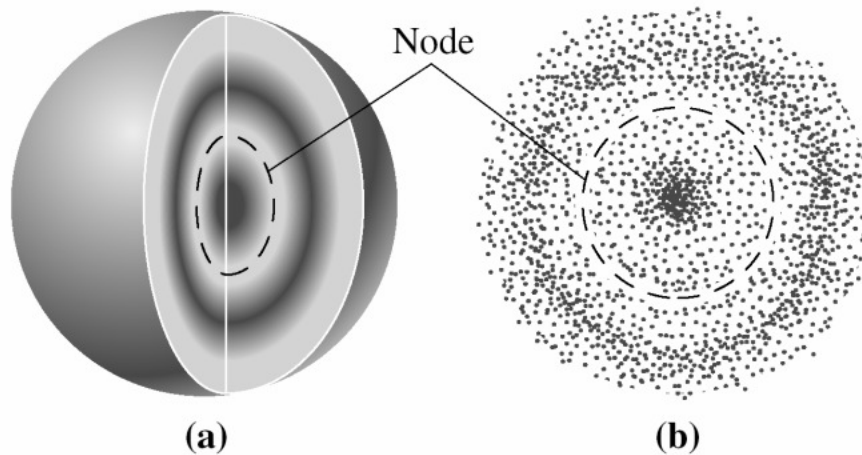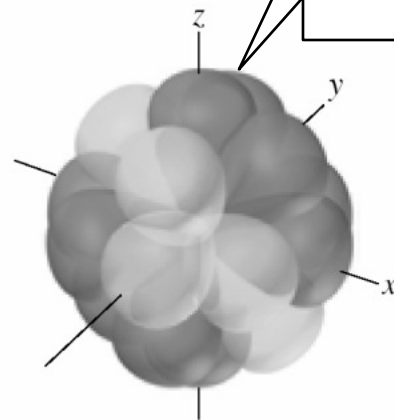

p_x orbital

p_y orbital
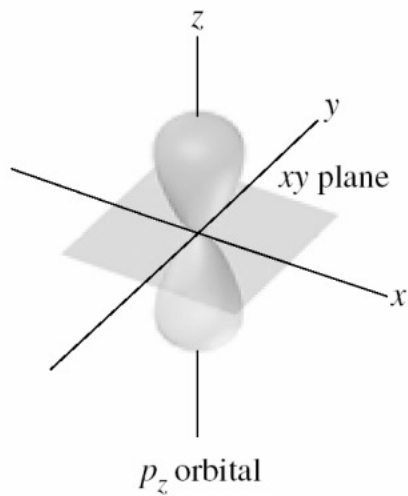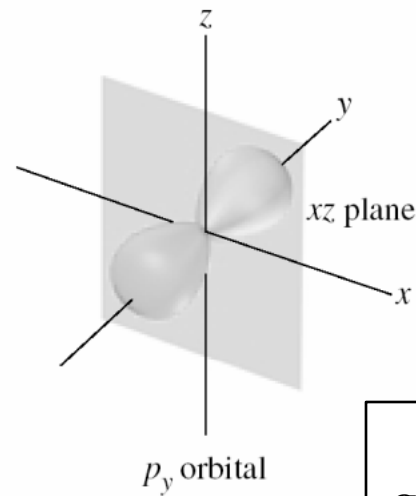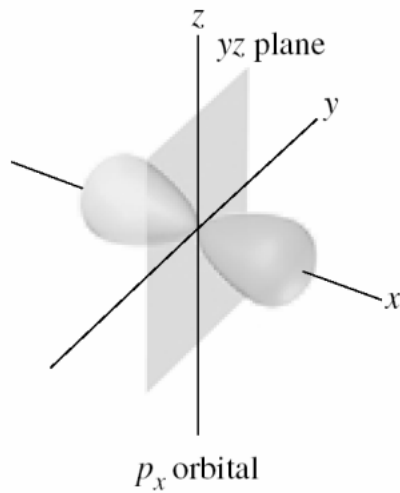
p_z orbital

Three values of m_l gives three p orbitals in the p subshell.

The five d *orbitals*

d_{xy} orbital

d_{xz} orbital

d_{yz} orbital

$d_{x^2-y^2}$ orbital
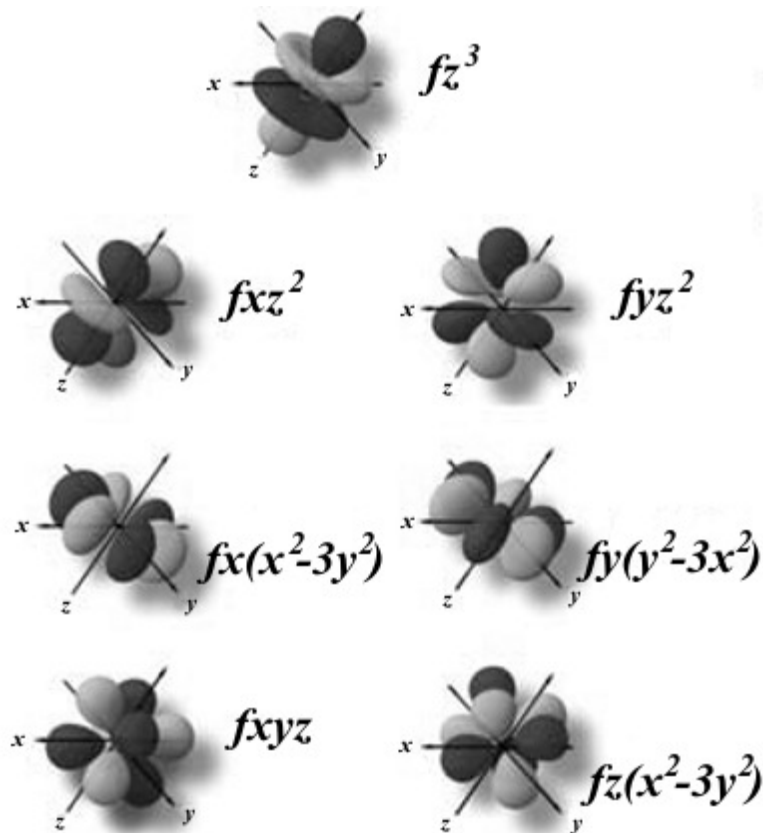
d_{z^2} orbital
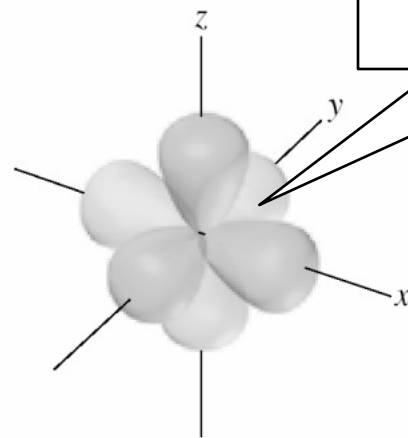
Five values of m_l (−2, −1, 0, 1, 2) gives five *d* orbitals in the *d* subshell.
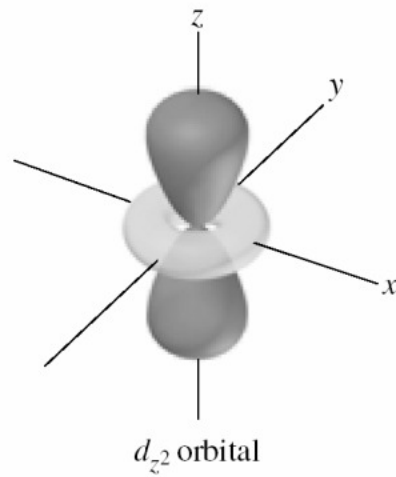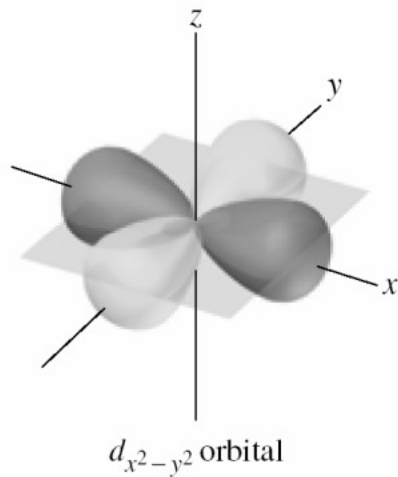
The seven f orbitals

Seven values of m_l (-3, -2, -1, 0, 1, 2, 3) gives seven f orbitals in the f subshell.

end of section

Schrödinger

- Cannot be solved for multielectron atoms
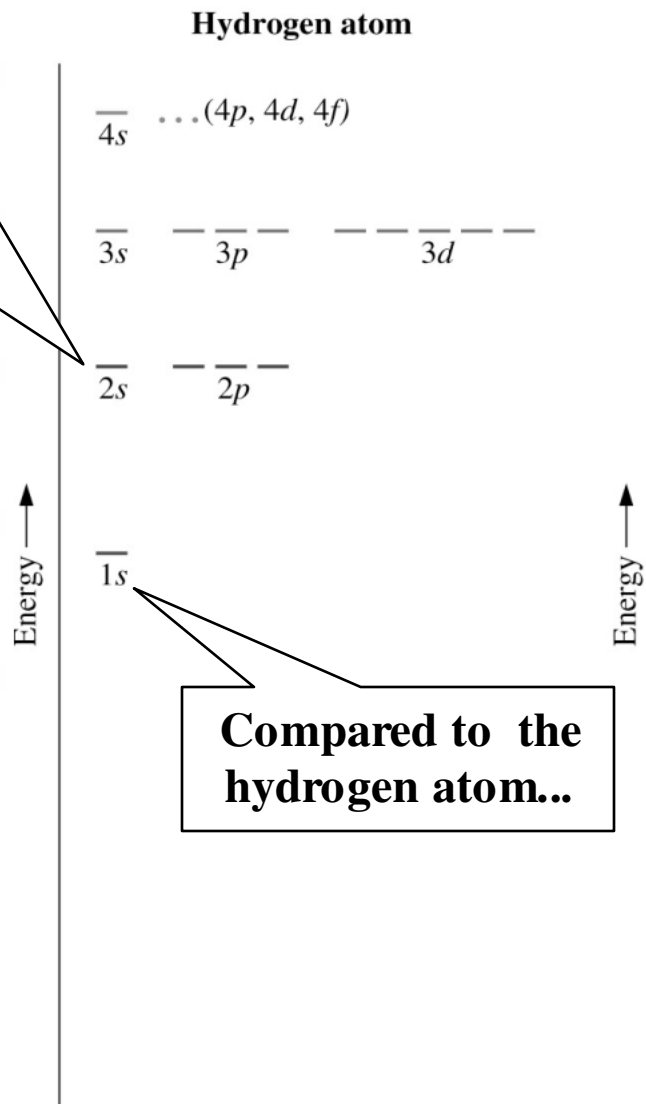- We must assume the orbitals are all hydrogen-like

Differences

- In the H atom, all subshells (*s,p,d,f*) of a principal shell are at the same energy
- This varies for other elements, though all orbitals *within* a subshell are at the same energy level. (2 slides ahead) (DEGENERATE orbitals)
- Orbital energies are lower in multielectron atoms than in H. (WHY????)
- In multielectron atoms, for higher numbered principal shells, some subshells have nearly identical energies.   (WHY???)

REMINDER

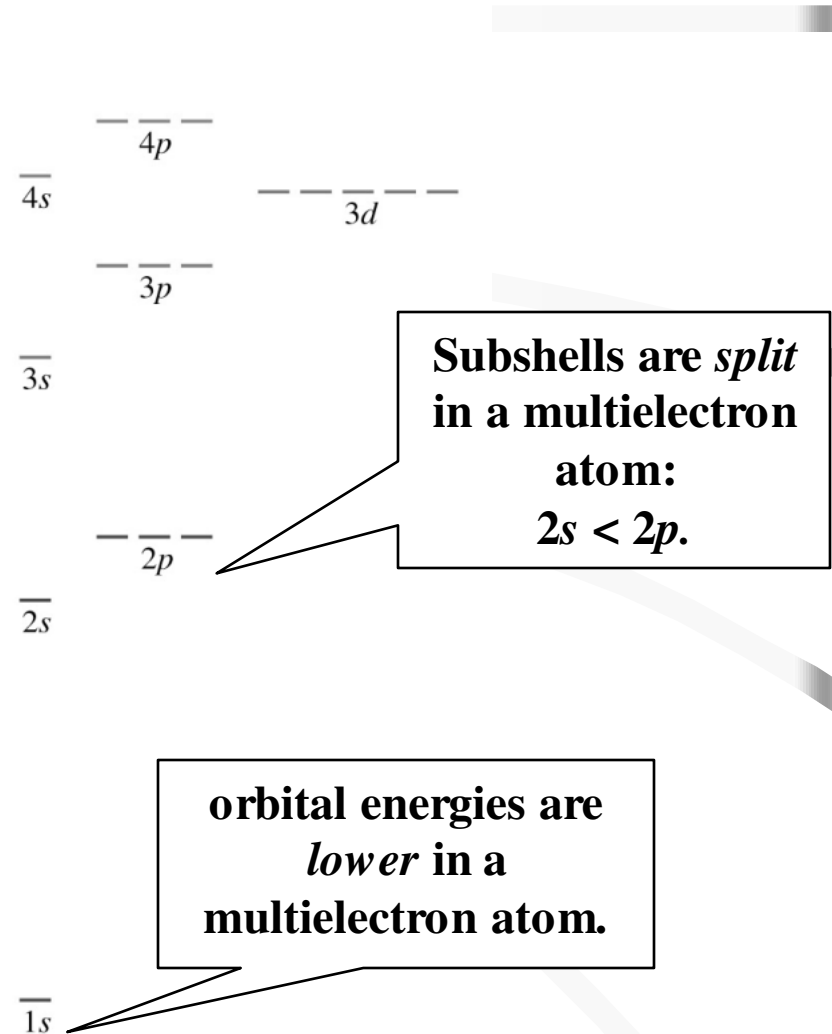ORBITALS

ARE

REGIONS OF PROBABILITY

Orbital energy diagrams

Subshells within a shell are at the *same* energy level in hydrogen: 2s = 2p.

Hydrogen atom

A typical multielectron atom

$\overline{4s}$ . . . (4p, 4d, 4f)

$\overline{3s}$ $\overline{3p}$ $\overline{3d}$

$\overline{2s}$ $\overline{2p}$

$\overline{1s}$

Energy

$\overline{4s}$

$\overline{4p}$

$\overline{3d}$

$\overline{3p}$

$\overline{3s}$

$\overline{2p}$

$\overline{2s}$

$\overline{1s}$

Energy

Compared to the hydrogen atom...

Subshells are *split* in a multielectron atom: 2s < 2p.

orbital energies are *lower* in a multielectron atom.

Electron configuration

- Describes the distribution of electrons among the various orbitals in the atom.
- Electron configuration is represented in two ways:
- *s p d f* notation
  - Numbers denote principal shell
  - Letters denote subshell
  - Superscripts denote number of electrons per subshell
  - Electrons occupy orbitals of the lowest energy available

- Orbital diagram

Electrons are in the *l* = 0 (*s*) subshell.
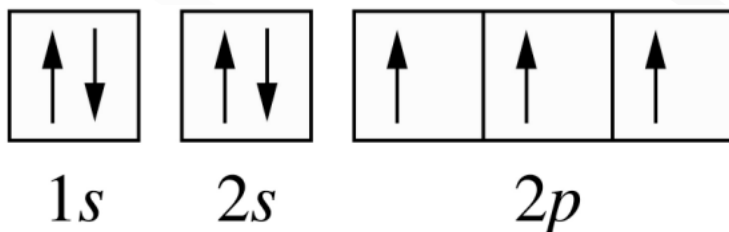
Two electrons in the 1*s* subshell.

$1s^2$

Electrons occupy the *n* = 1 energy level.

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1*s*   2*s*   2*p*

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s p d f *notation (cont'd)*

- No two electrons can have the same set of 4 quantum numbers

- Thus, an orbital can accommodate at most 2 electrons (Wolfgang Pauli, 1926)– The *Pauli Exclusion Principle*

- Electrons enter empty orbitals whenever possible when faced with a set of identical-energy orbitals (Hund's rule)

- Electrons in half-filled orbitals have the same (parallel) spins

- Therefore, when drawing *ground state* electron configurations, the aufbau ("building up") principle is employed
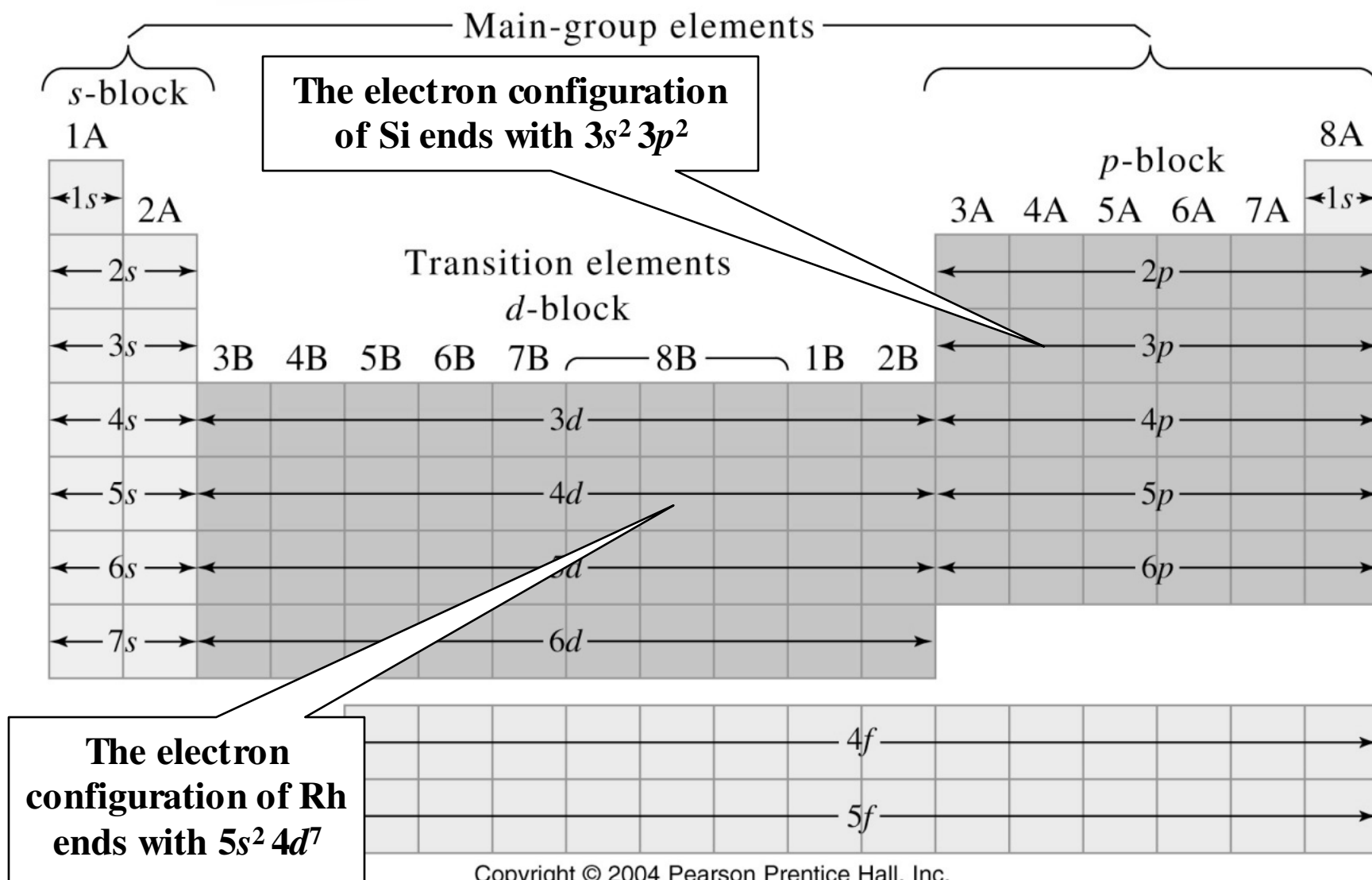
s p d f *notation (cont'd)*

- 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, 5*f*, 6*d*, 7*p*

- To remember the above, use the figure, or better yet, **USE THE PERIODIC TABLE**

1s
2s   2p
3s   3p   3d
4s   4p   4d   4f
5s   5p   5d   5f
6s   6p   6d
7s   7p
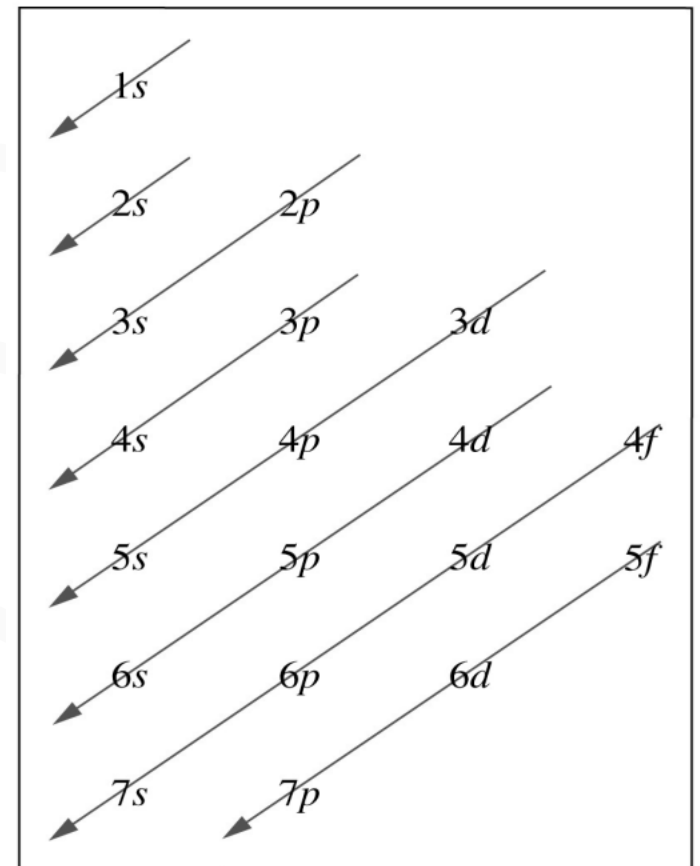
Using the periodic table to write e⁻ configurations

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Exceptions to aufbau

- Cr and Cu are examples where the observed configuration (confirmed experimentally) is not as expected due to a *hyperstability* of a FILLED or HALF-FILLED subshell

Exceptions to the Aufbau principle (cont'd)

Half-filled d subshell plus half-filled s subshell has slightly lower in energy than $s^2 d^4$.

Filled d subshell plus half-filled s subshell has slightly lower in energy than $s^2 d^9$.

More exceptions occur farther down the periodic table. They aren't always predictable, because energy levels get closer together.

		$3d$	$4s$	
Sc	[Ar]			$[Ar]3d^1 4s^2$
Ti	[Ar]			$[Ar]3d^2 4s^2$
V	[Ar]			$[Ar]3d^3 4s^2$
Cr	[Ar]			$[Ar]3d^5 4s^1$
Mn	[Ar]			$[Ar]3d^5 4s^2$
Fe	[Ar]			$[Ar]3d^6 4s^2$
Co	[Ar]			$[Ar]3d^7 4s^2$
Ni	[Ar]			$[Ar]3d^8 4s^2$
Cu	[Ar]			$[Ar]3d^{10} 4s^1$
Zn	[Ar]			$[Ar]3d^{10} 4s^2$

Exceptions to the Aufbau principle (cont'd)

1A												3A	4A	5A	6A	7A	8A
1 H $1s^1$	2A																2 He $1s^2$
3 Li $2s^1$	4 Be $2s^2$	3B	4B	5B	6B	7B	8B			1B	2B	5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
55 Cs $6s^1$	56 Ba $6s^2$	57 *La $5d^16s^2$	72 Hf $5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
87 Fr $7s^1$	88 Ra $7s^2$	89 †Ac $6d^17s^2$	104 Rf $6d^27s^2$	105 Db $6d^37s^2$	106 Sg $6d^47s^2$	107 Bh	108 Hs	109 Mt	110	111	112						

- s-block elements
- d-block elements
- p-block elements
- f-block elements

58 Ce $4f^26s^2$	59 Pr $4f^36s^2$	60 Nd $4f^46s^2$	61 Pm $4f^56s^2$	62 Sm $4f^66s^2$	63 Eu $4f^76s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^96s^2$	66 Dy $4f^{10}6s^2$	67 Ho $4f^{11}6s^2$	68 Er $4f^{12}6s^2$	69 Tm $4f^{13}6s^2$	70 Yb $4f^{14}6s^2$	71 Lu $4f^{14}5d^16s^2$
90 Th $6d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^67s^2$	95 Am $5f^77s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^97s^2$	98 Cf $5f^{10}7s^2$	99 Es $5f^{11}7s^2$	100 Fm $5f^{12}7s^2$	101 Md $5f^{13}7s^2$	102 No $5f^{14}7s^2$	103 Lr $5d^{14}6d^17s^2$

Example

- What is the electron configuration of Cs?

- ***Noble-gas-core (condensed) abbreviation***: Another example of chemists' shorthand. The portion of the config. that corresponds to the electron config. of the nearest previous noble gas is replaced with a bracketed chemical symbol. It's easier to write …

$$(Z = 3) \quad \text{Li} \ \textbf{[He]}2\text{s}^1$$
$$(Z = 22) \ \text{Ti} \ \textbf{[Ar]}4\text{s}^2 3\text{d}^2$$

Example

- Give the complete ground-state electron configuration of a strontium atom
  (a) in *spdf* notation and
  (b) in the noble-gas-core abbreviated notation
  (c) in the orbital box diagram notation.

Valence electrons

- The outermost shell of electrons is known as the *valence shell*
- The inner electrons are the *core electrons*
- When writing the configuration of *ions*, add or remove electrons to/from the valence shell
- Often results in noble gas configuration
- EXCEPTION: Transition elements- outer *s* electrons are lost first
- If two species have the same electron configuration, they are said to be *isoelectronic*

Valence electrons and core electrons

- The **valence shell** is the outermost occupied principal shell. The valence shell contains the **valence electrons**.

- For main group elements, the number of valence shell electrons is the same as the periodic table group number (2A elements: two valence electrons, etc.)

  The period number is the same as the principal quantum number n of the electrons in the valence shell.

- Electrons in inner shells are called **core electrons.**

Five valence electrons, for which $n = 4$

Example: As
$$[Ar]\ 4s^2\ 3d^{10}4p^3$$

28 core electrons
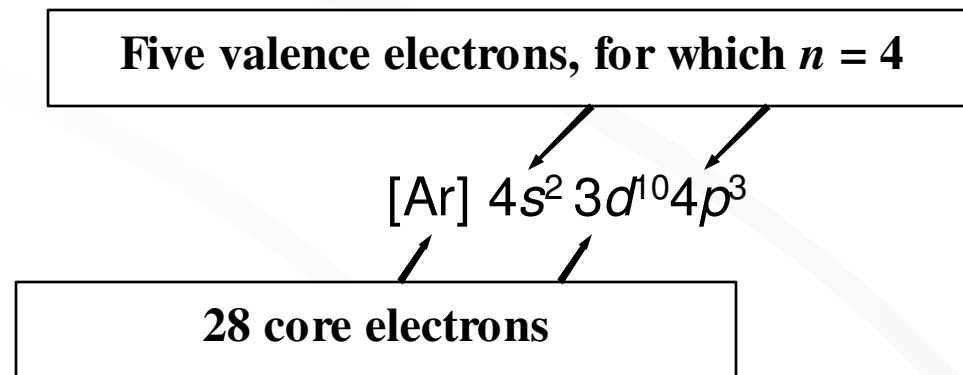
Electron configurations of ions

- To obtain the electron configuration of an **anion** by the aufbau process, we simply **add** the additional electrons to the valence shell of the neutral nonmetal atom.

- The number added often completes the shell.

- A nonmetal monatomic ion usually attains the electron configuration of a noble gas atom.

  O^{2-} :   [Ne]

  Br^- :   [Kr]

Electron configurations of ions (cont'd)

- A metal atom loses electrons to form a **cation**.
- Electrons are **removed** from the configuration of the atom.
- The first electrons lost are those of the **highest principal** quantum number.
- If there are two subshells with the same highest principal quantum number, electrons are lost from the subshell with the higher *l*.

Electron configurations of ions *(cont'd)*

Atom	Ion	(or)
F $1s^2\,2s^2 2p^5$	F$^-$ $1s^2\,2s^2 2p^6$	[Ne]
S [Ne] $3s^2\,3p^4$	S^{2-} [Ne] $3s^2\,3p^6$	[Ar]
Sr [Kr] $5s^2$	Sr^{2+} [Kr] $\cancel{5s^2}$	[Kr]
Ti [Ar] $4s^2\,3d^2$	Ti^{4+} [Ar] $\cancel{4s^2\,3d^2}$	[Ar]
Fe [Ar] $4s^2\,3d^6$	Fe^{2+} [Ar] $\cancel{4s^2}\,3d^6$	[Ar] $3d^6$

What would be the configuration of Fe^{3+}? Of Sn^{2+}?

Valence electrons are lost first.

e^- configuration of ions (cont'd)

Table 8.3 Electron Configurations of Some Metal Ions

Noble Gas			Pseudo–Noble Gas[a]		18 + 2[b]	Various	
Li^+	Be^{2+}	Al^{3+}	Cu^+	Zn^{2+}	In^+	Cr^{2+}:	$[Ar]3d^4$
Na^+	Mg^{2+}		Ag^+	Cd^{2+}	Tl^+	Cr^{3+}:	$[Ar]3d^3$
K^+	Ca^{2+}		Au^+	Hg^{2+}	Sn^{2+}	Mn^{2+}:	$[Ar]3d^5$
Rb^+	Sr^{2+}				Pb^{2+}	Mn^{3+}:	$[Ar]3d^4$
Cs^+	Ba^{2+}				Sb^{3+}	Fe^{2+}:	$[Ar]3d^6$
					Bi^{3+}	Fe^{3+}:	$[Ar]3d^5$
						Co^{2+}:	$[Ar]3d^7$
						Co^{3+}:	$[Ar]3d^6$
						Ni^{2+}:	$[Ar]3d^8$

[a] In the pseudo–noble gas configuration, all valence electrons are lost and the remaining $(n-1)$ shell has 18 electrons in the configuration $(n-1)s^2(n-1)p^6(n-1)d^{10}$.

[b] In the 18 + 2 configuration, $(n-1)s^2(n-1)p^6(n-1)d^{10}ns^2$, two valence electrons remain.

Magnetism

- *Diamagnetic* atoms have all electrons paired
- *Paramagnetic* atoms have some unpaired electrons
- *Ferromagnetism* is the exceptionally strong attractions of a magnetic field for iron and a few other substances.
- Despite the fact that your instructor's thesis centered on this topic, we will not discuss it further

Periodic properties

- Certain physical and chemical properties recur at regular intervals (Mendeleev, anyone?), and/or vary in regular fashion, when the elements are arranged according to increasing atomic number.
- Melting point, boiling point, hardness, density, physical state, and chemical reactivity are periodic properties.
- We will examine several periodic properties that are readily explained using electron configurations.
  - Atomic radii
  - Effective nuclear charge
  - Covalent radii
  - Ionic radii
  - Ionization energy
  - Electron affinity

Periodic properties: atomic radius

- Half the distance between the nuclei of two atoms is the **atomic radius.**

  Covalent radius: half the distance between the nuclei of two identical atoms joined in a *molecule*.

