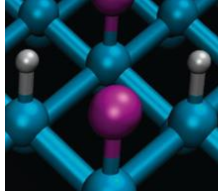
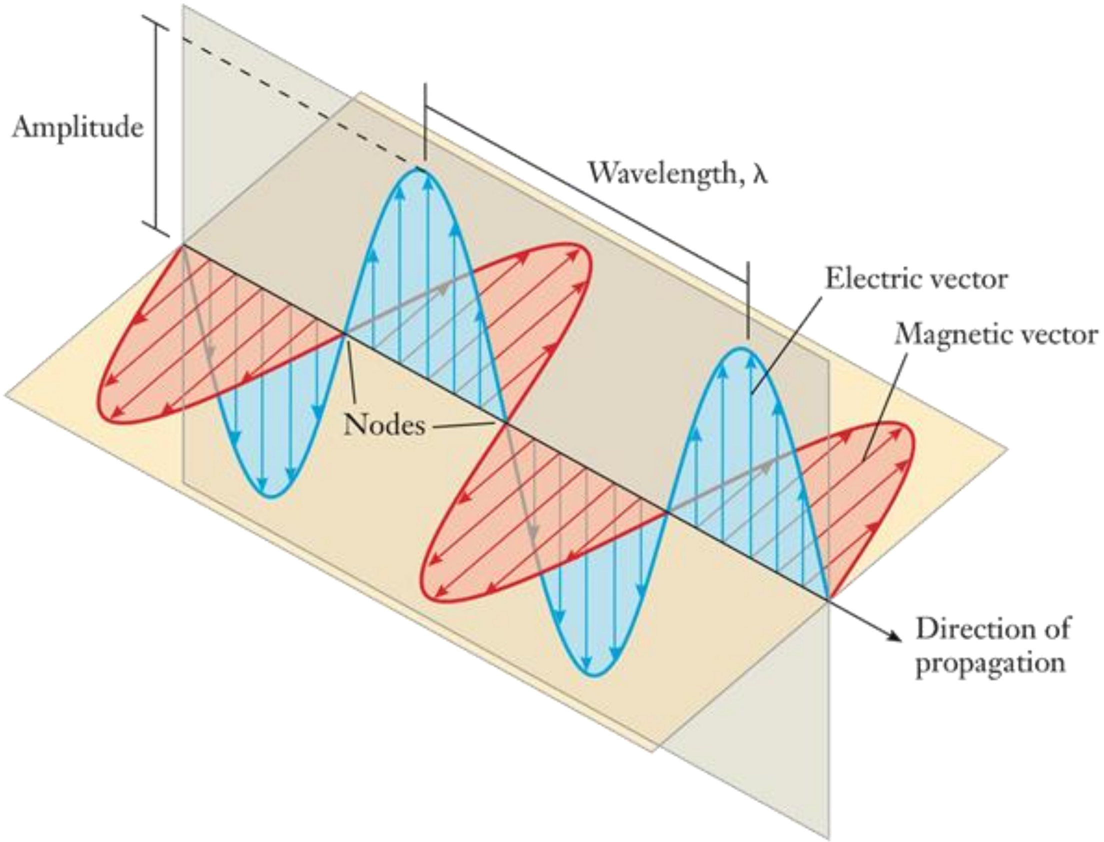


Chapter **6**

The Periodic Table and Atomic Structure

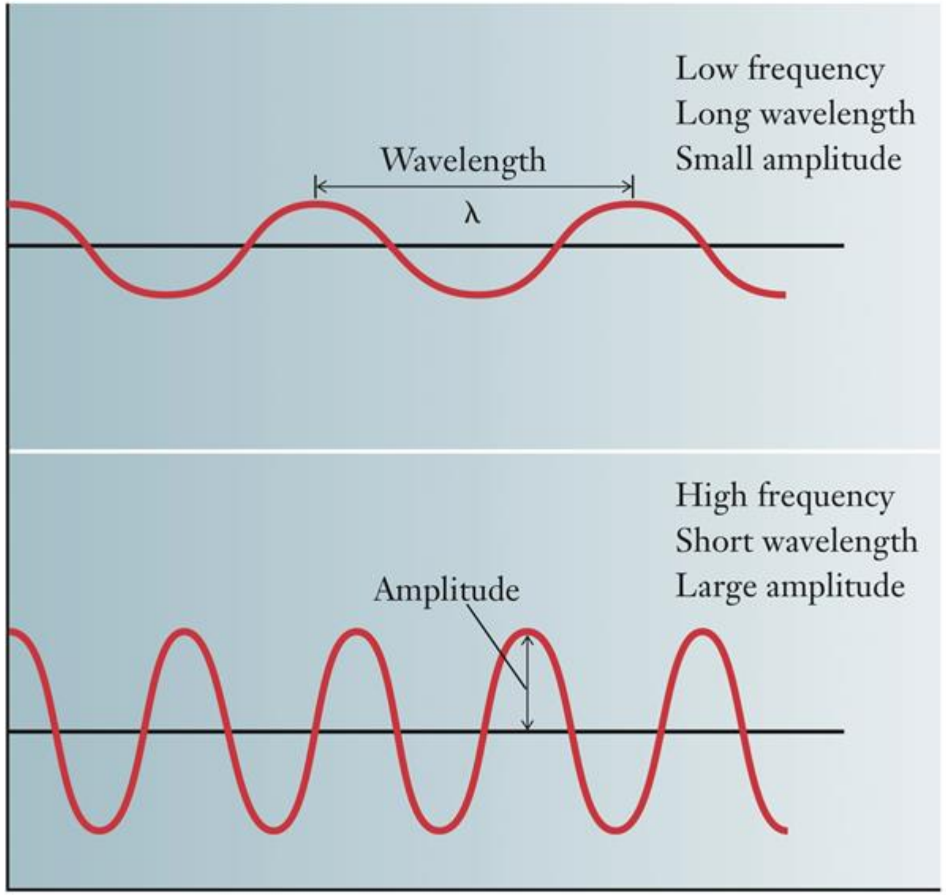
The Electromagnetic Spectrum

- Visible light is the small portion of the electromagnetic radiation spectrum detected by our eyes
  - Described as a wave traveling through space
- Forms of electromagnetic radiation include radio waves, microwaves, and X-rays
  - There are two components to electromagnetic radiation, an electric field and a magnetic field

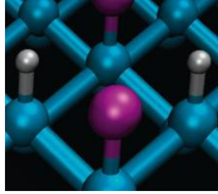


The Wave Nature of Light

- Wavelength, λ, is the distance between two corresponding points on a wave
- Amplitude is the size or height of a wave
- Frequency, *v*, is the number of cycles of the wave passing a given point per second, usually expressed in Hz
  - Frequency is inversely proportional to wavelength



