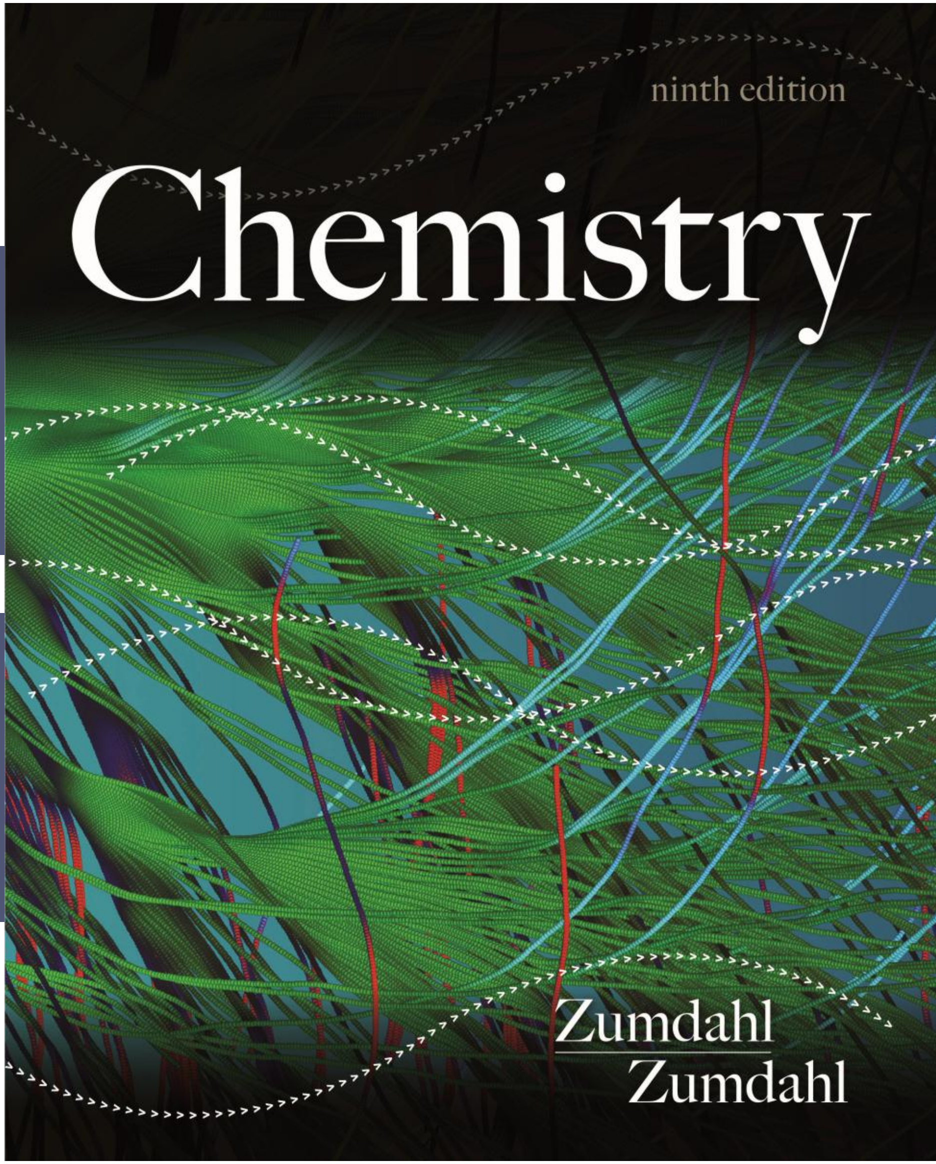

Chapter 7

Atomic Structure and Periodicity

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Electromagnetic Radiation

- One of the means by which energy travels through space
- Exhibits wavelike behavior
- Travels at the speed of light in a vacuum

Characteristics of Waves

- **Wavelength** (λ): Distance between two consecutive peaks or troughs in a wave
- **Frequency** (ν): Number of waves (cycles) per second that pass a given point in space
- Speed of light (c) = 2.9979×10^8 m/s

Relationship between Wavelength and Frequency

- Short-wavelength radiation has a higher frequency when compared to long-wavelength radiation
  - This implies an inverse relationship between wavelength and frequency

$$\lambda \propto 1/\nu \qquad \text{Or} \qquad \lambda\nu = c$$

    - λ - Wavelength in meters
    - ν - Frequency in cycles per second
    - c - Speed of light (2.9979×10^8 m/s)

Figure 7.1 - The Nature of Waves

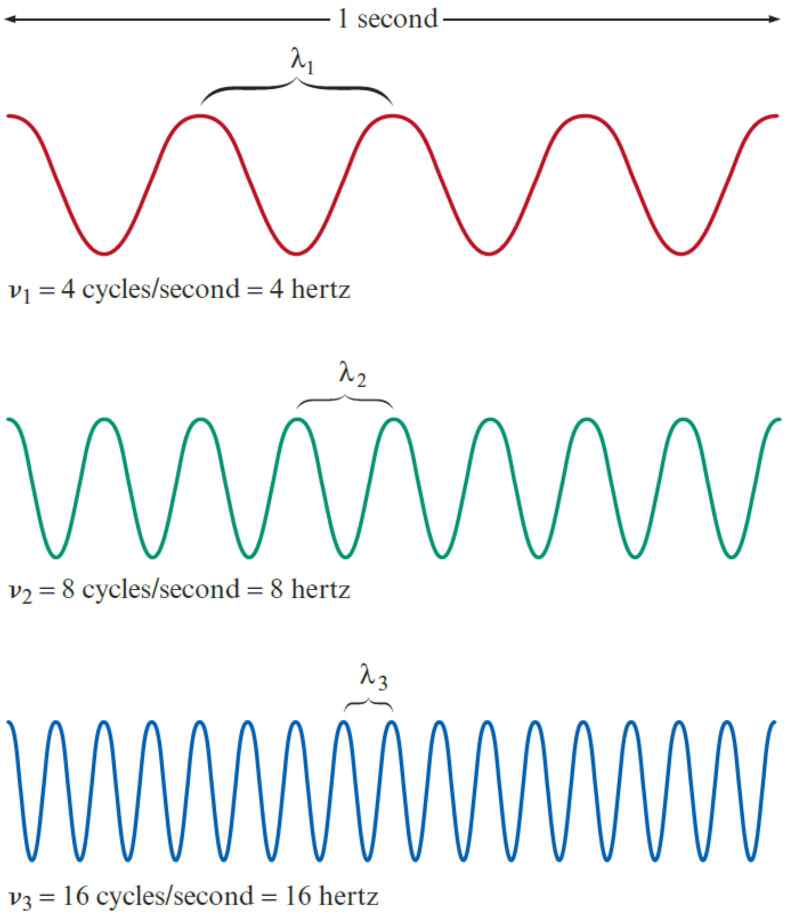
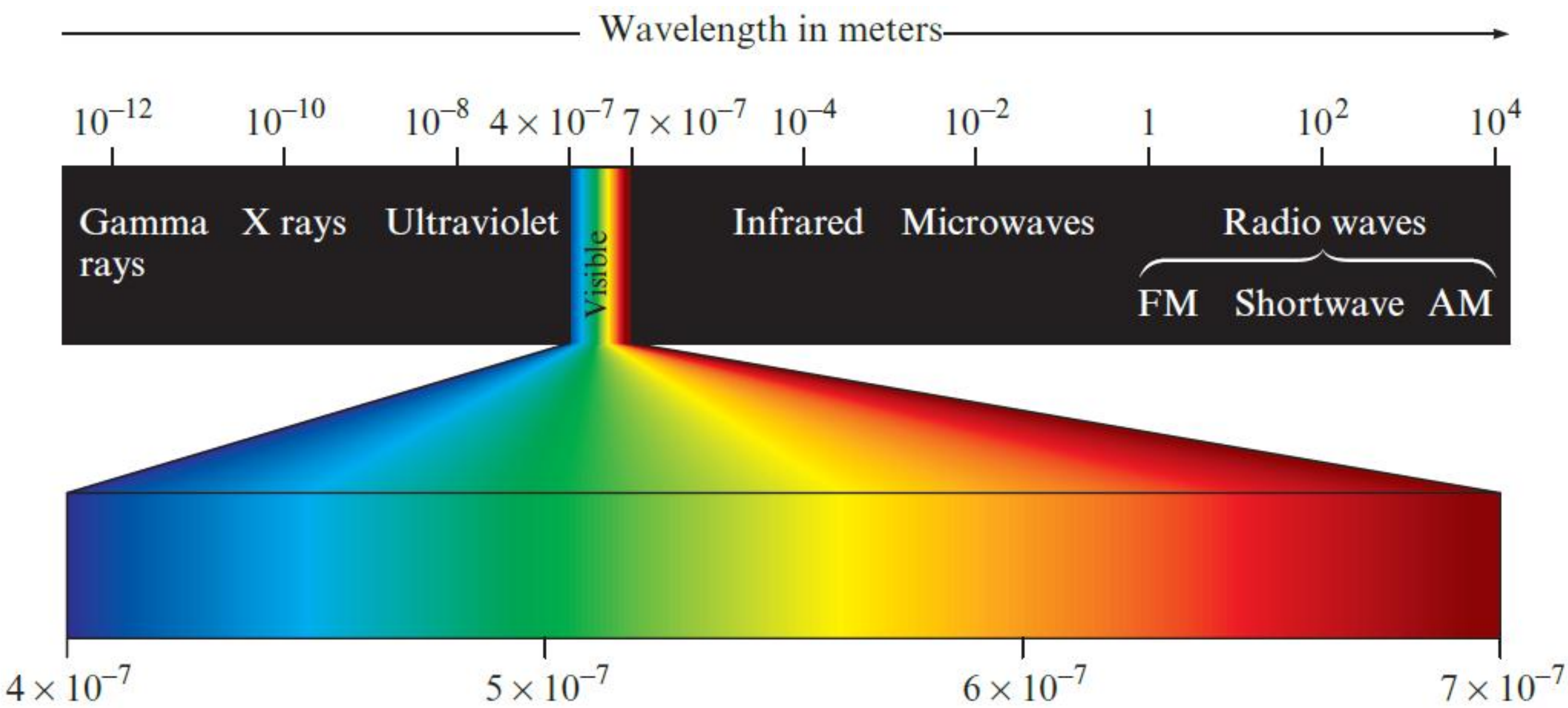


Figure 7.2 - Classification of Electromagnetic Radiation



Interactive Example 7.1 - Frequency of Electromagnetic Radiation

- The brilliant red colors seen in fireworks are due to the emission of light with wavelengths around 650 nm when strontium salts such as $Sr(NO_3)_2$ and $SrCO_3$ are heated
  - This can be easily demonstrated in the lab by dissolving one of these salts in methanol that contains a little water and igniting the mixture in an evaporating dish
  - Calculate the frequency of red light of wavelength 6.50×10^2 nm

Interactive Example 7.1 - Solution

- We can convert wavelength to frequency using the following equation:

$$\lambda\nu = c \quad \text{or} \quad \nu = \frac{c}{\lambda}$$

  - Where,
    - $c = 2.9979 \times 10^8$ m/s
    - $\lambda = 6.50 \times 10^2$ nm

Interactive Example 7.1 - Solution (Continued)

- Changing the wavelength to meters, we have

$$6.50 \times 10^{2}\ \cancel{\text{nm}} \times \frac{1\ \text{m}}{10^{9}\ \cancel{\text{nm}}} = 6.50 \times 10^{-7}\ \text{m}$$

- And

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^{8}\ \cancel{\text{m}}/\text{s}}{6.50 \times 10^{-7}\ \cancel{\text{m}}}$$

$$= 4.61 \times 10^{14}\ \text{s}^{-1}$$

$$= 4.61 \times 10^{14}\ \text{Hz}$$

Max Planck

- Postulated that energy can be gained or lost only in whole-number multiples of $h\nu$
  - **Planck's constant** = h = 6.626×10^{-34} J · s
  - Change in energy (ΔE) can be represented as follows:

$$\Delta E = nh\nu$$

    - n - Integer
    - h - Planck's constant
    - ν - Frequency of electromagnetic radiation absorbed or emitted

Conclusions from Planck's Postulate

- Energy is **quantized** and can occur in discrete units of $h\nu$
  - Quantum - A packet of energy
    - A system can transfer energy only in whole quanta
    - Energy seems to have particulate properties

Interactive Example 7.2 - The Energy of a Photon

- The blue color in fireworks is often achieved by heating copper(I) chloride (CuCl) to about 1200° C
  - Then the compound emits blue light having a wavelength of 450 nm
  - What is the increment of energy (the quantum) that is emitted at 4.50×10^2 nm by CuCl?

Interactive Example 7.2 - Solution

- The quantum of energy can be calculated from the following equation:

$$\Delta E = h\nu$$

  - The frequency ν for this case can be calculated as follows:

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^{8} \cancel{\text{m}}/\text{s}}{4.50 \times 10^{-7} \cancel{\text{m}}} = 6.66 \times 10^{14} \text{ s}^{-1}$$

Interactive Example 7.2 - Solution (Continued)

- Therefore,

$$\Delta E = h\nu = \left(6.626 \times 10^{-34}\ \text{J} \cdot \cancel{\text{s}}\right)\left(6.66 \times 10^{14}\ \cancel{\text{s}^{-1}}\right)$$

$$= 4.41 \times 10^{-19}\ \text{J}$$

- A sample of CuCl emitting light at 450 nm can lose energy only in increments of 4.41×10^{-19} J, the size of the quantum in this case

Albert Einstein

- Proposed that electromagnetic radiation is a stream of particles called **photons**
  - The energy of each photon is given by:

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

    - h - Planck's constant
    - ν - Frequency of radiation
    - λ - Wavelength of radiation