  Metallic radius: half the distance between the nuclei of adjacent atoms in a *solid metal*.

Covalent radius: 133 pm

Internuclear distance: 266 pm
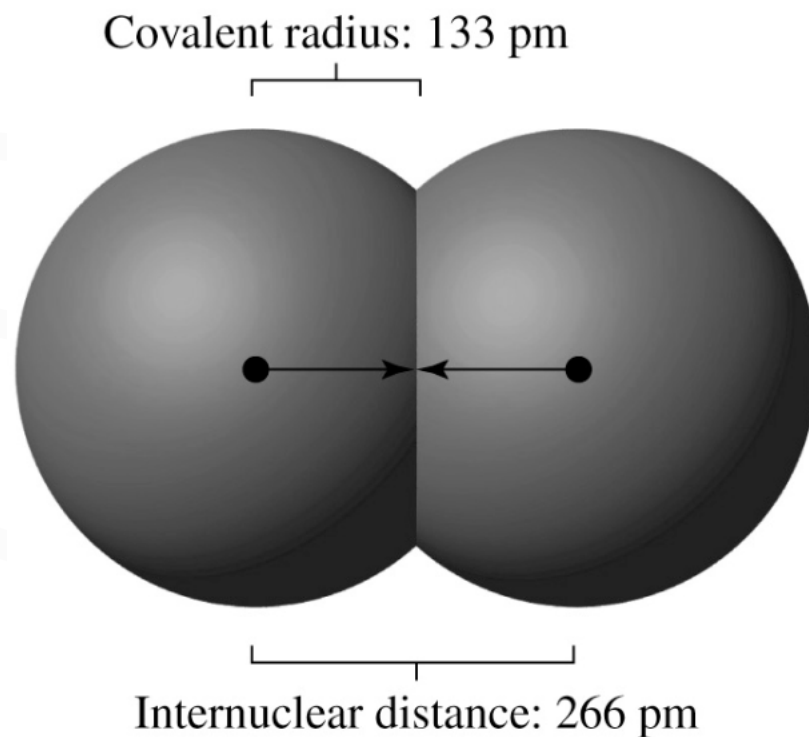
Atomic radius (cont'd)

- Atomic radius **increases** from top to bottom within a group.
- The value of n increases, moving down the periodic table.
- The value of n relates to the **distance** of an electron from the nucleus.
- Often in Angstroms (10^{-10}m) or picometers (10^{-12}m)

Atomic radius (cont'd)

- Atomic radius **decreases** from left to right within a period.
- Why? The **effective nuclear charge** (Z_{eff}) increases from left to right, increasing the attraction of the nucleus for the valence electrons, and making the atom smaller.

Mg has a greater effective nuclear charge than Na, and is *smaller* than Na.

10 core electrons screen the attraction of 10 protons.

Outer electron feels a net attraction of +1.

Two outer electrons feel a net attraction of +2.

$1s^2 2s^2 2p^6$

$11+$

$3s$

$1s^2 2s^2 2p^6$

$12+$

$3s^2$

Na

Mg
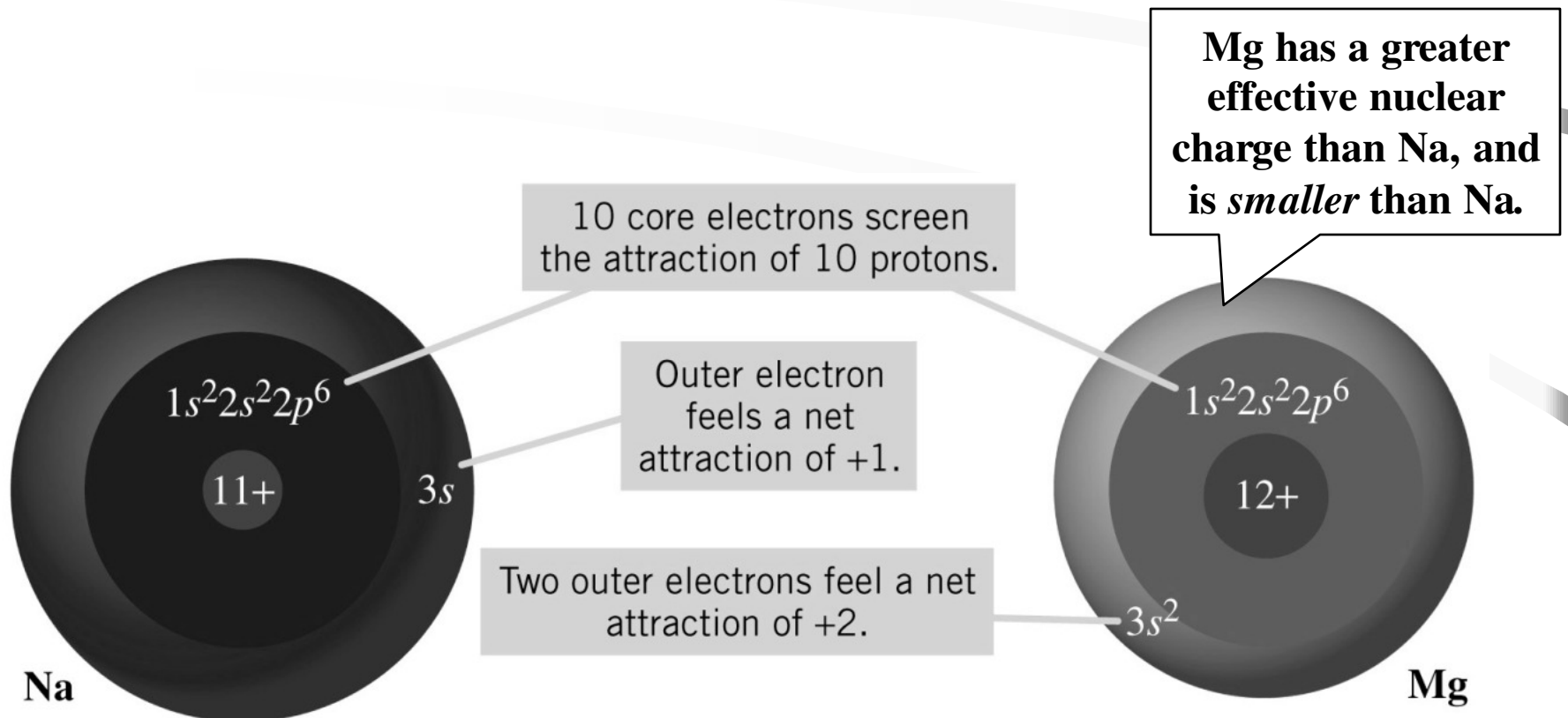
Atomic radii of the elements

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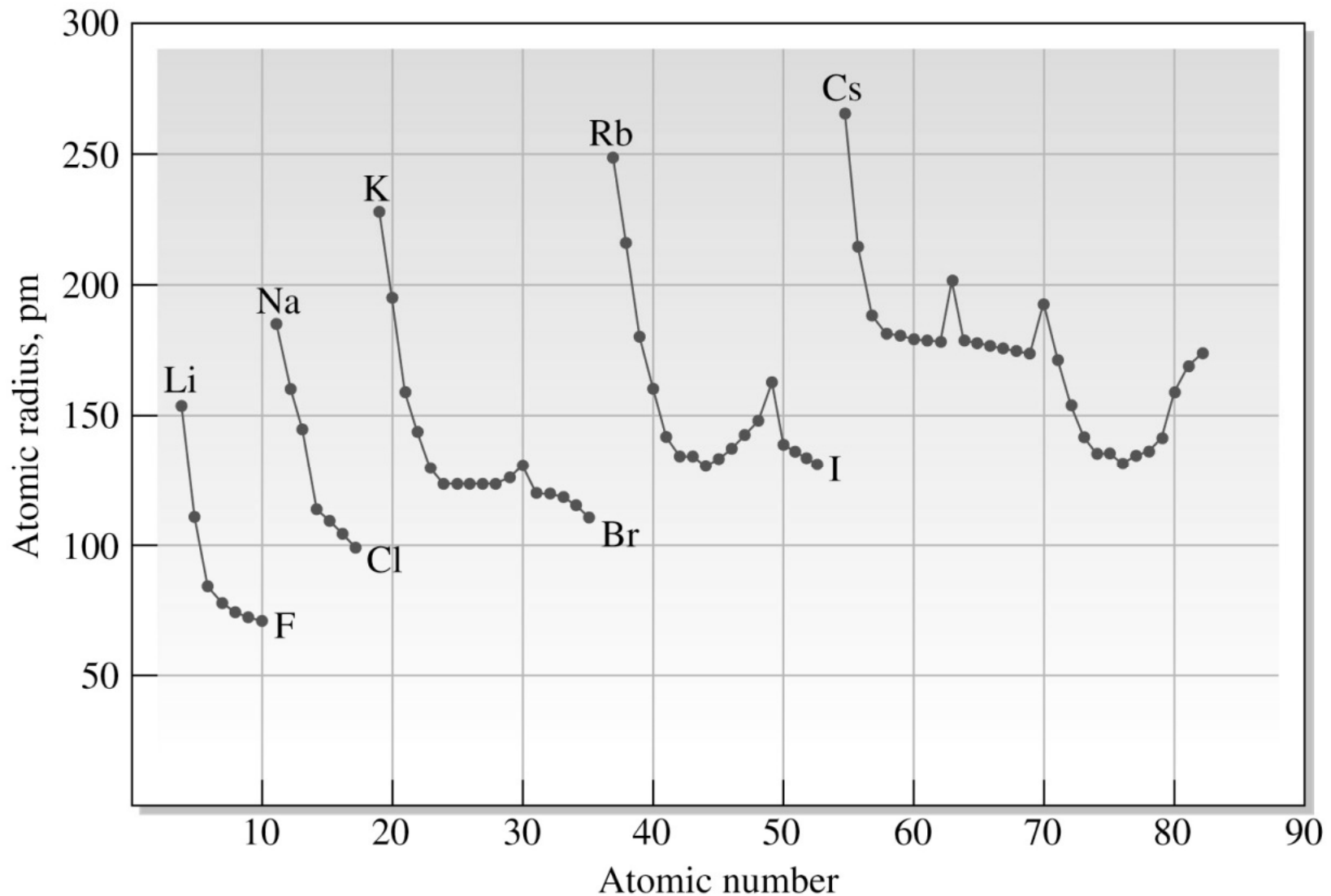
Example

- With reference only to a periodic table, arrange each set of elements in order of increasing atomic radius:
    - (a) Mg, S, Si
    - (b) As, N, P
    - (c) As, Sb, Se

Ionic radii

The **ionic radius** of each ion is the portion of the distance between the nuclei occupied by that ion.

Internuclear distance: 205 pm

Mg^{2+}

O^{2-}
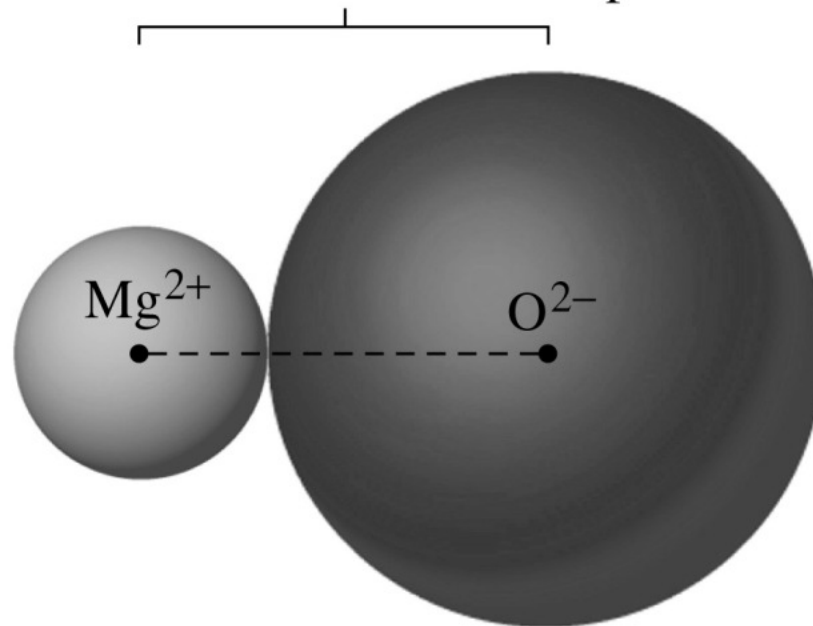
$r_{O^{2-}} = 140$ pm

$r_{Mg^{2+}} = 65$ pm

Ionic radii- cations

- *Cations* are **smaller** than the atoms from which they are formed; the value of *n* usually decreases. Also, there is less electron–electron repulsion.

Na	Mg	Ne	Na⁺	Mg²⁺
186 pm	160 pm	150 pm	99 pm	65 pm
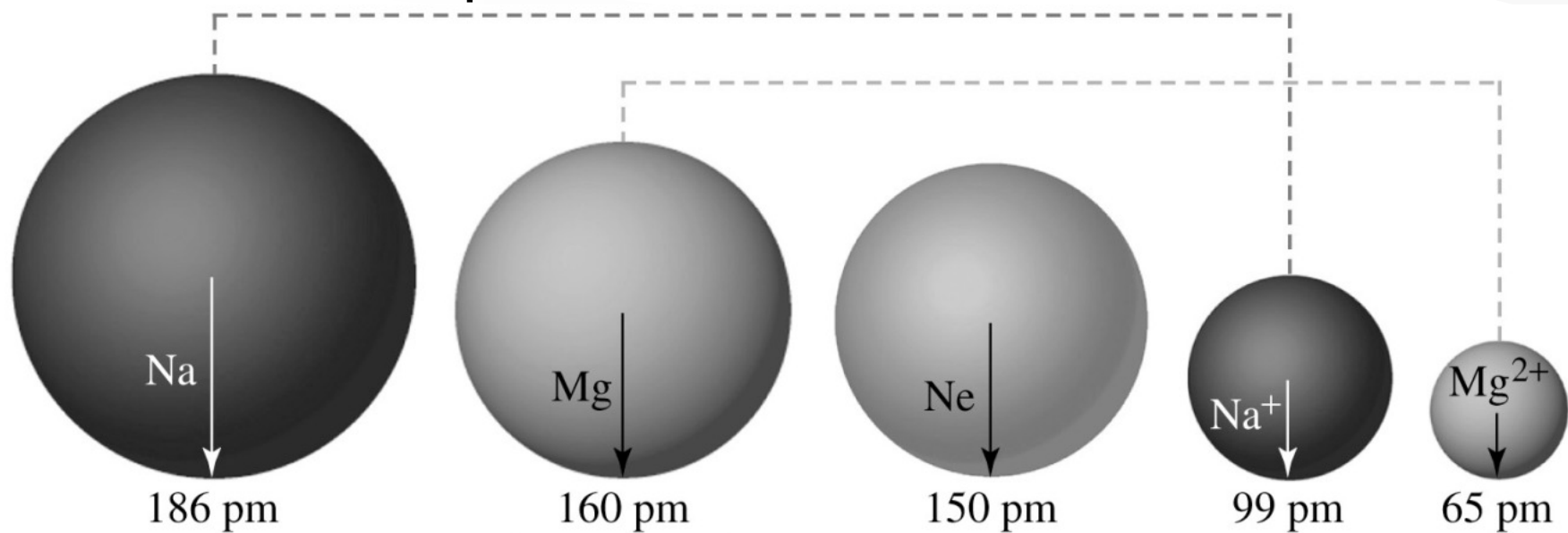
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Ionic radii- anions

- ***Anions*** are ***larger*** than the atoms from which they are formed.
- Effective nuclear charge is unchanged, but additional electron(s) increase electron–electron repulsion.
- ***Isoelectronic*** species have the same electron configuration; size decreases with effective nuclear charge.

Cl   +e⁻ →   Cl⁻

Cl   +e⁻ →   Cl⁻

Covalent radius	Anionic radius
99 pm	181 pm
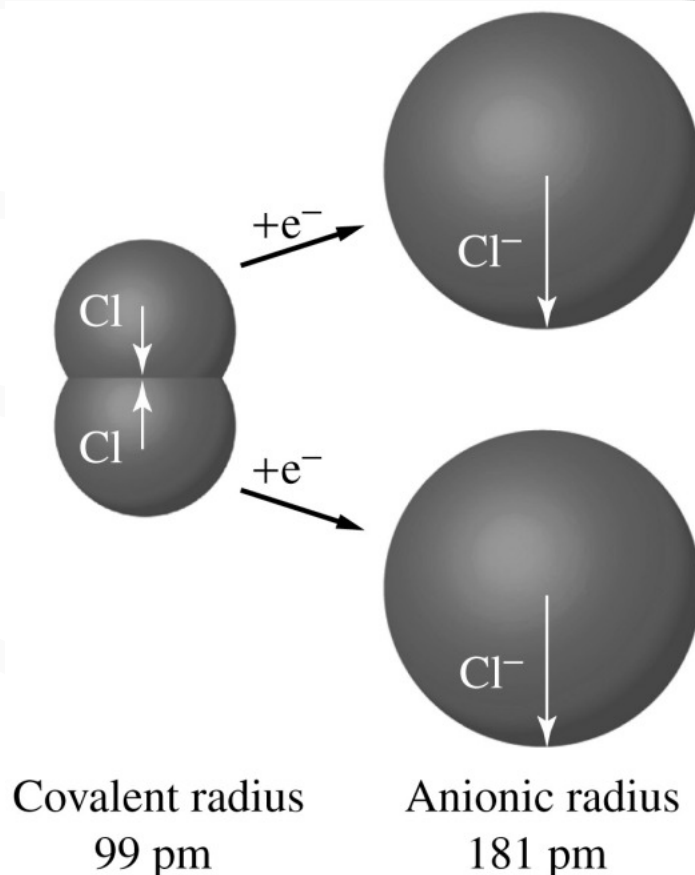
Some atomic and ionic radii

1A	2A
Li 152	Be 111
59 Li$^+$	31 Be^{2+}
Na 186	Mg 160
99 Na$^+$	65 Mg^{2+}
K 227	Ca 197
K$^+$ 138	99 Ca^{2+}
Rb 248	Sr 215
Rb$^+$ 148	113 Sr^{2+}
Cs 265	Ba 217
Cs$^+$ 169	135 Ba^{2+}

3A	4A	5A	6A	7A
B 80	C 77	N 75	O 73	F 71
20 B^{3+}		N^{3-} 171	O^{2-} 140	F$^-$ 133
Al 143	Si 118	P 110	S 103	Cl 99
50 Al^{3+}		P^{3-} 212	S^{2-} 184	Cl$^-$ 181
Ga 122	Ge 123	As 125	Se 116	Br 114
62 Ga^{3+}		69 As^{3+}	Se^{2-} 198	Br$^-$ 196
In 163	Sn 141	Sb 145	Te 143	I 133
92 In^{3+}	93 Sn^{2+}	89 Sb^{3+}	Te^{2-} 221	I$^-$ 220
Ti 170	Pb 175	Bi 155		
149 Tl$^+$	132 Pb^{2+}	96 Bi^{3+}		

3B	4B	5B	6B	7B	8B			1B	2B
Sc 161	Ti 145	V 132	Cr 125	Mn 124	Fe 124	Co 125	Ni 125	Cu 128	Zn 133
			Cr^{3+} 64		Fe^{3+} 67	Co^{3+} 64		Cu^{2+} 72	
83 Sc^{3+}	80 Ti^{2+}	72 V^{2+}	84 Cr^{2+}	91 Mn^{2+}	82 Fe^{2+}	82 Co^{2+}	78 Ni^{2+}	96 Cu$^+$	83 Zn^{2+}

Example

- Refer to a periodic table, but not to the previous figure, and arrange the following species in the expected order of increasing radius:
Ca^{2+}, Fe^{3+}, K^+, S^{2-}, Se^{2-}

Ionization energy

- **Ionization energy** (*IE*) is the energy required to remove an electron from a ground-state gaseous atom.
- *IE* is usually expressed in kJ per mole of atoms.

$$M(g) \rightarrow M^+(g) \ + \ e^- \qquad \Delta H = I_1$$
$$M^+(g) \rightarrow M^{2+}(g) \ + \ e^- \quad \Delta H = I_2$$
$$M^{2+}(g) \rightarrow M^{3+}(g) \ + \ e^- \ \Delta H = I_3$$
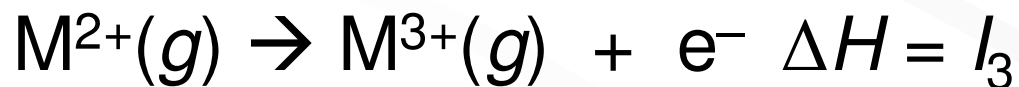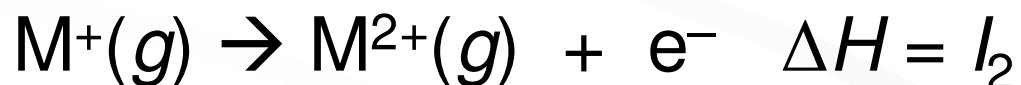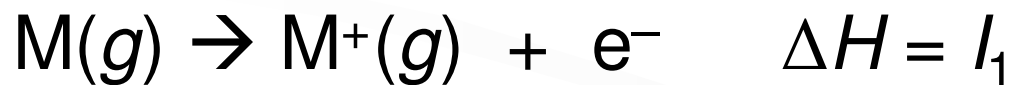
Trends in IE

- $I_1 < I_2 < I_3$
  - Removing an electron from a *positive ion* is more difficult than removing it from a *neutral atom*.
- A large jump in *I* occurs after valence electrons are completely removed (why?).
- I_1 **decreases** from top to bottom on the periodic table.
  - *n* increases; valence electron is farther from nucleus.
- I_1 generally **increases** from left to right, with exceptions.
  - Greater effective nuclear charge from left to right holds electrons more tightly.

Selected ionization energies

Compare I_2 to I_1 for a 2A element, then for the corresponding 1A element.

Why is I_2 for each 1A element so *much* greater than I_1?

Why don't we see the *same* trend for each *2A element*? $I_2 > I_1$ … but only about twice as great …

Table 8.4 Ionization Energies of Group 1A and Group 2A Elements, kJ/mol

	1A	2A
	Li	Be
I_1	520	900
I_2	7298	1757
	Na	Mg
I_1	496	738
I_2	4562	1451
	K	Ca
I_1	419	590
I_2	3051	1145
	Rb	Sr
I_1	403	550
I_2	2633	1064
	Cs	Ba
I_1	376	503
I_2	2230	965

Selected ionization energies

General trend in I_1: An increase from left to right, but …

…I_1 drops, moving from 2A to 3A.

The electron being removed is now a p electron (higher energy, easier to remove than an s).

Table 8.5 Ionization Energies of the Second- and Third-Period Elements, kJ/mol

	1A	2A	3A	4A	5A	6A	7A	8A
	Li	Be	B	C	N	O	F	Ne
I_1	520	900	801	1086	1402	1314	1681	2081
I_2	7298	1757	2427	2352	2856	3388	3374	3952
	Na	Mg	Al	Si	P	S	Cl	Ar
I_1	496	738	578	787	1012	999	1251	1521
I_2	4562	1461	1817	1577	190	2251	2298	2666

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I_1 drops again between 5A and 6A.

Repulsion of the paired electron in 6A makes that electron easier to remove.

First ionization energies

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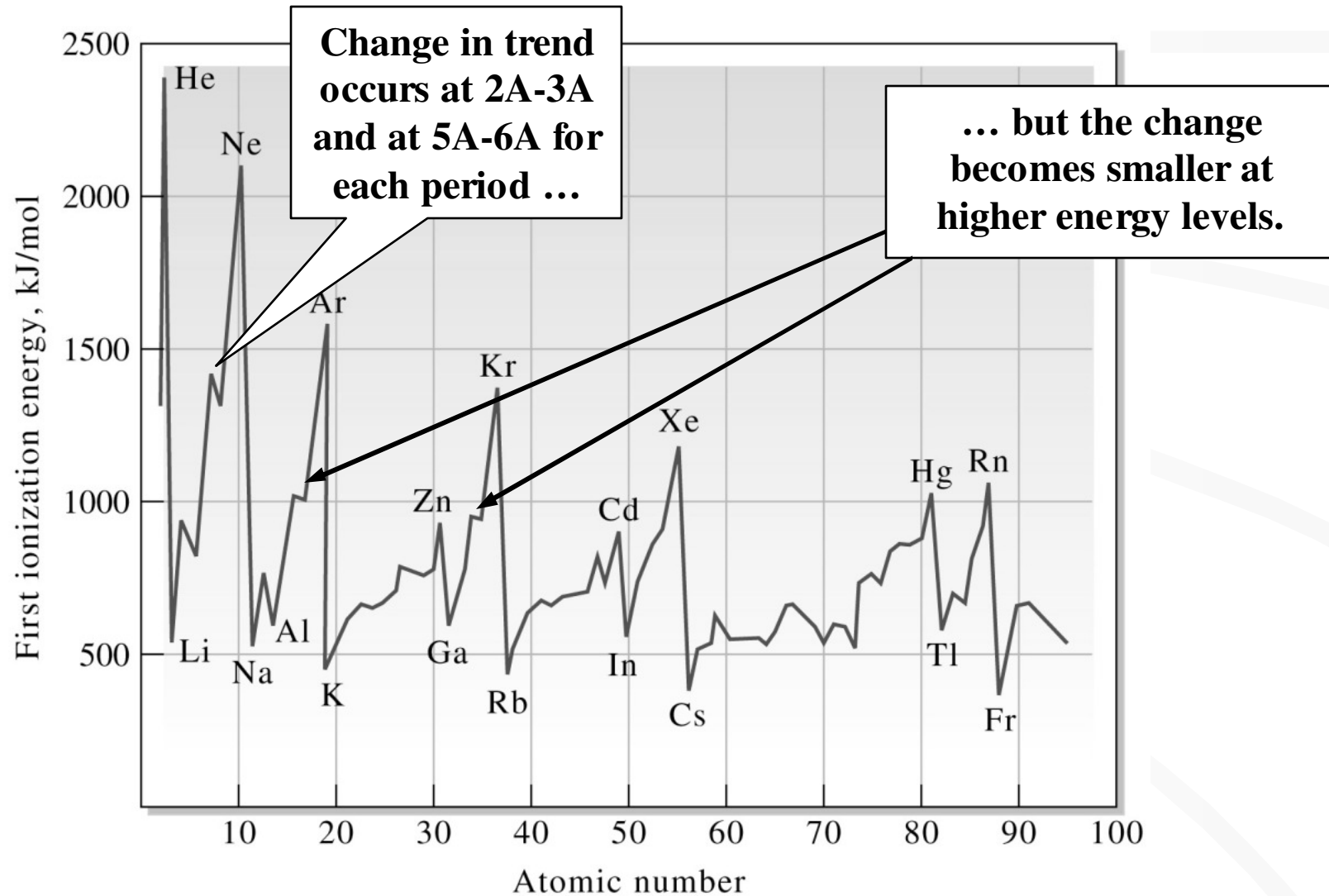
Example

- Without reference to the previous figure, arrange each set of elements in the expected order of increasing first ionization energy.
  (a) Mg, S, Si
  (b) As, N, P
  (c) As, Ge, P

Electron affinity

Electron affinity (*EA*) is the energy change that occurs when an electron is added to a gaseous atom:

$$M(g) \ + \ e^- \rightarrow M^-(g) \qquad\qquad \Delta H = EA_1$$
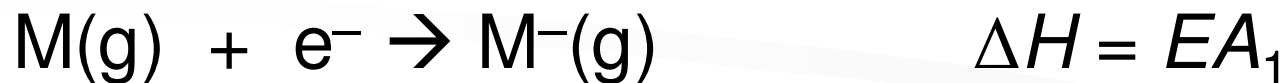
- A **negative** electron affinity means that the process is **exothermic**.
- Nonmetals generally have more affinity for electrons than metals do. (Nonmetals like to form anions!)
- Electron affinity generally is **more** negative or less positive on the right and toward the top of the periodic table.

Selected electron affinities

> The halogens have a greater affinity for electrons than do the alkali metals, as expected.

Table 8.6 Some Selected First Electron Affinities, kJ/mol

1A	2A	3A	4A	5A	6A	7A	8A
Li	Be	B	C	N	O	F	Ne
−60	>0	−27	−154	≈0	−141	−328	>0
Na					S	Cl	
−53					−200	−349	
K					Se	Br	
−48					−195	−325	
Rb					Te	I	
−47					−190	−295	
Cs					Po	At	
−46					−183	−270	

Other periodic properties (overview)

- Metallic character
  - Increases top to bottom
  - Decreases left to right
- Flame color
  - Due to electronic transitions
- Oxidizing and reducing power
  - Think of how easy it is to gain or lose electron(s)
- Acidic and basic character
  - Ditto!

Metals

- **Metals** have a small number of electrons in their valence shells and tend to form **positive** ions.

  - For example, an aluminum atom loses its three valence electrons in forming Al^{3+}.

- All s-block elements (except H and He), all d- and f-block elements, and some p-block elements are metals.

Metallic Character

- Metallic character is related to atomic radius and ionization energy.

- Metallic character generally **increases** from right to left across a period, and **increases** from top to bottom in a group.

More metallic character

More metallic character
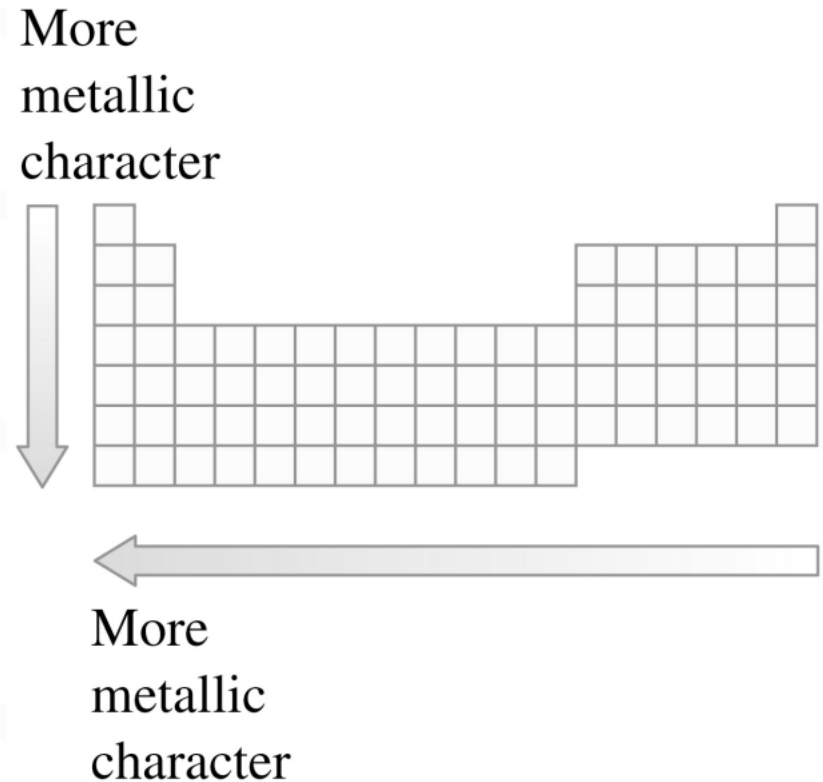
Nonmetals

- Atoms of a **nonmetal** generally have larger numbers of electrons in their valence shell than do metals.