The Wave Nature of Light



- Speed of light in a vacuum is a constant
  - *c* equals 2.99792458×10^{8} m/s
- Speed of light is defined as the product of frequency and wavelength

$$c = \lambda \nu$$

- The fourth variable of light is velocity

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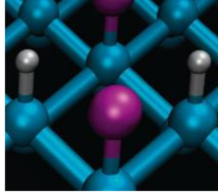
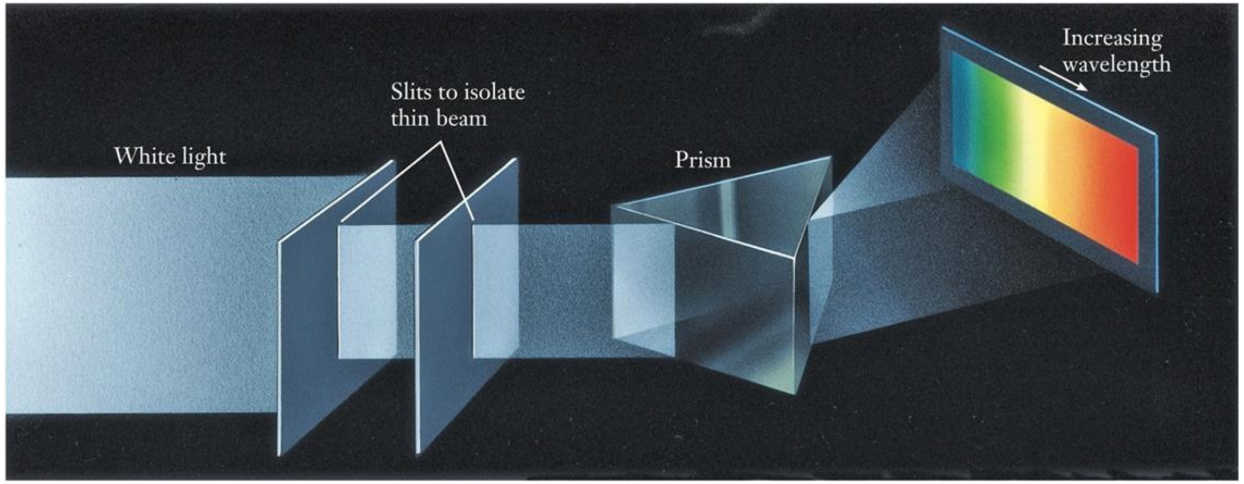
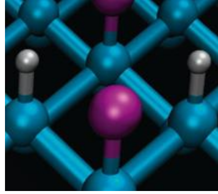
The Wave Nature of Light



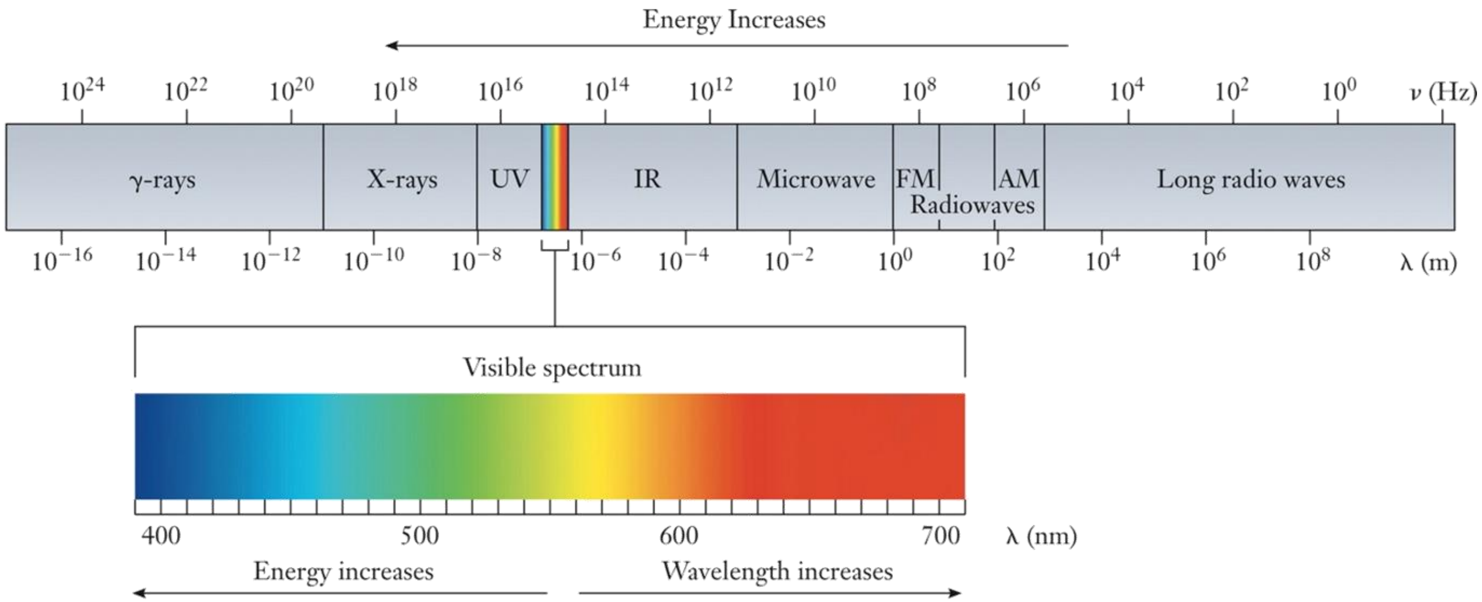
- Refraction is the bending of a wave when it passes from one medium to another of different refractive index
  - Speed of light changes
  - Light bends at an angle depending on its wavelength
  - Light separates into its component colors in order of their wavelengths





The Wave Nature of Light

- Electromagnetic radiation can be categorized in terms of its wavelength or frequency
  - Visible light is a small portion of the entire electromagnetic spectrum



Example Problem 6.1

- Carbon can be detected in an X-ray fluorescence experiment by monitoring the emission at a wavelength of 4.47 nm
  - What is the frequency of this light?