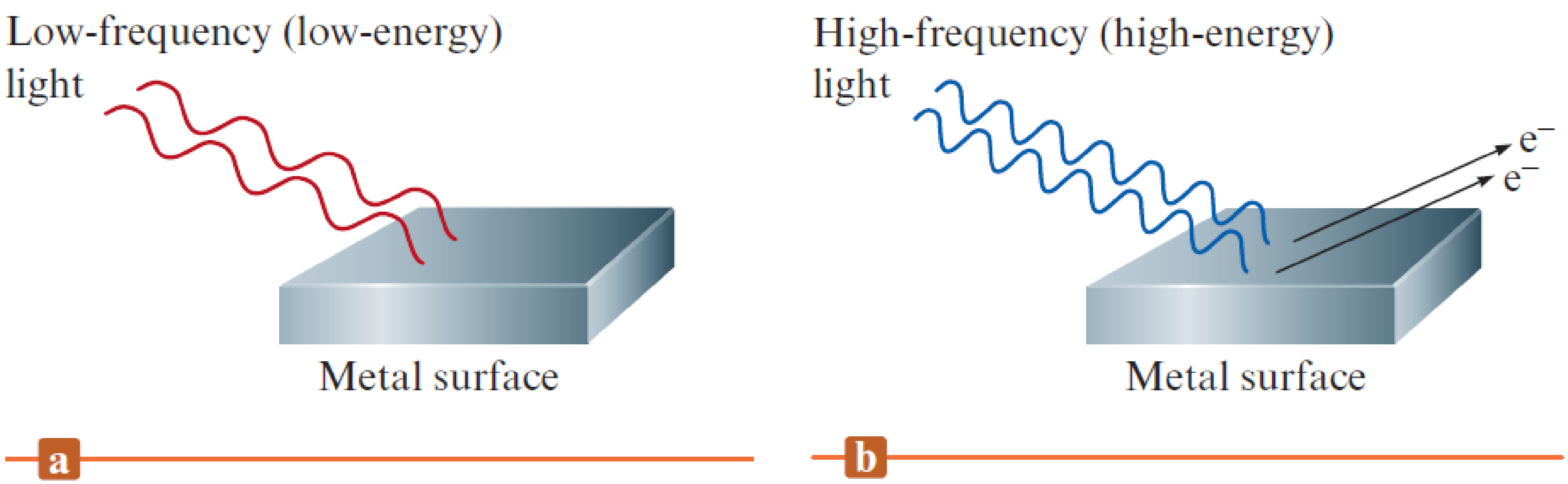
Photoelectric Effect

- Phenomenon in which electrons are emitted from the surface of a metal when light strikes it
- Observations
  - When frequency of light is varied, no electrons are emitted by a given metal below the threshold frequency (ν_0)
  - When $\nu < \nu_0$, no electrons are emitted, regardless of the intensity of the light

Photoelectric Effect (Continued 1)

- When $v > v_0$:
  - The number of electrons emitted increases with the intensity of the light
  - The kinetic energy (KE) of the emitted electrons increases linearly with the frequency of the light
- Assumptions
  - Electromagnetic radiation is quantized
  - v_0 represents the minimum energy required to remove the electron from the surface of the metal

Figure 7.4 - The Photoelectric Effect



Photoelectric Effect (Continued 2)

- Minimum energy required to remove an electron $= E_0 = h\nu_0$
- When $\nu > \nu_0$, energy in excess of that required to remove the electron is given to the electron as kinetic energy (KE)

$$\mathrm{KE}_{\text{electron}} = \frac{1}{2}m\upsilon^2 = h\nu - h\nu_0$$

Photoelectric Effect (Continued 3)

- Here,
  - m - Mass of electron
  - v^2 - Velocity of electron
  - $h\nu$ - Energy of incident photon
  - $h\nu_0$ - Energy required to remove electron from metal’s surface

Einstein's Theory of Relativity

- Einstein proposed that energy has mass

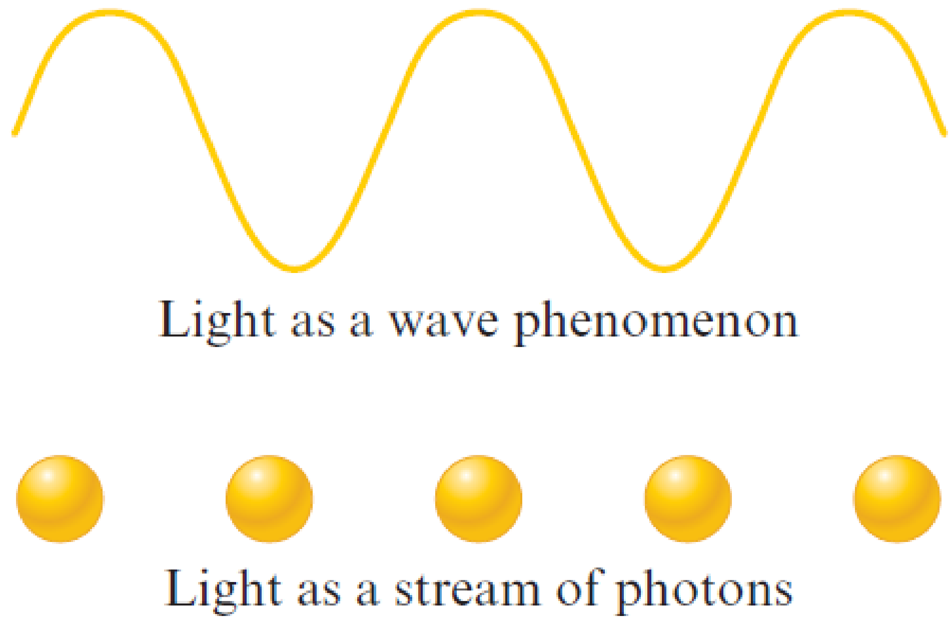
$$E = mc^2$$

  - When rearranged, this relation can be used to determine the mass associated with a quantity of energy

$$m = \frac{E}{c^2}$$

Dual Nature of Light

- Electromagnetic radiation exhibits wave and particulate properties



Louis de Broglie

- Ascertained if matter that is assumed to be particulate exhibits wave properties

$$m = \frac{h}{\lambda \nu}$$

Relationship between mass and wavelength for electromagnetic radiation

  - Rearranging to solve for λ gives de Broglie's equation
    - de Broglie's equation is used to calculate the wavelength of a particle

$$\lambda = \frac{h}{m\nu}$$

Interactive Example 7.3 - Calculations of Wavelength

- Compare the wavelength for an electron (mass = 9.11×10^{-31} kg) traveling at a speed of 1.0×10^{7} m/s with that for a ball (mass = 0.10 kg) traveling at 35 m/s

Interactive Example 7.3 - Solution

- We use the equation $\lambda = h/mv$, where
  - $h = 6.626 \times 10^{-34}$ J · s or 6.626×10^{-34} kg · m²/s
- Since 1 J = 1 kg · m²/s²:
  - For the electron,

$$\lambda_e = \frac{6.626 \times 10^{-34} \dfrac{\cancel{\text{kg}} \cdot \cancel{\text{m}} \cdot \text{m}}{\cancel{\text{s}}}}{\left(9.11 \times 10^{-31} \ \cancel{\text{kg}}\right)\left(1.0 \times 10^{7} \ \cancel{\text{m}} / \cancel{\text{s}}\right)} = 7.27 \times 10^{-11} \text{ m}$$

Interactive Example 7.3 - Solution (Continued)

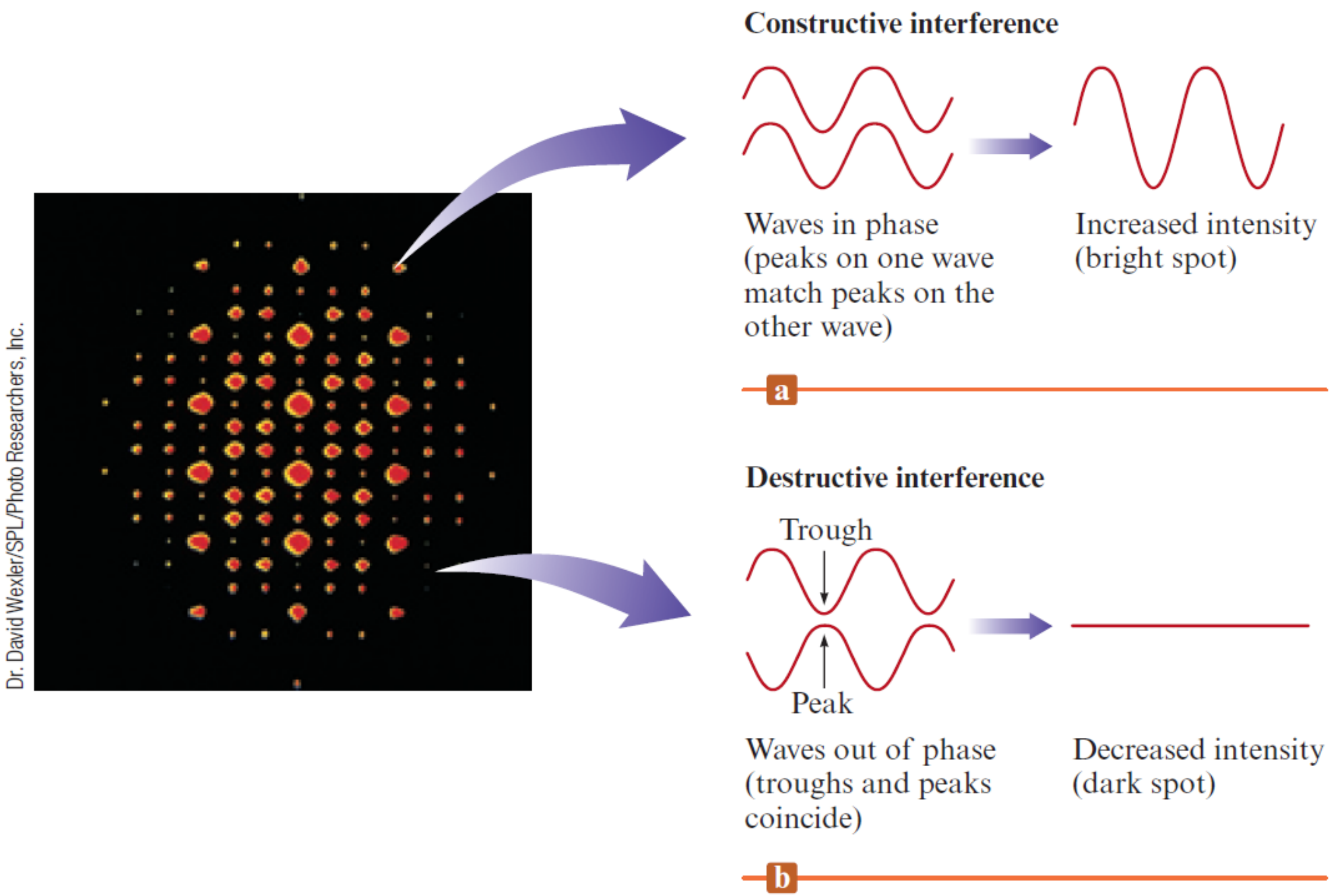
- For the ball,

$$\lambda_b = \frac{6.626 \times 10^{-34} \dfrac{\cancel{\text{kg}} \cdot \cancel{\text{m}} \cdot \text{m}}{\cancel{\text{s}}}}{\left(0.10 \ \cancel{\text{kg}}\right)\left(35 \ \cancel{\text{m}}/\cancel{\text{s}}\right)} = 1.9 \times 10^{-34} \ \text{m}$$

Diffraction

- Results when light is scattered from a regular array of points or lines
    - Colors result from various wavelengths of visible light that are not scattered in the same way
- Scattered radiation produces a **diffraction pattern** of bright spots and dark areas on a photographic plate
    - Explained in terms of waves

Figure 7.6 - Diffraction Pattern of a Beryl Crystal



Emission Spectrum of the Hydrogen Atom

- When a sample of hydrogen gas receives a high-energy spark, the H_2 molecules absorb energy, and some H—H bonds are broken
  - Resulting hydrogen atoms are excited
    - Atoms contain excess energy that is released by emitting light of various wavelengths to produce an emission spectrum

Continuous and Line Spectra

- **Continuous spectrum**: Results when white light is passed through a prism
  - Contains all the wavelengths of visible light
- **Line spectrum**: Shows only certain discrete wavelengths
  - Example - Hydrogen emission spectrum

Figure 7.7 (a) - A Continuous Spectrum

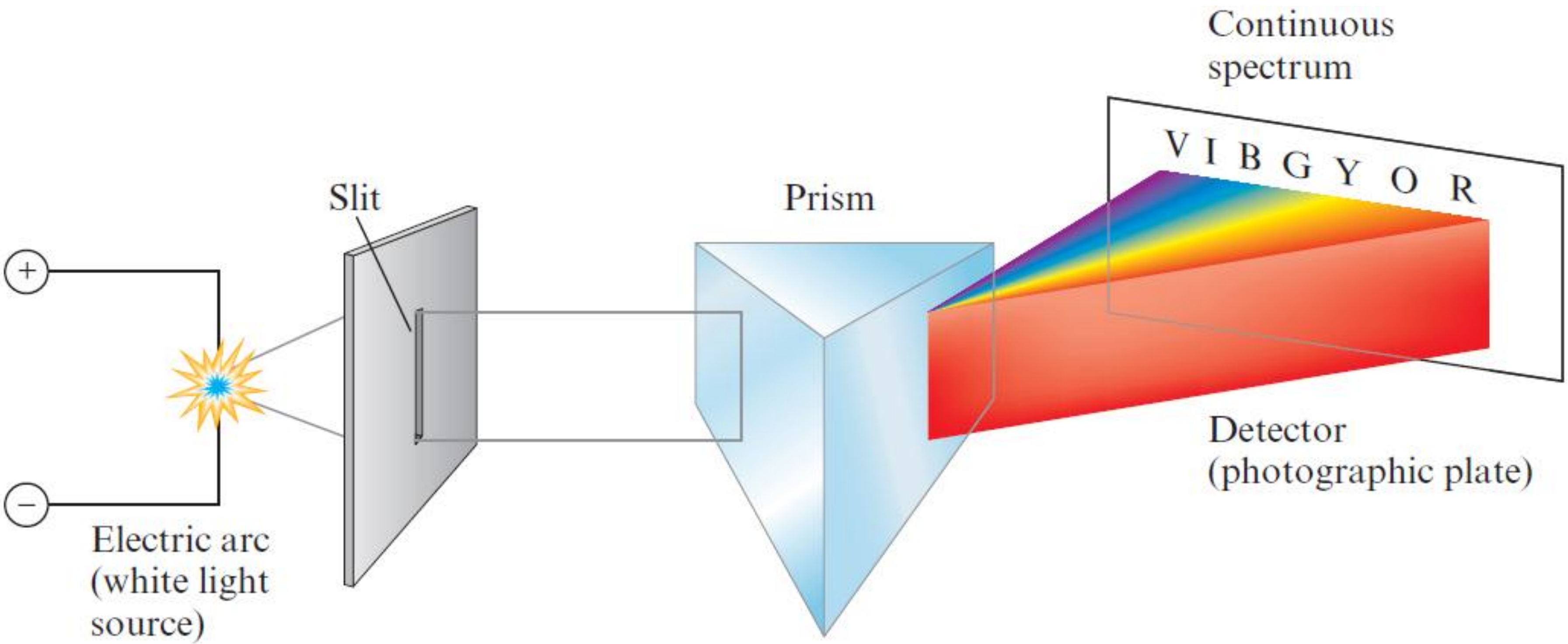
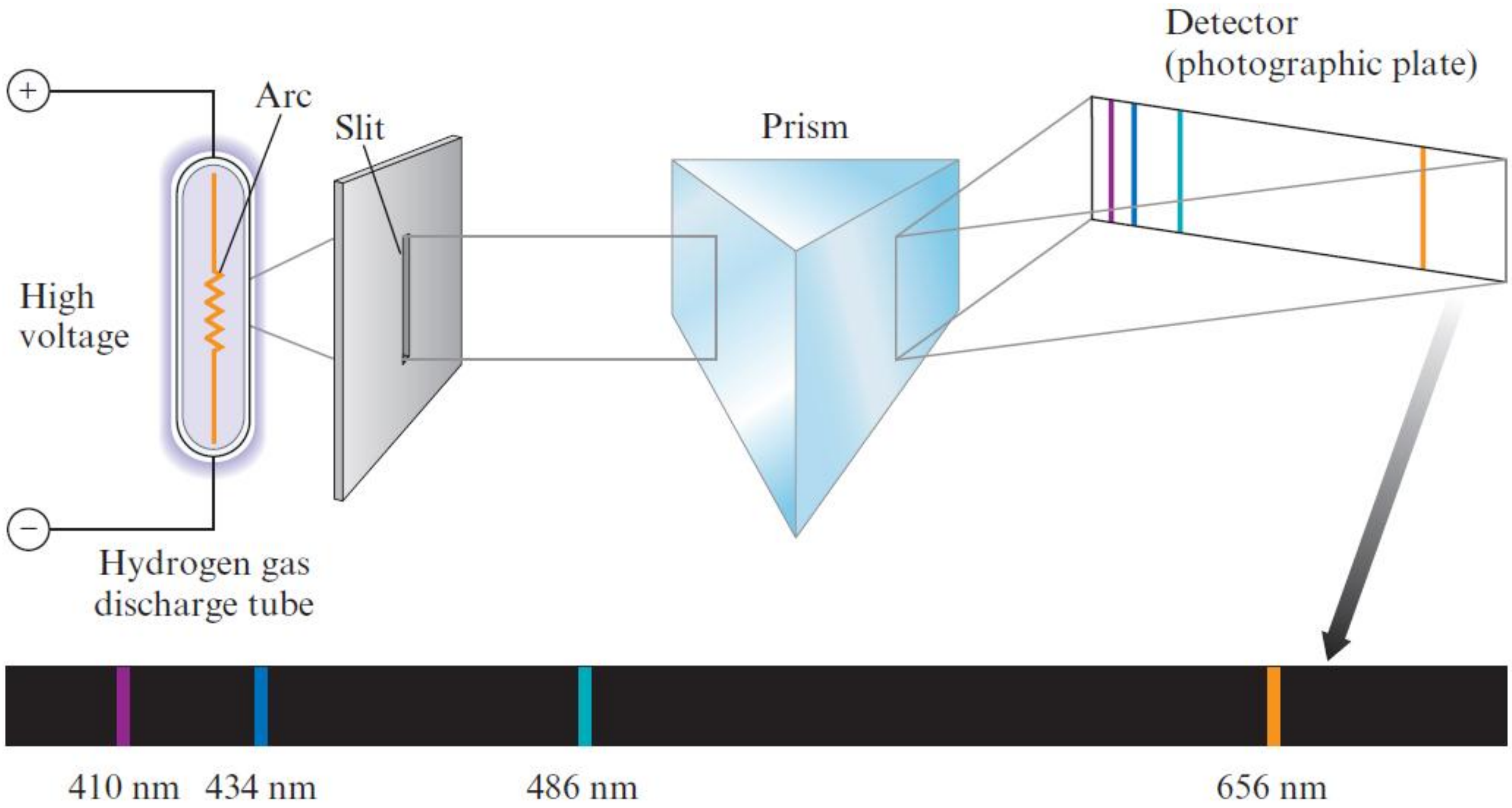