- Many nonmetals tend to form negative ions.

- All nonmetals (except H and He) are *p*-block elements.

  - Nonmetallic character generally increases right-to-left and increases bottom-to-top on the periodic table (the opposite of metallic character).

More
nonmetallic
character

More
nonmetallic
character
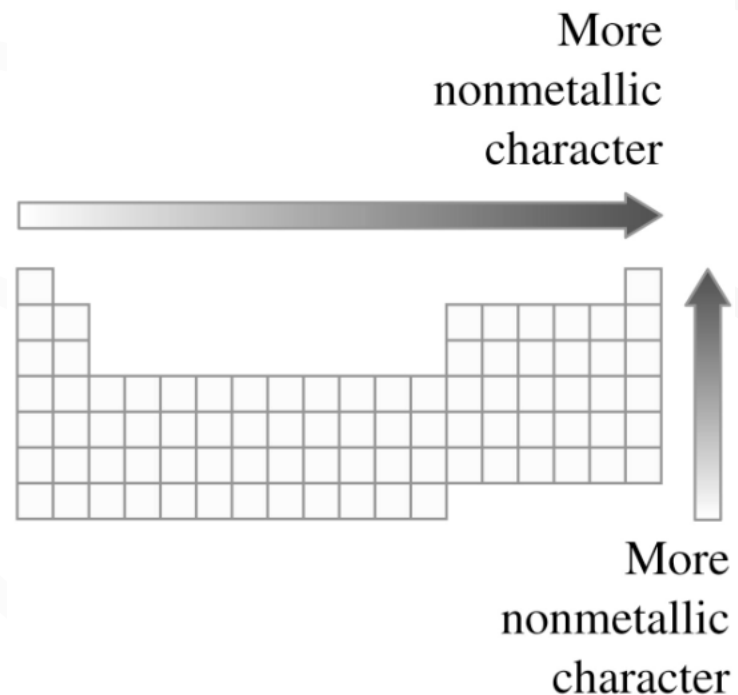
Metalloids

- A heavy stepped diagonal line separates metals from nonmetals; some elements along this line are called **metalloids**.

- Metalloids have properties of both metals and nonmetals.

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A Summary of trends

The noble gases

- The **noble gases** are on the far right of the periodic table between the highly active nonmetals of Group 7A and the very reactive alkali metals Group 1A.

- The noble gases rarely enter into chemical reactions because of their stable electron configurations.

- However, a few compounds of noble gases (except for He and Ne) have been made.

Other trends-
flame color

Atoms emit energy when electrons drop from higher to lower energy states.

Elements with low **first ionization energies** can be excited in a Bunsen burner flame, and often emit in the visible region of the spectrum.

Elements with high values of IE_1 usually require higher temperatures for emission, and the emitted light is in the UV region of the spectrum.
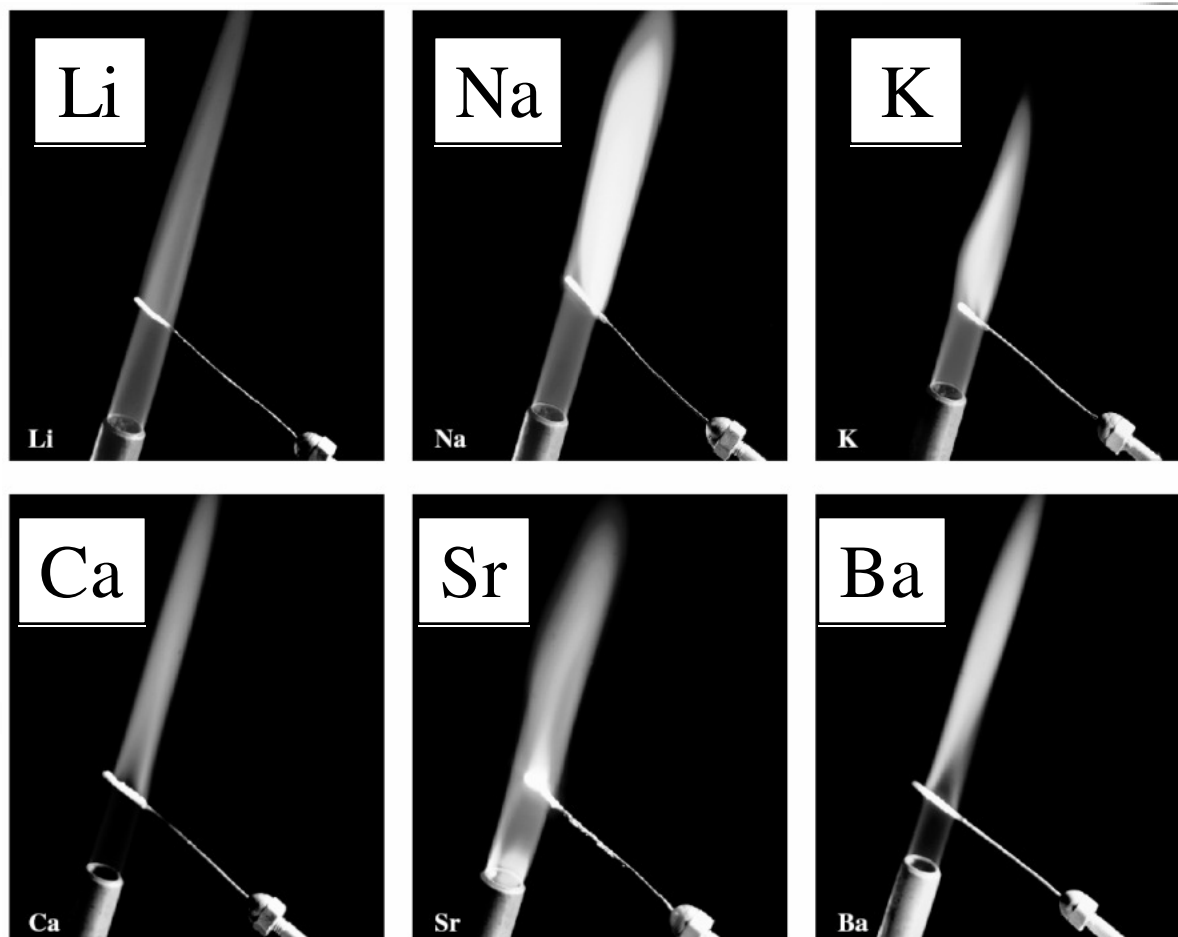
Oxidizing and reducing agents revisited

- The halogens (Group 7A) are good oxidizing agents.
- Halogens have a high affinity for electrons, and their oxidizing power generally varies with electron affinity.

When Cl_2 is bubbled into a solution containing colorless iodide ions …

… the chlorine oxidizes I^- to I_2, because EA_1 for Cl_2 is greater than EA_1 for I_2.
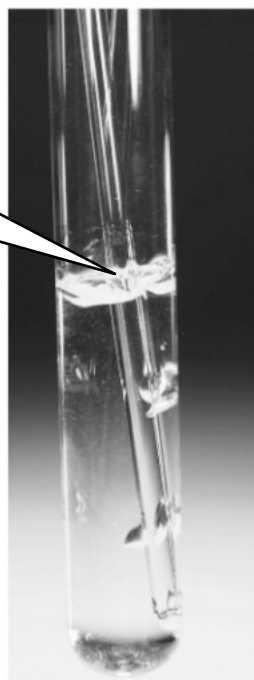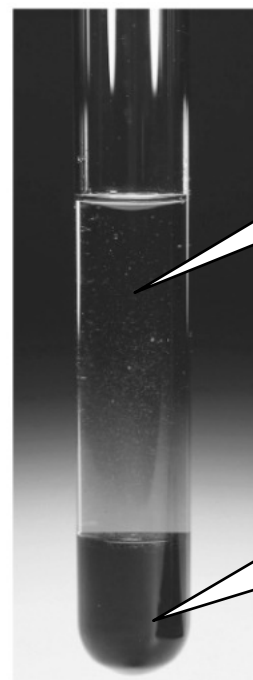
Displaced I_2 is brown in aqueous solution …

… but dissolves in CCl_4 to give a purple solution.

(a)   (b)

Oxidizing and reducing agents revisited (cont'd)

- The s-block elements are very strong reducing agents.
- All the IA metals and the heavier IIA metals will displace H_2 from water, in part because of their low values of IE_1.
- A low IE_1 means that the metal easily gives up its electron(s) to hydrogen in water, forming hydrogen gas.

Potassium metal reacts violently with water. The liberated H_2 ignites.
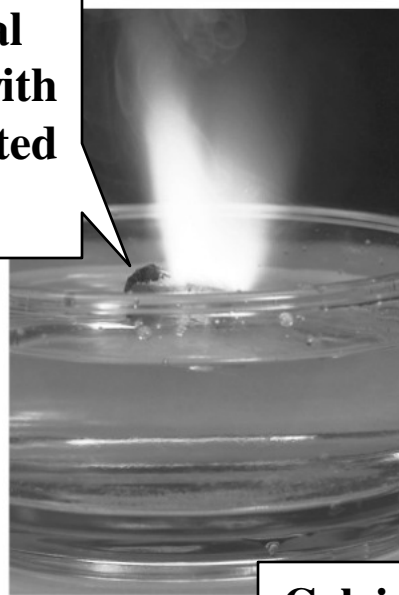
(a)

Calcium metal reacts readily with water …

(c)

… while magnesium is largely nonreactive toward cold water.
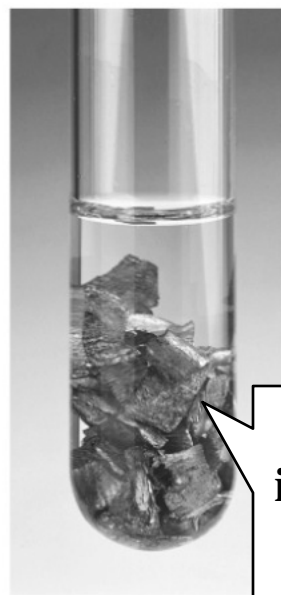
end of section

Reminder (again)

- As you remember, a chemical reaction is the formation and/or breaking of chemical bonds
- A chemical bond is a transfer or sharing of electrons

Chemical bonds

- *Chemical bonds* are the forces that hold atoms together in compounds
  - Bonds are *electrostatic* forces; attractions between opposite charges and repulsions between like charges

Nuclei attract electron(s)
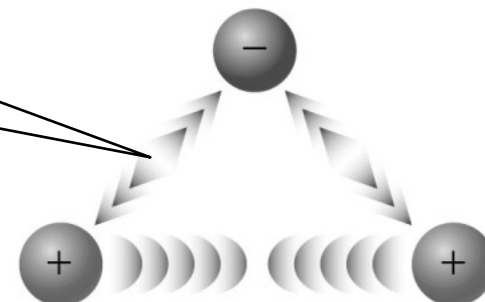
(a) H_2^+

Nuclei repel other nuclei
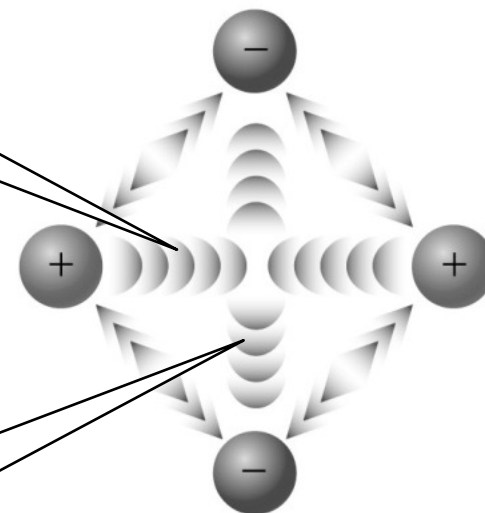
Electrons repel other electrons

(b) H_2

Chemical bonds (cont'd)

Closer than 74 pm, repulsion increases.

At 74 pm, attractive forces are at a maximum, energy is at a minimum.

= H atom

Higher energy than separated atoms

Potential energy

0

Internuclear distance

Lower energy than separated atoms

74 pm

−436 kJ/mol

Hydrogen nuclei far apart; just a little attraction.

Closer together; attraction increases.

Net repulsion
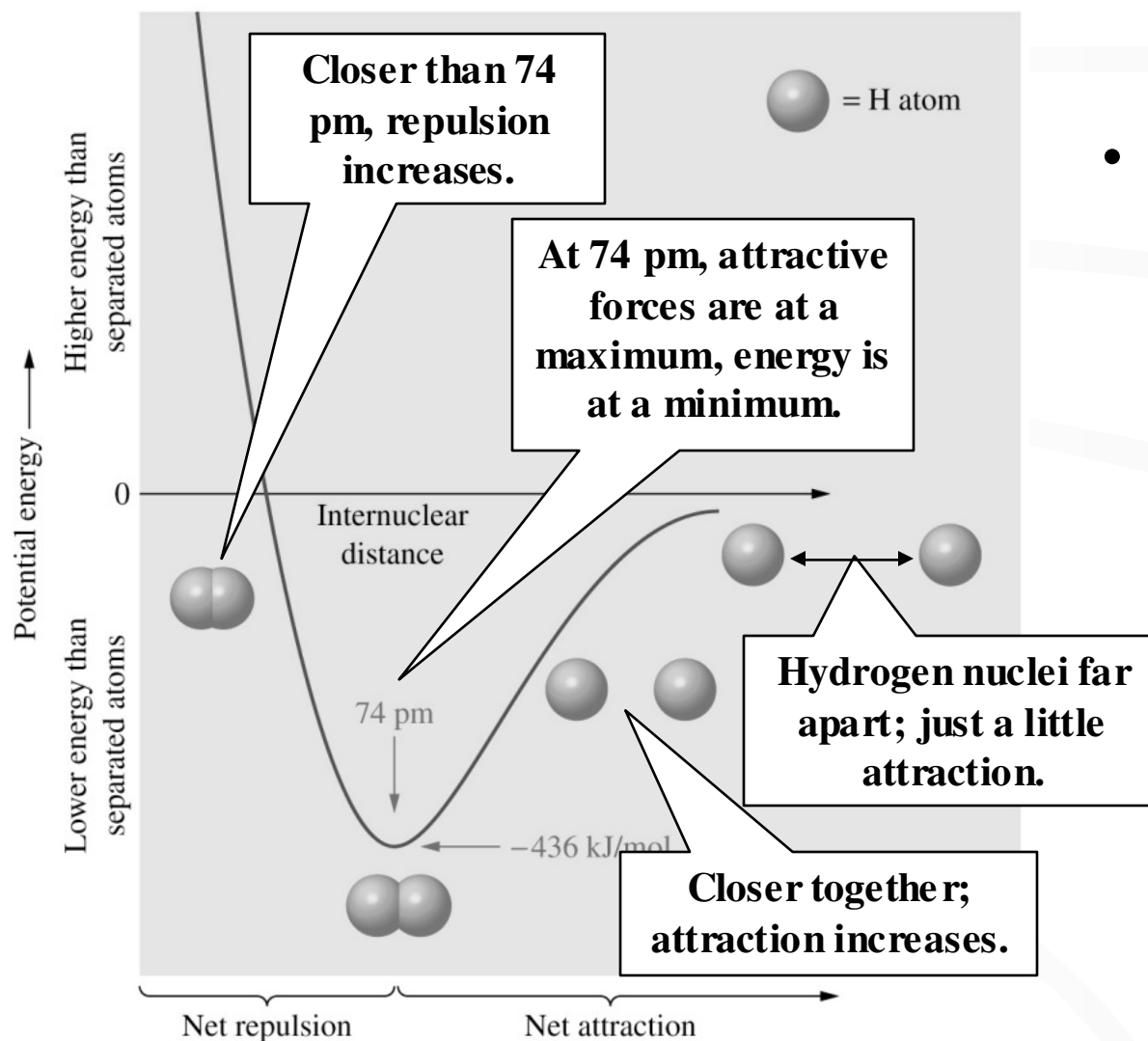
Net attraction

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- *Chemical bonds* are the forces that hold atoms together in compounds
  - When 2 atoms are brought together, there is an *optimum* distance where the unfavorable repulsions and the favorable attractions are maximized (see the *potential energy diagram* at left)

Chemical bonds (cont'd)

- Bonds are responsible for such physical properties as melting point and boiling point

- Bonds (and the type and number of atoms present) ultimately determine the shape of a molecule, and <u>structure determines function</u>

Lewis theory

- Valence electrons participate in bonding
- Metals and nonmetals combine by transferring electrons, forming cations and anions involved in ionic bonds
- Nonmetals combine with each other by sharing electron pairs (overlapping orbitals), forming covalent bonds
- Complete transfer is a 100% ionic "bond"
- Equal sharing is a 100% covalent bond
- The above are two extremes

Lewis theory (cont'd)

- When atoms gain, lose, or share electrons, atoms tend to acquire the electron configuration of a noble gas ("noble gas configuration")

- Remember, electrons are transferred, NOT protons, so the atom becomes an ion of the original element, not the noble gas itself... noble gas configurations are hyper-stable

- H, Li, and Be follow the duet rule (He configuration), while all other elements (except transition metals) follow the octet rule (Ne, Ar, Kr, Xe, Rn configuration with 8 (or 18) valence electrons)

Lewis symbols

- A *Lewis symbol* is the element's symbol with "dots" on 4 sides of it to represent the valence electrons
- Electrons are shown "unpaired" whenever possible (although the idea of electron spin had not been developed when Lewis developed his theories)

Lewis symbols (cont'd)

- In a **Lewis symbol**, the chemical symbol for the element represents the nucleus and core electrons of the atom.

- Dots around the symbol represent the **valence** electrons.

- In writing Lewis symbols, the first four dots are placed singly on each of the four sides of the chemical symbol. (Though spin was unknown at the time.)

- Dots are paired as the next four are added.

- Lewis symbols are used primarily for those elements that acquire noble-gas configurations when they form bonds.

1A	2A	3A	4A	5A	6A	7A	8A
Li·	Be·	·B·	·C·	·N:	·O:	:F:	:Ne:
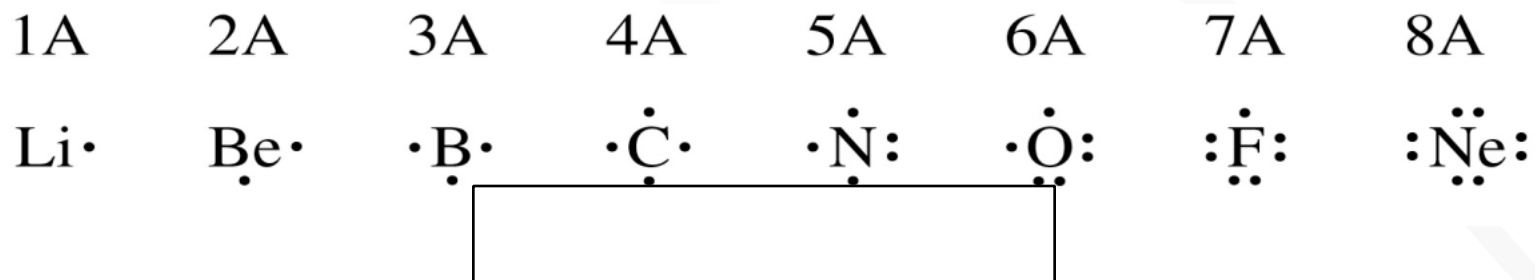
Reactions

- Reactions can be drawn showing the transfer of electrons
  - Looking at tables of ionization energy and electron affinity *along with the energies of some changes in state, lattice energies (2 slides ahead) and bond energies*, the energy of a reaction can be calculated (Ex.- the *enthalpy of formation* of NaCl seven slides ahead) just like with Hess' law

Ionic bonds and ionic crystals

- When atoms lose or gain electrons, they may acquire a noble gas configuration, but do not *become* noble gases.
- Because the two ions formed in a reaction between a metal and a nonmetal have opposite charges, they are strongly attracted to one another and form an **ion pair**.
- The net attractive electrostatic forces that hold the cations and anions together are **ionic bonds**.
- The highly ordered solid collection of ions is called an **ionic crystal**.

Formation of a crystal of sodium chloride
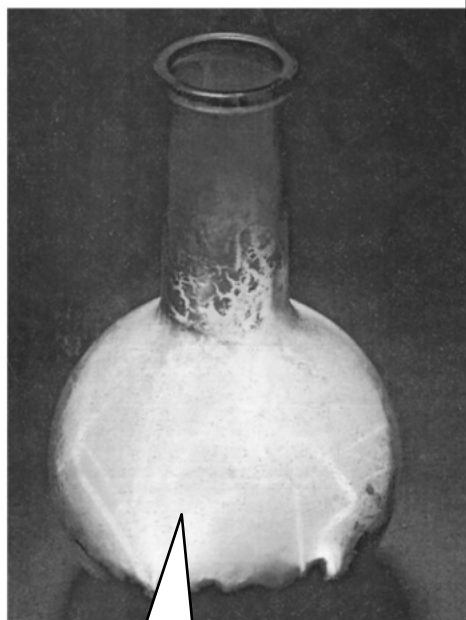
Na donates an electron to Cl …

… and opposites attract.

Sodium reacts violently in chlorine gas.

Using Lewis symbols to represent ionic bonding

- Lewis symbols can be used to represent ionic bonding between nonmetals and:
  the *s*-block metals, some *p*-block metals, and a few *d*-block metals.

- Instead of using complete electron configurations to represent the loss and gain of electrons, Lewis symbols can be used.

$$\left[\text{Na} \cdot \right] \; + \; \left[:\ddot{\text{Cl}}: \right] \; \longrightarrow \; \left[\text{Na} \right]^{+} \; + \; \left[:\ddot{\text{Cl}}: \right]^{-}$$
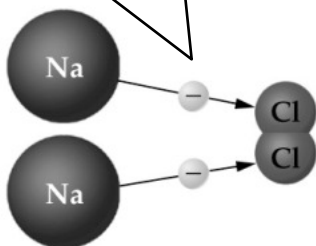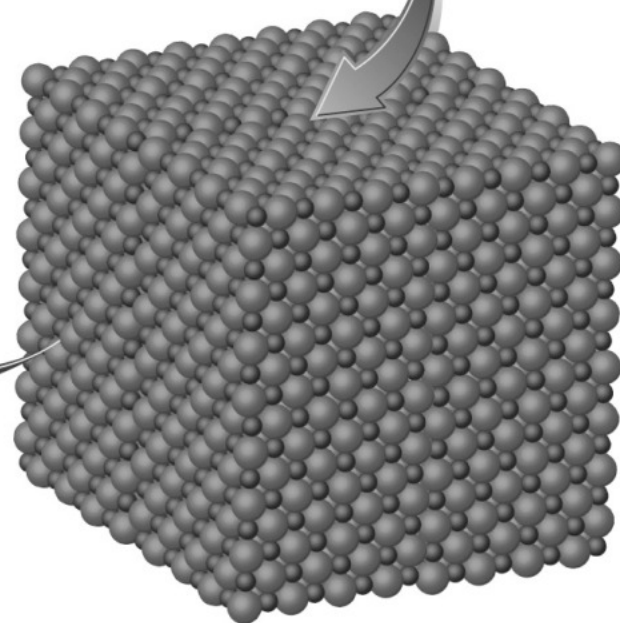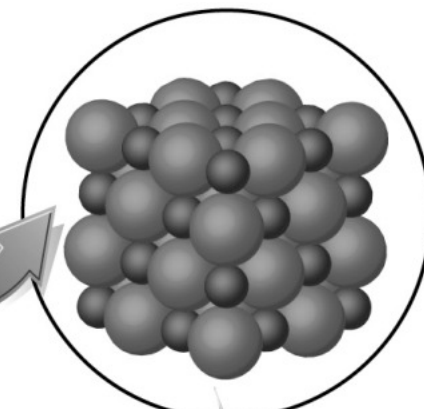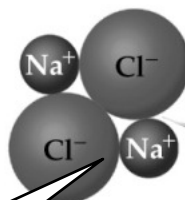
Example

- Use Lewis symbols to show the formation of ionic bonds between magnesium and nitrogen.

- What are the name and formula of the compound that results?

- (worked out next slide)

Example worked out

Strategy

First, we determine the number of electrons that must be lost by magnesium atoms and gained by nitrogen atoms so that the resulting ions have noble-gas electron configurations.
Then we can combine Lewis symbols for the ions in the appropriate proportions to produce a neutral formal unit, from which we can deduce the compound's name and formula.

Solution

Mg atoms (group 2A) lose their two valence electrons, and N atoms (group 5A) gain three additional valence electrons. To produce an electrically neutral formula unit, three Mg atoms must lose a total of six electrons and two N atoms must gain a total of six:

$$3\left[\mathrm{Mg}\right]^{2+} + 2\left[:\ddot{\mathrm{N}}:\right]^{3-}$$

The compound is magnesium nitride, Mg_3N_2.

□ **Exercise**

Use Lewis symbols to show the formation of ionic bonds between barium and iodine.
What are the name and formula of the compound that results?

□ **Exercise**

Use Lewis symbols to show the formation of ionic bonds in aluminum oxide.

Energy changes in ionic compound formation

$$Na(g) \rightarrow Na^+(g) + e^- \qquad IE_1 = +496 \text{ kJ/mol}$$

$$Cl(g) + e^- \rightarrow Cl^-(g) \qquad EA_1 = -349 \text{ kJ/mol}$$

- From the data above, it doesn't appear that the formation of NaCl from its elements is energetically favored. However …

- … the **enthalpy of formation** of the ionic compound is more important than either the first ionization energy or electron affinity.

- The overall enthalpy change can be calculated using a step-wise procedure called the **Born–Haber cycle**.

Energy changes in
ionic compound formation *(cont'd)*

- The Born–Haber cycle is a hypothetical process, in which ΔH_f is represented by several steps.
- What law can be used to find an enthalpy change that occurs in steps??

$Na^+(g) + Cl(g) + e^-$

③ $\Delta H_3 = +496$ kJ   ④ $\Delta H_4 = -349$ kJ

$Na^+(g) + Cl^-(g)$

$Na(g) + Cl(g)$

$Na(g) + \frac{1}{2} Cl_2(g)$ ② $\Delta H_2 = +122$ kJ

$Na(s) + \frac{1}{2} Cl_2(g)$ ① $\Delta H_1 = +107$ kJ   ⑤ $\Delta H_5 = -787$ kJ

START

$\Delta H_f^\circ[NaCl(s)] = -411$ kJ

$NaCl(s)$

END

ΔH_f° for NaCl is very negative because …

… ΔH_5—the lattice energy—is very negative.
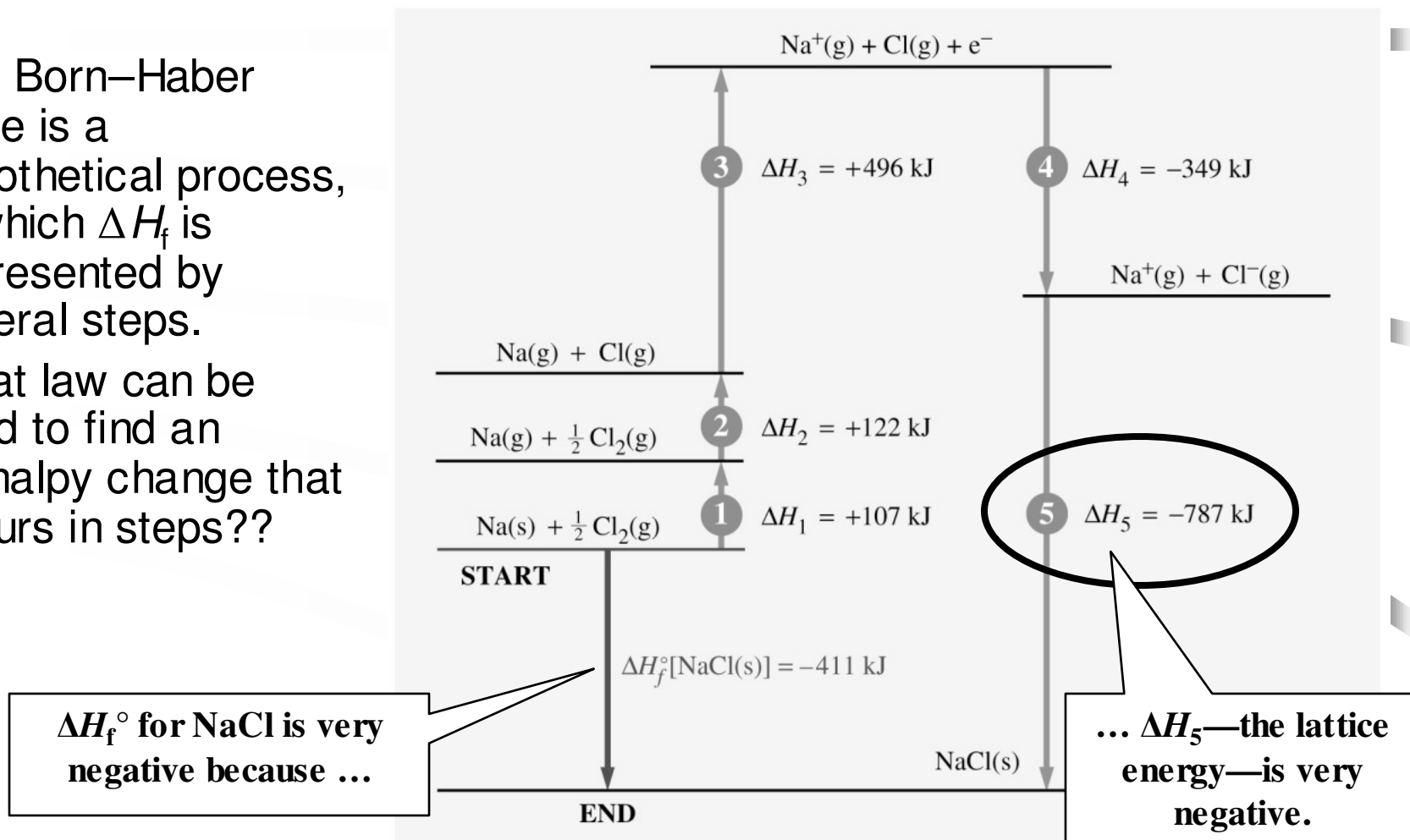
Example

- Use the following data to determine the lattice energy of $MgF_2(s)$:
  - enthalpy of sublimation of Mg: +146kJ/mol;
  - I_1 for Mg: +738kJ/mol;
  - I_2 for Mg: +1451kJ/mol;
  - bond-dissociation energy of $F_2(g)$: +159kJ/mol F_2;
  - electron affinity of F: -328 kJ/mol F;
  - enthalpy of formation of $MgF_2(s)$: -1124kJ/mol
- (worked out next slide)

Example worked out

Strategy

The approach we need here differs in three ways from the one used for NaCl(s). (1) The compound $MgF_2(s)$ has two anions for each cation in the crystal. Therefore, in the step where $F_2(g)$ dissociates, we need the bond-dissociation energy based on 1 mol of $F_2(g)$ in order to get 2 mol of F(g). Similarly, in the electron affinity step, we must produce 2 mol of $F^-(g)$ rather than 1 mol. (2) Because the magnesium cation carries a 2+ charge, we must include two ionization steps and both I_1 and I_2 in our calculation. (3) The enthalpy of formation of $MgF_2(s)$ is given, and our unknown is the lattice energy.