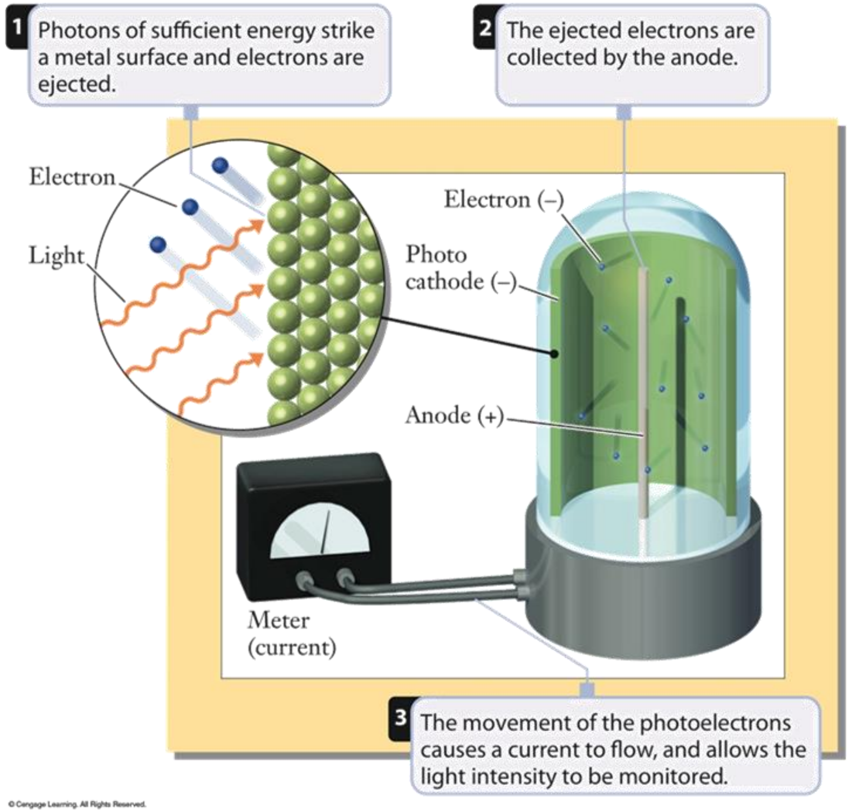
$$c = \lambda \cdot \nu$$

$$\Rightarrow \nu = \frac{c}{\lambda} = \frac{2.99 \times 10^{8}}{4.47 \times 10^{-6}} =$$

The Particulate Nature of Light

- Photoelectric effect occurs when light strikes a metal surface and causes electrons to be ejected
    - Energy from the light is transferred to the electrons in the metal
    - With sufficient energy, electrons break free from the metal
    - When more energy is given to electrons, they travel faster and have higher kinetic energy as they leave the metal

The Particulate Nature of Light

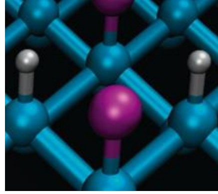


- The photoelectric effect is used in photocathodes
  - Light strikes the cathode and ejects electrons
  - Ejected electrons are collected at the anode
    - Positive voltage applied here ensures electrons travel in desired direction
  - Current flow is used to monitor light intensity

The Particulate Nature of Light

- The photoelectric effect is not explained using a wave description but is explained by modeling light as a particle
- Wave–particle duality: Depending on the situation, light is best described as a wave or a particle
  - Light is best described as a particle when light is imparting energy to another object
  - Light is described as a collection of packets of energy called photons
  - Neither waves nor particles provide an accurate description of all the properties of light
    - Model that best describes the properties being examined should be used

The Particulate Nature of Light



- The energy of a photon, *E*, is proportional to its frequency, *v*
  - It is inversely proportional to the wavelength, *λ*

$$E = h\nu = \frac{hc}{\lambda}$$

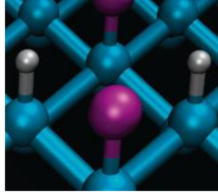
  - h denotes Planck’s constant, which is equal to $6.626 \times 10^{-34}\ \text{J} \cdot \text{s}$

Example Problem 6.2

- Chromium can be detected in atomic absorption spectroscopy by monitoring the absorbance of UV light at a wavelength of 357.8 nm
  - What is the energy of a photon of this light?

$$E = h\nu = 6.626 \times 10^{-34} \times \frac{2.99 \times 10^{14}}{357.8 \times 10^{-6}} =$$

The Particulate Nature of Light



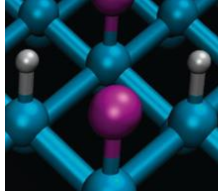
- Binding energy is the energy holding an electron to a metal
  - Threshold frequency, v_0, is the minimum frequency of light needed to emit an electron
  - For frequencies below the threshold frequency, no electrons are detected
  - For frequencies above the threshold frequency, extra energy is imparted to the electrons as kinetic energy
    - E_{photon} = Binding E + Kinetic E
      - This explains the photoelectric effect

Example Problem 6.3

- In a photoelectric experiment, ultraviolet light with a wavelength of 337 nm was directed at the surface of a piece of potassium metal. The kinetic energy of the ejected electrons was measured as 2.30×10^{-19} J
  - What is the electron binding energy for potassium?

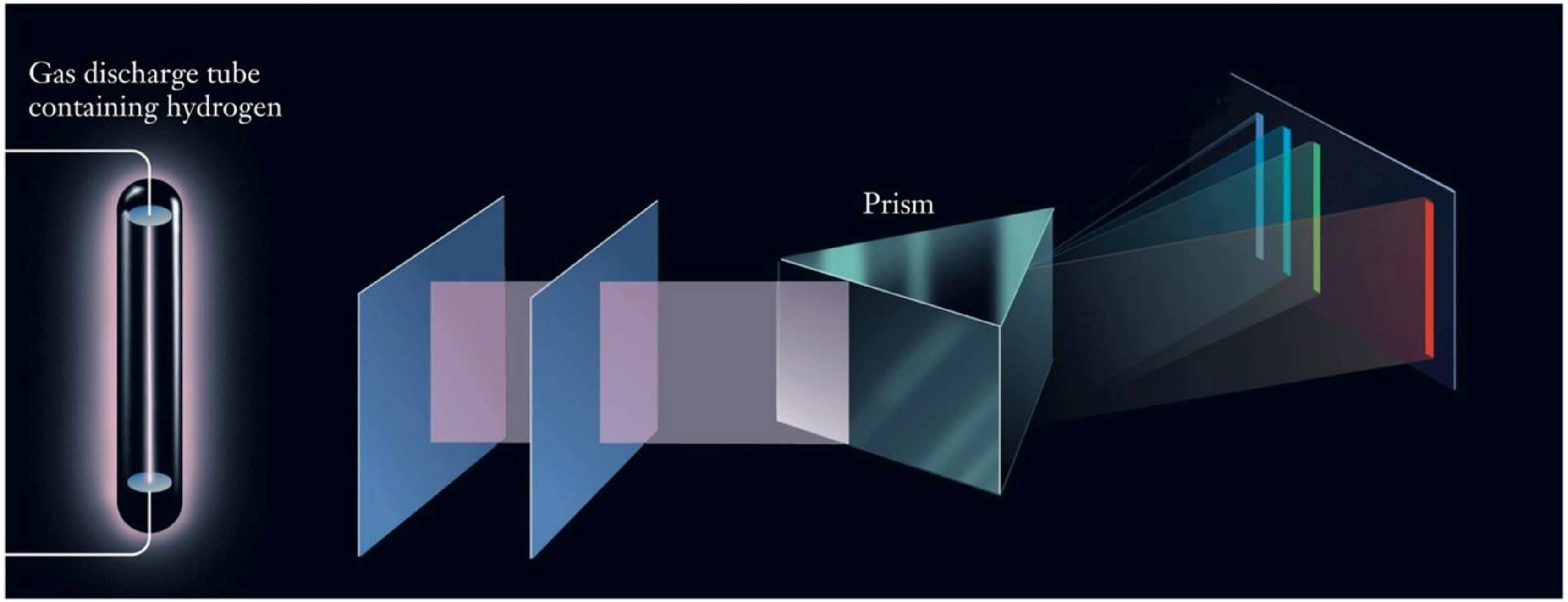
$$E_b = E_p - E_b$$
$$= h \cdot \nu - E_b$$
$$= \frac{h \cdot c}{\lambda} - E_b$$
$$= \frac{6.626 \times 10^{-34} \times 2.99 \times 10^{8}}{3.37 \times 10^{-7}} - 2.30 \times 10^{-19}$$