Figure 7.7 (b) - The Hydrogen Line Spectrum



Significance of the Line Spectrum of Hydrogen

- Only certain energies are allowed for the electron in the hydrogen atom
  - Change between two discrete energy levels emits a photon of light

Critical Thinking

- We now have evidence that electron energy levels in the atoms are quantized
  - Some of this evidence is discussed in this chapter
  - What if energy levels in atoms were not quantized?
    - What are some differences we would notice?

Quantum Model for the Hydrogen Atom - Niels Bohr

- **Quantum model**: The electron in a hydrogen atom moves around the nucleus in certain allowed circular orbits
  - Tendency of the revolving electrons to fly off the atom can be balanced by its attraction to the positively charged nucleus
  - Assumption - Angular momentum of the electron occurs in certain increments
    - Angular momentum = mass × velocity × orbital radius

Figure 7.9 (a) - An Energy-Level Diagram for Electronic Transitions

- Bohr's model gave hydrogen atom energy levels consistent with the hydrogen emission spectrum

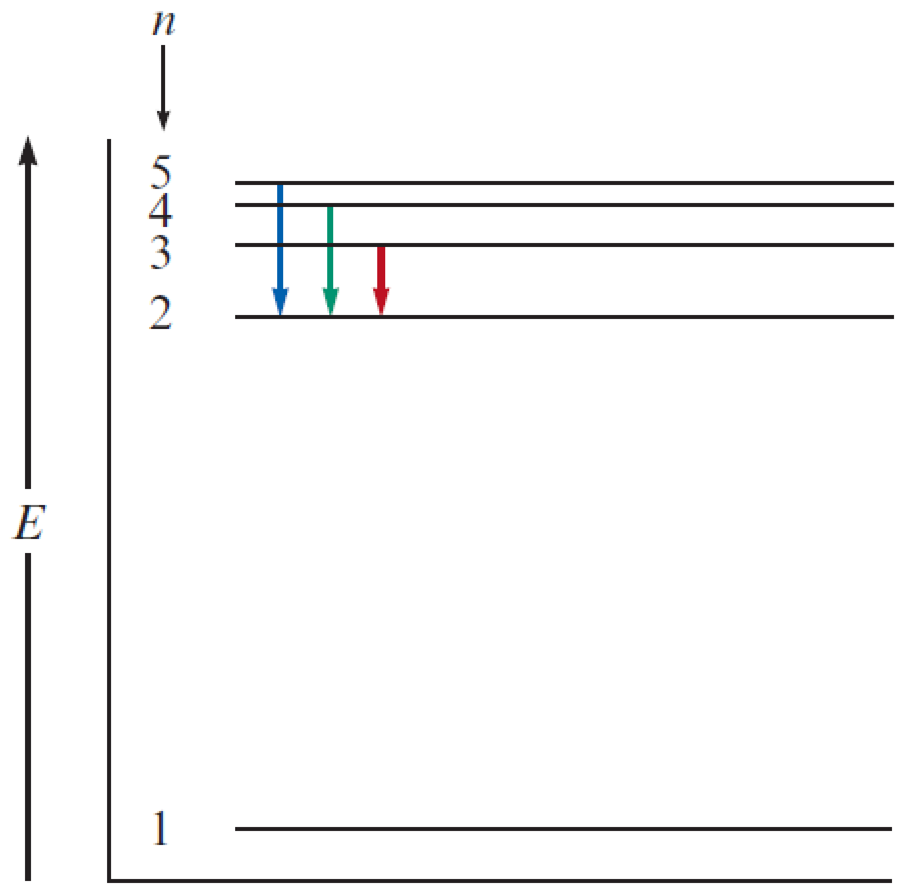
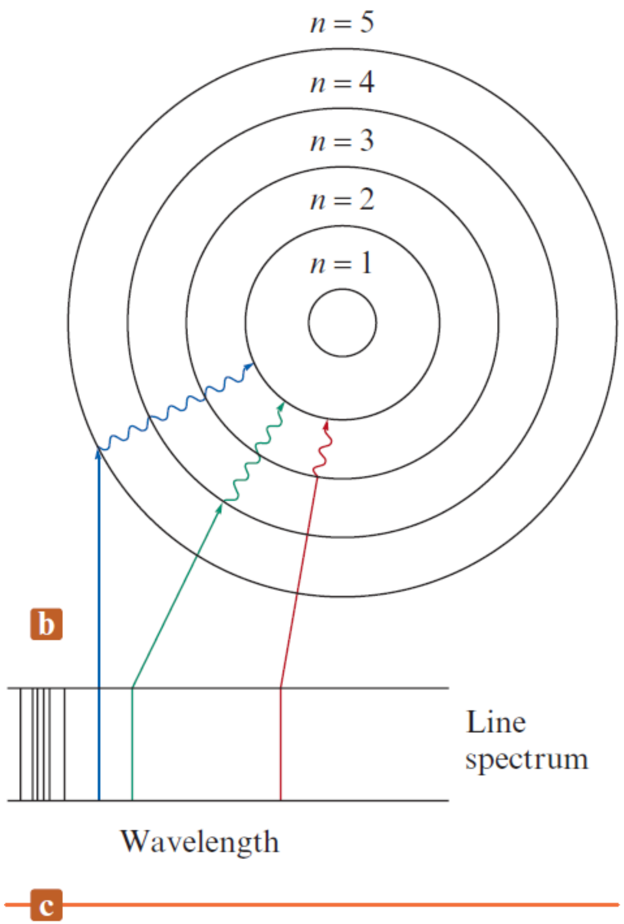


Figure 7.9 (b and c) - Electronic Transitions in the Bohr Model for the Hydrogen Atom

b) An orbit-transition diagram, which accounts for the experimental spectrum
c) The resulting line spectrum on a photographic plate is shown



Bohr's Model

- Expression for energy levels available to the electrons in the hydrogen atom

$$E = -2.178 \times 10^{-18}\text{J}\left(\frac{Z^2}{n^2}\right)$$

  - *n* - An integer (A large *n* value implies a large orbit radius)
  - *Z* - Nuclear charge

Bohr's Model (Continued)

- Negative sign implies that the energy of the electron bound to the nucleus is lower than it would be if the electron were at an infinite distance from the nucleus

$$E = -2.178 \times 10^{-18}\,\mathrm{J}\left(\frac{Z^2}{\infty}\right) = 0$$

  - Energy of the electron in any orbit is negative relative to the reference state ($n = \infty$)
  - **Ground state**: Lowest possible energy state

Calculation of Change in Energy (ΔE) and Wavelength of the Emitted Photon

- ΔE = energy of final state – energy of initial state
  - The negative sign indicates that the atom has lost energy and is now in a more stable state
  - Energy is carried away from the atom by the production (emission) of a photon
- Calculation of the wavelength of the emitted photon

$$\Delta E = h\left(\frac{c}{\lambda}\right) \text{ or } \lambda = \frac{hc}{\Delta E}$$

Interactive Example 7.4 - Energy Quantization in Hydrogen

- Calculate the energy required to excite the hydrogen electron from level $n = 1$ to level $n = 2$
  - Also calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach this excited state

Interactive Example 7.4 - Solution

- Use the following equation, with $Z = 1$:

$$E = -2.178 \times 10^{-18}\text{J}\left(\frac{Z^2}{n^2}\right)$$

$$E_1 = -2.178 \times 10^{-18}\text{J}\left(\frac{1^2}{1^2}\right) = -2.178 \times 10^{-18}\text{J}$$

$$E_2 = -2.178 \times 10^{-18}\text{J}\left(\frac{1^2}{2^2}\right) = -5.445 \times 10^{-19}\text{J}$$

Interactive Example 7.4 - Solution (Continued 1)

$$\Delta E = E_2 - E_1 = \left(-5.445 \times 10^{-19}\text{J}\right) - \left(-2.178 \times 10^{-18}\text{J}\right)$$
$$= 1.633 \times 10^{-18}\ \text{J}$$

- The positive value for ΔE indicates that the system has gained energy
  - The wavelength of light that must be absorbed to produce this change can be calculated using $\lambda = hc/\Delta E$

Interactive Example 7.4 - Solution (Continued 2)

$$\lambda = \frac{hc}{\Delta E} = \frac{\left(6.626 \times 10^{-34}\ \cancel{J} \cdot \cancel{s}\right)\left(2.9979 \times 10^{8}\ \text{m}/\cancel{s}\right)}{1.633 \times 10^{-18}\ \cancel{J}}$$

$$\lambda = 1.216 \times 10^{-7}\ \text{m}$$

Bohr's Model - Conclusions

- Correctly fits the quantized energy levels of the hydrogen atom
  - Postulates only certain allowed circular orbits for the electron
- As the electron becomes more tightly bound, its energy becomes more negative relative to the zero-energy reference state
  - As the electron is brought closer to the nucleus, energy is released from the system

Equation for an Electron Moving from One Level to Another

$$\Delta E = \text{energy of level } n_{\text{final}} - \text{ energy of level } n_{\text{initial}}$$

$$= E_{\text{final}} - E_{\text{initial}}$$

$$= \left(-2.178 \times 10^{-18}\ \text{J}\right)\left(\frac{1^2}{n_{\text{final}}{}^2}\right) - \left(-2.178 \times 10^{-18}\ \text{J}\right)\left(\frac{1^2}{n_{\text{initial}}{}^2}\right)$$

$$\Delta E = \left(-2.178 \times 10^{-18}\ \text{J}\right)\left(\frac{1^2}{n_{\text{final}}{}^2} - \frac{1^2}{n_{\text{initial}}{}^2}\right)$$

Example 7.5 - Electron Energies

- Calculate the energy required to remove the electron from a hydrogen atom in its ground state

Example 7.5 - Solution

- Removing the electron from a hydrogen atom in its ground state corresponds to taking the electron from $n_{\text{initial}} = 1$ to $n_{\text{final}} = \infty$
  - Thus,

$$\Delta E = \left(-2.178 \times 10^{-18}\ \text{J}\right)\left(\frac{1^2}{n_{\text{final}}^{\ 2}} - \frac{1^2}{n_{\text{initial}}^{\ 2}}\right)$$

$$= \left(-2.178 \times 10^{-18}\ \text{J}\right)\left(\frac{1}{\infty} - \frac{1}{1^2}\right)$$

Example 7.5 - Solution (Continued)

$$\Delta E = -2.178 \times 10^{-18}\ \mathrm{J}\left(0-1\right) = 2.178 \times 10^{-18}\ \mathrm{J}$$

- The energy required to remove the electron from a hydrogen atom in its ground state is 2.178×10^{-18} J