Solution

The setup that follows incorporates all of the steps needed to determine the unknown lattice energy of $MgF_2(s)$ from the given data.

Sublimation:	$Mg(s) \longrightarrow Mg(g)$	$\Delta H_1 = +146$ kJ
Bond dissociation:	$F_2(g) \longrightarrow 2F(g)$	$\Delta H_2 = +159$ kJ
First ionization:	$Mg(g) \longrightarrow Mg^+(g) + e^-$	$\Delta H_3 = +738$ kJ
Second ionization:	$Mg^+(g) \longrightarrow Mg^{2+}(g) + e^-$	$\Delta H_4 = +1451$ kJ
Electron gain:	$2F(g) + 2e^- \longrightarrow 2F^-(g)$	$\Delta H_5 = 2(-328$ kJ$)$
Unknown:	$Mg^{2+}(g) + 2F^- \longrightarrow MgF_2(s)$	$\Delta H_6 = $ lattice energy
Overall:	$Mg(s) + F_2(g) \longrightarrow MgF_2(s)$	$\Delta H_f^\circ = -1124$ kJ

The enthalpy of formation is equal to the sum of the energies of the individual processes.

$$\Delta H_f^\circ = -1124 \text{ kJ} = (146 + 159 + 738 + 1451 - 656) \text{ kJ} + \text{lattice energy}$$

Rearranging the summed expression, we solve for the lattice energy.

Lattice energy $= (-1124 - 146 - 159 - 738 - 1451 + 656)$ kJ $= -2962$ kJ

The lattice energy is -2962 kJ/mol $MgF_2(s)$.

Lewis structures of simple molecules
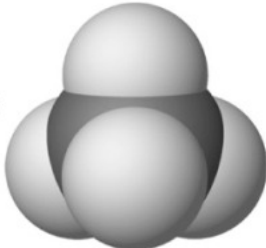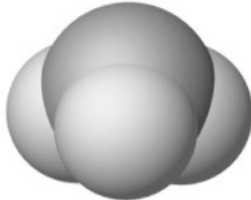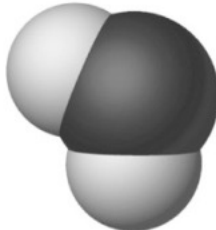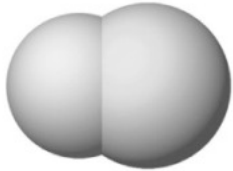
- A **Lewis structure** is a combination of Lewis symbols that represents the formation of covalent bonds between atoms.

- In most cases, a Lewis structure shows the bonded atoms with the electron configuration of a noble gas; that is, the atoms obey the *octet rule*. (H obeys the *duet rule*.)

- The shared electrons can be counted for each atom that shares them, so each atom may have a noble gas configuration.

Lewis structures *(cont'd)*

- The shared pairs of electrons in a molecule are called **bonding pairs**.

- The bonding pair is represented by a dash (—).

- The other electron pairs, which are not shared, are called **nonbonding pairs**, or **lone pairs**.

- Two electrons from one element form a **coordinate covalent** bond (like in H_3O^+).

Each chlorine atom "sees" an octet of electrons.

Bonding pair

Lone pair

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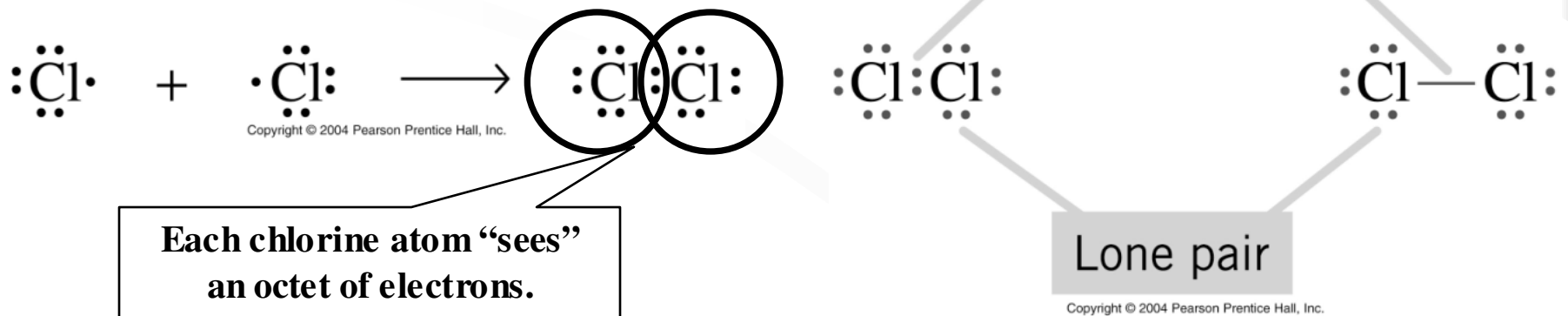
Some illustrative compounds

Group:	4A	5A	6A	7A
Lewis symbol:	·Ċ·	·N̈·	·Ö:	·F̈:
Lewis structure:	H—C—H (with H above and H below)	H—N̈—H (with H below)	H—Ö: (with H below)	H—F̈:
Name and formula:	Methane, CH_4	Ammonia, NH_3	Water, H_2O	Hydrogen fluoride, HF
Geometric shape:				

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- Note that the two-dimensional Lewis structures do not necessarily show the correct *shapes* of the three-dimensional molecules. Nor are they intended to do so.

- The Lewis structure for water may be drawn with all three atoms in a line: H–O–H.

- We will learn how to predict *shapes* of molecules in Chapter 10.

Multiple covalent bonds

- The covalent bond in which one pair of electrons is shared is called a **single bond**.
- Multiple bonds can also form:
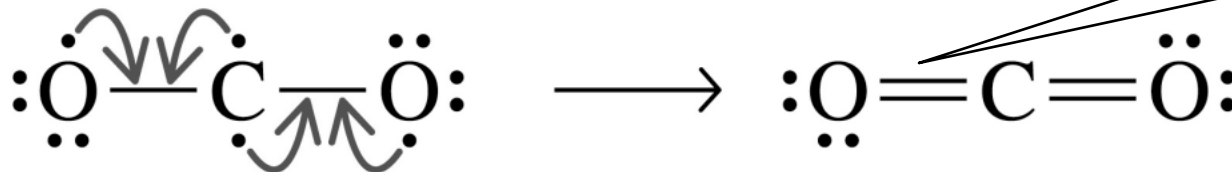
In a **double bond** two pairs of electrons are shared.

$$:\ddot{O}-C-\ddot{O}: \longrightarrow :\ddot{O}=C=\ddot{O}:$$

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$$:N-N: \longrightarrow :N\equiv N:$$
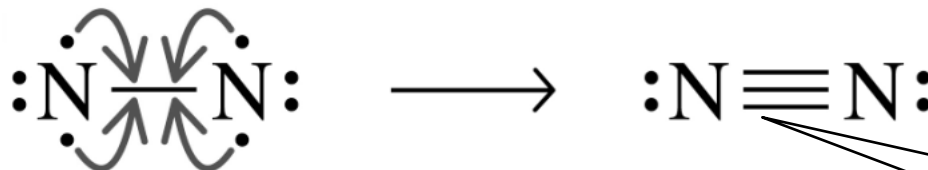
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In a **triple bond** three pairs of electrons are shared.

Note that each atom obeys the octet rule, even with multiple bonds.
(Again, movement of a single electron <u>should</u> be represented by a single-headed arrow.)

Polar covalent bonds and electronegativity

- Sharing is not always equal
- **ELECTRONEGATIVITY** (**EN**) is a measure of the ability of an atom to attract its bonding electrons to itself.
- EN is related to ionization energy and electron affinity.
- The greater the EN of an atom in a molecule, the more strongly the atom attracts the electrons in a covalent bond.

Electronegativity generally *increases* from left to right within a period, and it generally *increases* from the bottom to the top within a group.

Increasing electronegativity

Increasing electro-negativity
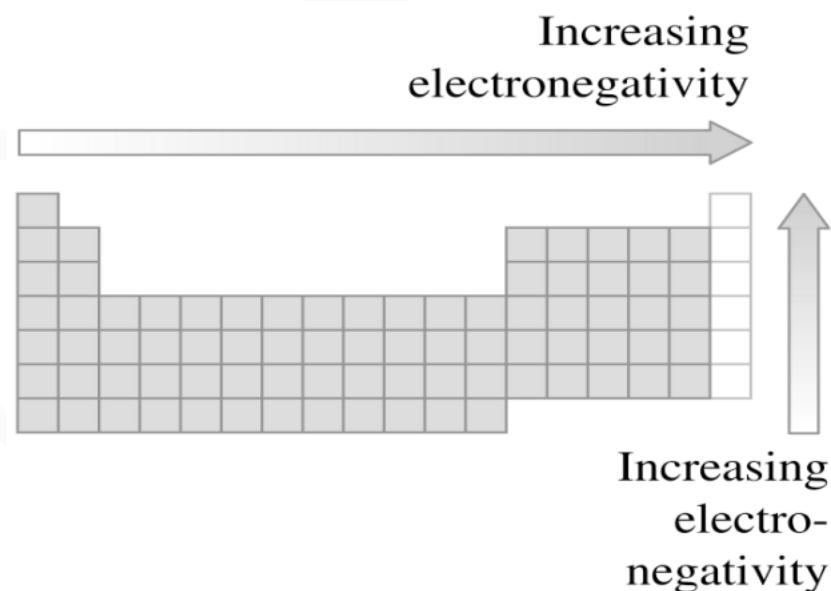
Pauling's electronegativities

F is the most electronegative, Fr is the least...
(It wouldn't hurt to remember the four elements of highest electronegativity: N, O, F, and Cl.)

Below 1.0	2.0–2.4
1.0–1.4	2.5–2.9
1.5–1.9	3.0–4.0

Period	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
1	H 2.1																
2	Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
3	Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4	K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.7	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
5	Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
6	Cs 0.7	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
7	Fr 0.7	Ra 0.9	Ac† 1.1														

*Lanthanides: 1.1–1.3
†Actinides: 1.3–1.5

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Electronegativity (cont'd)

- The greater the difference in electronegativity the greater the *ionic character*...the more ionic character to the bond, the more *polar* it is.
- A diatomic molecule is completely *nonpolar*.
- Polarity is drawn using an arrow with a cross through the tail (3 slides ahead).
- "Partially positive" atoms are denoted by a "delta-plus" ($\delta+$), partially negative atoms are denoted by a "delta-minus"($\delta-$).

Electronegativity difference and bond type
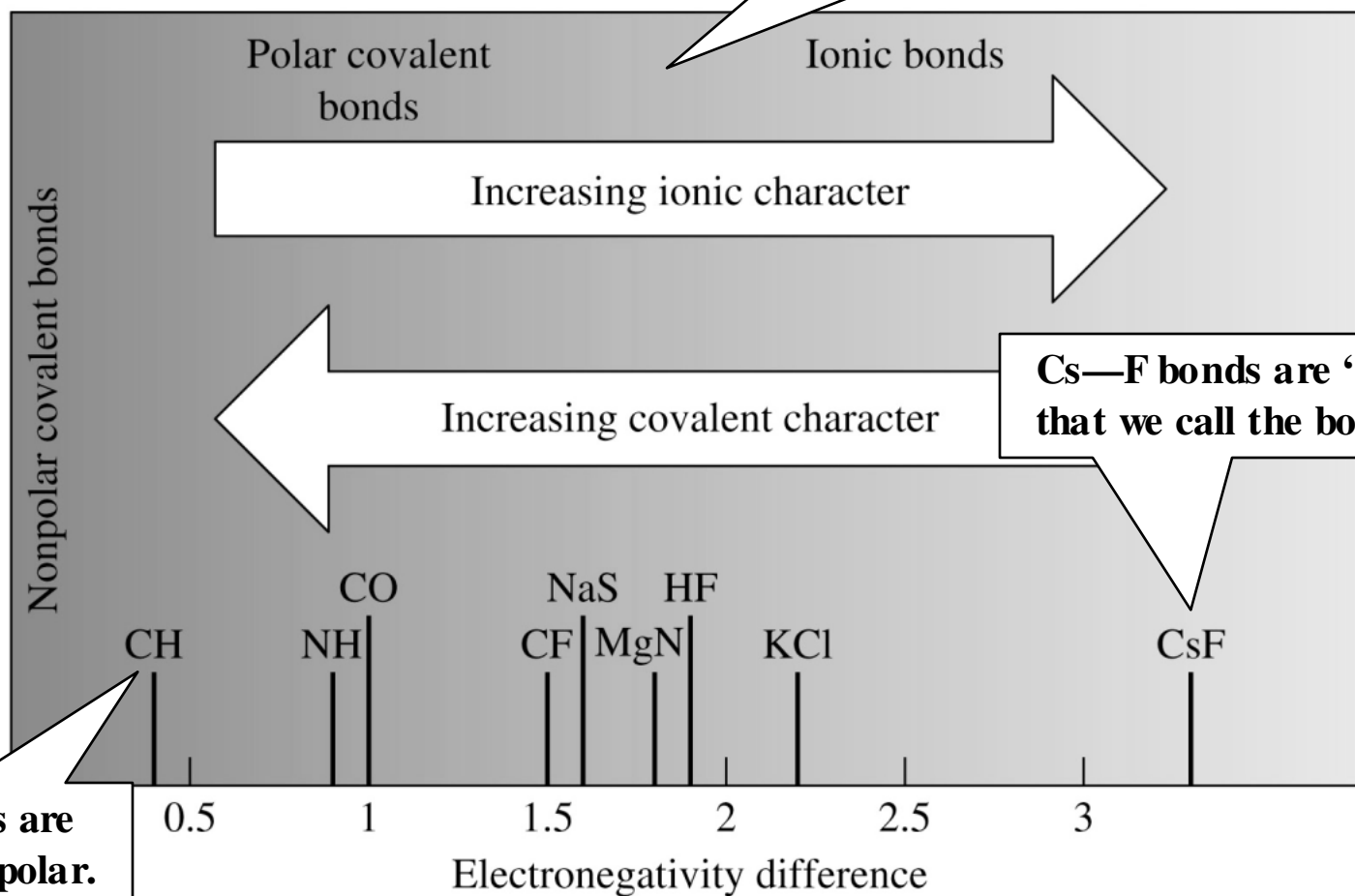
Depicting polar covalent bonds

Nonpolar covalent bond

In nonpolar bonds, electrons are shared *equally*.

H   H
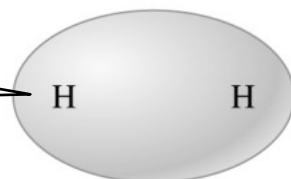
(a)

Unequal sharing in polar covalent bonds.

Polar covalent bond

H   Cl
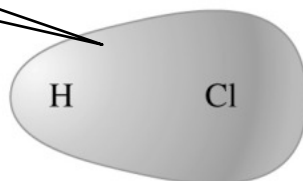
(b)

Polar bonds are often depicted using colors to show electrostatic potential (blue = positive, red = negative).
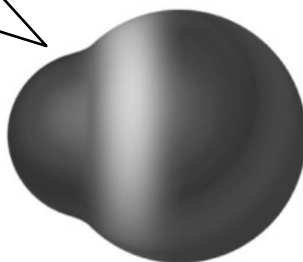
(c)

Polar bonds are also depicted by partial positive and partial negative symbols …

$$\delta+ \qquad \delta-$$

$$H - Cl$$
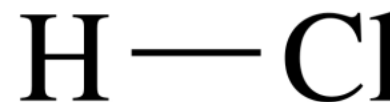
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… or with a cross-based arrow pointing to the more electronegative element.

$$+\!\longrightarrow$$

$$H - Cl$$

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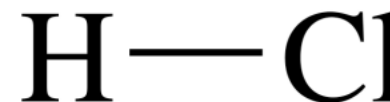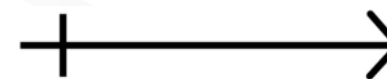
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Example

- Use electronegativity values to arrange the following bonds in order of increasing polarity:

  Br—Cl, Cl—Cl, Cl—F, H—Cl, I—Cl

- Worked out next slide

Example worked out

Strategy

We begin with the knowledge that the polar character of a bond is determined by electronegativity differences. For the individual electronegativities of the atoms, we turn to Figure 9.8.

Solution

The electronegativities (EN) and electronegativity differences are

EN:	2.8	3.0	3.0	3.0	3.0	4.0	2.1	3.0	2.5	3.0
	Br — Cl		Cl — Cl		Cl — F		H — Cl		I — Cl	
ΔEN:	0.2		0.0		1.0		0.9		0.5	

The order of increasing polarity is therefore

$$Cl — Cl < Br — Cl < I — Cl < H — Cl < Cl — F.$$

☐ Exercise 9.5A

Use electronegativity values to arrange the following bonds in order of increasing polarity:
C — Cl, C — H, C — Mg, C — O, C — S

☐ Exercise 9.5B

(a) Of the elements carbon, silicon, bromine, sulfur, nitrogen, chlorine, arsenic, fluorine, and selenium, which two form the covalent bond that has the most ionic character?

(b) Which two form the covalent bond that has the least ionic character?

Writing Lewis structures: skeletal structures

- The SKELETAL STRUCTURE shows the arrangement of atoms.
- Lewis structures have terminal atoms drawn around a central atom....think of each atom as a four-sided box that must obey the octet (duet) rule.....draw dashes for single bonds, then add *lone pairs* of electrons to the terminal atoms to get an octet...then add lone pairs and/or form multiple bonds to central atoms as needed to account for the *total number of valence electrons*
- Hydrogen atoms are **terminal atoms** (bonded to only one other atom).
- The **central atom** of a structure usually has the **lowest** electronegativity.
- In oxoacids ($HClO_4$, HNO_3, etc.) hydrogen atoms are usually bonded to **oxygen** atoms.
- Molecules and polyatomic ions usually have compact, symmetrical structures.
- C, N, O, and S are often double bonded. C and N can be triple bonded.

Example

– Write the Lewis structure of nitrogen trifluoride, NF_3.

Solution

Step 1: *Determine the number of valence electrons.* In one N atom (group 5A) and three F atoms (group 7A), there are $5 + (3 \times 7) = 26$ valence electrons.

Step 2: *Write a skeletal structure.* The electronegativity of N is 3.0; that of F is 4.0. We expect a skeletal structure with N as a central atom and F as terminal atoms. The three nitrogen-to-fluorine bonds in this structure account for six electrons.

$$F\!-\!N\!-\!F$$
$$|$$
$$F$$
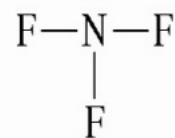
Step 3: *Complete the octets of terminals atoms.* We complete the octets of the F atoms by placing three lone pairs of electrons around each. This accounts for 18 additional electrons.

$$:\!\ddot{F}\!-\!N\!-\!\ddot{F}\!:$$
$$|$$
$$:\!\ddot{F}\!:$$
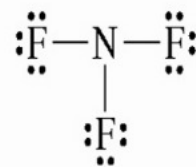
Step 4: *Assign lone pairs to central atom(s).* We have now assigned $6 + 18 = 24$ of the 26 valence electrons. We place the remaining two as a lone pair on the N atom.

$$:\!\ddot{F}\!-\!\ddot{N}\!-\!\ddot{F}\!:$$
$$|$$
$$:\!\ddot{F}\!:$$
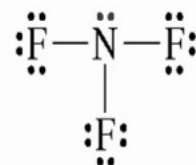
• Write the Lewis structure of hydrazine, N_2H_4.

Lewis structures are not always "right"–
The importance of experimental evidence

- The Lewis structure commonly drawn for oxygen is $:\ddot{O}\!=\!\ddot{O}:$

- But oxygen is **paramagnetic**, and therefore must have **unpaired** electrons.

- Lewis structures are a useful **tool**, but they do not always represent molecules correctly, even when the Lewis structure is plausible.
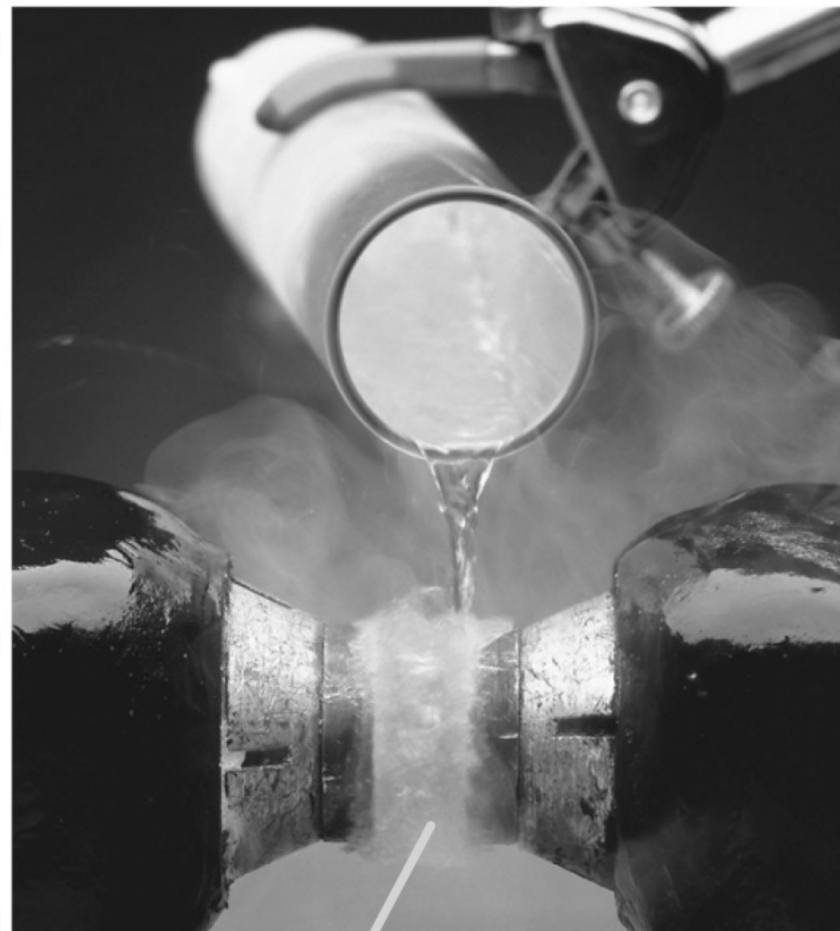
Liquid oxygen is paramagnetic and is held between the poles of the magnet.

Example

Write a plausible Lewis structure for phosgene, $COCl_2$.

Step 1: *Determine the number of valence electrons.*

In one C atom (group 4A), one O atom (group 6A), and two Cl atoms (group 7A), there are $4 + 6 + (2 \times 7) = 24$ valence electrons.

Step 2: *Write a skeletal structure.* The electronegativities are 2.5 for C, 3.5 for O, and 3.0 for Cl. We expect C, the least electronegative atom, to be the central atom, and O and Cl to be terminal atoms attached to it. This skeletal structure accounts for six of the valence electrons.

$$
\begin{array}{c}
\text{O} \\
| \\
\text{Cl}-\text{C}-\text{Cl}
\end{array}
$$
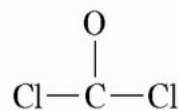
Step 3: *Complete the octets of terminal atoms.* Place three lone pairs around the O atom and three lone pairs around each of the Cl atoms, for a total of 18 electrons. This completes the octets of the terminal atoms.

$$
\begin{array}{c}
:\ddot{\text{O}}: \\
| \\
:\ddot{\text{C}}\text{l}-\text{C}-\ddot{\text{C}}\text{l}:
\end{array}
$$
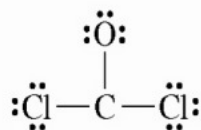
Step 4: *Assign lone pairs to central atom(s).* Up to this point, we have assigned $6 + 18 = 24$ of the 24 valence electrons, so there are none available to complete the octet of the central C atom. Therefore we must go to step 5.

Step 5: *Form multiple bonds to complete octets of central atom(s).* Complete the octet on the C atom by shifting a lone pair of electrons from the O atom to form a carbon-to-oxygen double bond. (C and O are two atoms that are able to form a double bond.)

$$
\begin{array}{c}
:\ddot{\text{O}}: \\
\curvearrowleft \\
:\ddot{\text{C}}\text{l}-\text{C}-\ddot{\text{C}}\text{l}:
\end{array}
\longrightarrow
\begin{array}{c}
:\ddot{\text{O}} \\
\| \\
:\ddot{\text{C}}\text{l}-\text{C}-\ddot{\text{C}}\text{l}:
\end{array}
$$
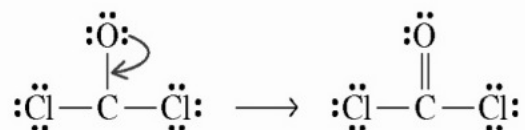
Formal charge

- **Formal charge** is the difference between the number of valence electrons in a free (uncombined) atom and the number of electrons assigned to that atom when bonded to other atoms in a Lewis structure.
- Formal charge is a **hypothetical** quantity; a useful tool in predicting reactivity.
- Usually, the **most plausible** Lewis structure is one with no formal charges.
- When formal charges are required, they should be as small as possible.
- Negative formal charges should appear on the most electronegative atoms. *Makes sense, right?*
- Adjacent atoms in a structure should *not* carry formal charges of the same sign.

Formal charge illustrated
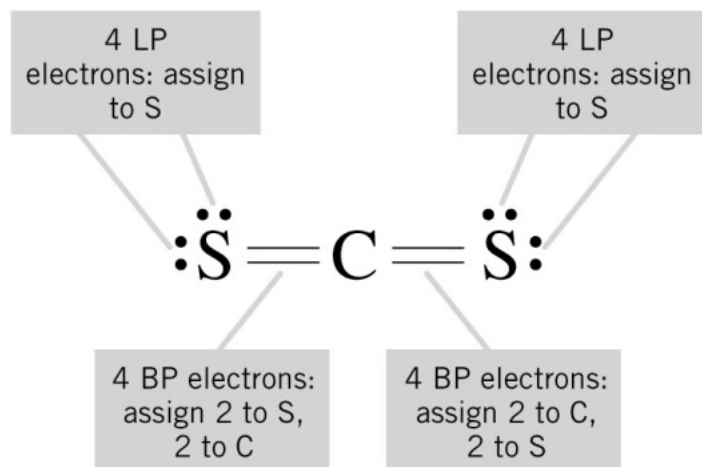
	S	C	S
Valence electrons	6	4	6
Electrons assigned	6	4	6
Formal charge	0	0	0

(a)
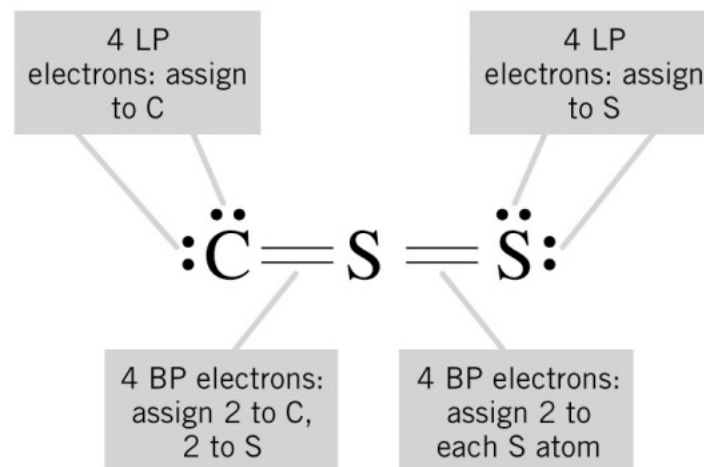
	C	S	S
Valence electrons	4	6	6
Electrons assigned	6	4	6
Formal charge	−2	+2	0

(b)

✓ yes   ✗ no

Example

- Before, we wrote a Lewis structure for the molecule $COCl_2$, shown here as structure (a). Show that structure (a) is more plausible than (b) or (c).
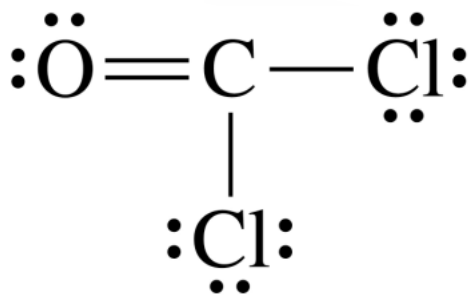
(a)
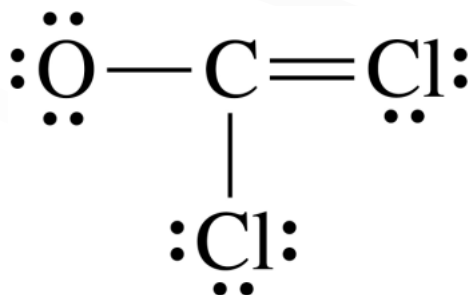
(b)
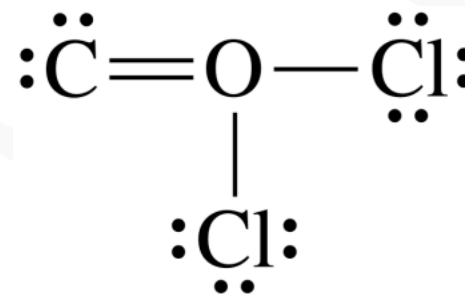
(c)

Resonance: delocalized bonding

- When a molecule or ion can be represented by two or more plausible Lewis structures that differ **only in the distribution of electrons**, the true structure is a composite, a hybrid, of them.
- The different plausible structures are called **resonance structures**.
- The actual molecule or ion that is a hybrid of the resonance structures is called a **resonance hybrid**.
- Electrons that are part of the resonance hybrid are spread out over several atoms and are referred to as being **delocalized**.

Three **pairs of electrons are distributed among** *two* **bonds.**

$$\overset{-1}{:\ddot{O}}—\overset{+1}{\ddot{O}}\!=\!\ddot{O}: \longleftrightarrow :\ddot{O}\!=\!\overset{+1}{\ddot{O}}—\overset{-1}{\ddot{O}}:$$

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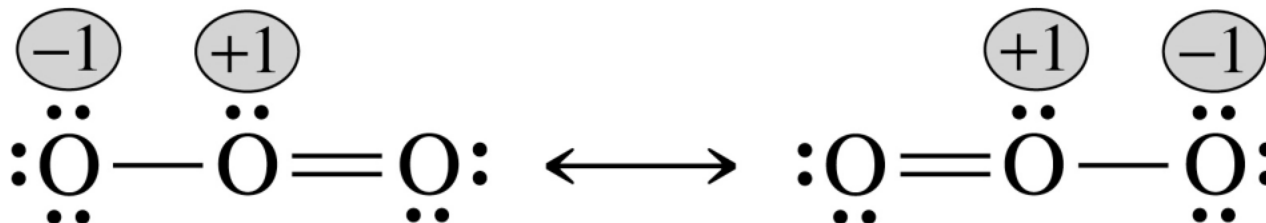
Example

- Write three equivalent Lewis structures for the SO_3 molecule that conform to the octet rule, and describe how the resonance hybrid is related to the three structures.