Atomic Spectra



- Atomic spectra: Particular pattern of wavelengths absorbed and emitted by an element
  - Wavelengths are well separated or discrete
  - Wavelengths vary from one element to the next
- Atoms can only exist in a few states with very specific energies
  - When light is emitted, the atom goes from a higher energy state to a lower energy state

Atomic Spectra



- Electrical current dissociates molecular H_2 into excited atoms, which emit light that separates into four discrete wavelengths after being passed through a prism

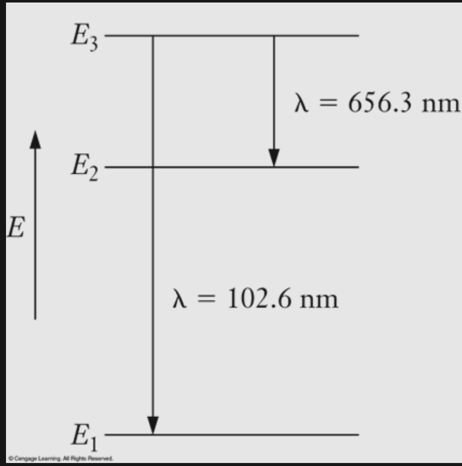
Example Problem 6.4

- When a hydrogen atom undergoes a transition from E_3 to E_1, it emits a photon with λ = 102.6 nm. Similarly, if the atom undergoes a transition from E_3 to E_2, it emits a photon with λ = 656.3 nm
    - Find the wavelength of light emitted by an atom making a transition from E_2 to E_1

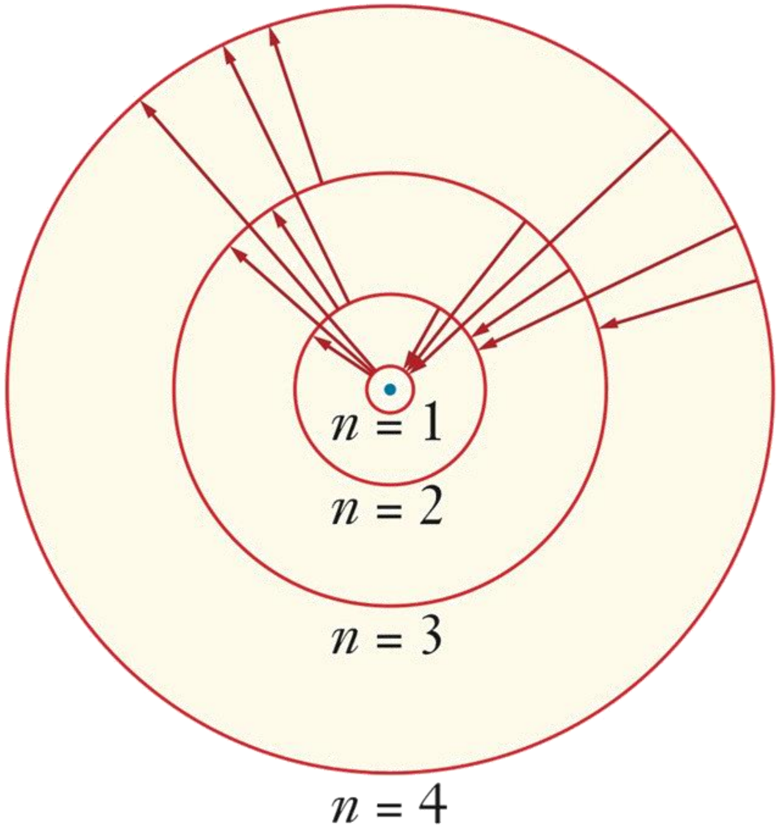
$$\Delta E = \frac{h\cdot c}{\lambda_1} - \frac{h \cdot c}{\lambda_2} = \frac{hc}{\lambda}$$

$$= hc\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)$$

$$\lambda_0 = \left(\frac{\lambda_1 \lambda_2}{\lambda_2 - \lambda_1}\right)$$

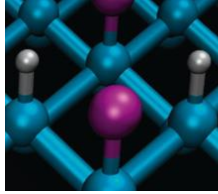


The Bohr Atom

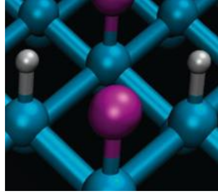


- Bohr model has electrons orbiting the nucleus in stable orbits
- Although not a completely accurate model, it can be used to explain absorption and emission
  - Electrons move from low energy to higher energy orbits by absorbing energy
  - Electrons move from high energy to lower energy orbits by emitting energy
  - Electron energy is quantized

The Bohr Atom



- Excited state: It is the grouping of electrons that is not at the lowest possible energy state
- Ground state: It is the grouping of electrons that is at the lowest possible energy state
  - Atoms return to ground state by emitting radiation