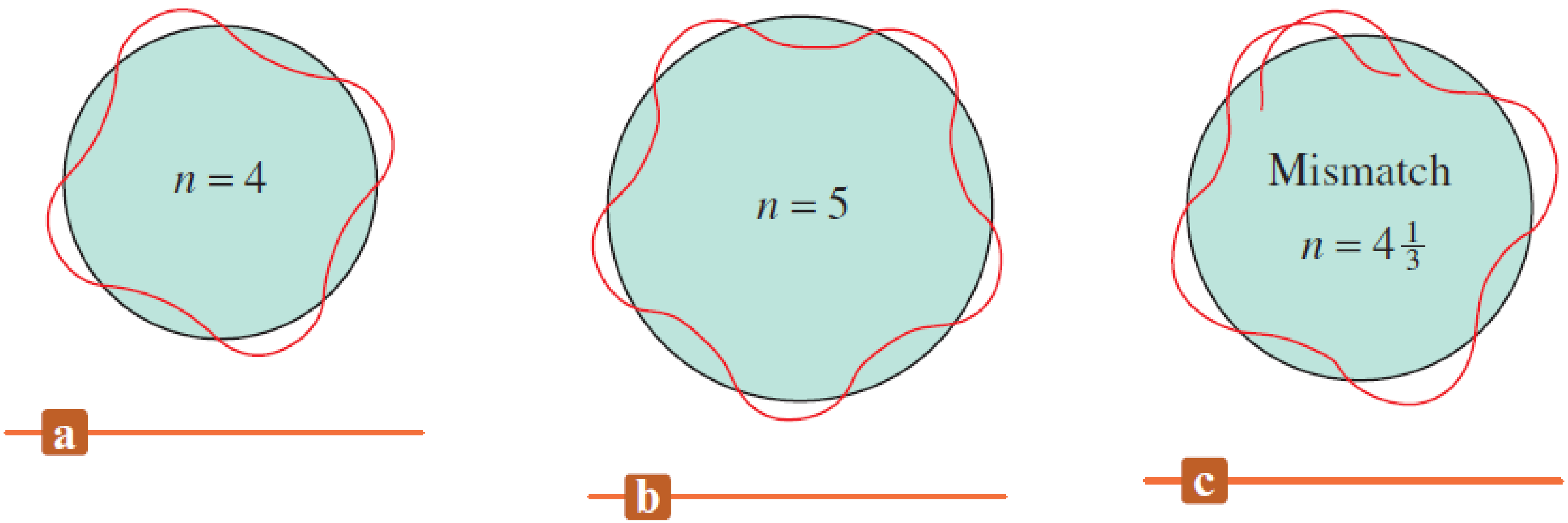
Exercise

- Calculate the maximum wavelength of light capable of removing an electron for a hydrogen atom from the energy state characterized by:
  - $n = 1$ **λ = 91.20 nm**
  - $n = 2$ **λ = 364.8 nm**

Wave Mechanics in Hydrogen

- The electron in a hydrogen atom is imagined to be a standing wave
  - Only certain circular orbits have a circumference into which a whole number of wavelengths of the standing electron wave will fit
  - Other orbits produce destructive interference of the standing electron wave and are not allowed

Figure 7.11 - Hydrogen Electron Visualized as a Standing Wave



Erwin Schrödinger and Quantum Mechanics

- Schrödinger's equation

$$\hat{H}\psi = E\psi$$

  - ψ - **Wave function**
    - Function of the coordinates of the electron's position in three-dimensional space
  - $\hat{H}$ - Operator
    - Contains mathematical terms that produce the total energy of an atom when applied to the wave function

Erwin Schrödinger and Quantum Mechanics (Continued)

- E - Total energy of the atom
  - Sum of the potential energy due to the attraction between the proton and electron and kinetic energy of the moving electron
- **Orbital**: Specific wave function
  - 1*s* orbital - Wave function corresponding to the lowest energy for the hydrogen atom
  - Wave function provides no information about the detailed pathway of an electron

Heisenberg's Uncertainty Principle

- There is a fundamental limitation to just how precisely we can know both the position and momentum of a particle at a given time

$$\Delta x \cdot \Delta(m\upsilon) \geq \frac{h}{4\pi}$$

  - Δx - Uncertainty in a particle's position
  - $\Delta(m\upsilon)$ - Uncertainty in particle momentum
    - Minimum uncertainty in the product $\Delta x \cdot \Delta(m\upsilon)$ is $h/4\pi$
  - h - Planck's constant

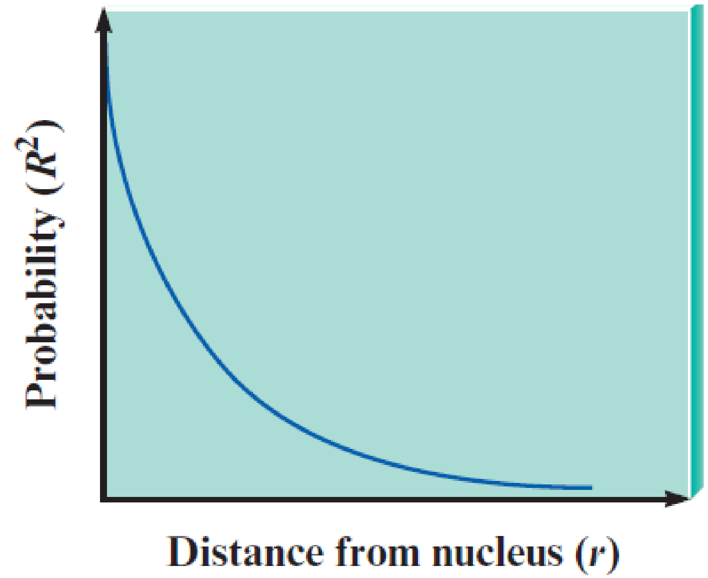
Square of a Wave Function

- Indicates the probability of finding an electron near a particular point in space
- Represented by probability distribution
  - **Probability distribution**: Intensity of color is used to indicate the probability value near a given point in space

Figure 7.12 - Probability Distribution for the Hydrogen 1*s* Wave Function (Orbital)

a

The probability distribution for the hydrogen 1s orbital in three-dimensional space



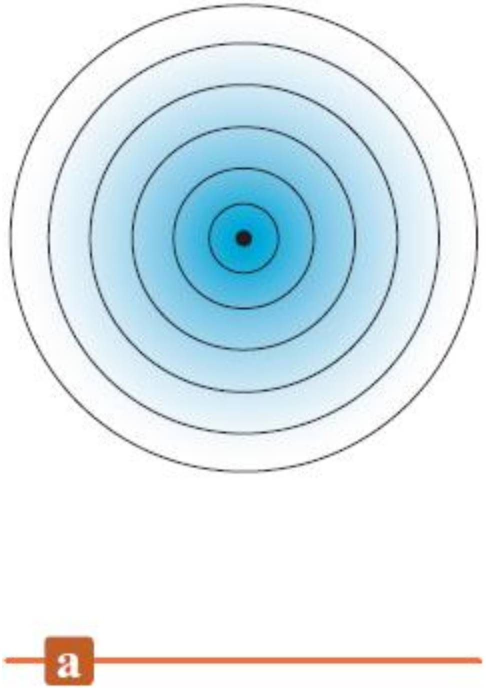
b

The probability of finding the electron at points along a line drawn from the nucleus outward in any direction for the hydrogen 1*s* orbital

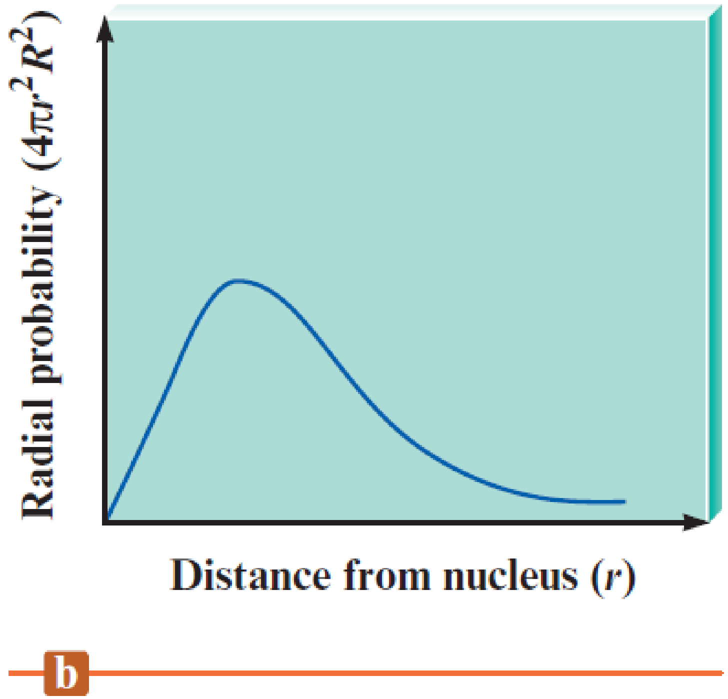
Radial Probability Distribution

- Plots the total probability of finding an electron in each spherical shell versus the distance from the nucleus
  - Probability of finding an electron at a particular position is greatest near the nucleus
  - Volume of the spherical shell increases with distance from the nucleus

Figure 7.13 - Radial Probability Distribution



Cross section of the hydrogen 1*s* orbital probability distribution divided into successive thin spherical shells



Plot of the total probability of finding the electron in each thin spherical shell as a function of distance from the nucleus

Characteristics of the Hydrogen 1*s* Orbital

- Maximum radial probability
  - Occurs at the distance of 5.29×10^{-2} nm or 0.529 Å from the nucleus
- Size
  - Radius of the sphere that encloses 90% of the total electron probability

Quantum Numbers

- Series of numbers that express various properties of an orbital
  - Principal quantum number (n)
  - Angular momentum quantum number (λ)
  - Magnetic quantum number (m_λ)

Principal Quantum Number (*n*)

- Has integral values (1, 2, 3, …)
- Related to the size and energy of an orbital
- As the value of *n* increases:
  - The orbital becomes larger
  - The electron spends more time away from the nucleus
  - The energy increases since the electron is less tightly bound to the nucleus
    - Energy is less negative

Angular Momentum Quantum Number (λ)

- Has integral values from 0 to $n - 1$ for each value of n
- Related to the shape of atomic orbitals
- Value of λ in each orbital is assigned a letter

Value of ℓ	0	1	2	3	4
Letter Used	*s*	*p*	*d*	*f*	*g*

  - Each set of orbitals with a given value of λ (**subshell**) is designated by giving the value of n and the letter for λ

Magnetic Quantum Number (m_λ)

- Has integral values between λ and –λ
  - Includes zero
- Value is related to the orientation of an orbital in space relative to the other orbitals in the atom

Subshells

- Each set of orbitals with a given value of λ is designated by giving the value of *n* and the letter for λ
  - Example - When $n = 2$ and $\lambda = 1$, the orbital is symbolized as 2*p*
    - There are three 2*p* orbitals with different orientations in space

Interactive Example 7.6 - Electron Subshells

- For principal quantum level n = 5, determine the number of allowed subshells (different values of λ), and give the designation of each

Interactive Example 7.6 - Solution

- For n = 5, the allowed values of λ run from 0 to 4 (n – 1 = 5 – 1)
  - Thus, the subshells and their designations are as follows:

$\lambda = 0$	$\lambda = 1$	$\lambda = 2$	$\lambda = 3$	$\lambda = 4$
5*s*	5*p*	5*d*	5*f*	5*g*

Exercise

- What are the possible values for the quantum numbers n, λ, and m_λ?

$$n = 1, 2, 3, \ldots$$

$$\lambda = 0, 1, 2, \ldots (n - 1)$$

$$m_\lambda = -\lambda, \ldots, -2, -1, 0, 1, 2, \ldots, +\lambda$$

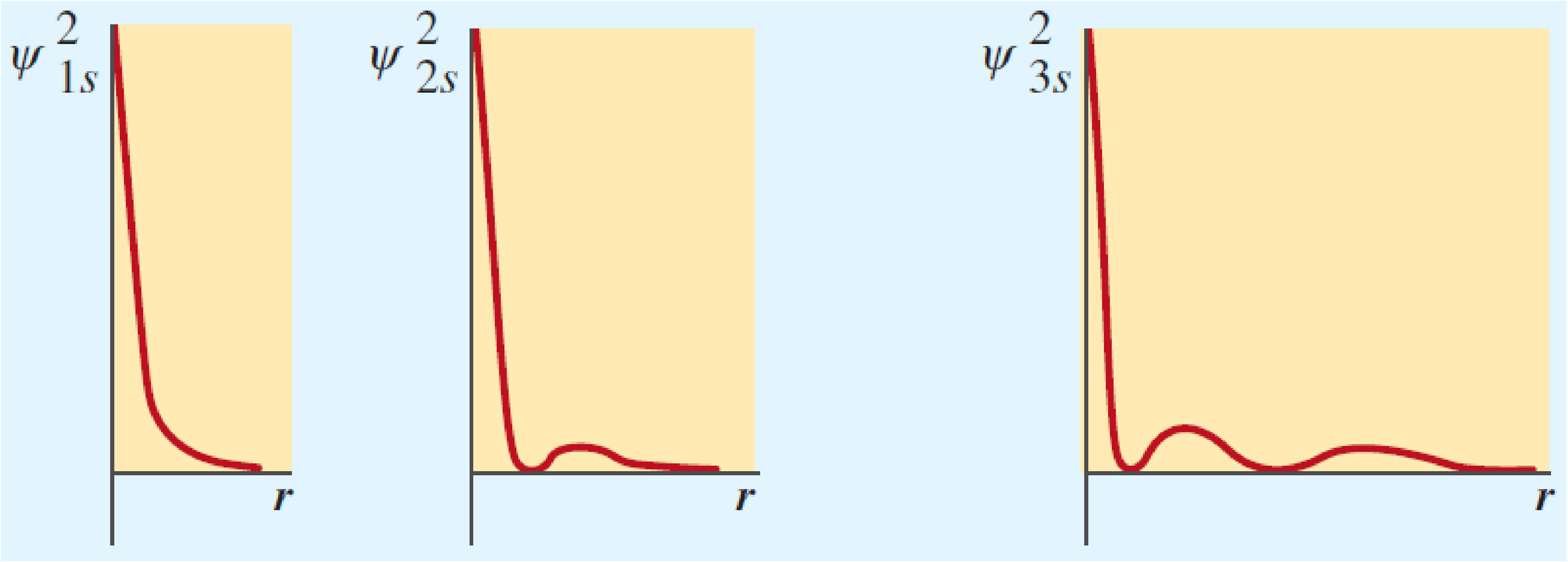
Orbitals in a Hydrogen Atom

- Each orbital in a hydrogen atom has a unique probability distribution
  - Contains 1*s*, 2*s*, and 3*s* orbitals
- **Nodes**: Areas of zero probability in an orbital
  - Known as **nodal surfaces**
  - Number of nodes increases as *n* increases

s Orbitals

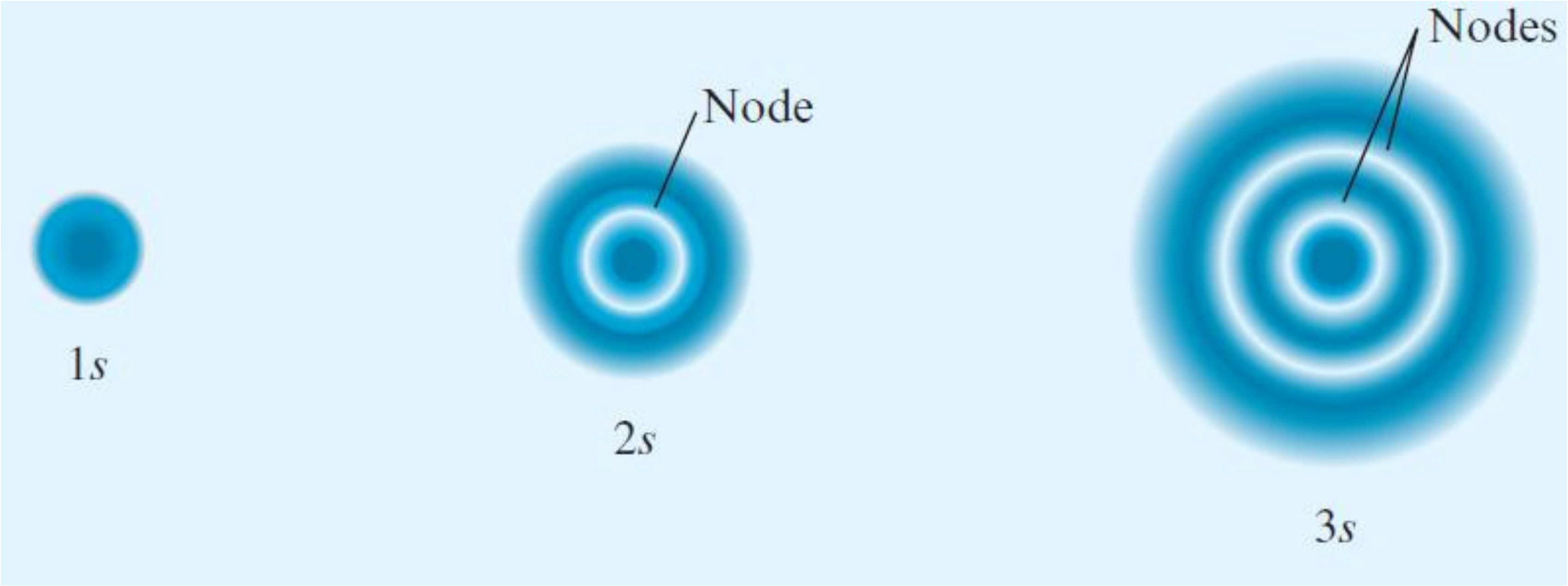
- Characterized by their spherical shape
  - Shape becomes larger as the value of *n* increases
- 2*s* and 3*s* orbitals have areas of high probability separated by areas of low probability
- Number of nodes is given by $n - 1$
- *s* orbital function is always positive in three-dimensional space