Step 1: *Determine the number of valence electrons.*

There are $6 + (3 \times 6) = 24$ valence electrons.

Step 2: *Write a skeletal structure.* The skeletal structure has sulfur, the atom of lower electronegativity, as the central atom.

$$O - \underset{\overset{|}{O}}{S} - O$$
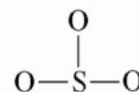
Step 3: *Complete the octets of terminal atoms.* Place three lone pairs of electrons on each O atom to complete its octet.
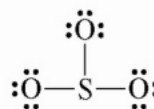
Step 4: *Assign lone pairs to central atom(s).* We have already assigned all 24 valence electrons; there are none left to place as lone pairs on the central atom. Because the S atom does not yet have an octet, we must go on to step 5.

Step 5: *Form multiple bonds to complete octets of central atom(s).* Move a lone pair of electrons from any terminal O atom to form a double bond to the central S atom. Because the double bond can go to any one of the three terminal O atoms, we get three equivalent structures that differ only in the position of the double bond.

Resonance structures
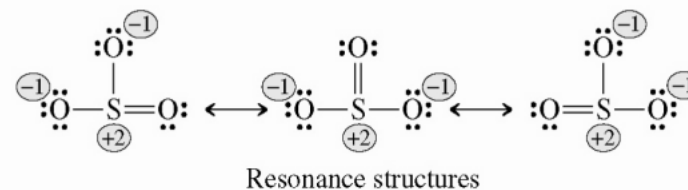
Molecules that do not follow the octet rule

- Molecules with an **odd number** of valence electrons have at least one of them unpaired and are called **free radicals**.
- Some molecules have **incomplete octets**. These are usually compounds of Be, B, or Al; they generally have some unusual bonding characteristics, and are often quite reactive.
- Some compounds have **expanded valence shells**, which means that the central atom has more than eight electrons around it.
- A central atom can have expanded valence if it is in the third period or lower (i.e., S, Cl, P).

Example

- Write the Lewis structure for bromine pentafluoride, BrF_5.

Step 1: *Determine the number of valence electrons.*

Both Br and F are in group 7A. All the atoms in the structure have seven valence electrons, and $7 + (5 \times 7) = 42$ valence electrons must appear in the Lewis structure.

Step 2: *Write a skeletal structure.* The skeletal structure has Br, the atom of lower electronegativity, as the central atom.
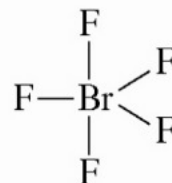
Step 3: *Complete the octets of terminal atoms.* To complete the octets of the F atoms, we place three lone pairs of electrons around each one.
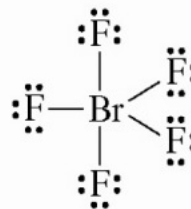
Step 4: *Assign lone pairs to central atom(s).* Through step 3, we have assigned 40 of the 42 valence electrons; two remain to be placed. They can be shown as a lone pair on the bromine atom. In this representation, the Br atom has an expanded valence shell containing 12 electrons.
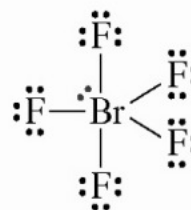
Example

- Indicate the error in each of the following Lewis structures. Replace each by a more acceptable structure(s).

a. :C≡N:

b. H—Ö=N—Ö:
with :O: above the N
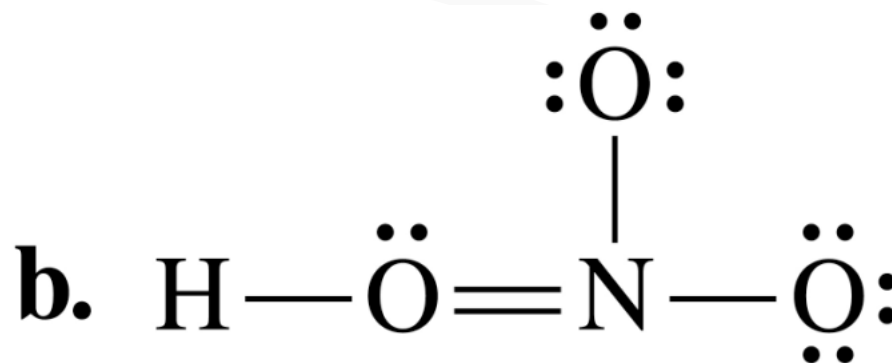
Bond order and bond length

- **_Bond order_** is the number of shared electron pairs in a bond.

- A single bond has BO = 1, a double bond has BO = 2, etc.

- **_Bond length_** is the distance between the nuclei of two atoms joined by a covalent bond.

- Bond length depends on the particular atoms in the bond and on the bond order.

H—H
74 pm

O=O
121 pm

F—F
143 pm

Cl—Cl
199 pm

I—I
266 pm
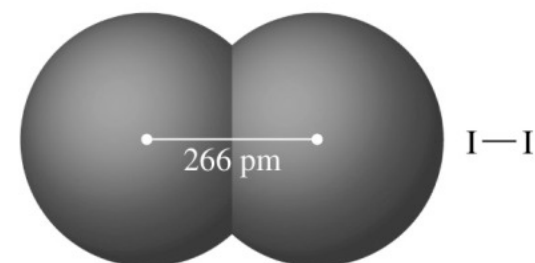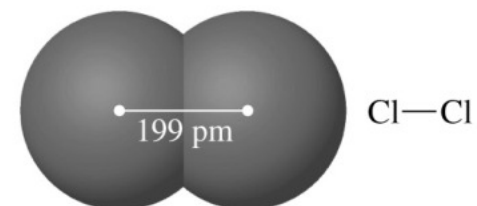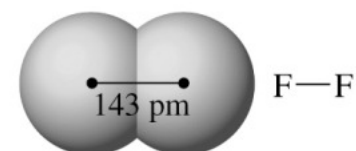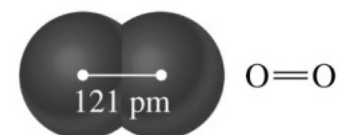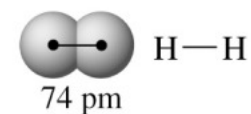
Bond energy

- **Bond-dissociation energy** (**D**) is the energy required to break one mole of a particular type of covalent bond in a *gas*-phase compound.

- Energies of some bonds can differ from compound to compound, so we use an **average** bond energy.

The H—H bond energy is precisely known …

⬤⬤ + 436 kJ ⟶ ⬤ + ⬤
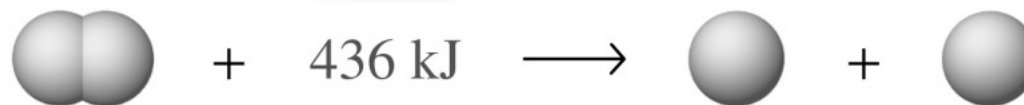
… while the O—H bond energies for the two bonds in H_2O are different.

⬤⬤ + 499 kJ ⟶ ⬤⬤ + ⬤

⬤⬤ + 428 kJ ⟶ ⬤⬤ + ⬤
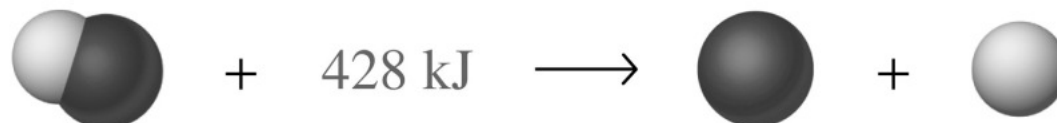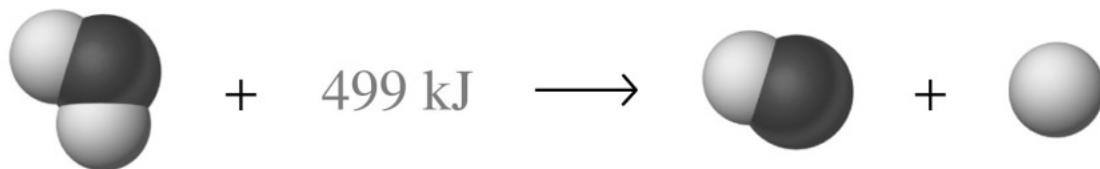
Table 9.1 Some Representative Bond Lengths and Bond Energies

Bond	Bond Length, pm	Bond Energy,[a] kJ/mol	Bond	Bond Length, pm	Bond Energy,[a] kJ/mol
H—H	74	436	C—O	143	360
H—C	110	414	C=O	120	736[b]
H—N	100	389	C—Cl	178	339
H—O	97	464	N—N	145	163
H—S	132	368	N=N	123	418
H—F	92	565	N≡N	110	946
H—Cl	127	431	N—O	136	222
H—Br	141	364	N=O	120	590
H—I	161	297	O—O	145	142
C—C	154	347	O=O	121	498
C=C	134	611	F—F	143	159
C≡C	120	837	Cl—Cl	199	243
C—N	147	305	Br—Br	228	193
C=N	128	615	I—I	266	151
C≡N	116	891			

[a] Bond-dissociation energy for the bonds in diatomic molecules (H_2, HF, HCl, HBr, HI, N_2, O_2, F_2, Cl_2, Br_2 and I_2) and average bond energies for the other bonds.

[b] The value for the CO bond in CO_2 is considerably different: 799 kJ/mol.

Trends in bond lengths and energies

- The *higher* the order (for a particular type of bond), the **shorter** and the **stronger** (higher energy) the bond.
- A N=N *double* bond is shorter and stronger than a N–N *single* bond.
- There are *four* electrons between the two positive nuclei in N=N. This produces more electrostatic attraction than the two electrons between the nuclei in N–N.

Example

- Estimate the length of
  (a) the nitrogen-to-nitrogen bond in N_2H_4 and
  (b) the bond in BrCl.

(a) The Lewis structure

$$H-\overset{..}{N}-\overset{..}{N}-H$$
$$\,\,\,\,\,\,\,\,\,\,\,|\,\,\,\,\,\,\,\,|$$
$$\,\,\,\,\,\,\,\,\,\,\,H\,\,\,\,\,H$$
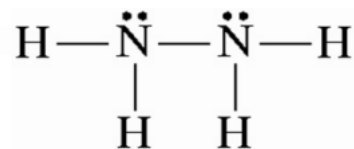
is a plausible one: valence-shell octets for the N atoms, duets for the H atoms, and formal charges of 0.
The nitrogen-to-nitrogen bond is single, and from Table 9.1 we find its bond length to be 145 pm.

(b) To get the Lewis structure of BrCl, we imagine substituting one Br atom for one Cl atom in the Lewis structure of Cl_2, arriving at the structure
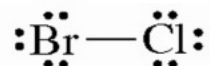
$$:\overset{..}{\underset{..}{Br}}-\overset{..}{\underset{..}{Cl}}:$$

The BrCl molecule contains a Br—Cl single bond with a length approximately one-half the Cl—Cl bond length *plus* one-half the Br—Br bond length. From Table 9.1, we get $\left[\left(\frac{1}{2} \times 199\right) + \left(\frac{1}{2} \times 228\right)\right] = 214$ pm.

Calculations involving bond energies

For the reaction $N_2(g)$ + $2\,H_2(g)$ → $N_2H_4(g)$ to occur …

… we must
supply **946 kJ …**

When the bonds of the product *form*, **163 kJ plus 4(389 kJ) of energy is** *liberated*.

436

946

H−H

N≡N

H

H

N ←→ N

−389

H   H
| /
N−N
/   \
H   H

−389

−389

H−H

436

H

H

−389

−163

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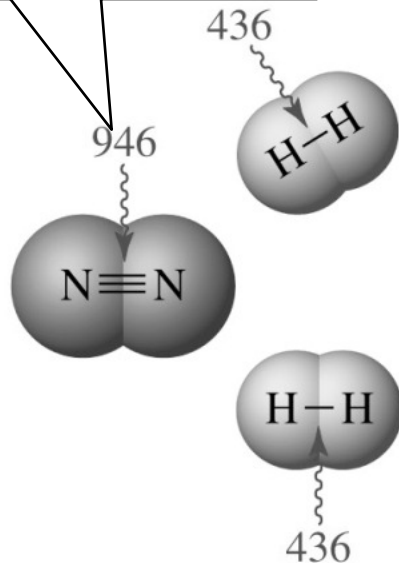
… plus 2(436 kJ), to *break* **bonds of the reactants.**
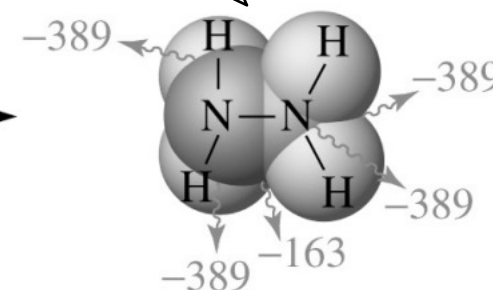
$$\Delta H = (+946\text{ kJ}) + 2(+436\text{ kJ}) + (-163\text{ kJ}) + 4(-389\text{ kJ})$$

Flashback: alkenes and alkynes

- Hydrocarbons with double or triple bonds between carbon atoms are called **unsaturated hydrocarbons**.
- **Alkenes** are hydrocarbons with one or more C=C double bonds.
- The simplest alkene is C_2H_4, ethene (ethylene).
- **Alkynes** are hydrocarbons that have one or more carbon–carbon triple bonds.
- The simplest alkyne is C_2H_2, ethyne (acetylene).

Molecular models of ethene and ethyne

space-filling models

H   H
 \ /
  C=C
 / \
H   H

Structural formula

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$CH_2\!\!=\!\!CH_2$ or $H_2C\!\!=\!\!CH_2$
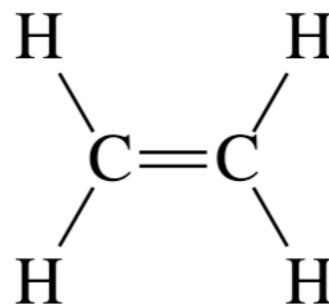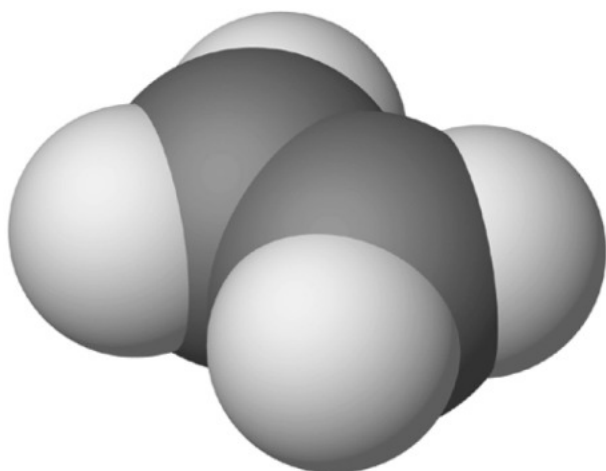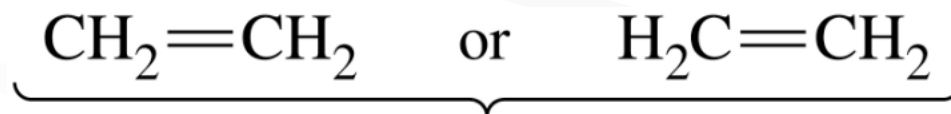
Condensed structural formula

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H:C:::C:H   or $H\!-\!C\!\equiv\!C\!-\!H$
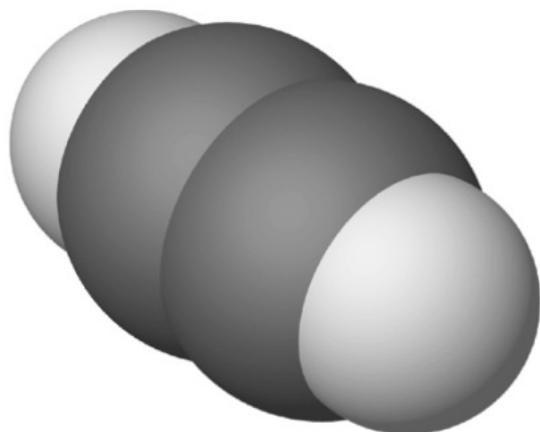
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Fats and oils

- Triglycerides are composed of glycerol plus three long-chain carboxylic (fatty) acids
- What's the difference between a fat and an oil? Fats are solids at RT, Oils are liquids
- Unsaturated fats become saturated upon *hydrogenation* (Fig. 13.21)
- Your book also has a nice bromination picture in this chapter

(a) $CH_3(CH_2)_7C=C(CH_2)_7COOH$

Nickel surface

(b) $CH_3(CH_2)_7$ — $CH_3(CH_2)_7$ ... $(CH_2)_7COOH$

(c) $CH_3(CH_2)_7$ ... $(CH_2)_7COOH$

(d) $CH_3(CH_2)_7$ ... $(CH_2)_7COOH$

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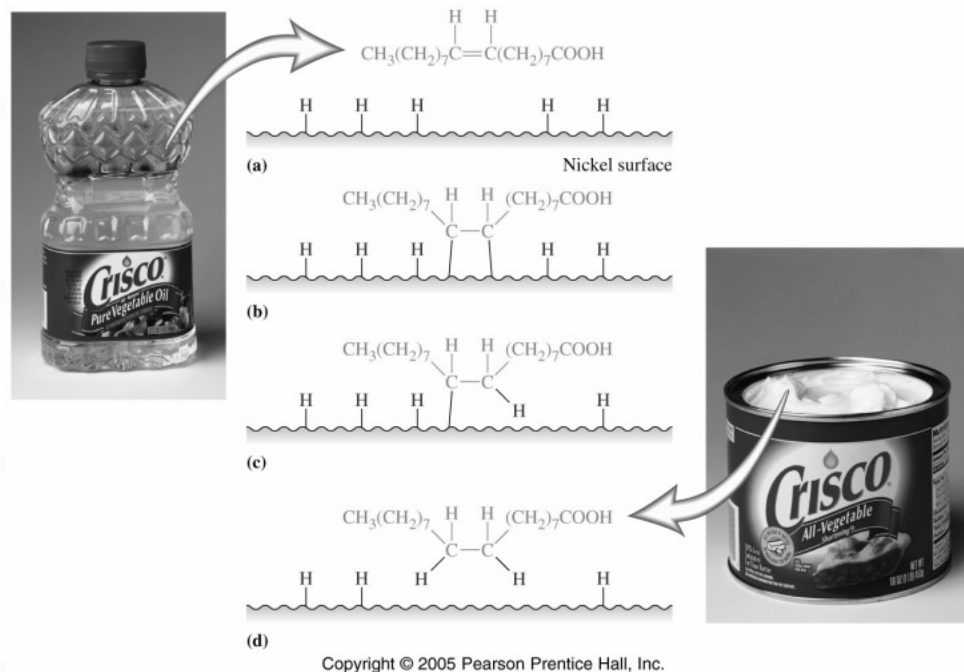
Polymers

- **Polymers** are compounds in which many identical molecules have been joined together.
- **Monomers** are the simple molecules which join together to form polymers.
- Often, the monomers have double or triple bonds.
- The process of these molecules joining together is called **polymerization**.
- Many everyday products and many biological compounds are polymers.

Formation of polyethylene
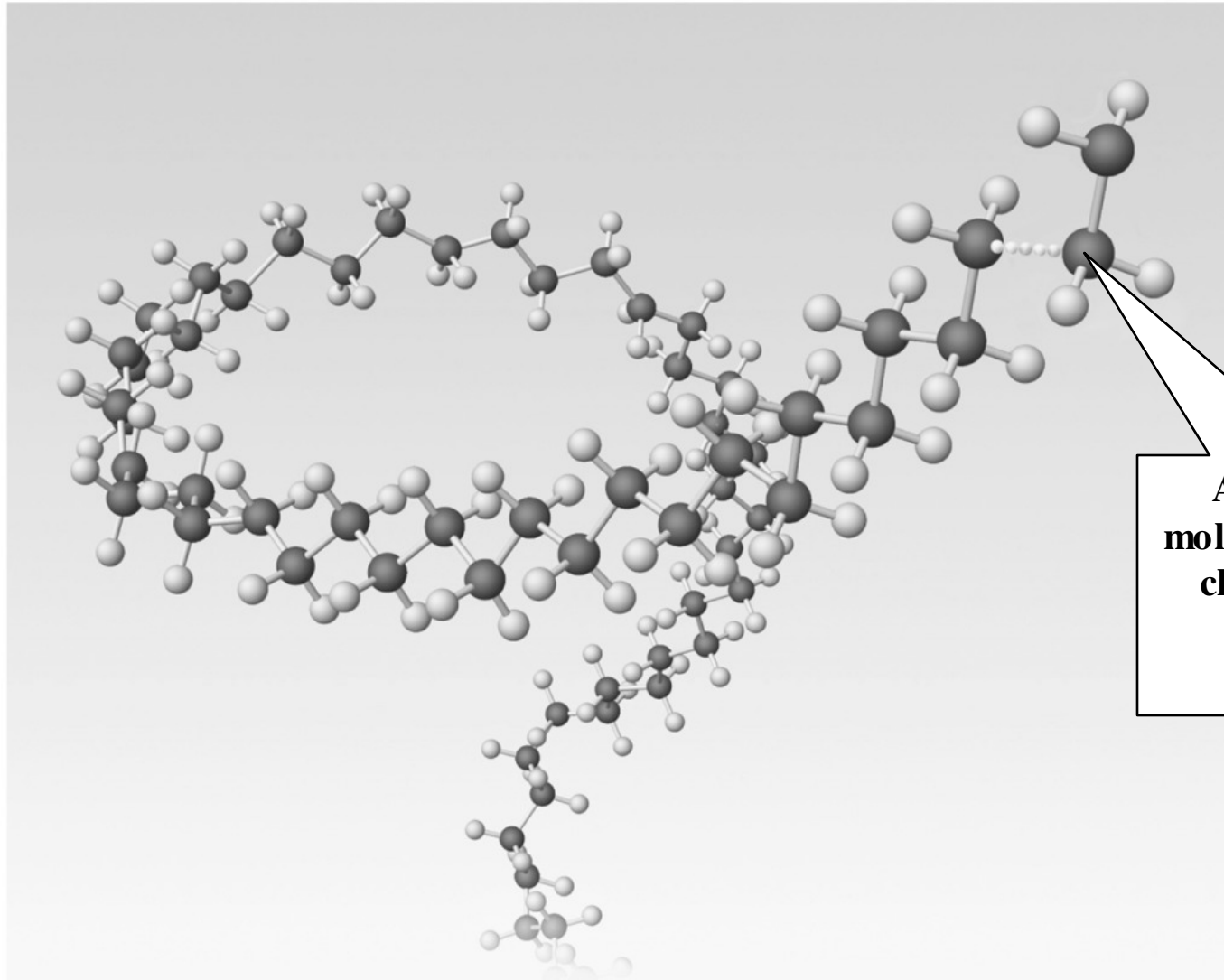
Another ethylene molecule adds to a long chain formed from more ethylene molecules.

Table 9.2 A Selection of Addition Polymers

Monomer	Polymer	Polymer Name	Some Uses
$H_2C{=}CH_2$	$\left[\begin{array}{c} H \quad H \\ \mid \quad \mid \\ -C-C- \\ \mid \quad \mid \\ H \quad H \end{array}\right]_n$	Polyethylene	Plastic bags, milk bottles, toys, electrical insulation, plastic wrap, paper coatings, food containers and lids, storage containers, laboratory bottles, wastebaskets
$H_2C{=}CH{-}CH_3$	$\left[\begin{array}{c} H \quad H \\ \mid \quad \mid \\ -C-C- \\ \mid \quad \mid \\ H \quad CH_3 \end{array}\right]_n$	Polypropylene	Indoor–outdoor carpeting, bottles, insulating sportswear, tear-resistant envelopes, labels, disposable clothing and protective outerwear, moisture-resistant packaging, chemical-resistant plumbing pipe
$H_2C{=}CH{-}Cl$	$\left[\begin{array}{c} H \quad H \\ \mid \quad \mid \\ -C-C- \\ \mid \quad \mid \\ H \quad Cl \end{array}\right]_n$	Poly(vinyl chloride), PVC	Plastic wrap, simulated leather (Naugahyde), T-shirt printing, garden hoses, clear flexible tubing, "soft" toys, plumbing fixtures and pipe, vinyl flooring, rainwear
$F_2C{=}CF_2$	$\left[\begin{array}{c} F \quad F \\ \mid \quad \mid \\ -C-C- \\ \mid \quad \mid \\ F \quad F \end{array}\right]_n$	Polytetrafluoroethylene, Teflon	Nonstick coating for cooking utensils, electrical insulation, chemical-resistant laboratory ware, coatings for clothing and carpet

Plastics

- Although plastics are marked recyclable 1-7, most areas only recycle plastics 1 and 2

  ⟨1⟩ PETE - Polyethylene terephthalate (**PET**)

  ⟨2⟩ HDPE - High-density polyethylene (**HDPE**)

  ⟨3⟩ V - Polyvinyl chloride (**PVC**)

  ⟨4⟩ LDPE - Low-density polyethylene (**LDPE**)

  ⟨5⟩ PP - Polypropylene (**PP**)

  ⟨6⟩ PS - Polystyrene (**PS**)

  ⟨7⟩ OTHER **7** - Other resins, like acrylonitrile butadine styrene (**ABS**)

end of section

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

B—A—B

B

⟹

B   B
 \   /
   A
   |
   B

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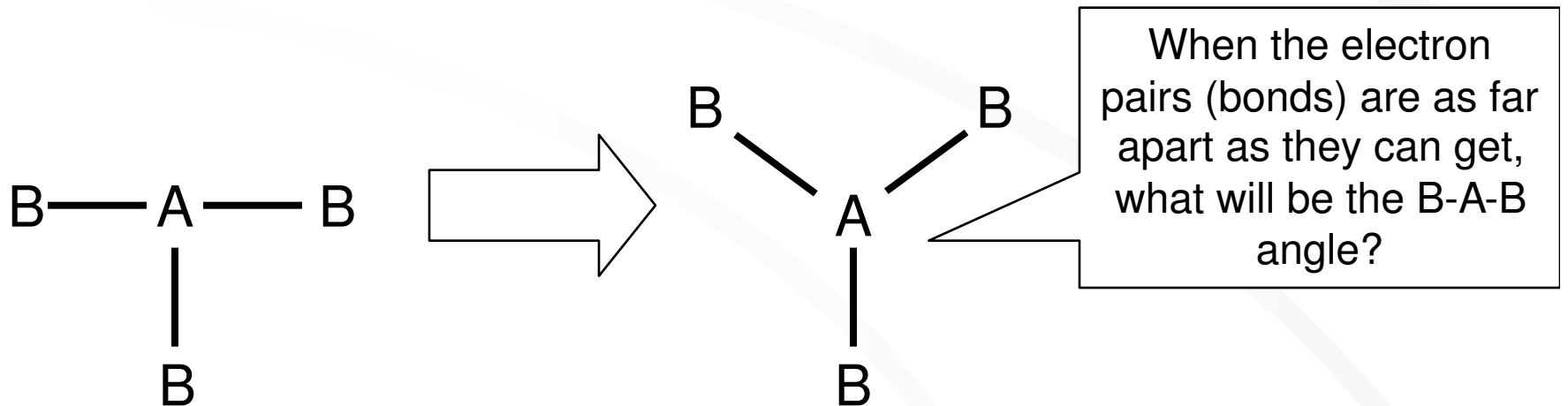
Electron group geometry

- 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)
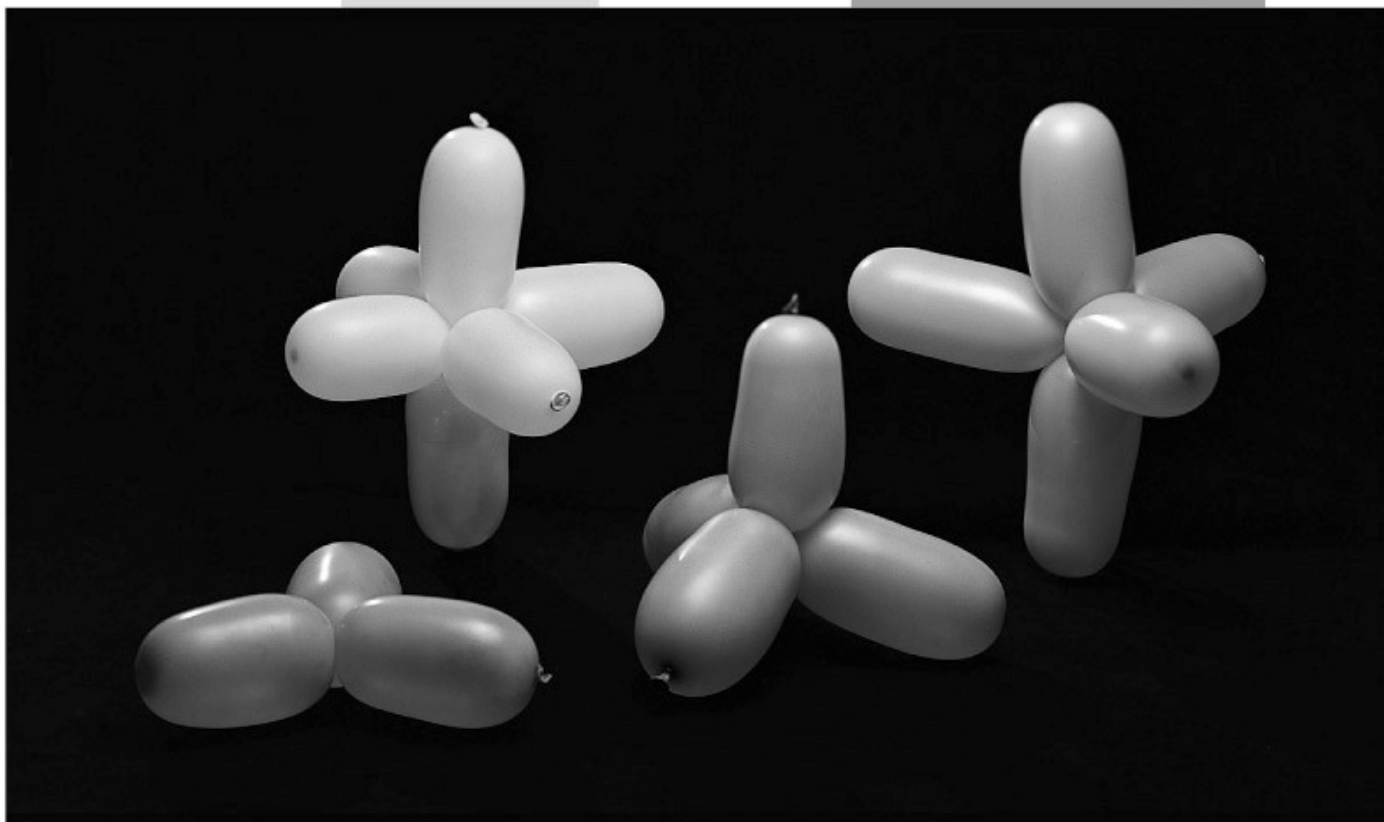
VSEPR notation

- central atoms are denoted "A"

- terminal atoms are denoted "X"

- lone pairs are denoted "E"

Thus, water is AX_2E_2
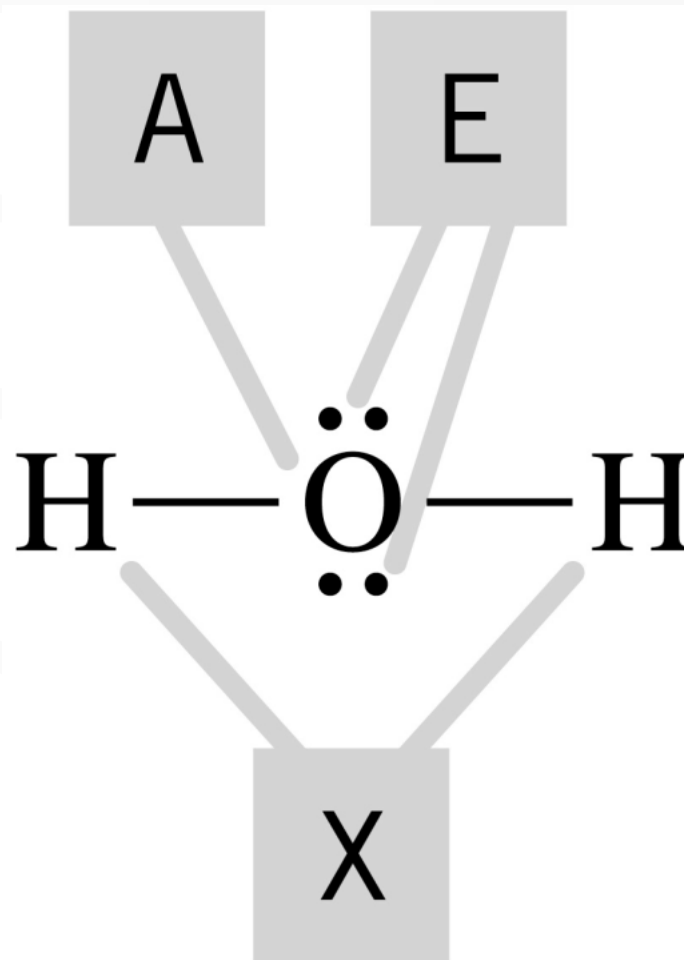
Molecular geometries

- 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!
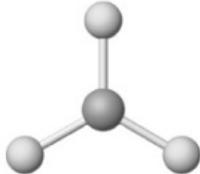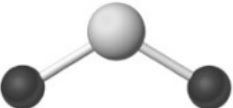
- For structures with no lone pairs on the central atom (AXn), the molecular ~~geometry~~ SHAPE is the same as the electron-group geometry.