The Quantum Mechanical Model of the Atom

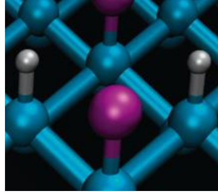
- Quantum mechanical model replaced the Bohr model of the atom
  - Bohr model depicted electrons as particles in circular orbits of fixed radius
  - Quantum mechanical model depicts electrons as waves spread out or delocalized through a region of space called an orbital
  - The energy of the orbitals is quantized like the Bohr model

The Quantum Mechanical Model of the Atom

- Diffraction of electrons was shown in 1927
  - Electrons exhibit wave-like behavior
- Wave behavior was described using a wave function, called as the Schrödinger equation
  - *H* is an operator, *E* is the energy, and ψ is the wave function

$$H\psi = E\psi$$

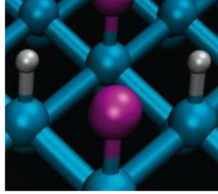
Quantum Numbers



- Each solution of the wave function defines an orbital
  - Each solution is labeled by a letter and number combination: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, etcetera
  - An orbital in quantum mechanical terms is actually a region of space rather than a particular point

- Quantum numbers are the solutions to the functions used to solve the wave equation
  - Quantum numbers are used to name atomic orbitals
  - Vibrating string fixed at both ends can be used to illustrate a function of the wave equation

Quantum Numbers



- When solving the Schrödinger equation, three quantum numbers are used
  - Principal quantum number, *n*, where *n* = 1, 2, 3, 4, 5, …
  - Secondary quantum number, ℓ
  - Magnetic quantum number, m_ℓ

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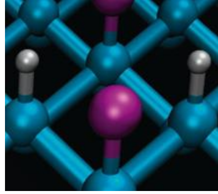

Quantum Numbers

- The principal quantum number, *n*, defines the shell in which a particular orbital is found
  - *n* must be a positive integer
  - *n* = 1 is the first shell, *n* = 2 is the second shell, and so on
  - Each shell has different energies

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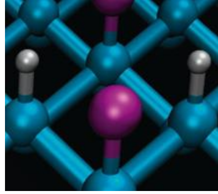
Quantum Numbers



- The secondary quantum number, ℓ, indexes energy differences between orbitals in the same shell of an atom
- ℓ has integer values from 0 to $n - 1$
  - ℓ specifies subshells
  - Each shell contains as many ℓ-values as its value of n

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Quantum Numbers

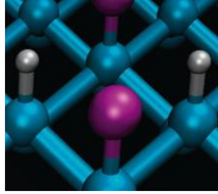
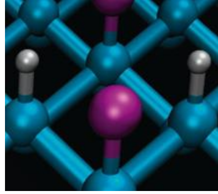


Table 6.1 Letter designations for naming orbitals

ℓ-value	0	1	2	3	4
Letter designation	*s*	*p*	*d*	*f*	*g*

Quantum Numbers



- The third quantum number is the magnetic quantum number, which is labeled m_ℓ
  - It has integer values
  - It may be either positive or negative
  - It must have an absolute value less than or equal to ℓ
  - For $\ell = 1$, $m_\ell = -1$, 0, or $+1$

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Quantum Numbers

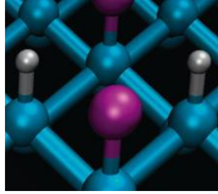


Table 6.2 Allowed combinations of quantum numbers

Relationships among values of the different quantum number are illustrated. This table allows us to make another observation about quantum numbers. If we count the total number of orbitals in each shell, it is equal to the square of the principal quantum number, n^2.

Value of n	Values for ℓ (letter designation)	Values for m_ℓ	Number of Orbitals
1	0 (*s*)	0	1
2	0 (*s*)	0	1
	1 (*p*)	−1, 0, 1	3
3	0 (*s*)	0	1
	1 (*p*)	−1, 0, 1	3
	2 (*d*)	−2, −1, 0, 1, 2	5
4	0 (*s*)	0	1
	1 (*p*)	−1, 0, 1	3
	2 (*d*)	−2, −1, 0, 1, 2	5
	3 (*f*)	−3, −2, −1, 0, 1, 2, 3	7

- Note the relationship between the number of orbitals within *s*, *p*, *d*, *f*, and m_ℓ