Figure 7.14 (a) - Representations of the Hydrogen 1*s*, 2*s*, and 3*s* Orbitals



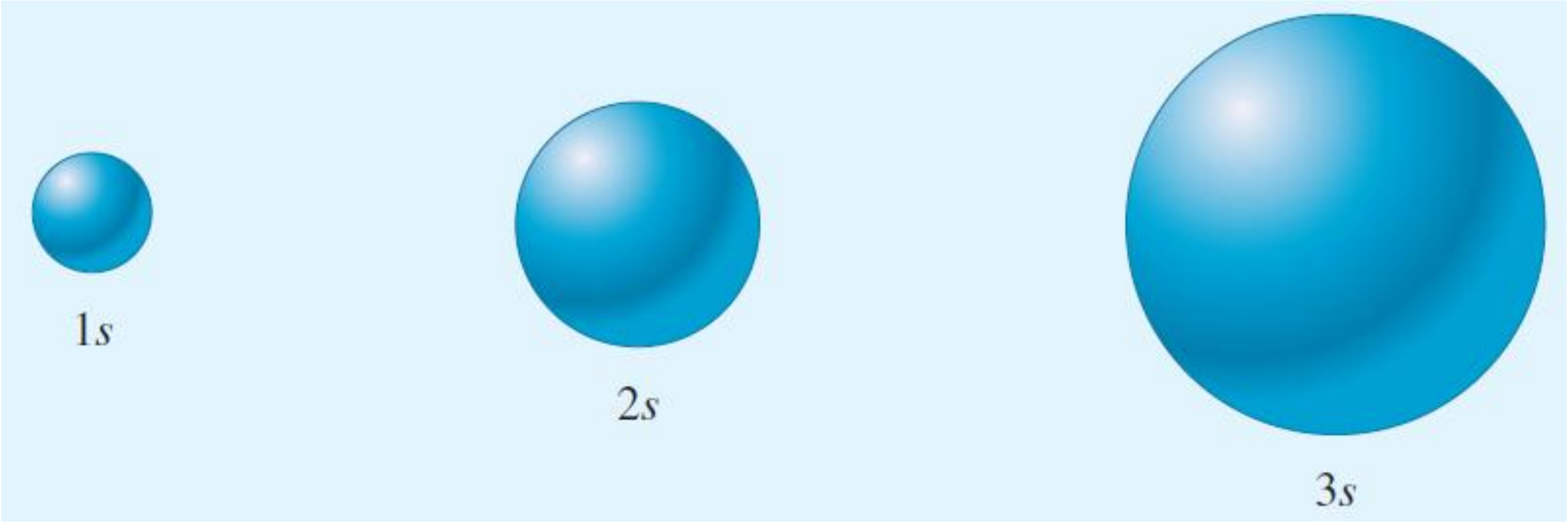
The square of the wave function

Figure 7.14 (b) - Representations of the Hydrogen 1*s*, 2*s*, and 3*s* Orbitals



"Slices" of the three-dimensional electron density

Figure 7.14 (c) - Representations of the Hydrogen 1*s*, 2*s*, and 3*s* Orbitals



The surfaces that contain 90% of the total electron probability

p Orbitals

- Have two lobes separated by a node at the nucleus
  - Labeled according to the axis of the *xyz* coordinate system along which the lobes lie
- *p* orbital functions have different signs in different regions of space
- Have positive and negative phases

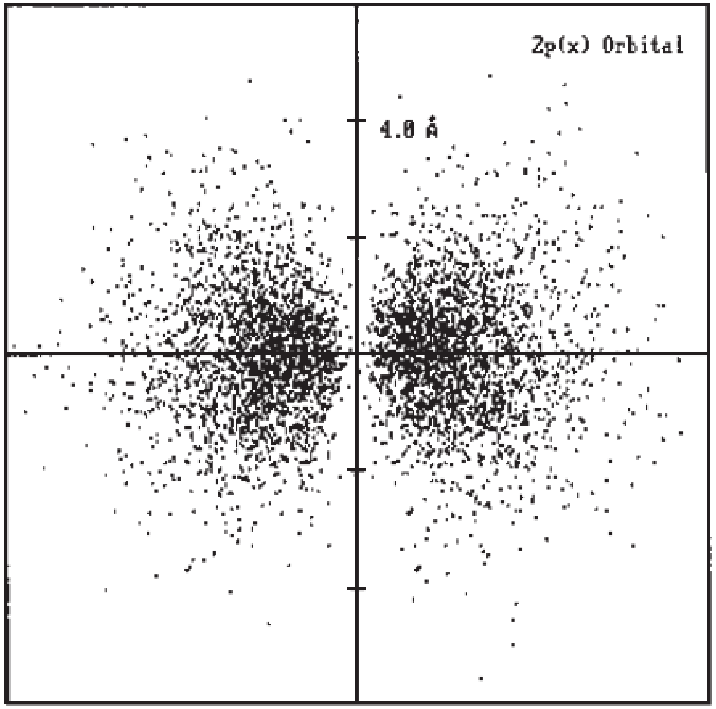


Figure 7.15 - Boundary Surface Representations of all Three 2*p* Orbitals

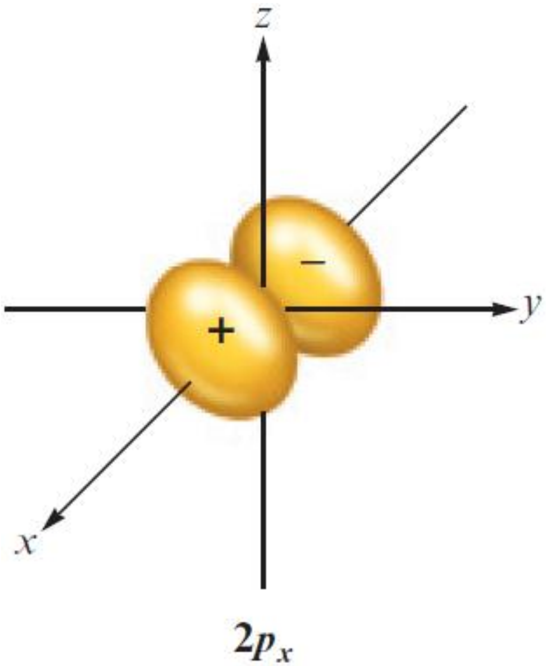


Figure 7.16 - A Cross Section of the Electron Probability Distribution for a 3*p* Orbital

d Orbitals

- Do not correspond to principal quantum levels n = 1 and n = 2
  - First appear in level n = 3
- Have two different fundamental shapes
  - d_{xz}, d_{yz}, d_{xy}, and $d_{x^2-y^2}$ have four lobes centered in the plane indicated in the orbital label
  - d_{z^2} orbital has a unique shape

Figure 7.17 (a) - Electron Density Plots of Selected 3*d* Orbitals

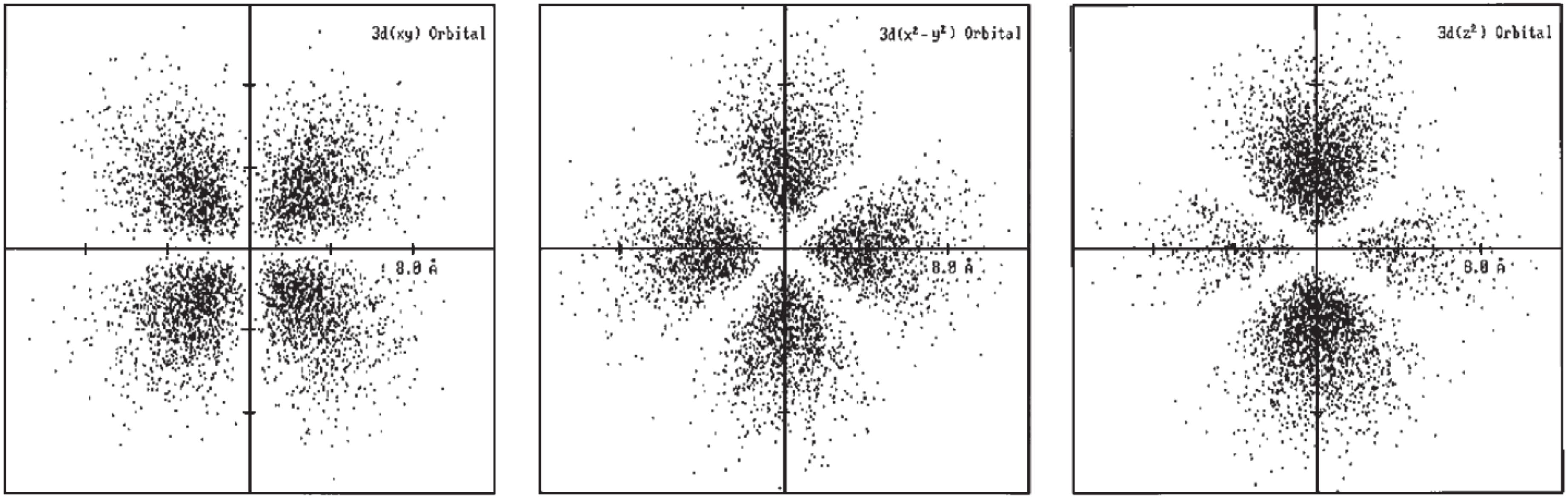
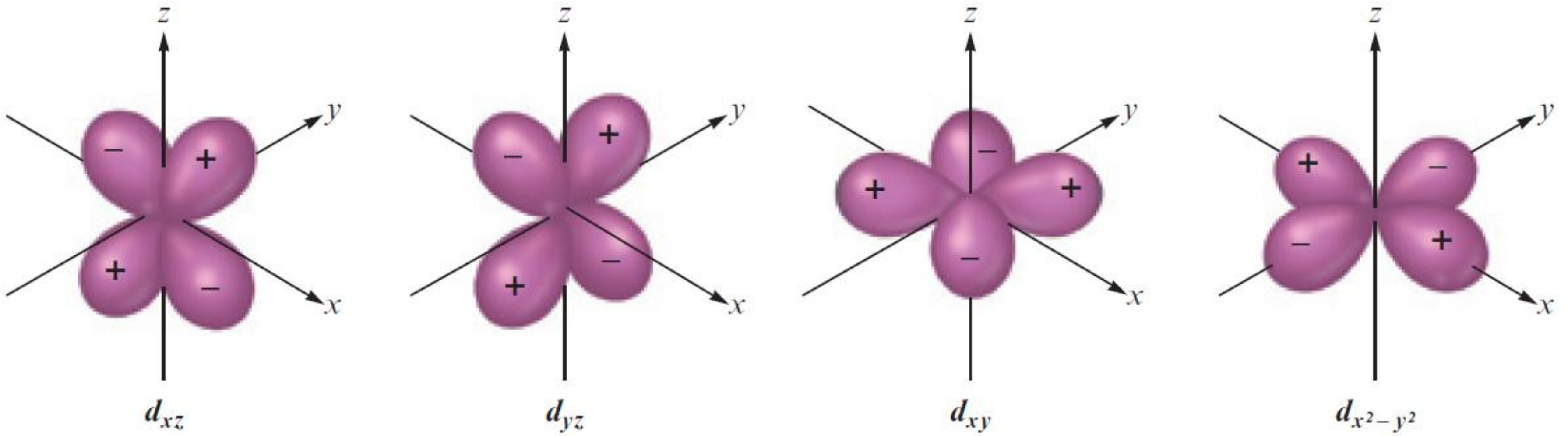
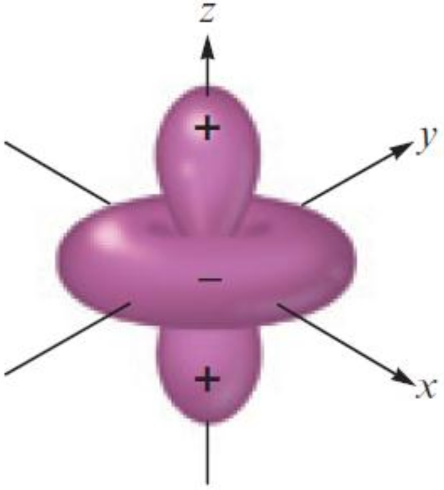


Figure 7.17 (b) - The Boundary Surfaces of Four 3*d* Orbitals, with the Signs (Phases) Indicated



Unique Shape of the d_{z^2} Orbital

- Two lobes run along the *z* axis and a belt is centered in the *xy* plane
- *d* orbitals for levels $n > 3$ look like the 3*d* orbitals
  - Have larger lobes