- 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
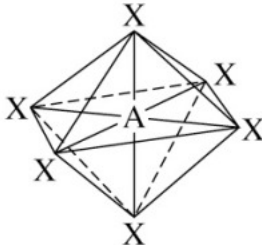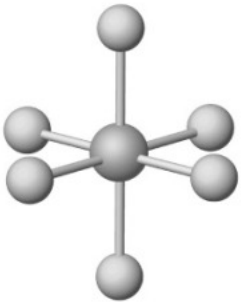- AX_5E vs AX_6
- AX_4E_2 vs AX_6
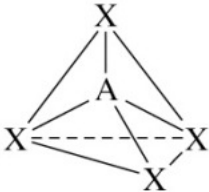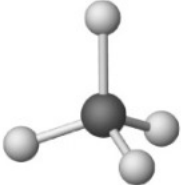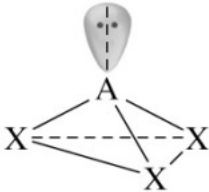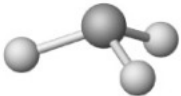
Shape and geometry

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

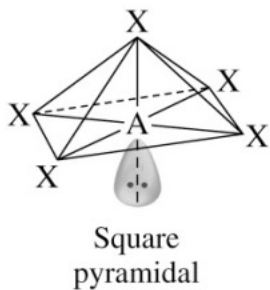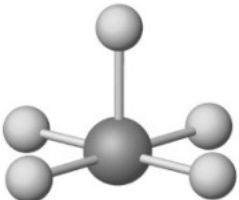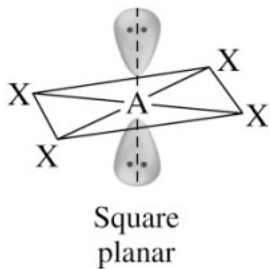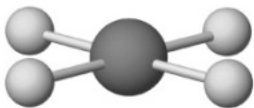| Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
2	Linear	0	AX_2	X—A—X Linear	180°	$BeCl_2$	
3	Trigonal planar	0	AX_3	Trigonal planar	120°	BF_3	
3	Trigonal planar	1	AX_2E	Angular	120°	SO_2	
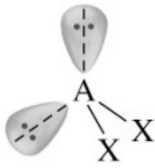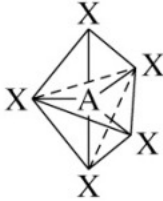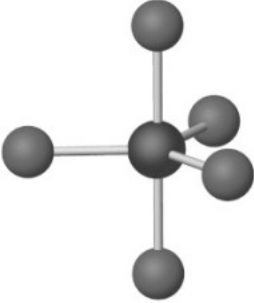
Shape and geometry (cont'd)

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	
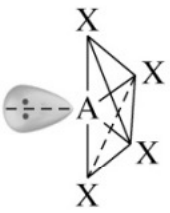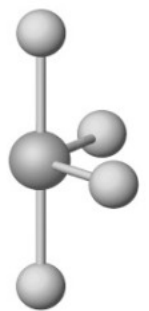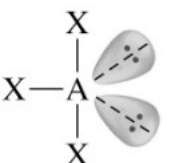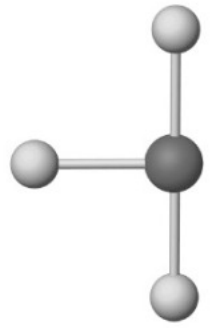
Shape and geometry (cont'd)

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	
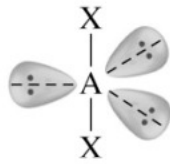
Shape and geometry (cont'd)

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)
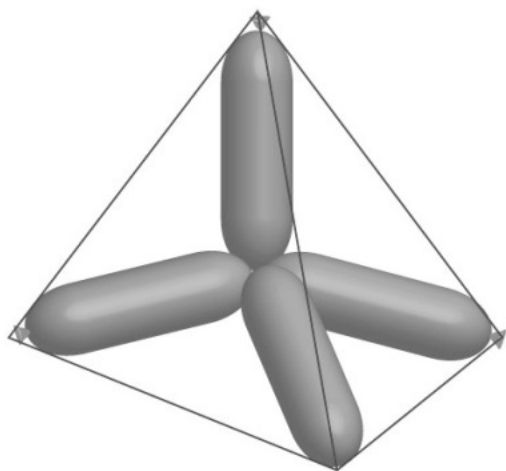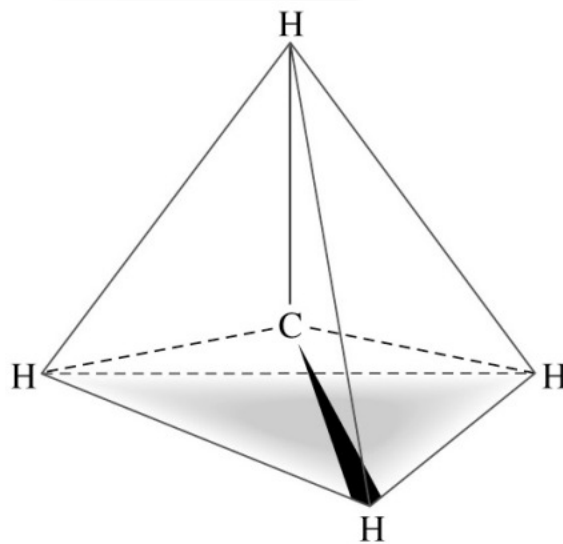
(b)
VSEPR notation: AX_4
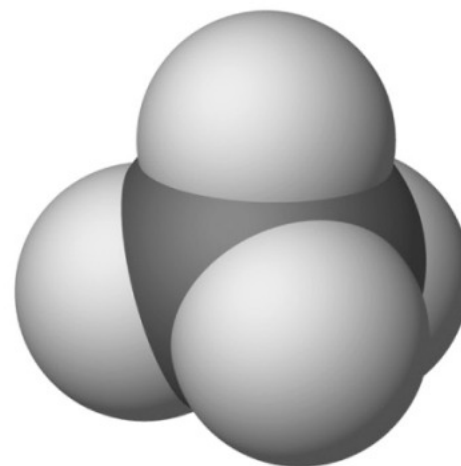
(c)

Molecular shape of water
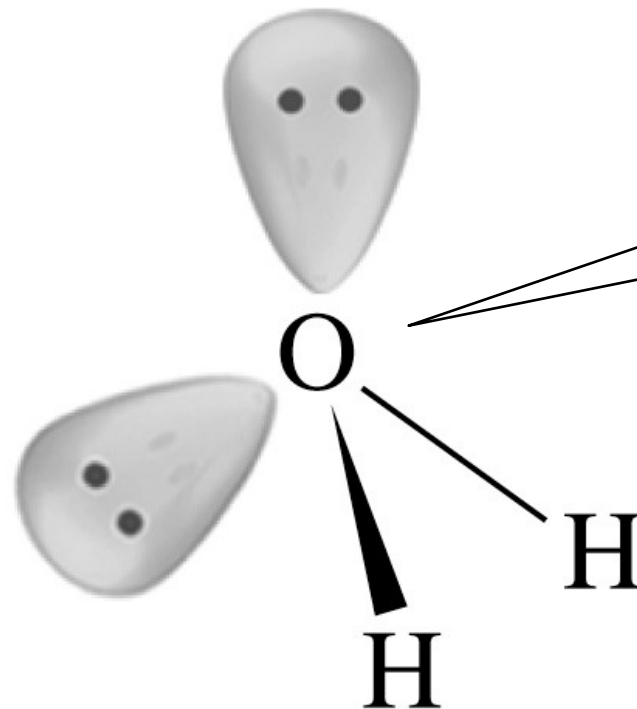
Is the water molecule tetrahedral?

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 **debye (D).**
- One debye (D) is equal to 3.34×10^{-30} C m.

Polar molecules in an electric field

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

(a)

(b)
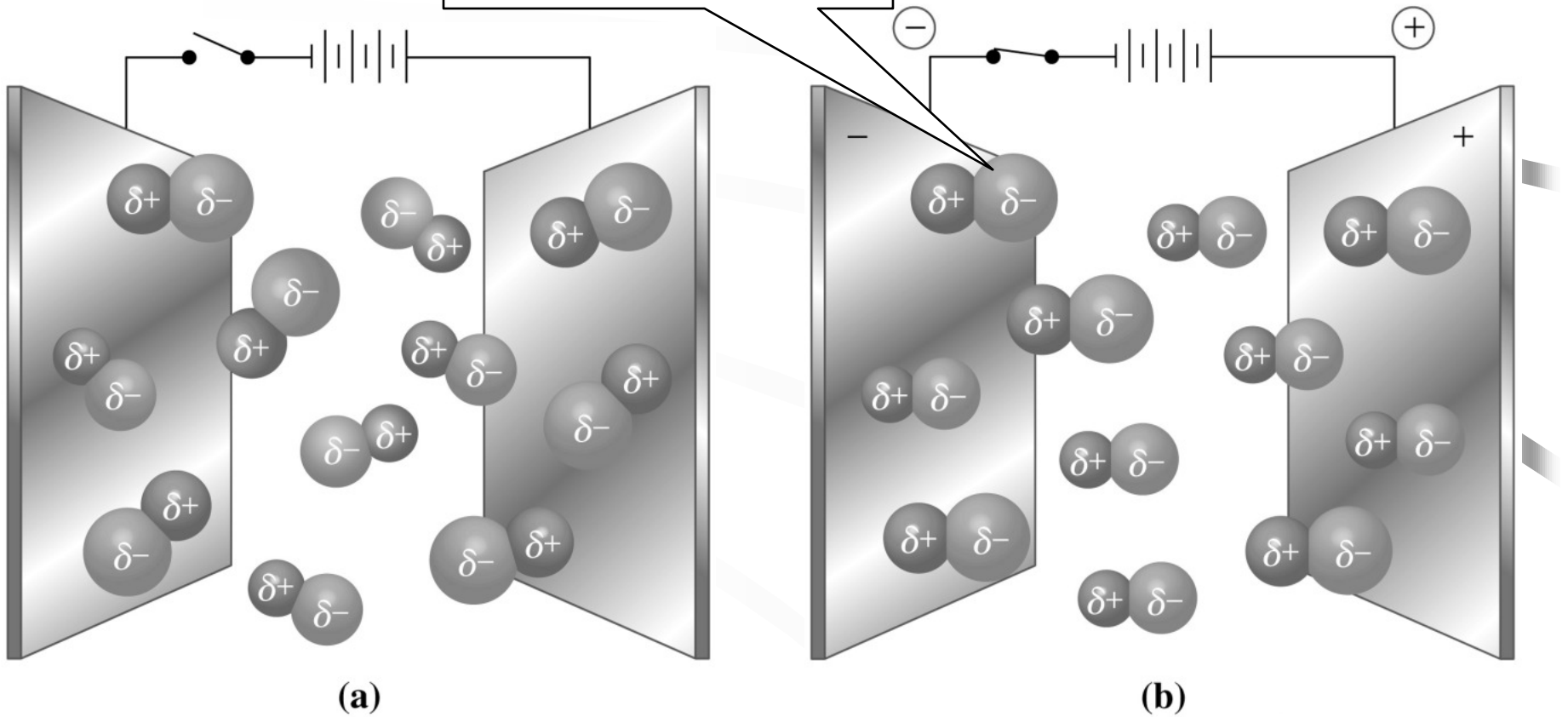
Bond Dipoles and Molecular Dipoles

- 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 ($\mu = 0$ D).

No net dipole

- The water molecule has polar bonds also, but is an **angular** molecule.

- The bond dipoles do **not** cancel (m = 1.84 D), so water is a **polar** molecule.
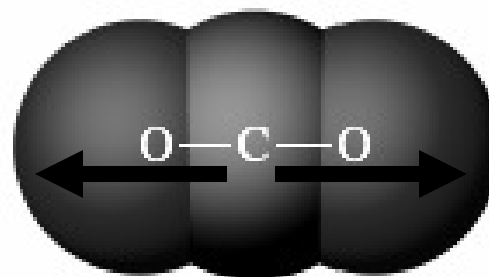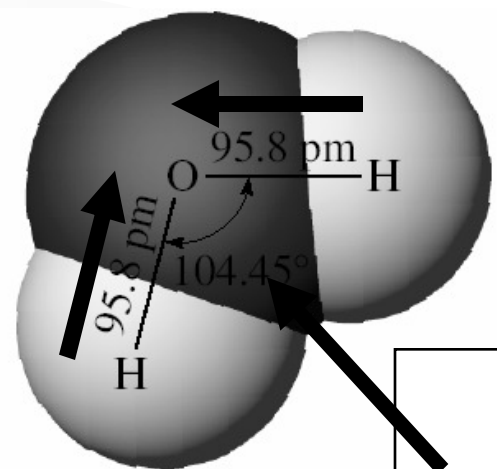
Net dipole

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.
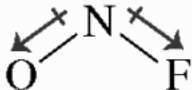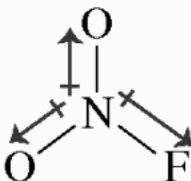

Cl

H

Cl⋯⋯C⋯⋯Cl

Cl⋯⋯C⋯⋯Cl

Cl

Cl

(a)

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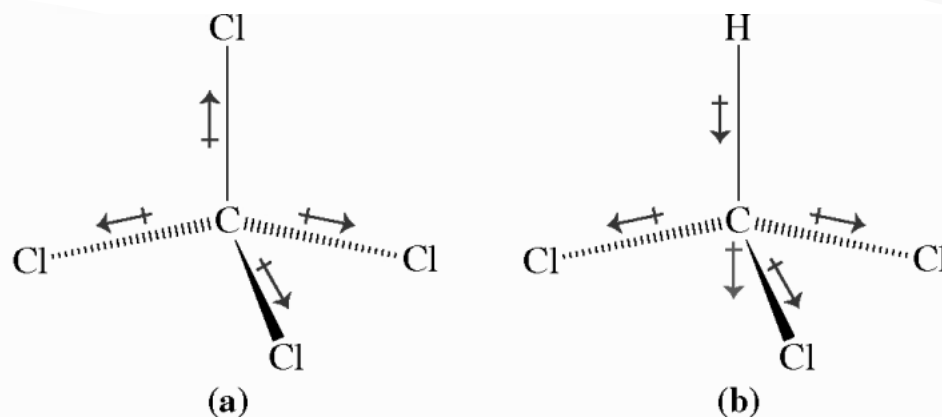
▲ FIGURE 10.9   **Molecular geometry and molecular dipoles**
The bond dipoles are represented by black cross-based arrows ⟵→
(a) The individual bond dipoles cancel, and there is no molecular dipole.
(b) All the bond dipoles point downward and combine to form a molecular dipole (red arrow).

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.
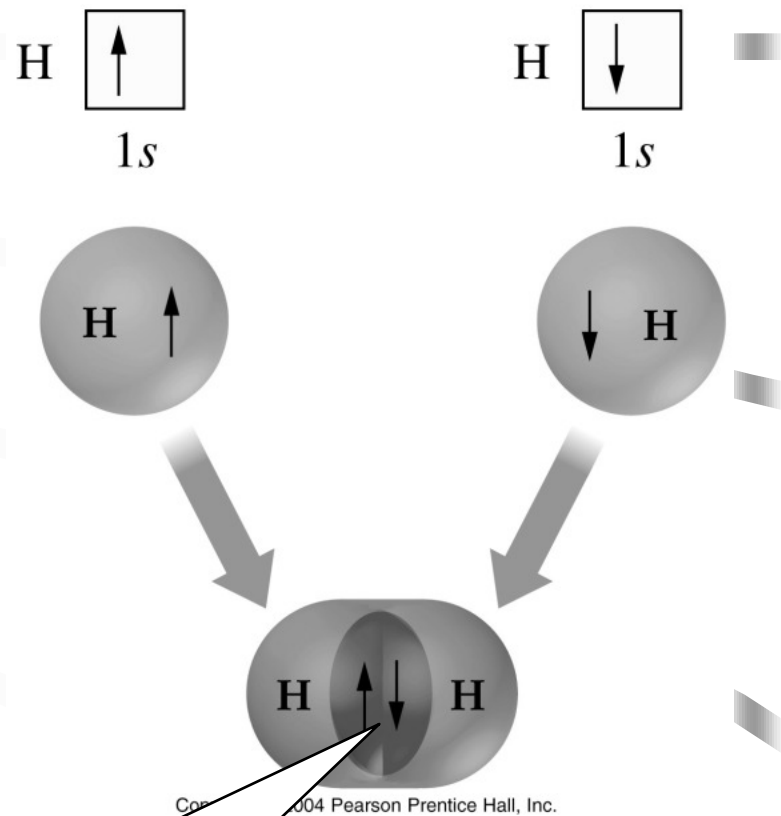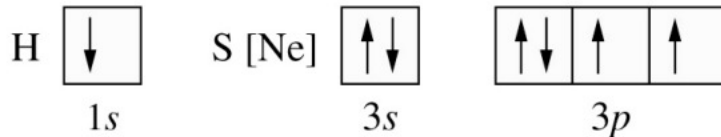

Overlap region between nuclei has high electron density

Bonding in H₂S
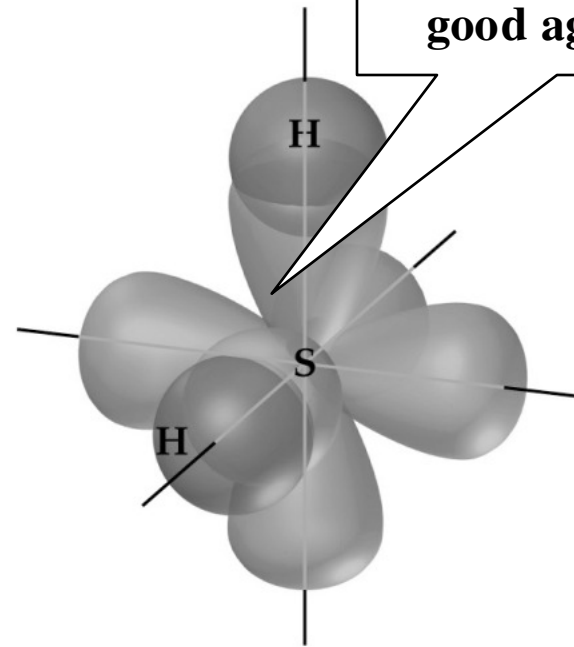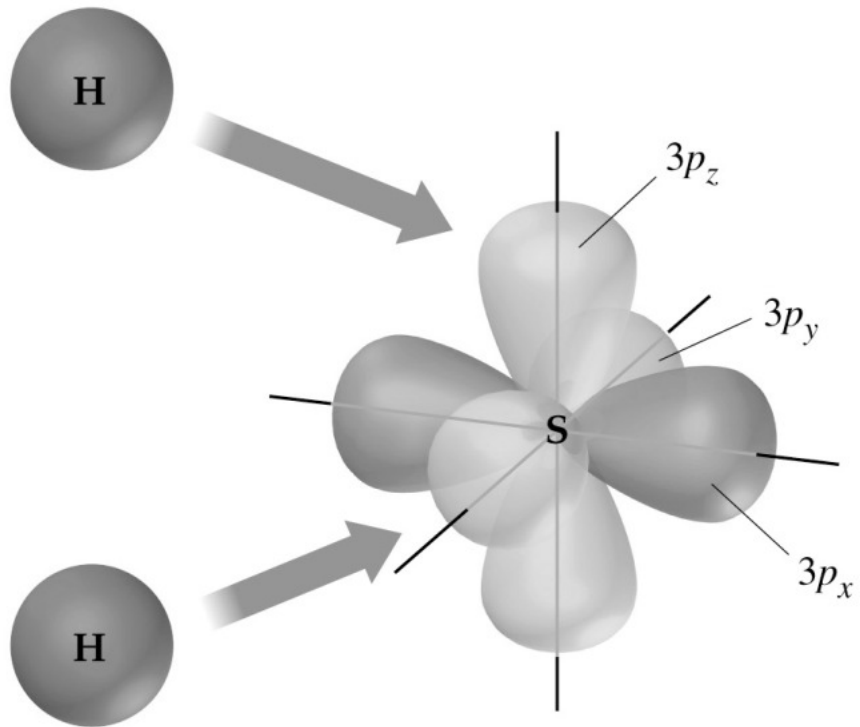
The measured bond angle in H₂S is 92°; good agreement.

3p_z

3p_y

S

3p_x

H

H

(a) Isolated atoms

(b) H₂S

H ↓
1s

S [Ne] ↑↓
3s

↑↓ ↑ ↑
3p

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"
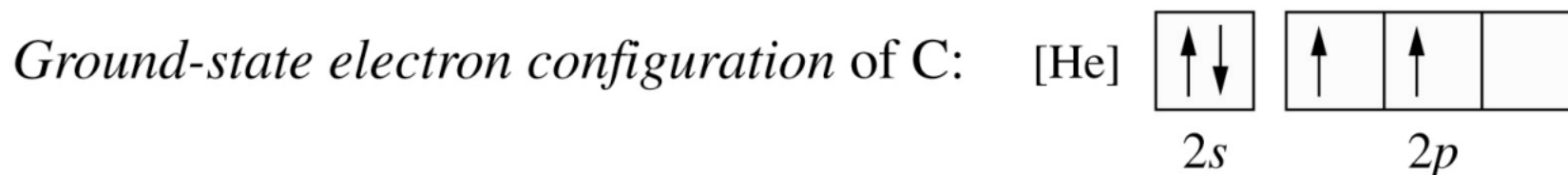- sp^3 orbitals
- sp^2 orbitals
- sp orbitals
- d hybrids

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]

2s   2p

- We can **hybridize** the four orbitals holding valence electrons; mathematically combine the wave functions for the 2s orbital and the three 2p 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).
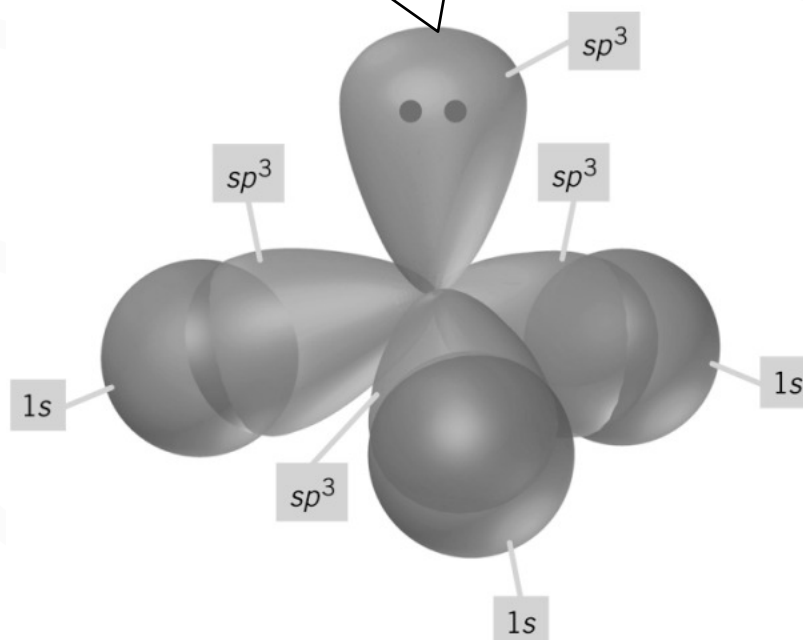
The sp³ hybridization scheme

| Four AOs … | … form four new hybrid AOs. |
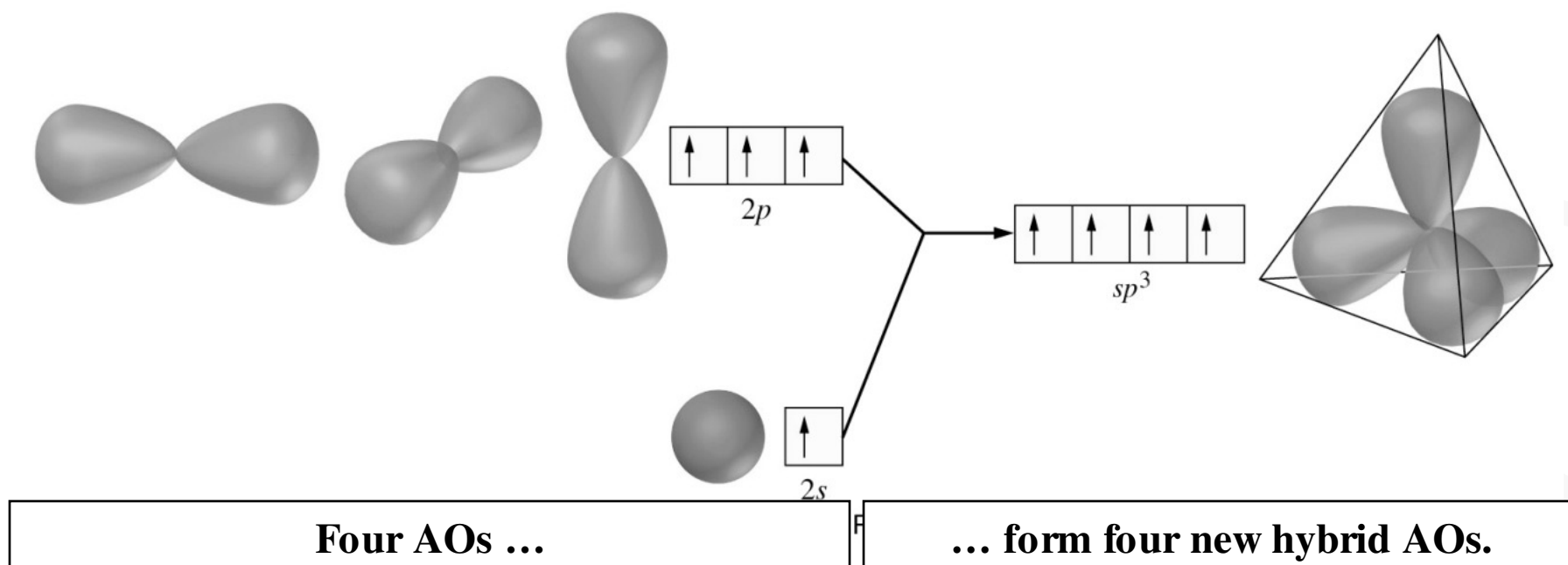
Methane and ammonia

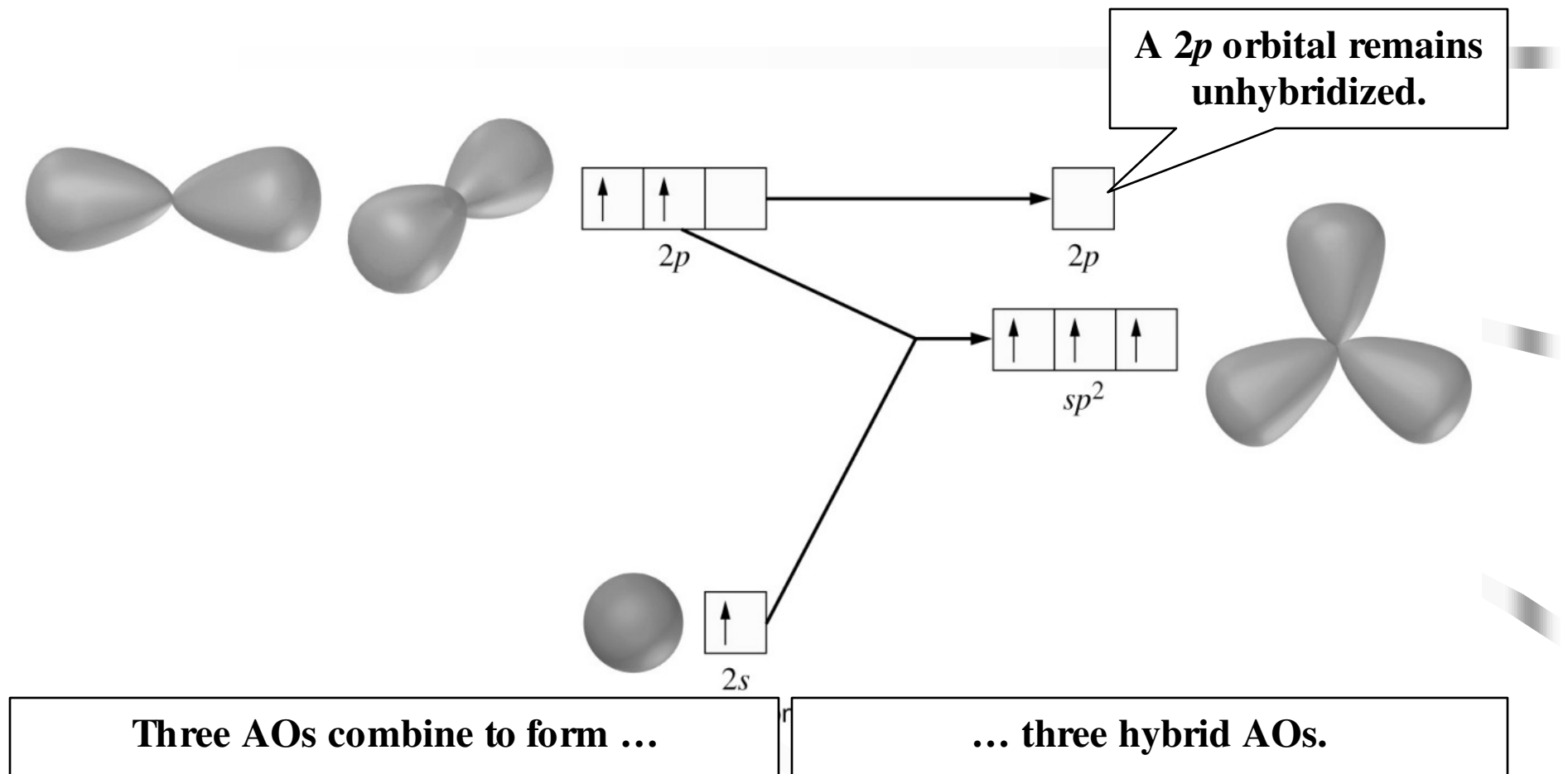In methane, each hybrid orbital is a bonding orbital
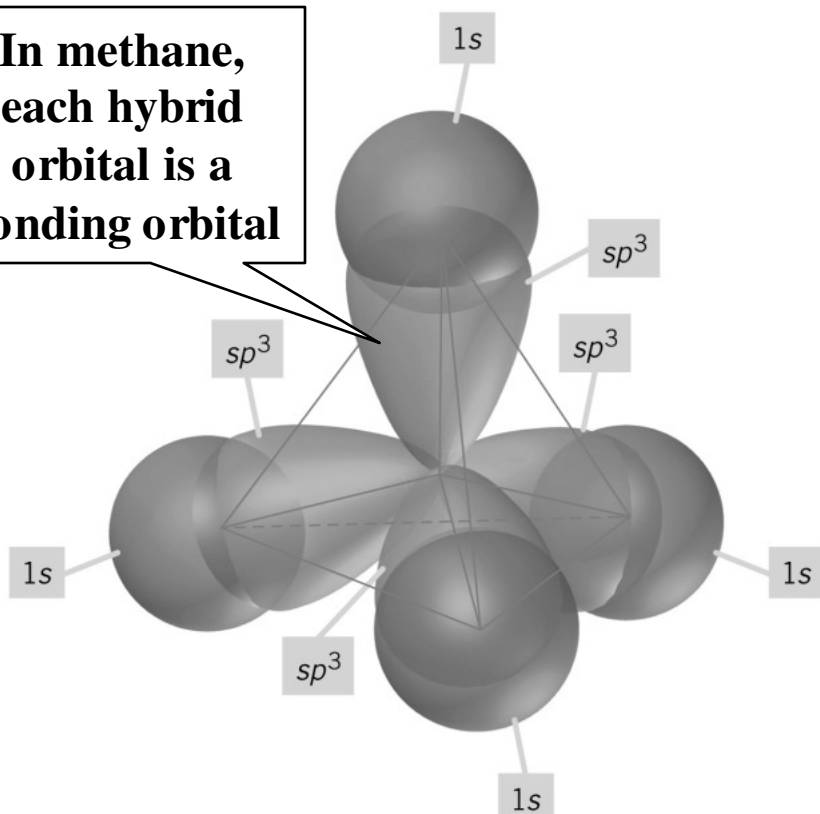
Four sp^3 hybrid orbitals: tetrahedral
Four electron groups: tetrahedral
Coincidence? Hardly.