Example Problem 6.5

- Write all of the allowed sets of quantum numbers for a 3p orbital

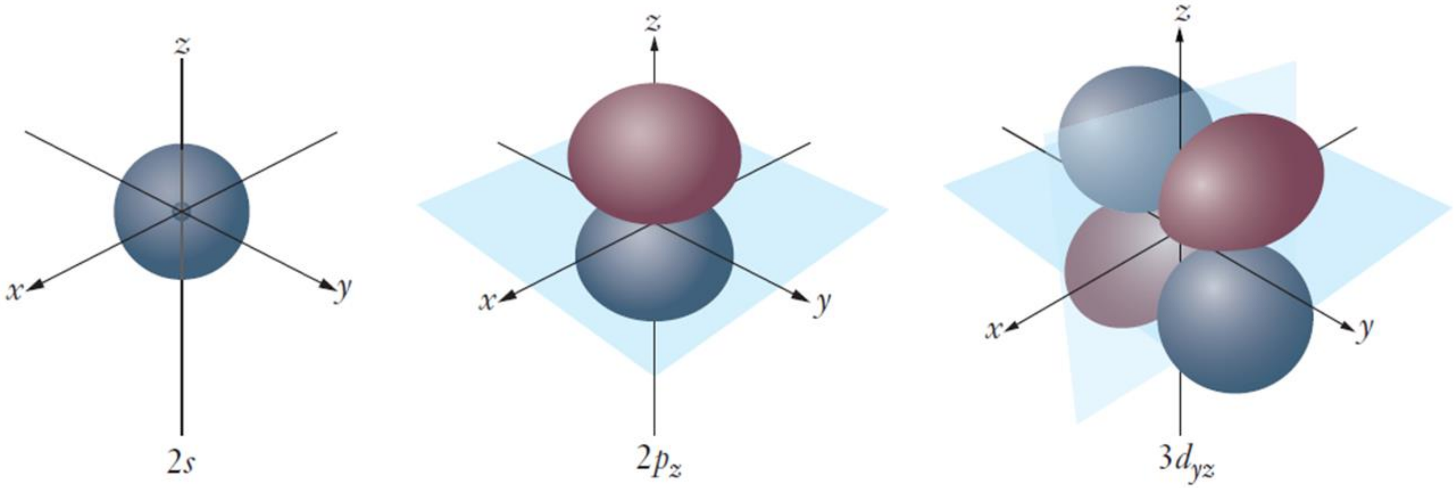
For 3p $n=3$ and $l=1$

$n > l \geq |m_l|$

So

n	l	m_l
3	1	-1
3	1	0
3	1	1

Visualizing Orbitals

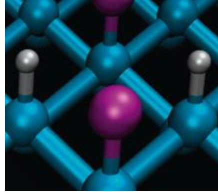


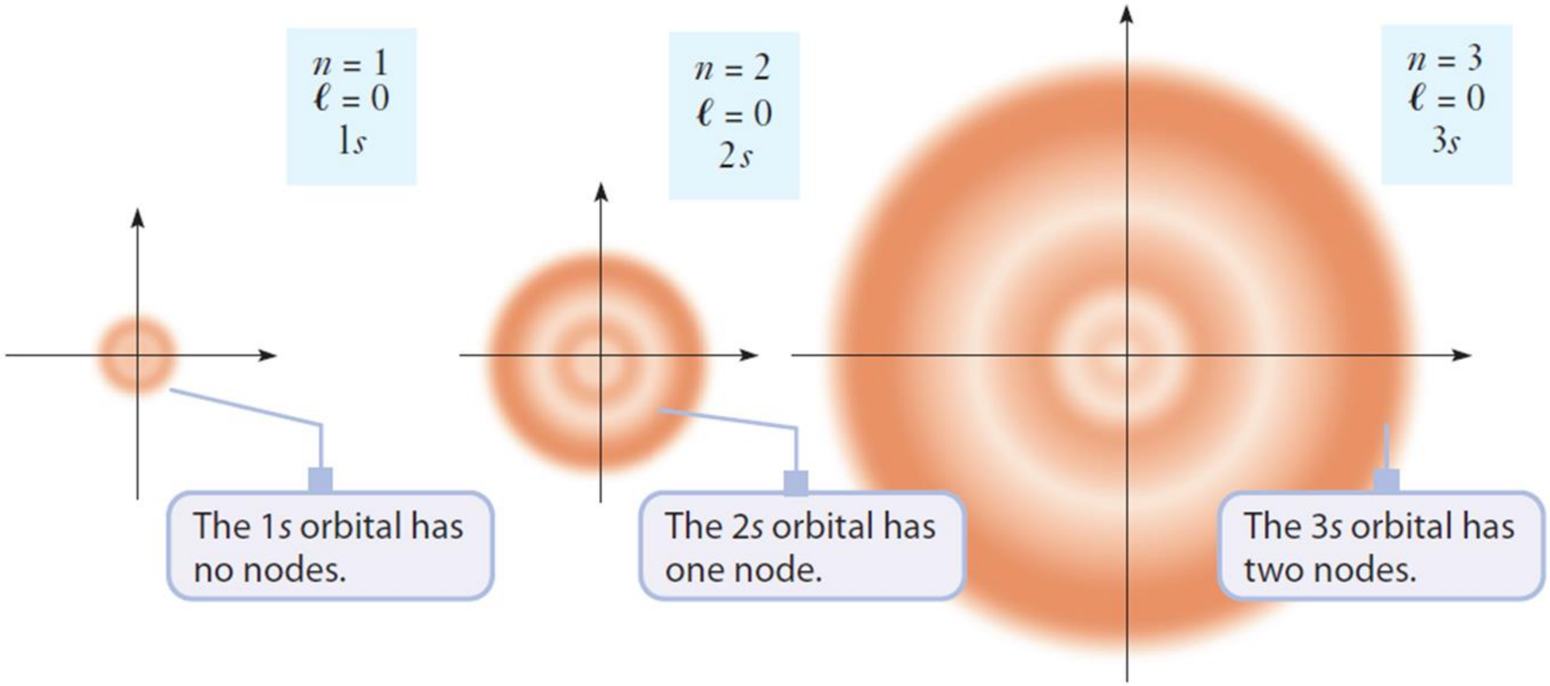
- *s* orbitals are spherical
- *p* orbitals have two lobes separated by a nodal plane
  - A nodal plane is a plane where the probability of finding an electron is zero
  - Here, it is the *xy* plane
- *d* orbitals have more complicated shapes due to the presence of two nodal planes

Visualizing Orbitals

- Nodes are explained using the uncertainty principle
  - It is impossible to determine both the position and momentum of an electron simultaneously and with complete accuracy
  - Orbitals provide us the probability of finding an electron
- The radial part of the wave function describes how the probability of finding an electron varies with distance from the nucleus
  - Spherical nodes are generated by the radial portion of the wave function