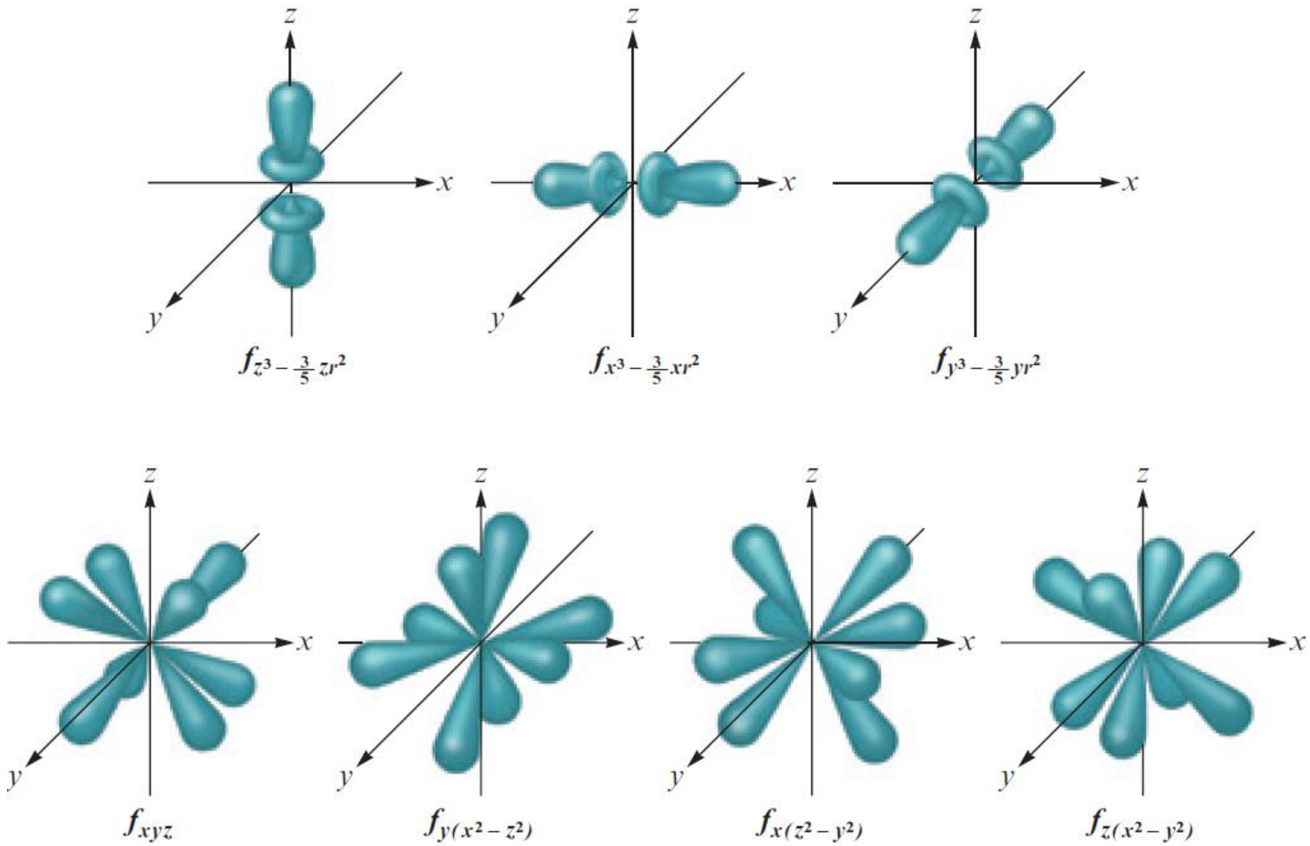


d_{z^2}

f Orbitals

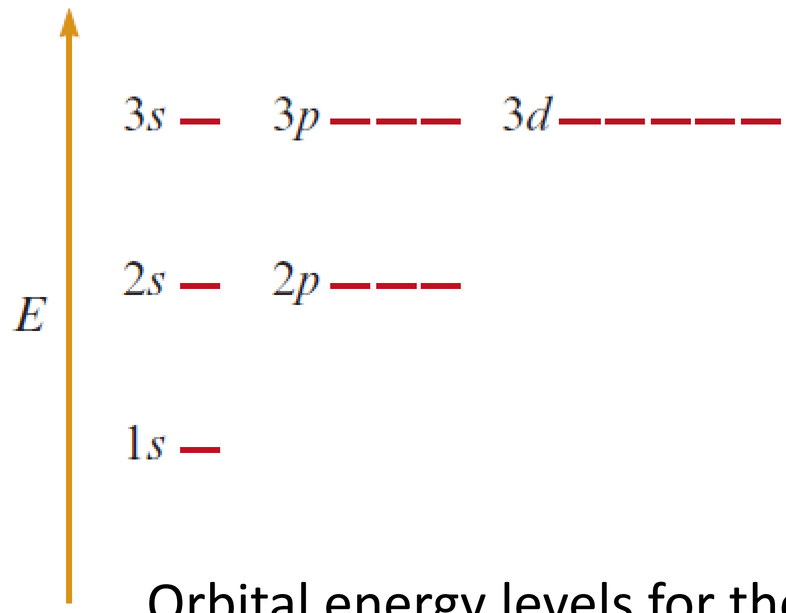
- First occur in level *n* = 4
- Not involved in bonding in any compounds
  - Shapes and labels are simply included for the purpose of completeness

Figure 7.18 - Representation of the 4*f* Orbitals in Terms of Their Boundary Surfaces



Degenerates

- All orbitals with the same value of *n* have the same energy



Orbital energy levels for the hydrogen atom

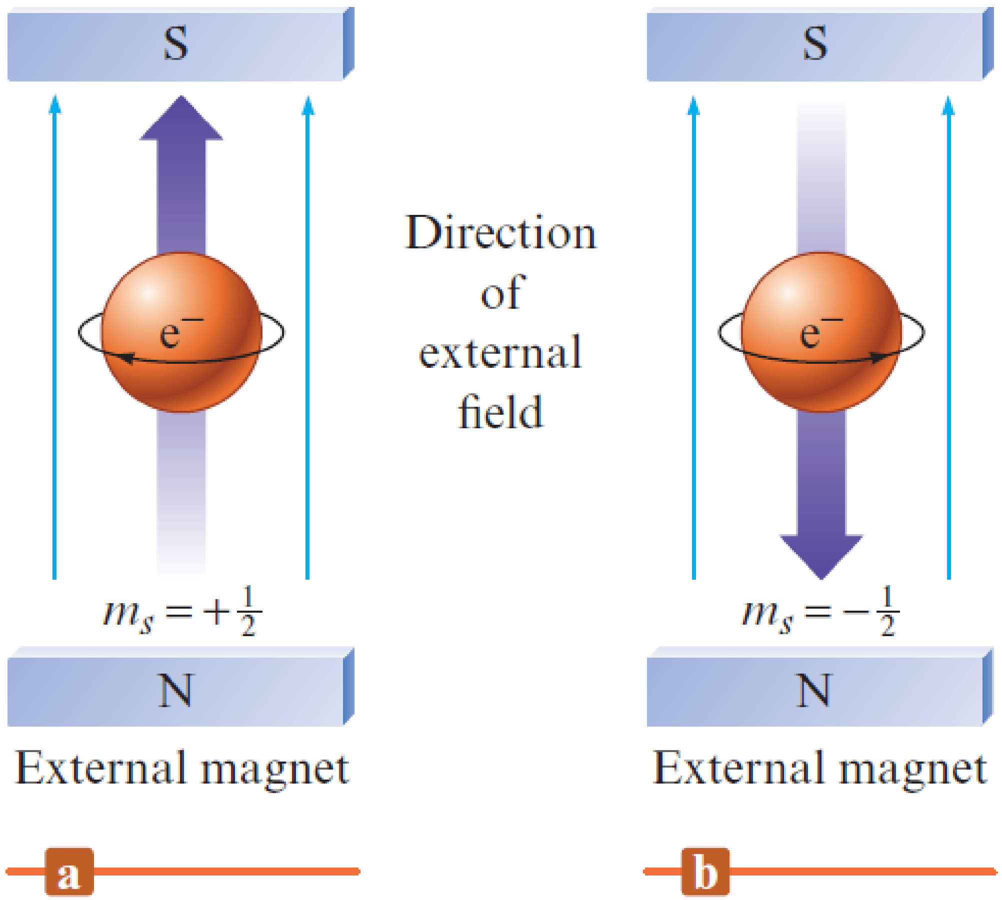
Energy States of a Hydrogen Atom

- Ground state - Lowest energy state
  - Electron resides in 1*s* orbital
- An excited state can be produced by transferring the electron to a higher-energy orbital

Electron Spin and the Pauli Exclusion Principle

- **Electron spin quantum number** (m_s)
  - Can be +½ or –½, implying that electron can spin in one of two opposite directions
- **Pauli exclusion principle**: In a given atom, no two electrons can have the same set of four quantum numbers
  - An orbital can hold only two electrons, and they must have opposite spins

Figure 7.20 - The Spinning Electron



Polyelectronic Atoms

- Atoms with more than one electron
- Electron correlation problem
  - Since the electron pathways are unknown, the electron repulsions cannot be calculated exactly
  - Approximation used to treat a system using the quantum mechanical model
    - Treat each electron as if it were moving in a field of charge

Polyelectronic Atoms (Continued)

- For a given principal quantum level, the orbitals vary in energy as follows:

$$E_{ns} < E_{np} < E_{nd} < E_{nf}$$

  - Electrons prefer the orbitals in the order *s*, *p*, *d*, and then *f*

Penetration Effect

- 2*s* electron penetrates to the nucleus more than once in the 2*p* orbital
  - Causes an electron in a 2*s* orbital to be attracted to the nucleus more strongly than an electron in a 2*p* orbital
    - The 2*s* orbital is lower in energy than the 2*p* orbitals in a polyelectronic atom

Figure 7.22 (a) - Radial Probability Distribution for an Electron in a 3*s* Orbital

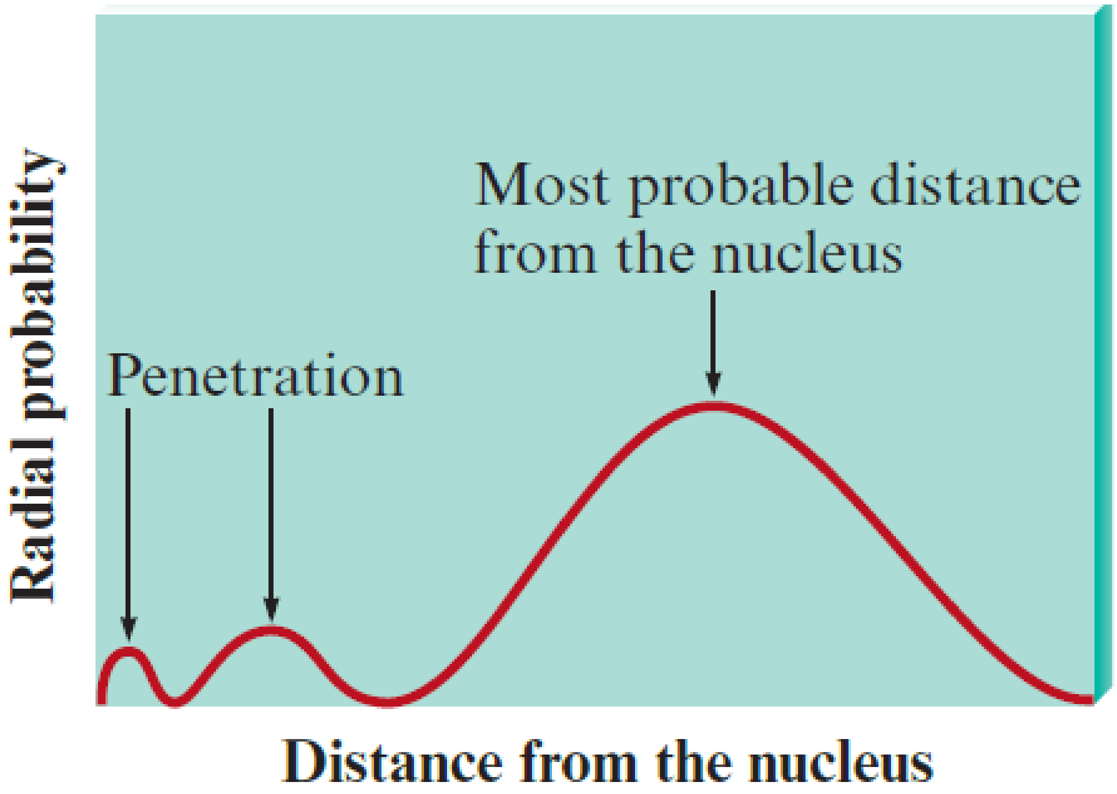


Figure 7.22 (b) - Radial Probability Distribution for the 3*s*, 3*p*, and 3*d* Orbitals

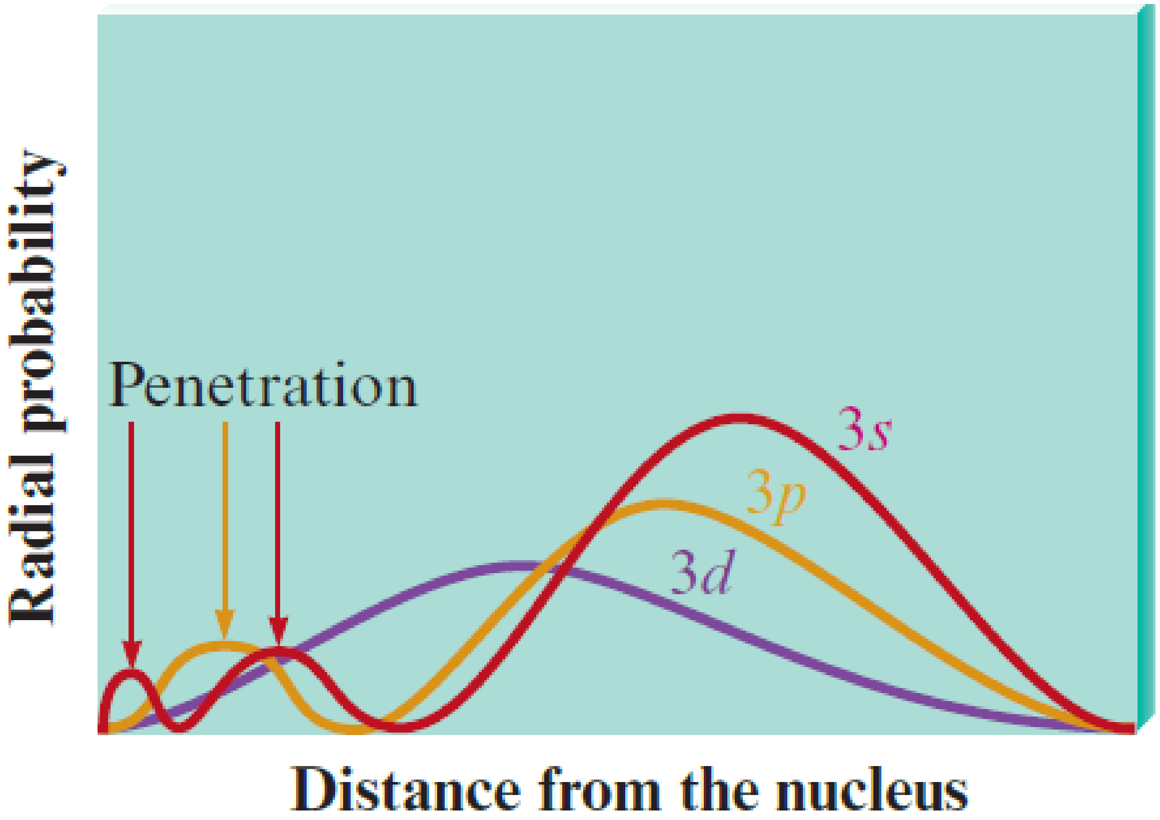
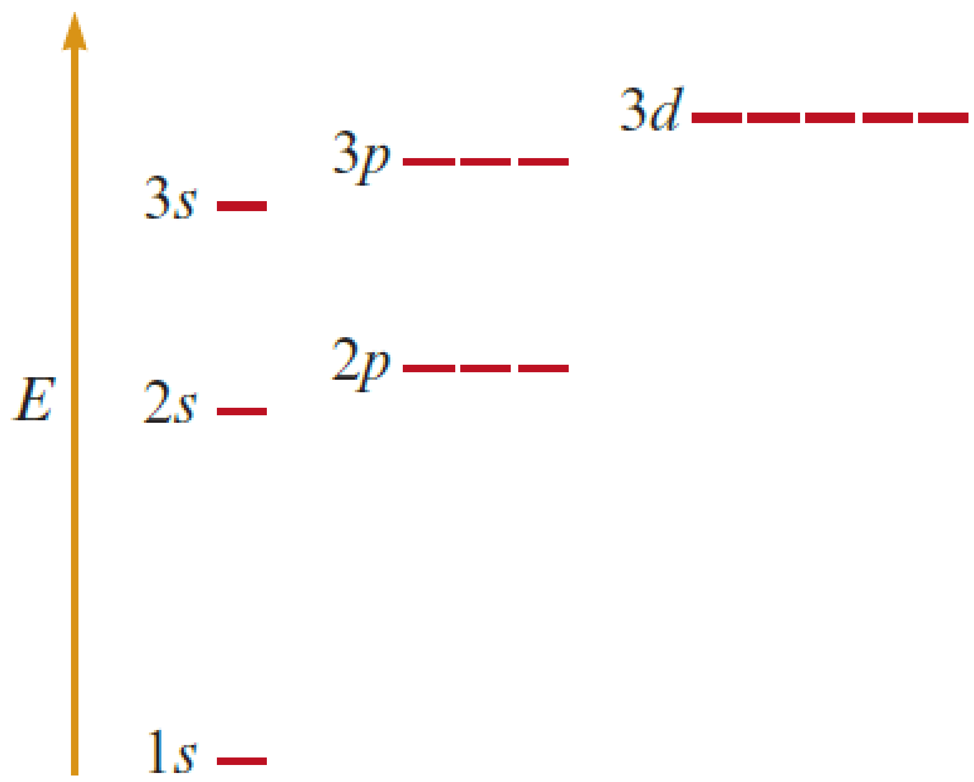