In ammonia, one of the hybrid orbitals contains the lone pair that is on the nitrogen atom
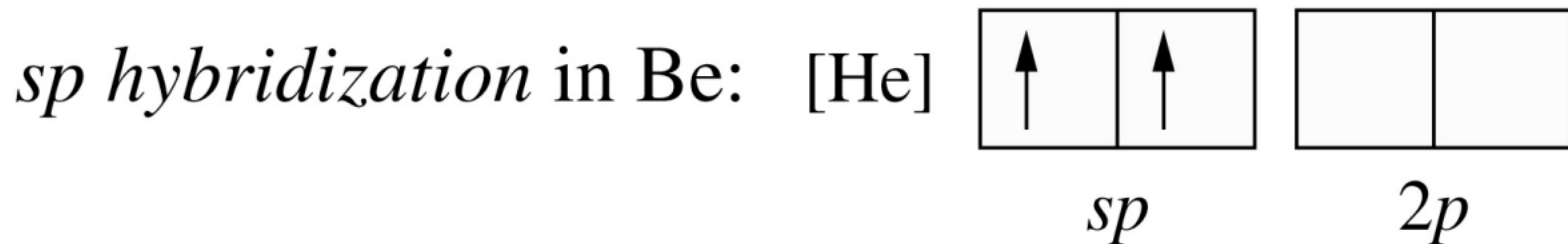
sp^2 *hybridization*

- 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.

sp^2 *hybridization* in **B**:   [He] ↑ ↑ ↑ □
                                                    sp^2 $2p$

The sp² hybridization scheme in boron

A **2p** orbital remains unhybridized.

2p

sp²

2p

2s

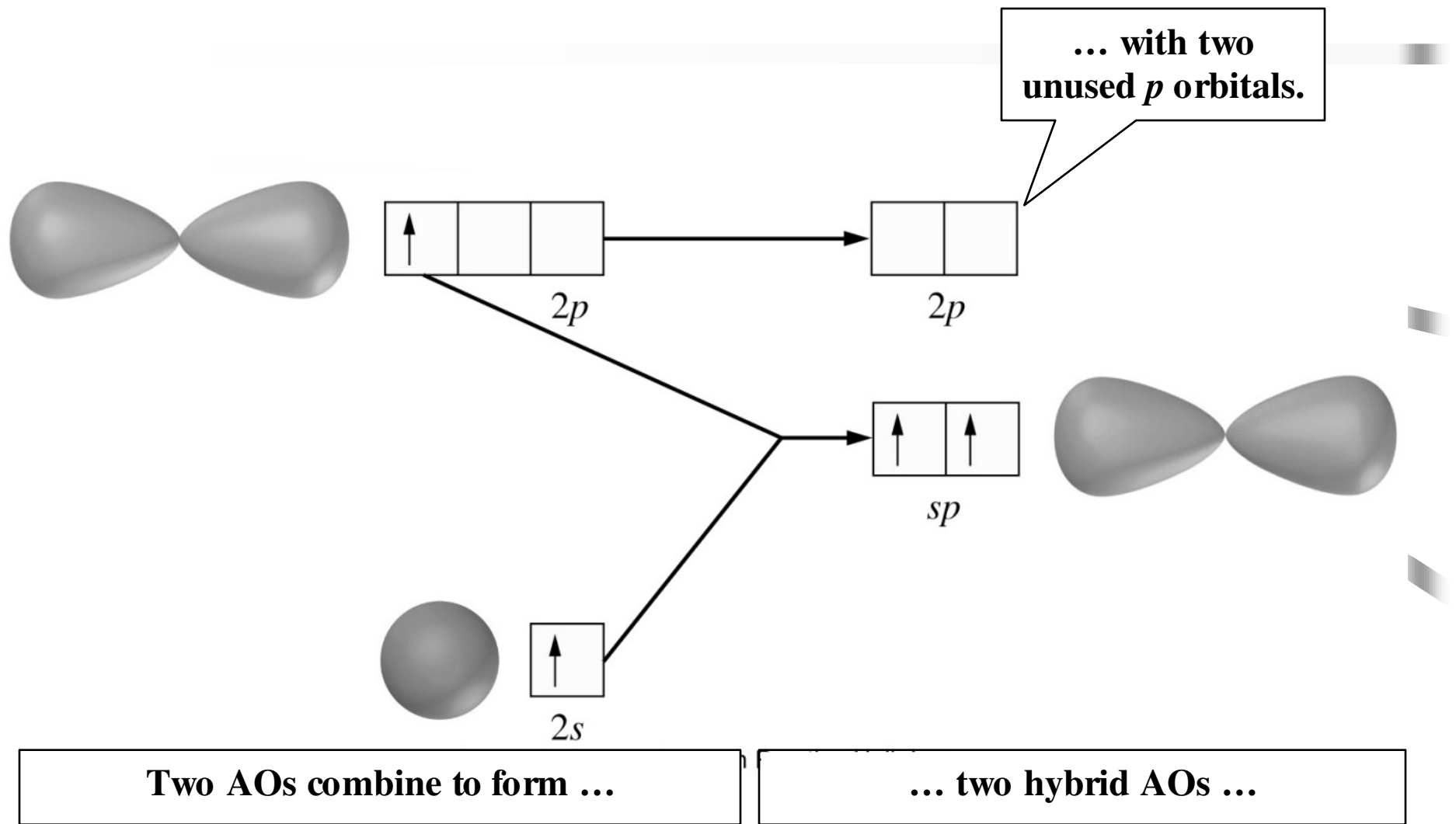| Three AOs combine to form … | … three hybrid AOs. |

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:**   [He]   ↑ ↑   sp   2p

sp *hybridization in Be*

… with two unused *p* orbitals.

2p

2p

sp

2s

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 **sp³d** hybrid orbitals.

- This hybridization scheme gives trigonal bipyramidal electron-group geometry.
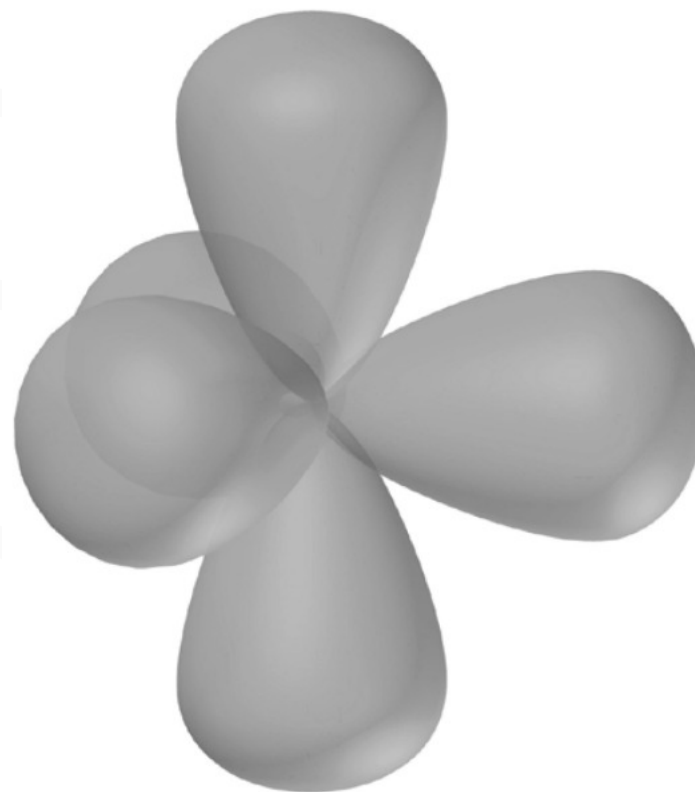
Hybrid orbitals involving d subshells (cont'd)

- By hybridizing one *s*, three *p*, and two *d* orbitals, we get five **sp^3d^2** hybrid orbitals.

- This hybridization scheme gives octahedral geometry.
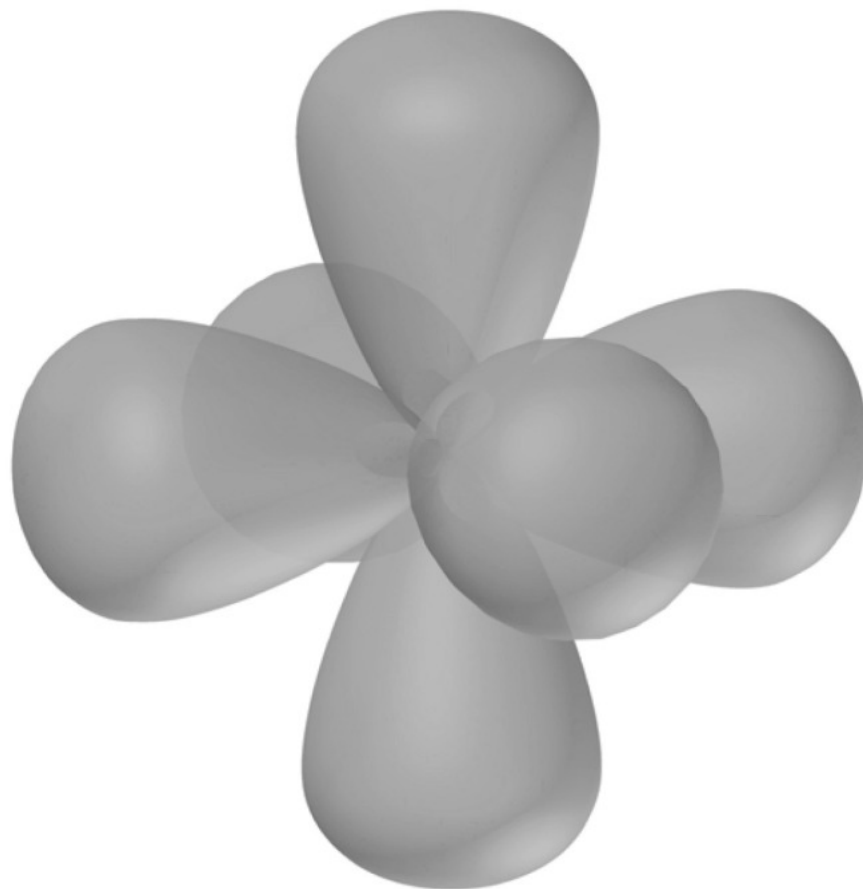
Predicting hybridization schemes

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

sp^3d^2 *hybridization* in I:

↑↓	↑	↑	↑	↑	↑			

sp^3d^2 5d

- 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.
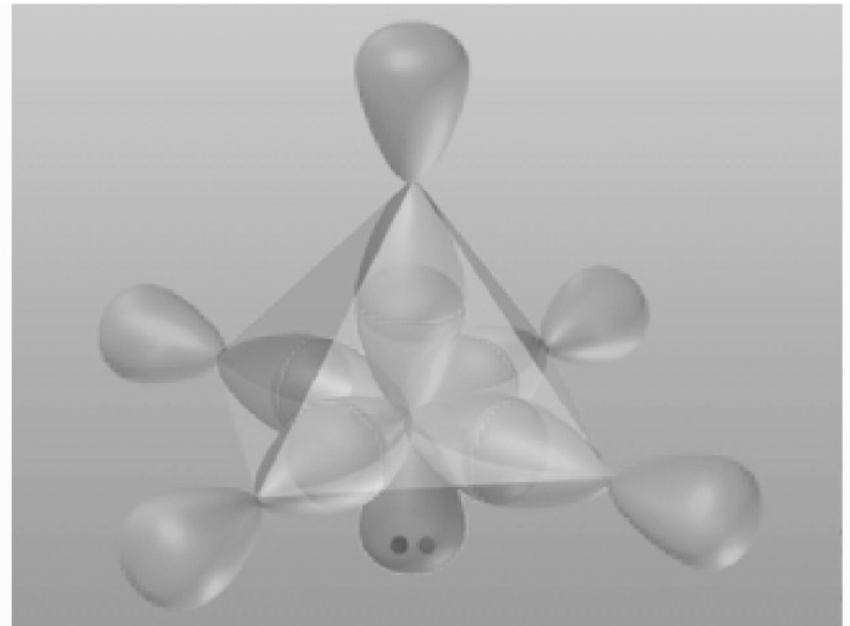
▲ FIGURE 10.19   **Bonding scheme for iodine pentafluoride, IF_5**
The orbitals around the central I atom are six sp^3d^2 hybrid orbitals. One of them (red) is occupied by the LP electrons. The other five are the bonding orbitals. Each bond involves the overlap of an I sp^3d^2 hybrid orbital with a $2p$ 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

- 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.
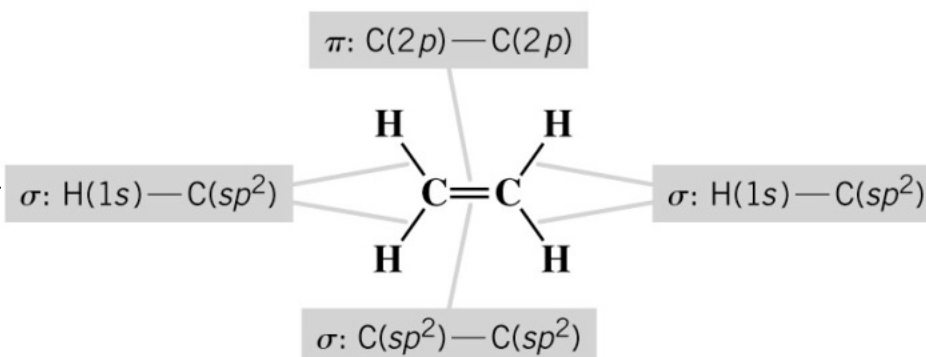
VB theory for ethylene, C_2H_4
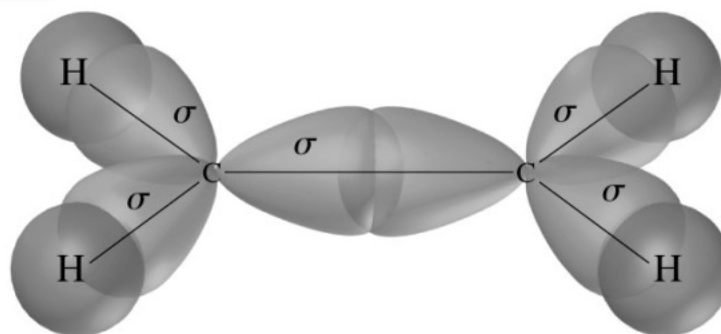
(a) The σ-bond framework

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

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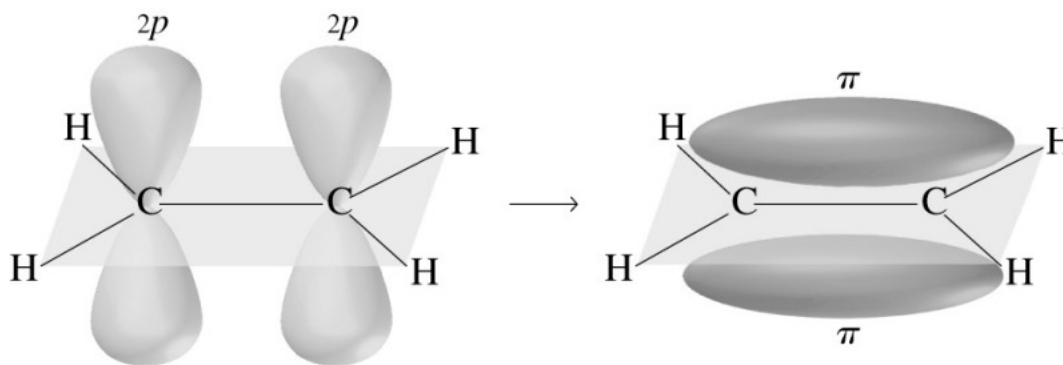
(b) The formation of a π-bond by the overlap of the half-filled $2p$ orbitals

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

π: C($2p$) — C($2p$)

σ: H($1s$) — C(sp^2)   C=C σ: H($1s$) — C(sp^2)

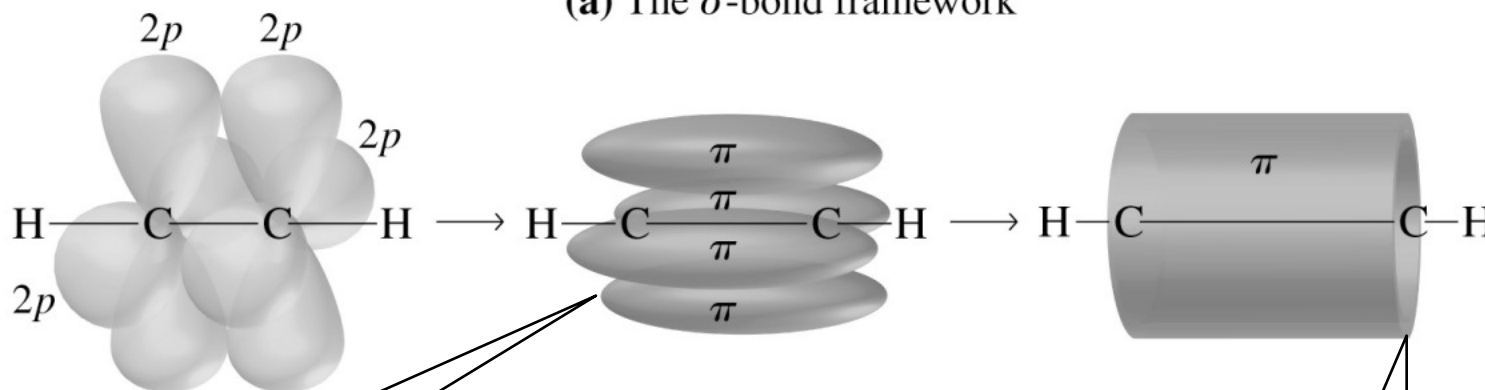σ: C(sp^2) — C(sp^2)

(c) Hybridization and bonding scheme

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VB theory for acetylene, C_2H_2
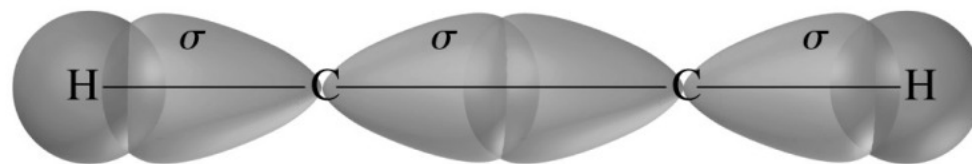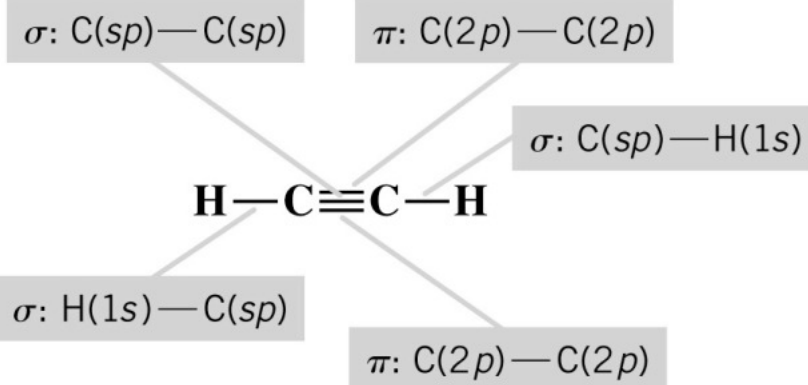

(a) The σ-bond framework

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

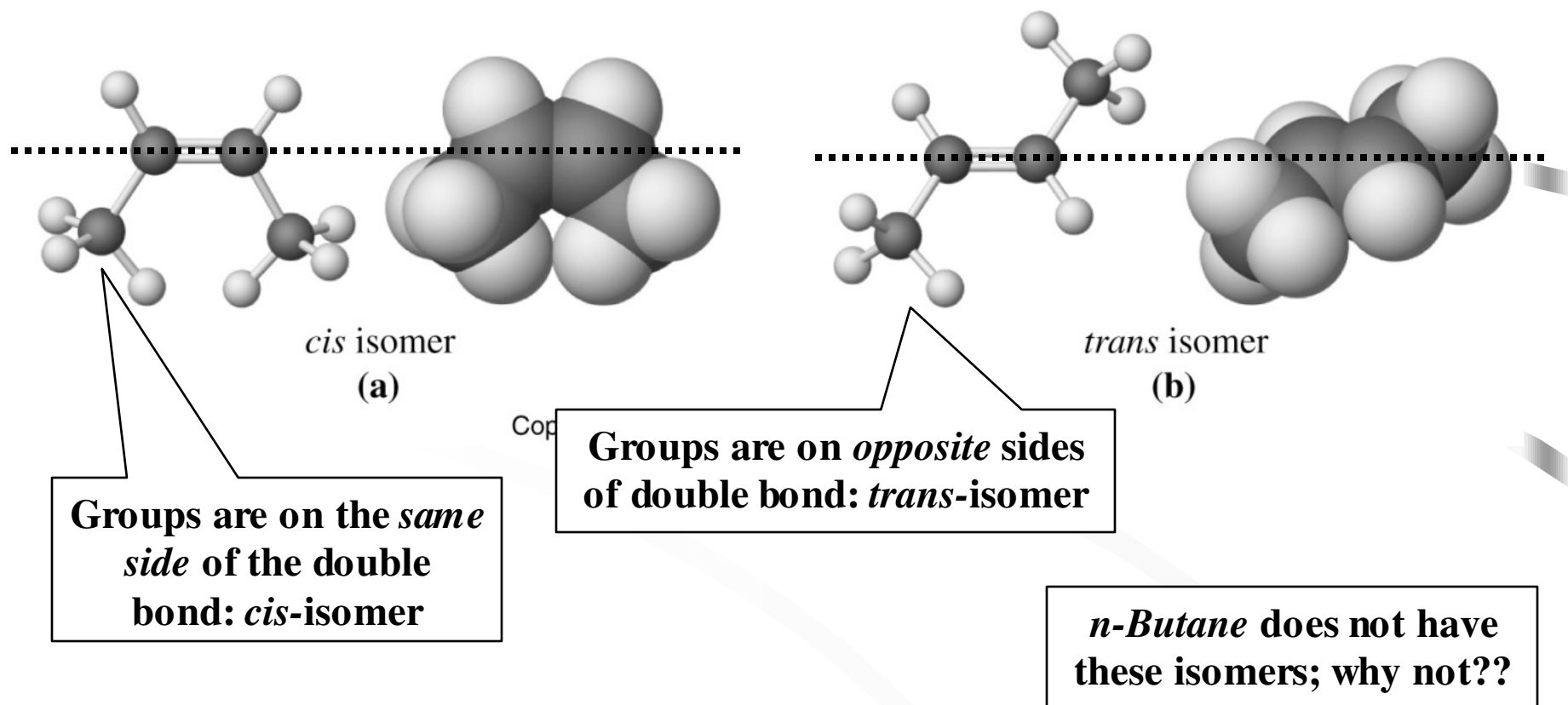Two π-bonds (above and below, and front and back) from $2p$–$2p$ overlap …

σ: C(sp)—C(sp)   π: C($2p$)—C($2p$)

σ: C(sp)—H($1s$)

H—C≡C—H

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

σ: H($1s$)—C(sp)

π: C($2p$)—C($2p$)

(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?
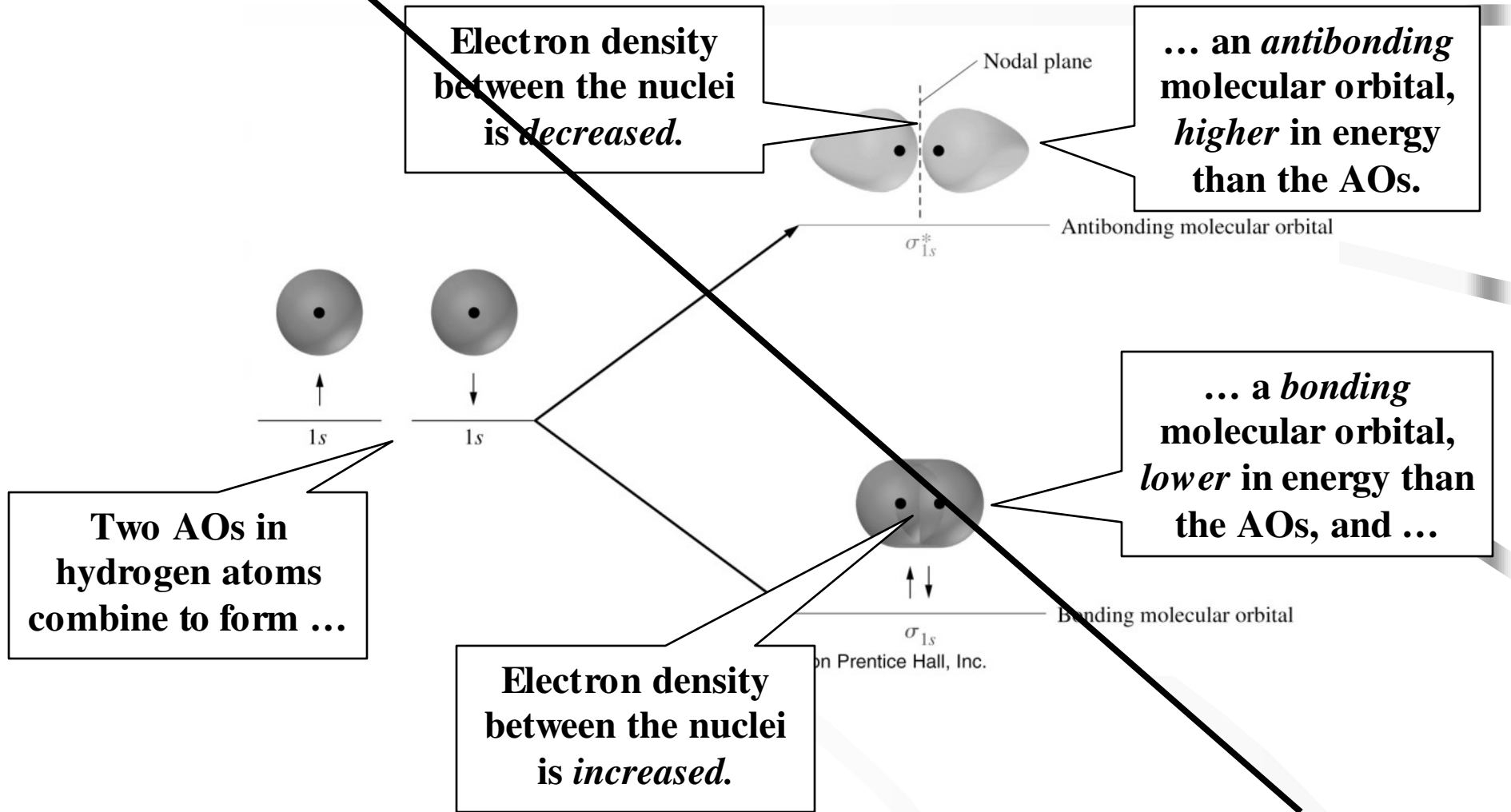
Molecular orbital theory (MO theory)

- 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.
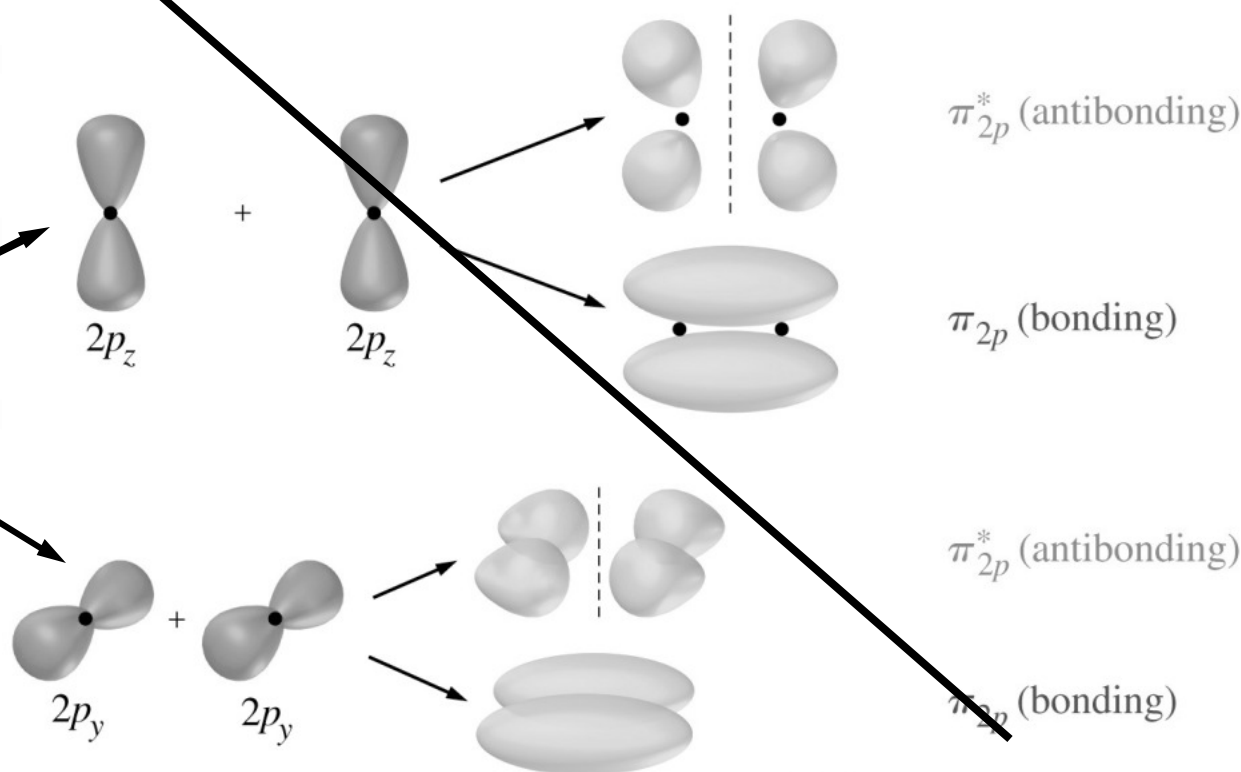- There are *nonbonding* orbitals which we will not discuss.