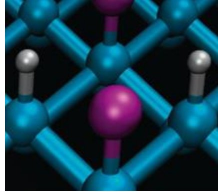
Visualizing Orbitals

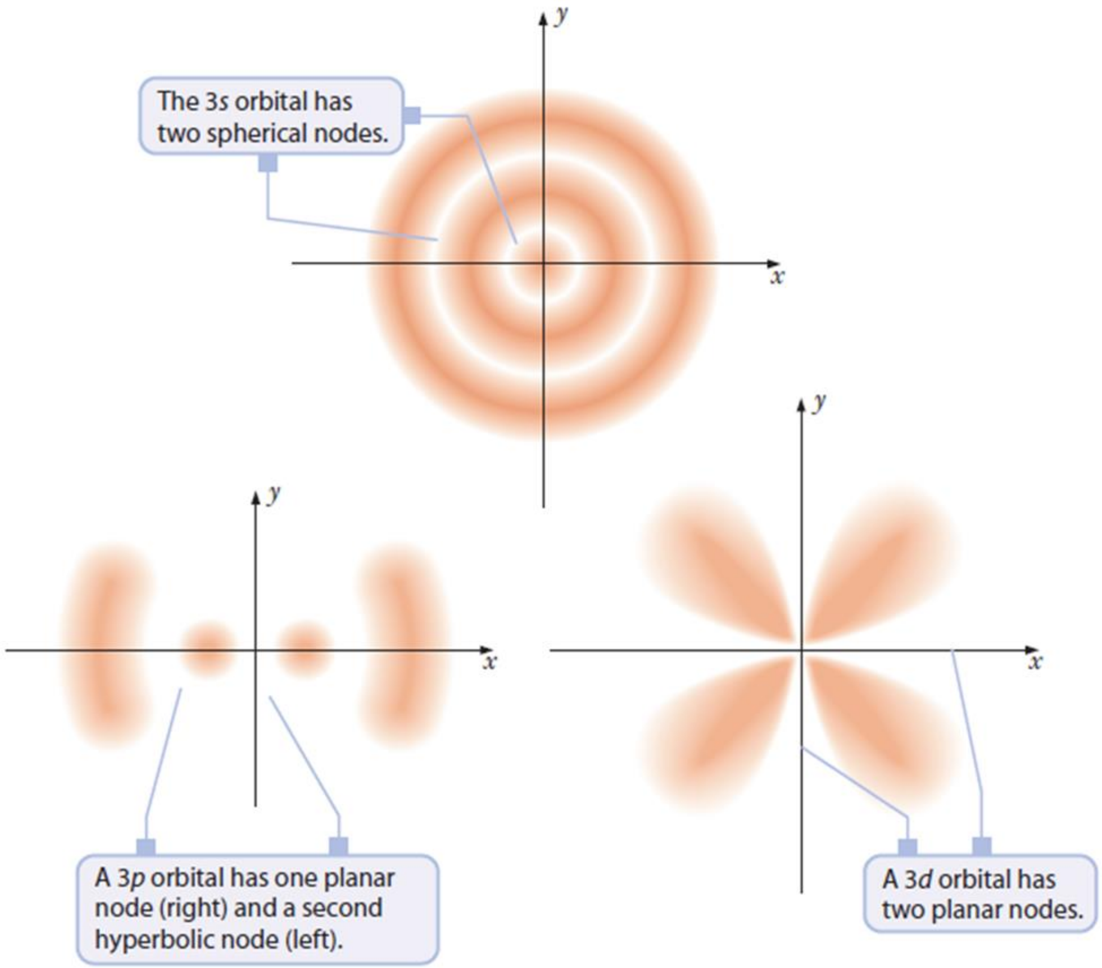




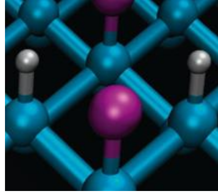
Cross-sectional views of the 1*s*, 2*s*, and 3*s* orbitals

Visualizing Orbitals





- Electron density plots for 3*s*, 3*p*, and 3*d* orbitals showing the nodes in each orbital



The Pauli Exclusion Principle and Electron Configurations

- The spin quantum number, m_s, determines the number of electrons that can occupy an orbital
  - m_s assumes only two possible values of ±½ or −½
  - Electrons are described as “spin up” or “spin down”
  - An electron is specified by using a set of four quantum numbers

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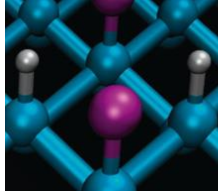
The Pauli Exclusion Principle and Electron Configurations



- The Pauli exclusion principle states that no two electrons in an atom may have the same set of four quantum numbers
  - Two electrons can have the same values of the first three quantum numbers but must have different values of m_s
  - There can be only two electrons maximum per orbital
  - Two electrons occupying the same orbital are spin paired
    - One with + ½ spin and the other with − ½ spin

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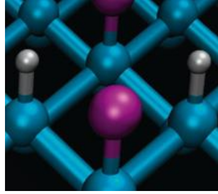
Orbital Energies and Electron Configurations

- Electrons in smaller orbitals are held more tightly and have lower energies
  - Orbital size increases as the value of *n* increases
  - True for hydrogen atoms but not entirely true for multielectron atoms
    - As nuclear charge increases, the orbital size decreases
    - Electrons interact with other electrons as well as the positively charged nucleus

Orbital Energies and Electron Configurations



- For electrons in larger orbitals, the charge felt is a combination of the actual nuclear charge and the offsetting charge of electrons in lower orbitals
  - Masking of the nuclear charge is called shielding
  - Shielding results in a reduced, effective nuclear charge

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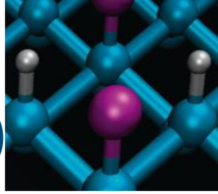
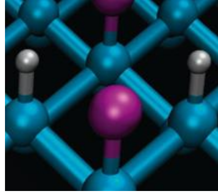
Orbital Energies and Electron Configurations (4 of 4)

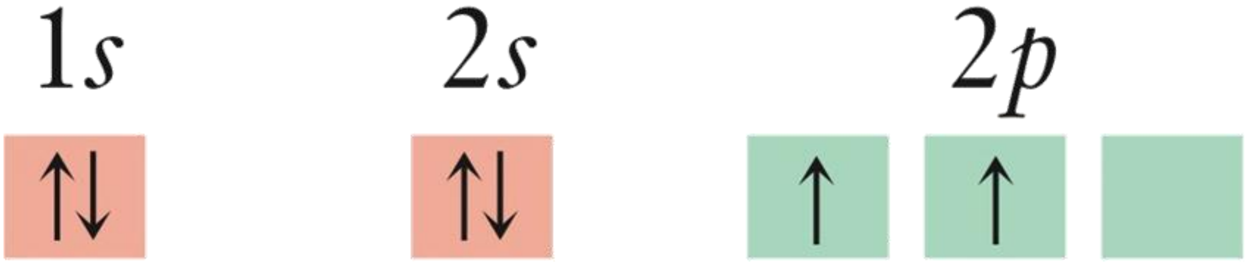


- The accepted order of orbital energies is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3d, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, 5*f*, 6*d*, and 7*p*
  - An orbital’s size and penetration when treated quantitatively produces the order of filling represented
- Electronic configurations are written in order of energy for atomic orbitals

Hund's Rule and the Aufbau Principle



- The Aufbau principle requires filling of orbitals starting with the lowest energy and proceeding to the next highest energy level
- Hund's rule states that within a subshell, electrons occupy orbitals individually and with parallel spins whenever possible
- Electron configurations are sometimes depicted using boxes to represent orbitals
- This depiction shows paired and unpaired electrons explicitly
  - See the example for carbon below:



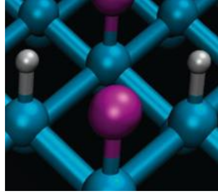
Example Problem 6.6

- What is the electron configuration for the sulfur atom?

$1s^2 2s^2 2p^6 3s^2 3p^4$

$[Ne] 3s^2 3p^4$

Hund’s Rule and the Aufbau Principle

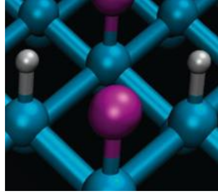


- A simplified depiction uses superscripts to indicate the number of electrons in an orbital set
    - $1s^2 2s^2 2p^2$ is the electronic configuration for carbon
- Shorthand for writing electronic configurations
    - Makes writing electron configurations less unwieldy
    - Relates electronic structure to chemical bonding
        - Electrons in outermost occupied orbitals give rise to the chemical reactivity of an element
- $[He]2s^2 2p^2$ is the shorthand for carbon

Example Problem 6.7

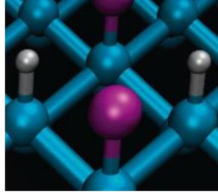
- What is the electron configuration (short hand notion) for the sulfur atom?