Figure 7.23 - Orders of the Energies of the Orbitals in the First Three Levels of Polyelectronic Atoms



Critical Thinking

- What if Bohr’s model was correct?
  - How would this affect the radial probability profiles in Figure 7.22?

The Periodic Table

- Originally constructed to represent the patterns observed in the chemical properties of the elements
- Johann Dobereiner
  - Attempted to expand his model of triads
    - Triads - Groups of three elements that have similar properties
- John Newlands - Suggested that elements should be arranged in octaves

The Modern Periodic Table

- Conceived by Julius Lothar Meyer and Dmitri Ivanovich Mendeleev
- Mendeleev's contributions
  - Emphasized the usefulness of the periodic table in predicting the existence and properties of still unknown elements
  - Used the table to correct several values of atomic masses

Figure 7.25 - Mendeleev's Early Periodic Table

TABELLE II

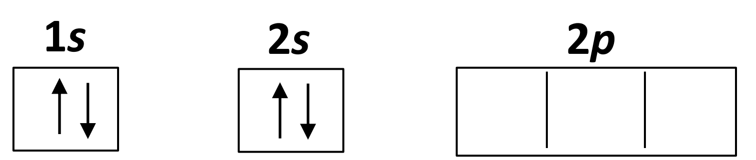
REIHEN	GRUPPE I. — R^2O	GRUPPE II. — RO	GRUPPE III. — R^2O^3	GRUPPE IV. RH^4 RO^2	GRUPPE V. RH^3 R^2O^5	GRUPPE VI. RH^2 RO^3	GRUPPE VII. RH R^2O^7	GRUPPE VIII. — RO^4
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	= 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	= 68	= 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	= 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

Public Domain

Aufbau Principle

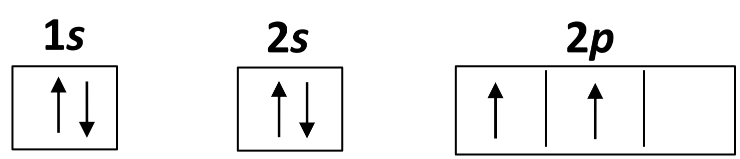
- As protons are added one by one to the nucleus to build up the elements, electrons are similarly added to hydrogen-like orbitals
  - Represented in orbital diagrams where the arrow represents electrons spinning in a specific direction
  - Example - Beryllium

Be: $1s^2 2s^2$



Hund's Rule

- Lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli principle in a particular set of degenerate orbitals
  - Unpaired electrons have parallel spins
- Example
  - C: $1s^2 2s^2 2p^2$



Valence Electrons

- Electrons present in the outermost principal quantum level of an atom
  - Essential for bonding
  - **Core electrons**: Inner electrons
- In the periodic table, elements in the same group have the same valence electron configuration
  - Elements with the same valence electron configuration exhibit similar chemical behavior

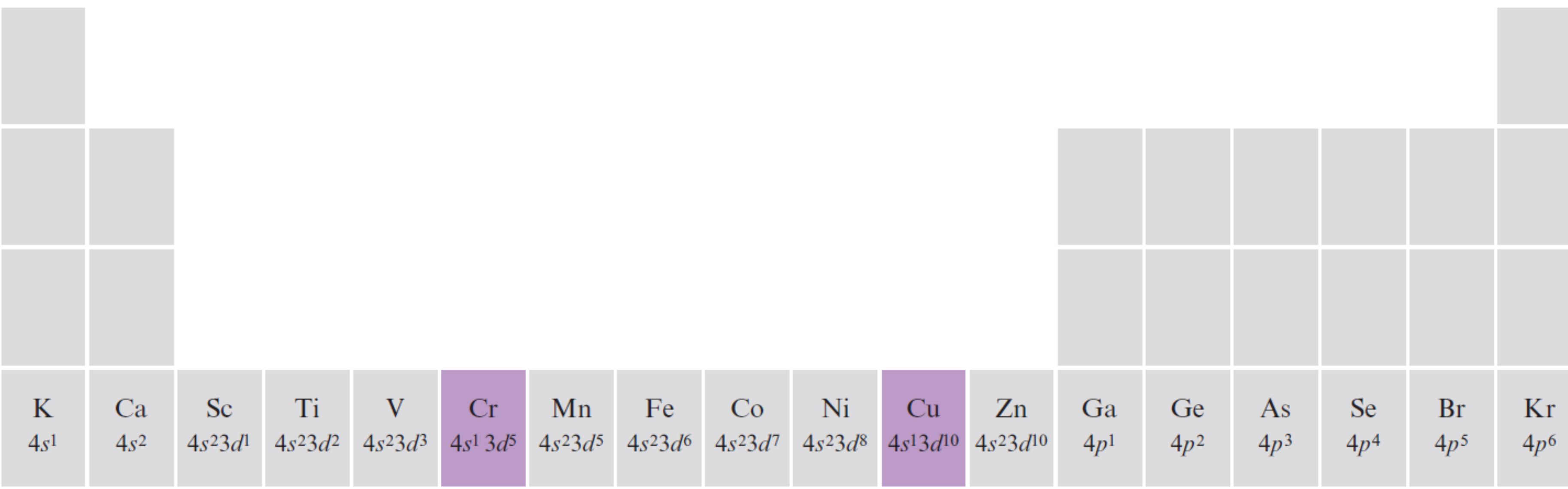
Figure 7.26 - Electron Configurations in the Type of Orbital Occupied Last for the First 18 Elements

H $1s^1$							He $1s^2$
Li $2s^1$	Be $2s^2$	B $2p^1$	C $2p^2$	N $2p^3$	O $2p^4$	F $2p^5$	Ne $2p^6$
Na $3s^1$	Mg $3s^2$	Al $3p^1$	Si $3p^2$	P $3p^3$	S $3p^4$	Cl $3p^5$	Ar $3p^6$

Electron Configuration of Transition Metals

- Configuration of transition metals is attained by adding electrons to the five 3*d* orbitals
- Examples
  - Scandium Sc: [Ar] $4s^2 3d^1$
  - Titanium Ti: [Ar] $4s^2 3d^2$
  - Vanadium V: [Ar] $4s^2 3d^3$

Figure 7.27 - Valence Electron Configurations for Potassium through Krypton



Electron Configuration - Some Essential Points

- (n + 1)s orbitals always fills before the nd orbitals
- **Lanthanide series**: Group of 14 elements that appear after lanthanum
  - Corresponds to the filling of the seven 4f orbitals
- **Actinide series**: Group of 14 elements that appear after actinium
  - Corresponds to the filling of seven 5f orbitals

Electron Configuration - Some Essential Points (Continued)

- Labels for Groups 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A indicate the total number of valence electrons for the atoms in these groups
- **Main-group** (**representative**) **elements**: Elements in groups labeled 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A
  - Members of these groups have the same valance electron configuration

Critical Thinking

- You have learned that each orbital is allowed two electrons, and this pattern is evident on the periodic table
  - What if each orbital was allowed three electrons?
    - How would this change the appearance of the periodic table?

Interactive Example 7.7 - Electron Configurations

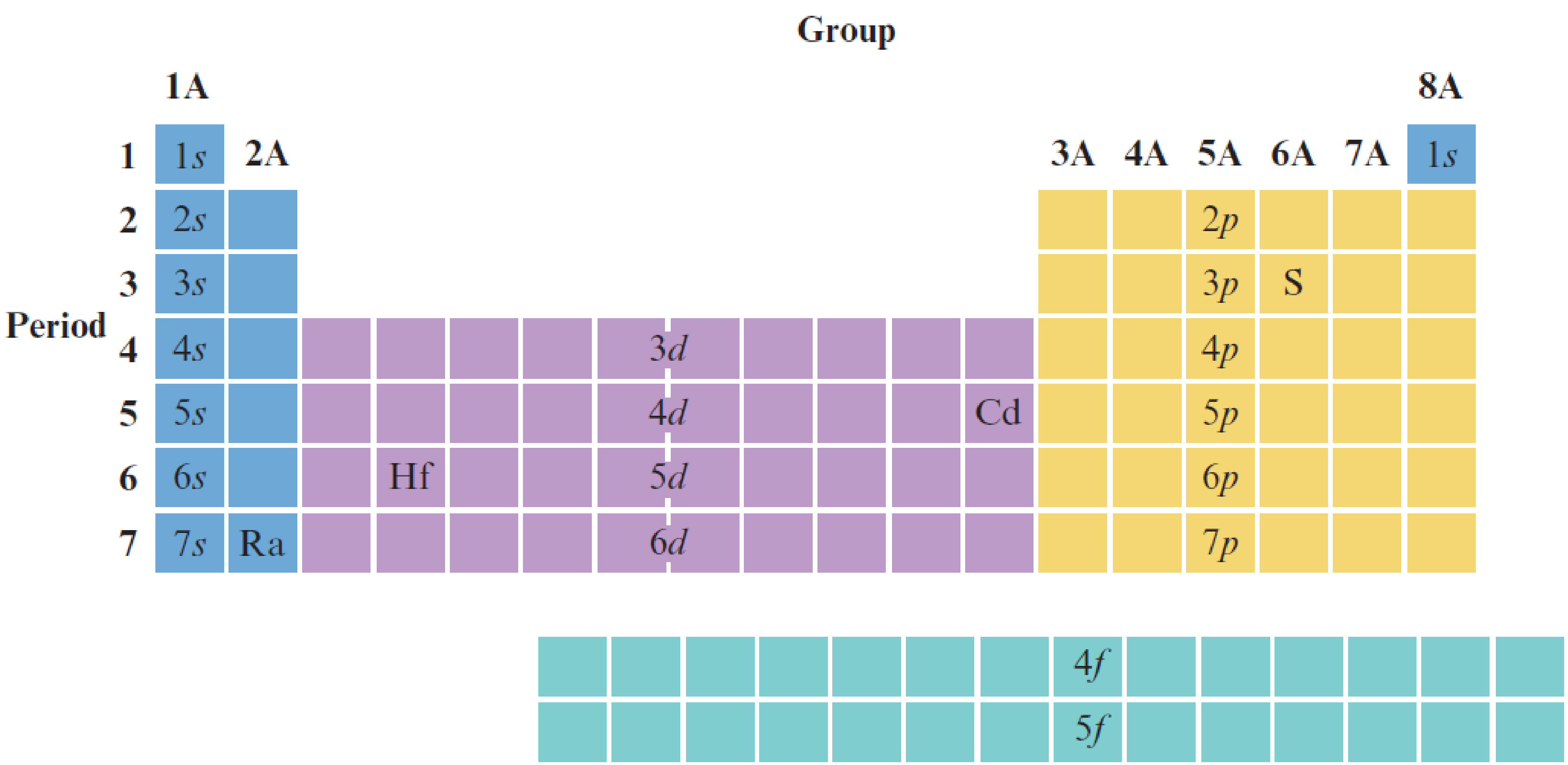
- Give the electron configurations for sulfur (S), cadmium (Cd), hafnium (Hf), and radium (Ra) using the periodic table inside the front cover of this book

Interactive Example 7.7 - Solution

- Sulfur is element 16 and resides in Period 3, where the 3*p* orbitals are being filled
  - Since sulfur is the fourth among the 3*p* elements, it must have four 3*p* electrons, and its configuration is:

$$\text{S:}\quad 1s^2 2s^2 2p^6 3s^2 3p^4 \text{ or } [\text{Ne}]3s^2 3p^4$$

Interactive Example 7.7 - Solution (Continued 1)



Interactive Example 7.7 - Solution (Continued 2)

- Cadmium is element 48 and is located in Period 5 at the end of the 4*d* transition metals
  - It is the tenth element in the series
    - Has 10 electrons in the 4*d* orbitals in addition to the 2 electrons in the 5*s* orbital
  - The configuration is:

Cd: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$ or $[Kr]5s^2 4d^{10}$

Interactive Example 7.7 - Solution (Continued 3)

- Hafnium is element 72 and is found in Period 6
  - Occurs just after the lanthanide series
  - The 4*f* orbitals are already filled
    - Hafnium is the second member of the 5*d* transition series and has two 5*d* electrons
  - The configuration is:

$$\text{Hf: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^2$$

$$\text{or } [\text{Xe}]6s^2 4f^{14} 5d^2$$

Interactive Example 7.7 - Solution (Continued 4)

- Radium is element 88 and is in Period 7 (and Group 2A)
  - Has two electrons in the 7*s* orbital
  - The configuration is:

Ra:

$$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^67s^2$$

or

$$[Rn]7s^2$$

Periodic Trends

- Ionization energy
- Electron affinity
- Atomic radius

Ionization Energy

- Energy required to remove an electron from a gaseous atom or ion

$$X(g) \rightarrow X^{+}(g) + e^{-}$$

- **First ionization energy** (I_1): Energy required to remove the highest-energy electron of an atom
  - Value of I_1 is smaller than that of the **second ionization energy** (I_2)

Ionization Energy Trends in the Periodic Table

- As we go across a period from left to right, I_1 increases
  - Electrons added in the same principal quantum level do not completely shield the increasing nuclear charge caused by the added protons
  - Electrons in the same principal quantum level are more strongly bound as we move from left to right on the periodic table

Ionization Energy Trends in the Periodic Table (Continued)

- As we go down a group, I_1 decreases
  - Electrons being removed are farther from the nucleus
  - As *n* increases, the size of the orbital increases
    - Removal of electrons becomes easier

Example 7.8 - Trends in Ionization Energies

- The first ionization energy for phosphorus is 1060 kJ/mol, and that for sulfur is 1005 kJ/mol
  - Why?