Types of MOs

Electron density between the nuclei is *decreased.*

Nodal plane

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

Antibonding molecular orbital

σ^*_{1s}

$1s$

$1s$

Two AOs in hydrogen atoms combine to form ...

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

Bonding molecular orbital

σ_{1s}

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Electron density between the nuclei is *increased.*

Homonuclear diatomic molecules of the second period elements

The two p_x orbitals combine to form *sigma* bonding and antibonding MOs.
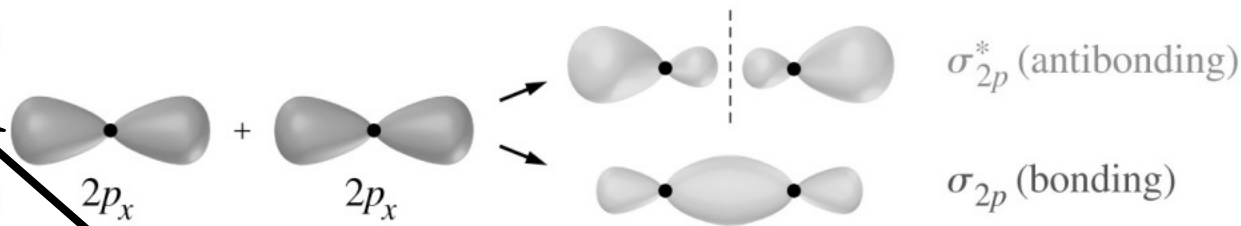
The two p_y orbitals and the two p_z orbitals give *pi* bonding and antibonding MOs.

$2p_x$ + $2p_x$ → σ^*_{2p} (antibonding), σ_{2p} (bonding)

$2p_z$ + $2p_z$ → π^*_{2p} (antibonding), π_{2p} (bonding)

$2p_y$ + $2p_y$ → π^*_{2p} (antibonding), π_{2p} (bonding)

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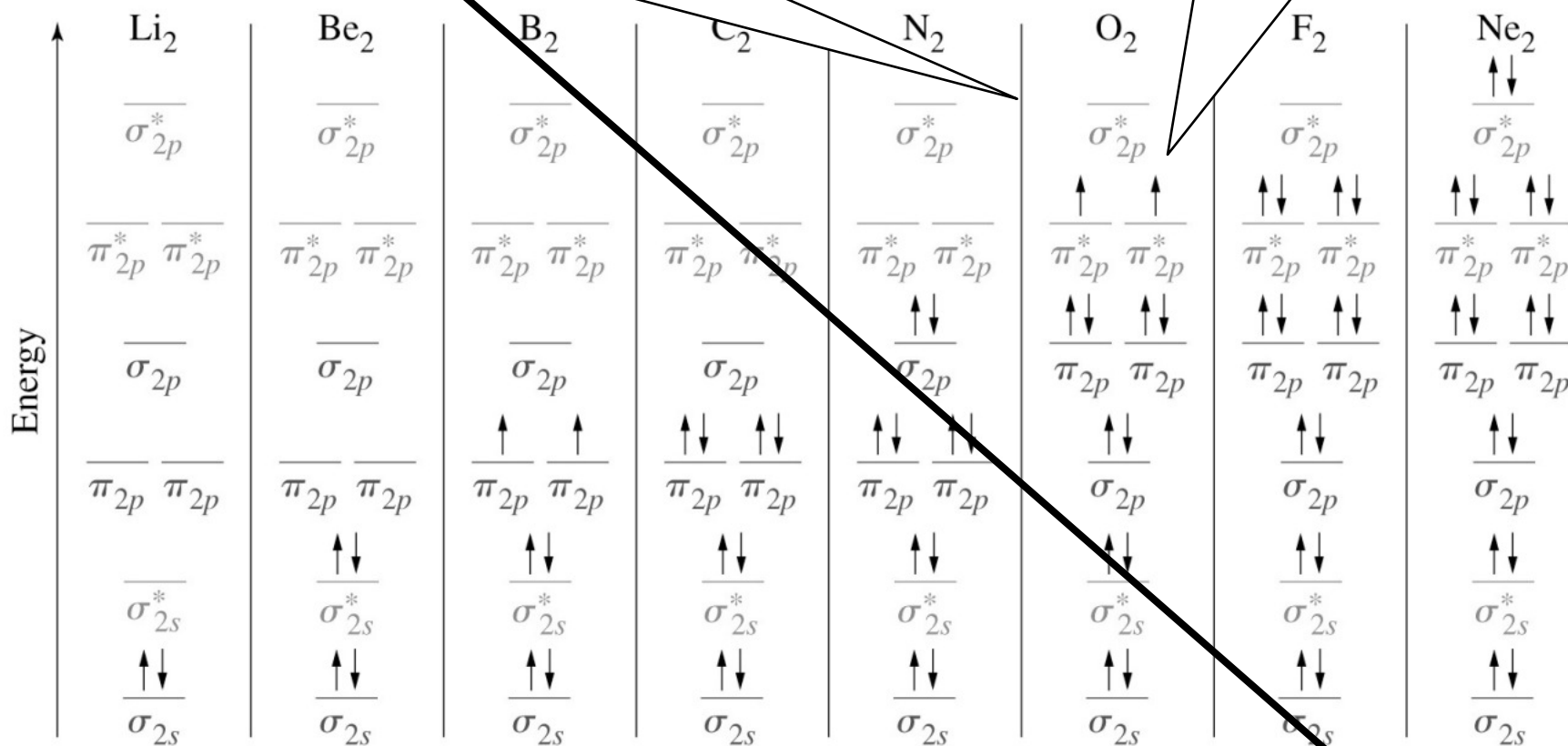
Electrons fill MOs in the same way that AOs are filled – lowest energy to highest energy.

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.
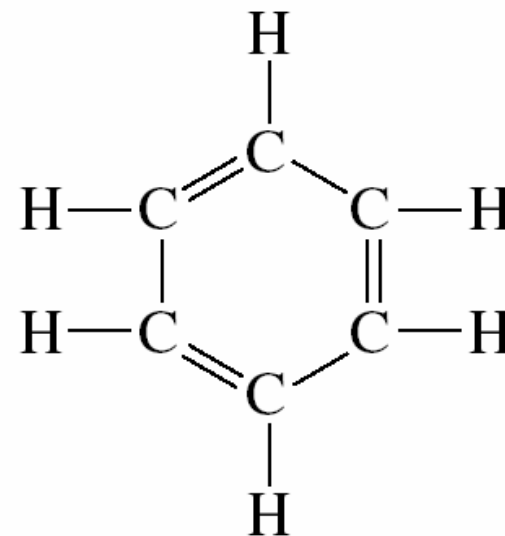
- Modern view: there are two resonance hybrids of benzene.

- The pi-electrons are not localized between any particular carbon atoms, but are **delocalized** among all six carbon atoms.
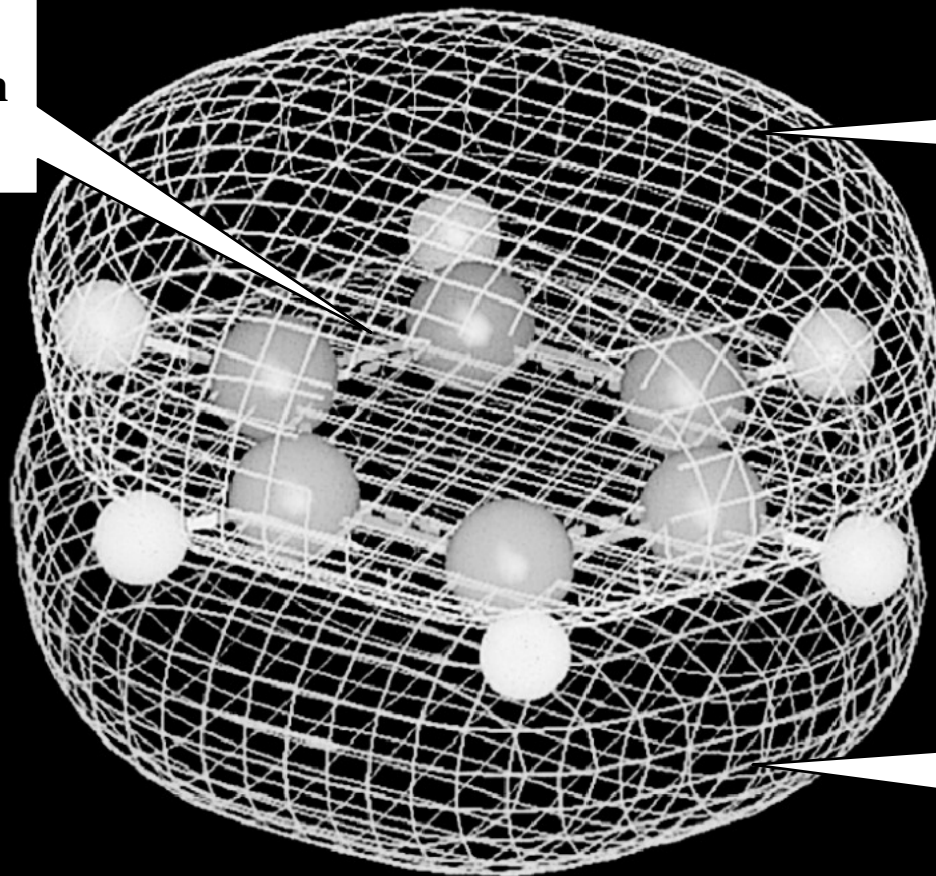
The σ-bonding framework in benzene
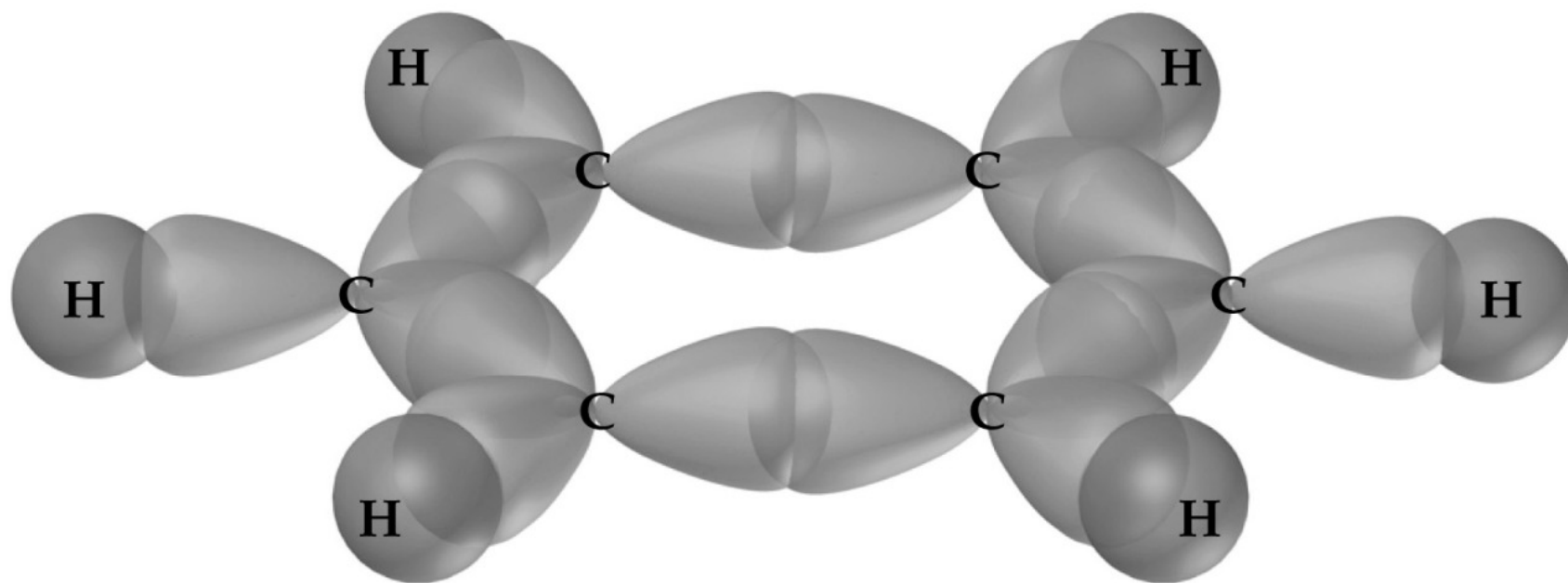
The π-bonding framework in benzene
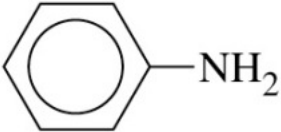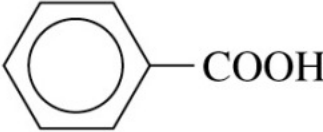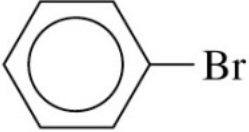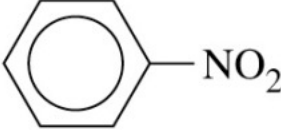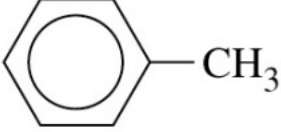
TABLE 10.3 Some Representative Aromatic Compounds

| Name	Structure	Typical Use(s)
Aniline	$\bigcirc$—NH$_2$	Starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
Benzoic acid	$\bigcirc$—COOH	Food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
Bromobenzene	$\bigcirc$—Br	Starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
Nitrobenzene	$\bigcirc$—NO$_2$	Starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
Phenol	$\bigcirc$—OH	Disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
Toluene	$\bigcirc$—CH$_3$	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 (+).
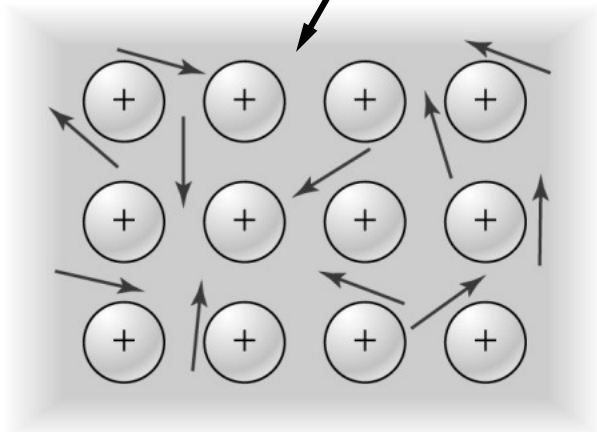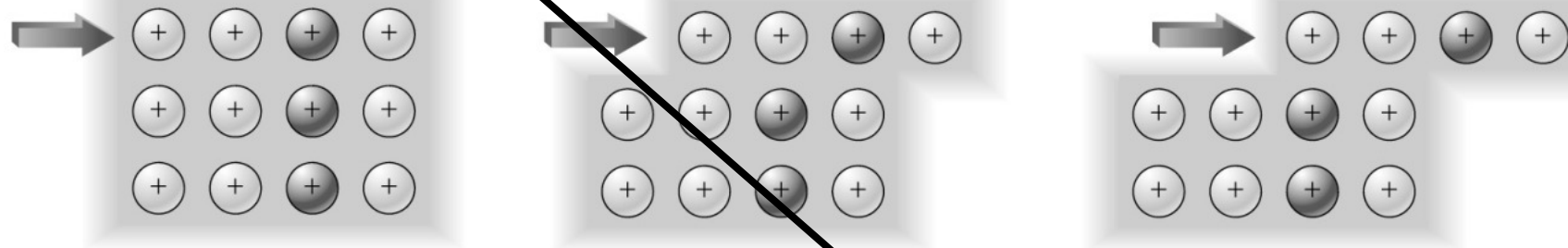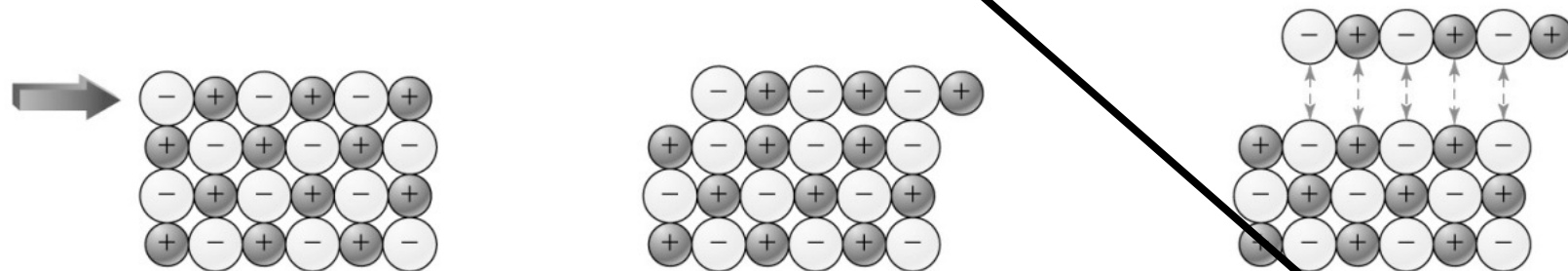
(a)
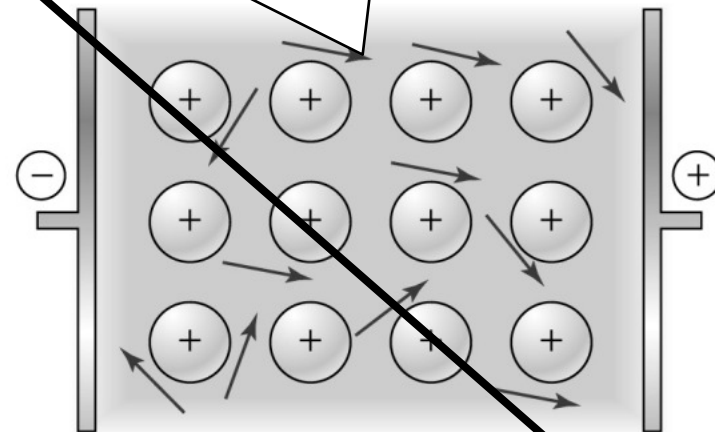
(b)

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.
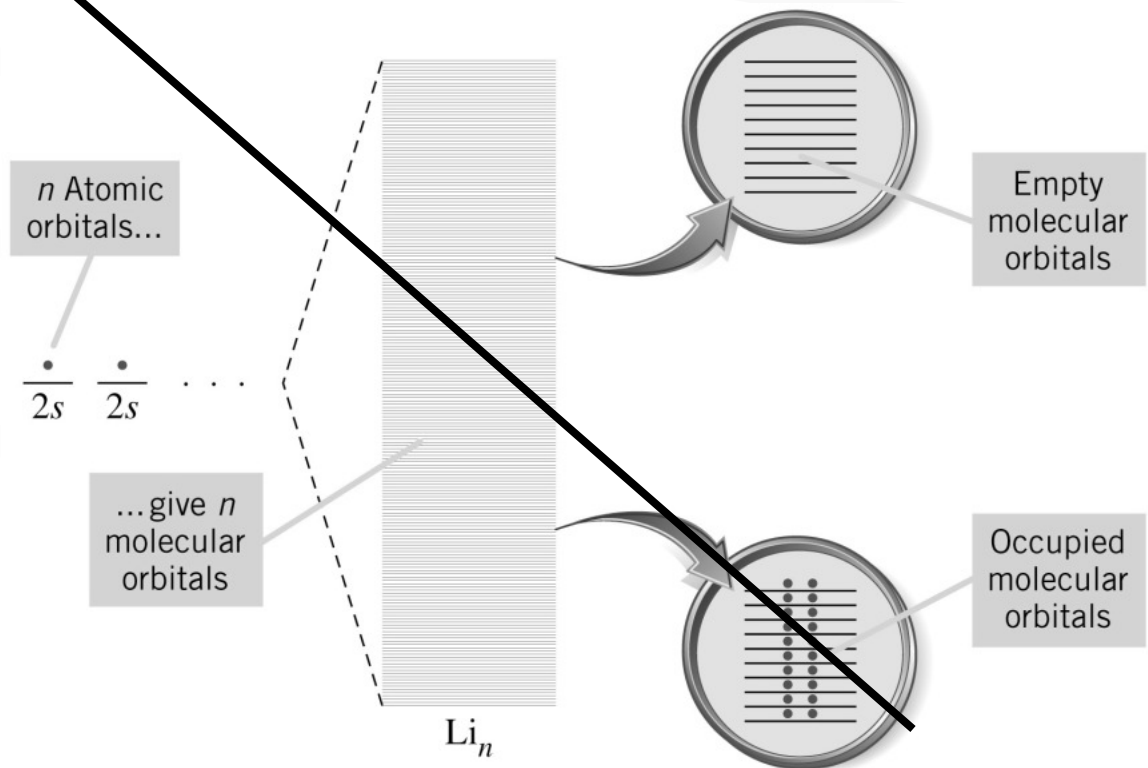

(a) Metal

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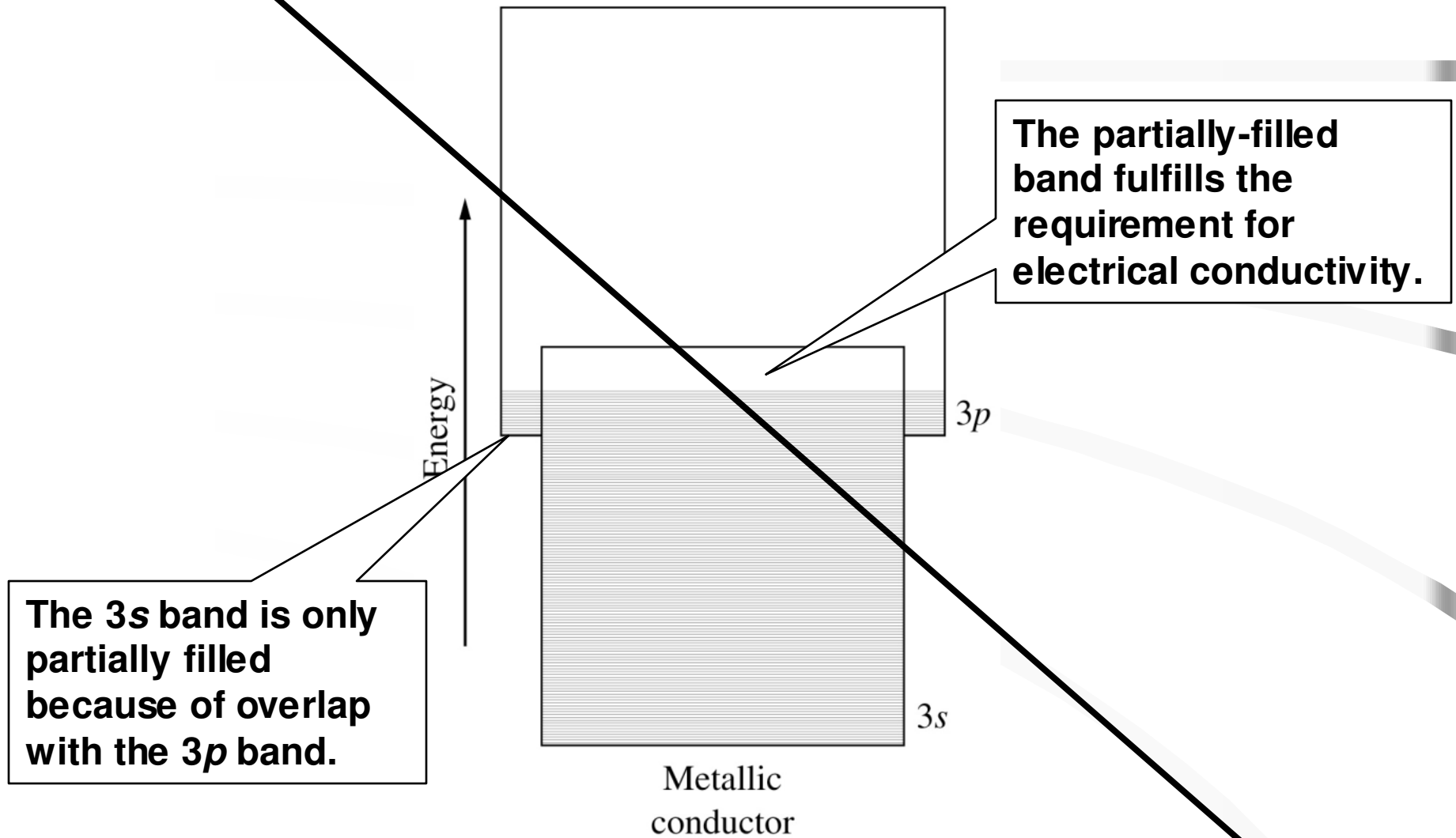
The spacing between electron energy levels is so minute in metals that the levels essentially merge into a *band*.

n Atomic orbitals...

$\overline{\underset{2s}{\bullet}} \quad \overline{\underset{2s}{\bullet}} \quad \cdots$

...give *n* molecular orbitals

Empty molecular orbitals

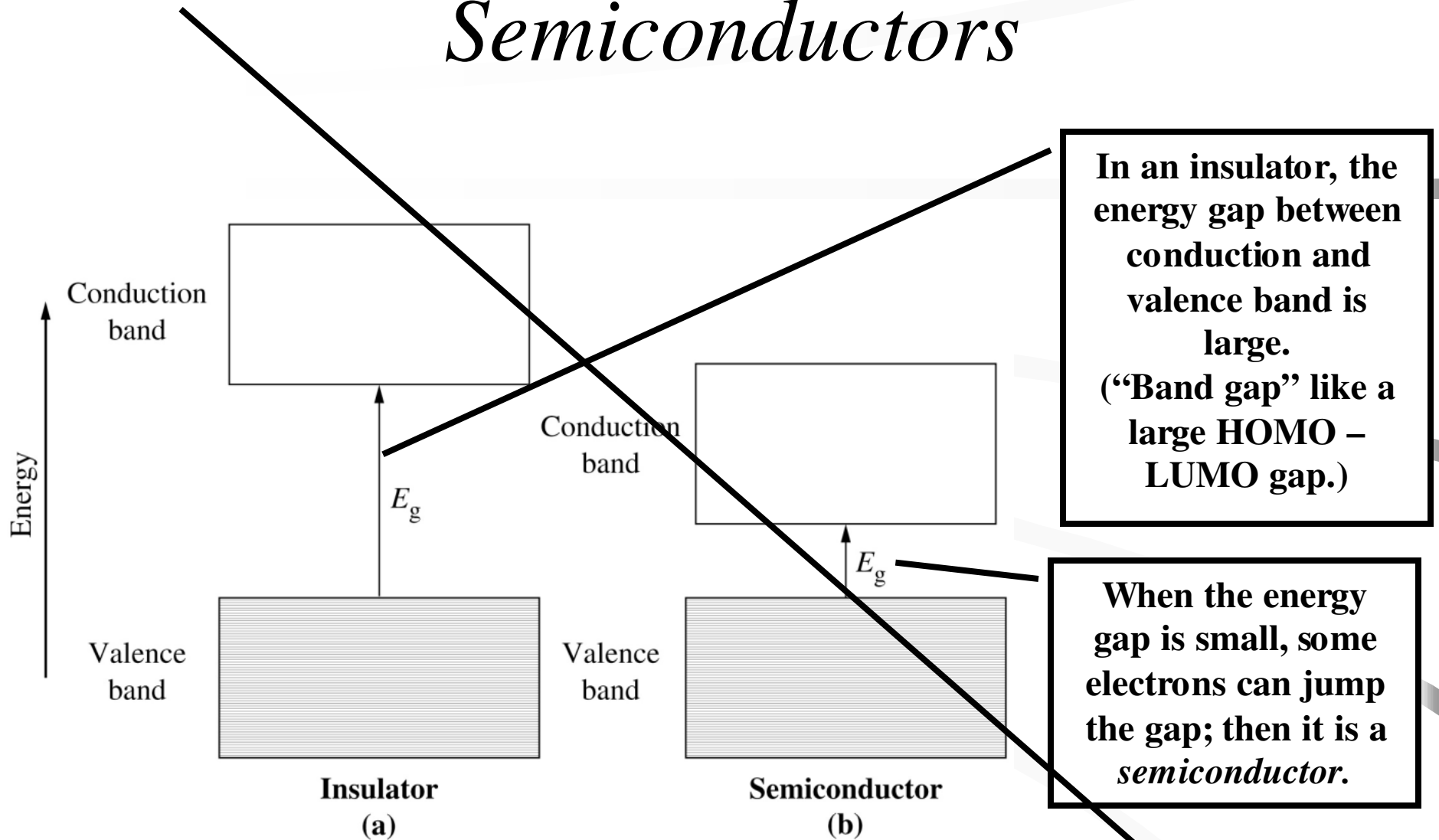Occupied molecular orbitals

Li_n

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

3p

3s

Metallic
conductor

Energy

Semiconductors

Conduction band

Energy

E_g

Valence band

Insulator
(a)

Conduction band

E_g

Valence band

Semiconductor
(b)

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*.

the end