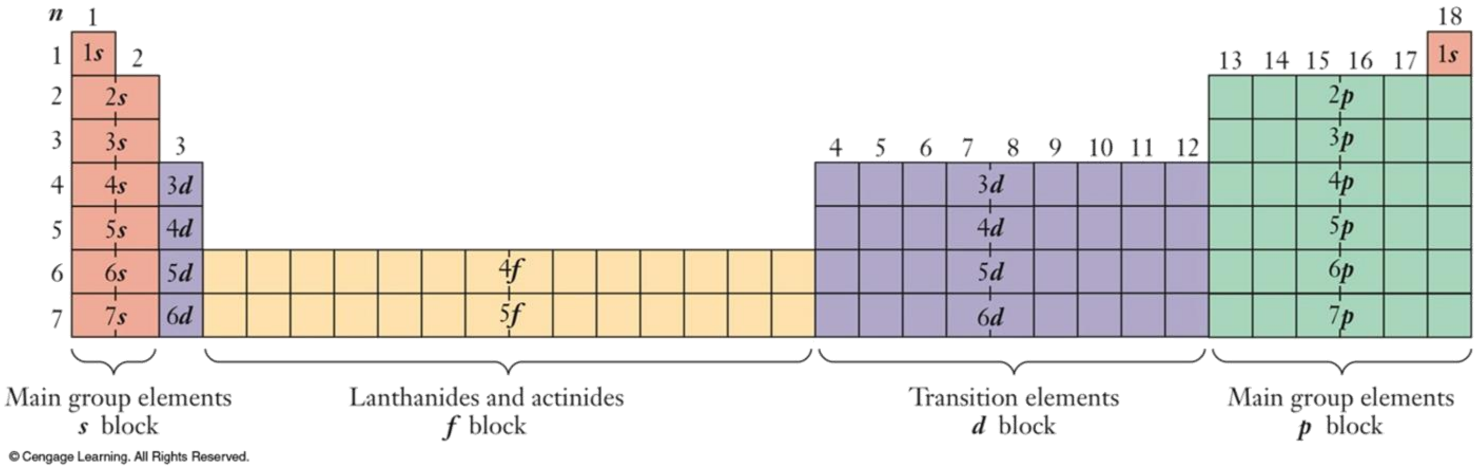
Hund's Rule and the Aufbau Principle



- The inner electrons, which lie closer to the nucleus, are referred to as core electrons
  - Core electrons can be represented by the atomic symbol of the noble gas elements with the same electronic configuration
- The outer electrons are usually referred to as valence electrons
  - Valence electrons are shown explicitly when a noble gas shorthand is used to write electronic configurations
  - Valence electrons determine reactivity

The Periodic Table and Electron Configurations (2 of 2)





- The shape of the periodic table can be broken down into blocks according to the type of orbital occupied by the highest energy electron in the ground state
- We find the element of interest in the periodic table and write its core electrons using the shorthand notation with the previous rare gas element
  - Then we determine the valence electrons by noting where the element sits within its own period in the table

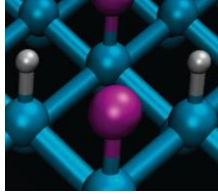
Example Problem 6.8

- Tungsten alloys are often used for parts that must withstand high temperatures
  - Use the periodic table to determine the electron configuration of tungsten, W

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

$[Xe]\ 5d^4 6s^2$

Periodic Trends in Atomic Properties



- Using the understanding of orbitals and atomic structure, it is possible to explain some periodic properties
  - Atomic size
  - Ionization energy
  - Electron affinity

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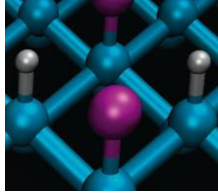
Atomic Size

- The shell in which the valence electrons are found affects atomic size
  - The size of the valence orbitals increases with *n*, so size must increase from top to bottom for a group
- The strength of the interaction between the nucleus and the valence electrons affects atomic size
  - The effective nuclear charge increases from left to right across a period, so the interaction between the electrons and the nucleus increases in strength
  - As interaction strength increases, valence electrons are drawn closer to the nucleus, decreasing atomic size

Ionization Energy



- Ionization energy is the energy required to remove an electron from a gaseous atom, forming a cation
  - Formation of X^{+} is the first ionization energy, X^{2+} would be the second ionization energy, etc.

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

  - The more strongly held an electron is, the higher the ionization energy must be
  - As valence electrons move further from the nucleus, they become easier to remove and the first ionization energy becomes smaller

CENGAGE

Ionization Energy

- From nitrogen to oxygen, there is a slight decrease in ionization energy
  - Nitrogen has a half-filled *p* subshell
  - Oxygen must pair two electrons in one 2*p* orbital
  - Ionization of oxygen relieves electron–electron repulsion, lowering its ionization energy
- Ionization energies increase with successive ionizations for a given element
  - Effective nuclear charge for valence electrons is larger for the ion than the neutral atom
- Filled subshells of electrons are difficult to break up, making it difficult to remove electrons from noble gases

Ionization Energy

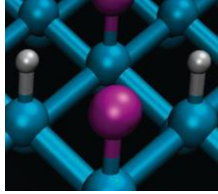


Table 6.5 Successive ionization energies

The first four ionization energies (all in kJ/mol) for the elements of the first three periods. Those ionizations with values shown in **shaded** cells with **bold** print involve removing the last electron from a particular shell. Further ionization requires removing an electron from a more stable filled shell, and this leads to a very large increase in ionization energy.

Z	Element	IE_1	IE_2	IE_3	IE_4
1	H	**1312**	–	–	–
2	He	2372	**5250**	–	–
3	Li	**520.2**	7298	11,815	–
4	Be	899.4	**1757**	14,848	21,007
5	B	800.6	2427	**3660**	25,026
6	C	1086	2353	4620	**6223**
7	N	1402	2856	4578	7475
8	O	1314	3388	5300	7469
9	F	1681	3374	6050	8408

The first four ionization energies in kJ/mol for elements Z = 1 to 9

CENGAGE

Electron Affinity

- Electron affinity is the energy required to place an electron on a gaseous atom, forming an anion

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

  - Electron affinities may have positive or negative values
    - Negative values—energy released
    - Positive values—energy absorbed
- Electron affinities increase or the numerical value becomes more negative from left to right for a period and bottom to top for a group
- The greater or more negative the electron affinity becomes, the more stable the anion will be