Example 7.8 - Solution

- Phosphorus and sulfur are neighboring elements in Period 3 of the periodic table and have the following valence electron configurations:
  - Phosphorus is $3s^2 3p^3$
  - Sulfur is $3s^2 3p^4$

Example 7.8 - Solution (Continued)

- Ordinarily, the first ionization energy increases as we go across a period, so we might expect sulfur to have a greater ionization energy than phosphorus
  - However, in this case the fourth *p* electron in sulfur must be placed in an already occupied orbital
    - The electron–electron repulsions that result cause this electron to be more easily removed than might be expected

Electron Affinity

- Energy change associated with the addition of an electron to a gaseous atom

$$X(g) + e^- \rightarrow X^-(g)$$

- As we go across a period from left to right, electron affinities become more negative
  - More negative the energy, greater the quantity of energy released

Electron Affinity (Continued)

- Depends on atomic number
  - Changes in electron repulsions can be considered as a function of electron configurations
- Becomes more positive as we go down a group
  - Electrons are added at increasing distances from the nucleus
  - Changes are relatively small

Atomic Radii

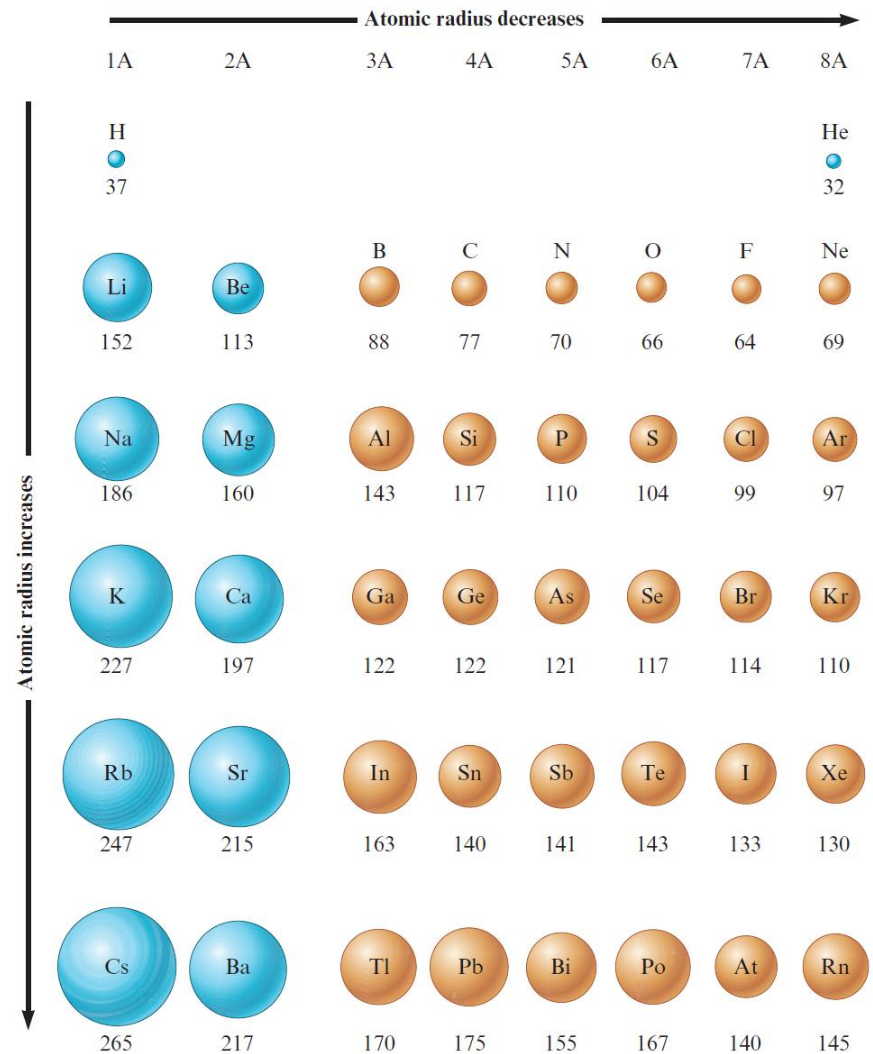
- Obtained by measuring the distance between atoms in a chemical compound
  - Covalent atomic radii - Determined from the distances between atoms in covalent bonds
  - Metallic radii - Obtained from half the distance between metal atoms in solid metal crystals

Trends in Atomic Radius

- Atomic radius decreases in going across a period from left to right
  - Caused due to increasing effective nuclear charge while going from left to right
    - Valence electrons are closer to the nucleus, which decreases the size of the atom
- Atomic radius increases down a group
  - Caused by the increase in orbital sizes in successive principal quantum levels

Section 7.12
Periodic Trends in Atomic Properties

Figure 7.35 - Atomic Radii for Selected Atoms



Interactive Example 7.10 - Trends in Radii

- Predict the trend in radius for the following ions:
  - Be^{2+}
  - Mg^{2+}
  - Ca^{2+}
  - Sr^{2+}

Interactive Example 7.10 - Solution

- All these ions are formed by removing two electrons from an atom of a Group 2A element
  - In going from beryllium to strontium, we are going down the group, so the sizes increase:

$$Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+}$$

Smallest radius (Be^{2+}) — Largest radius (Sr^{2+})

Information Contained in the Periodic Table

- The number and type of valence electrons primarily determine an atom's chemistry
- Electron configurations can be determined from the organization of the periodic table
- Certain groups in the periodic table have special names

Information Contained in the Periodic Table (Continued)

- Elements in the periodic table are divided into metals and nonmetals
  - Metals have low ionization energy
  - Nonmetals have large ionization energies and negative electron affinities
  - **Metalloids (semimetals)**: Elements that exhibit both metallic and nonmetallic properties

Figure 7.36 - Special Names for Groups in the Periodic Table

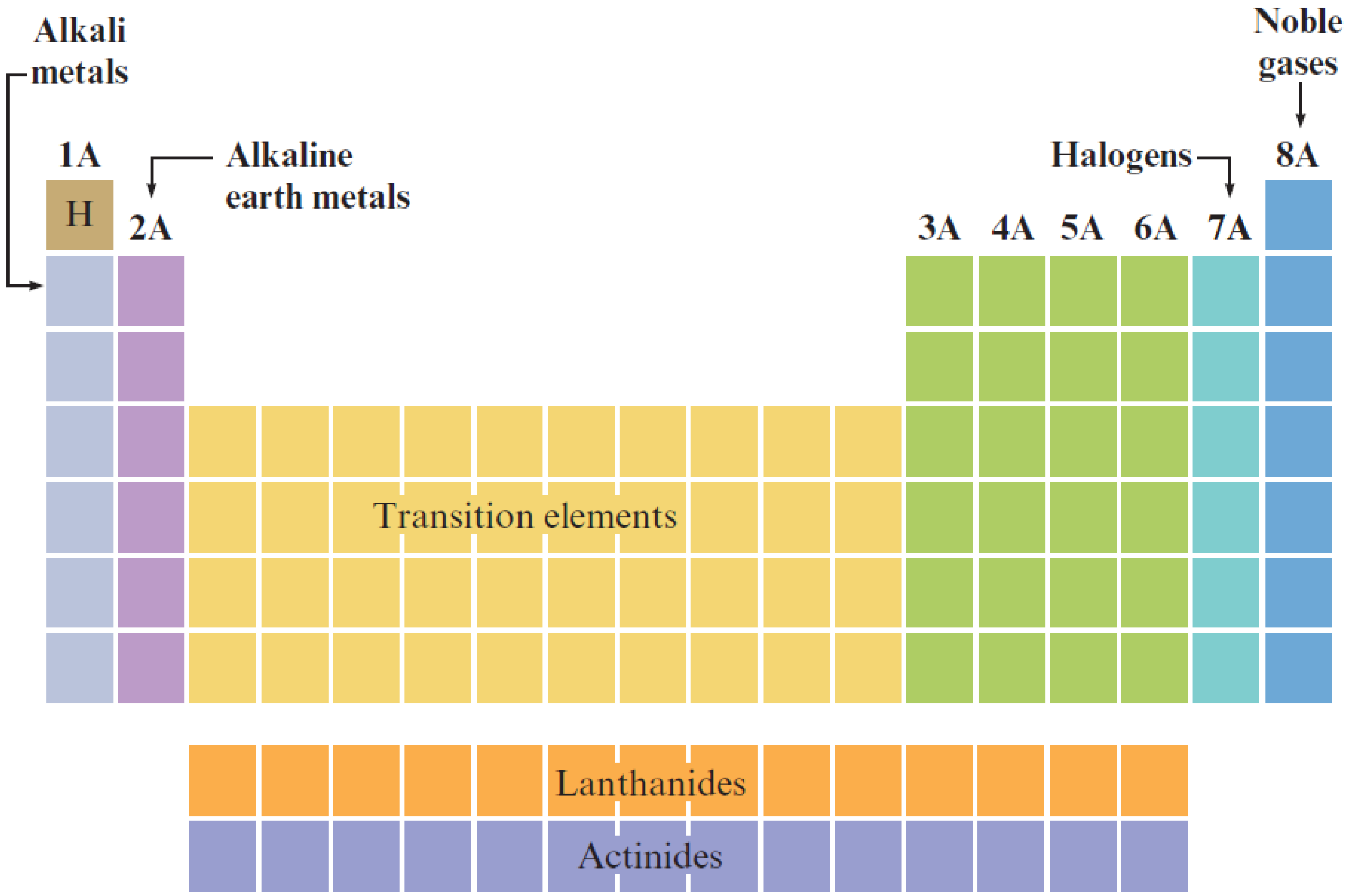
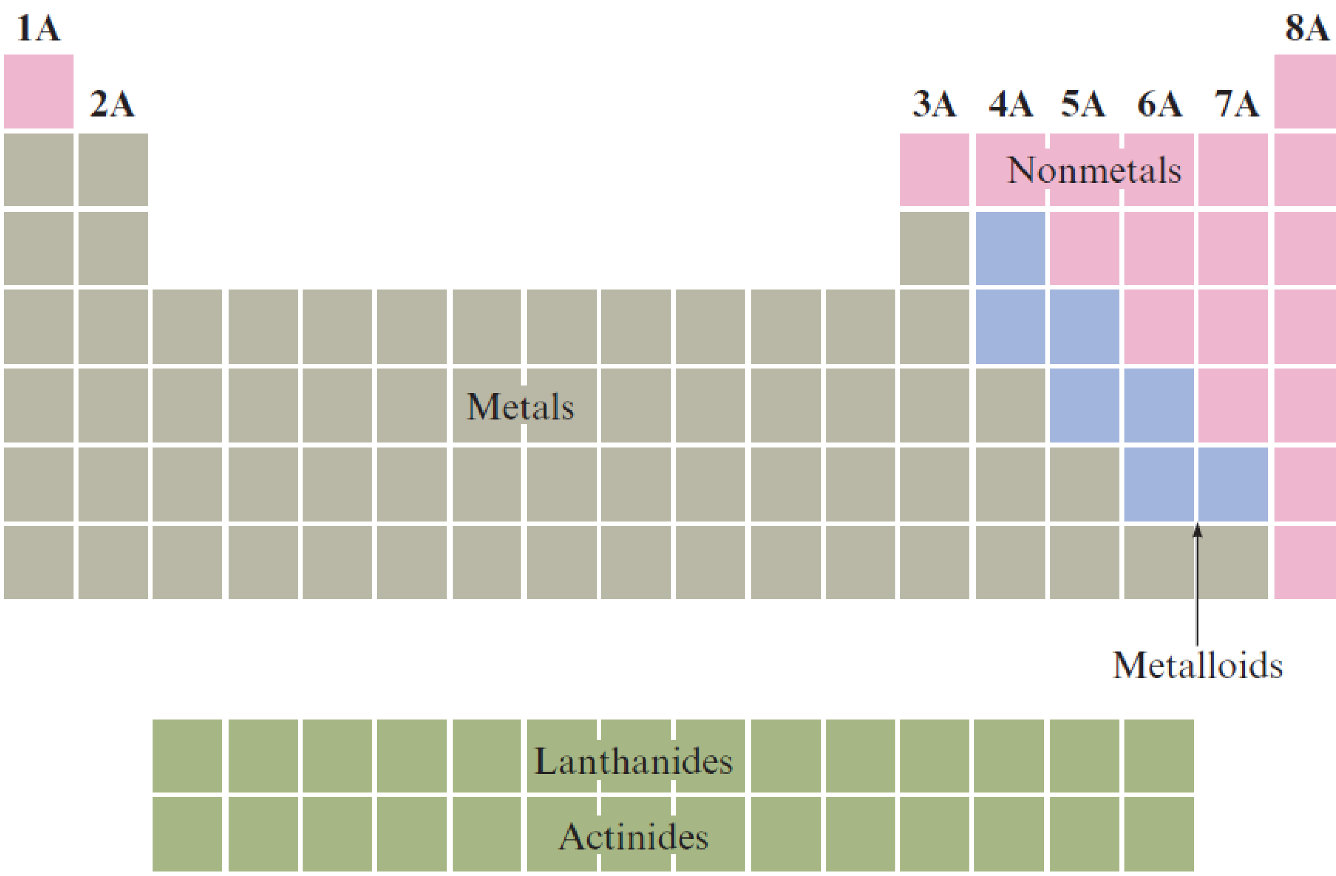


Figure 7.36 - Special Names for Groups in the Periodic Table (Continued)



The Alkali Metals

- Li, Na, K, Rb, Cs, and Fr
  - Most chemically reactive of the metals
  - React with nonmetals to form ionic solids
- Hydrogen
  - Exhibits nonmetallic character due to its small size

The Alkali Metals - Trends

- Going down the group:
  - The first ionization energy decreases
  - Atomic radius increases
  - Density increases
  - Melting and boiling points smoothly decrease in Group 1A

Chemical Properties of the Alkali Metals

- Group 1A elements are highly reactive
- Relative reducing abilities are predicted from the first ionization energies
  - Reducing abilities in aqueous solution are affected by the hydration of M^+ ions by polar water molecules
- Energy change for a reaction and the rate at which it occurs are not necessarily related