CHEMISTRY

Chapter 6 ELECTRONIC STRUCTURE AND PERIODIC PROPERTIES OF ELEMENTS

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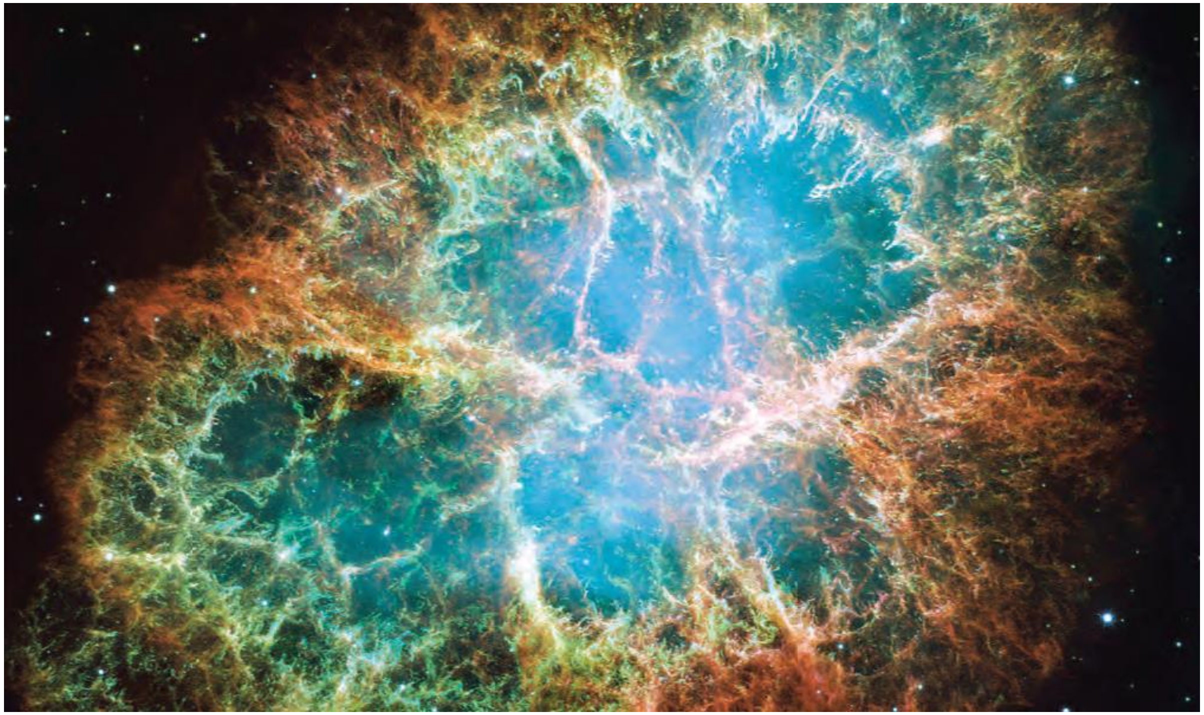
HW problems: 9, 11, 27, 35, 45, 49, 53, 61, 67, 71, 77



CH. 6 OUTLINE

6.1: Electromagnetic Energy

6.2: The Bohr Model

6.3: Development of Quantum Theory

6.4: Electronic Structure of Atoms (Electron Configurations)

6.5: Periodic Variations in Element Properties

6.1 ELECTROMAGNETIC ENERGY

- The nature of light has been a subject of inquiry since antiquity…. But focus on the chemistry here, not the physics. The point of all of this is that LIGHT has enabled chemists to EXPLORE atoms/molecules (spectroscopy).
- **In the seventeenth century, Isaac Newton said:**
  - ***White light consists of the individual colors of the rainbow combined together.***

  - ***Light was composed of streams of extremely tiny particles*** travelling at high speeds according to Newton's laws of motion.

LIGHT

- **Early in the nineteenth century, Thomas Young said:**
  - Light passing through narrow, closely spaced slits produced interference patterns.
  - Could not be explained in terms of Newtonian particles but could be easily ***explained in terms of waves.***

- **James Clerk Maxwell said:**
  - ***Light was the visible part of a vast spectrum of electromagnetic waves.***

- Particles and waves are connected on a fundamental level called ***wave-particle duality.***

WAVES

- A ***wave*** is an oscillation or periodic movement that can transport energy from one point in space to another.

- **Examples of waves:**
  - Shaking the end of a rope
  - Dropping a pebble into a pond.
  - The expansion of air that accompanies a lightning strike.

- In each of these cases, ***kinetic energy is transferred through matter*** (the rope, water, or air) while the matter remains essentially in place.

SPEED OF LIGHT

- Waves are not restricted to travel through only matter.

- ***Electromagnetic waves*** consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel.

- Electromagnetic waves can travel through a vacuum at a constant speed.

- This speed is known as the ***speed of light (c).***

- **$c = 2.998 \times 10^8$ m/s**

WAVE PROPERTIES

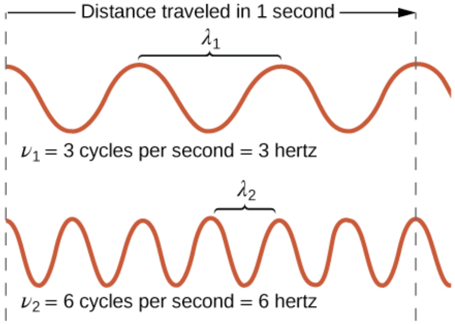
- All waves are characterized by the following:

1) Wavelength (λ)

- Distance between two consecutive peaks or troughs in a wave.

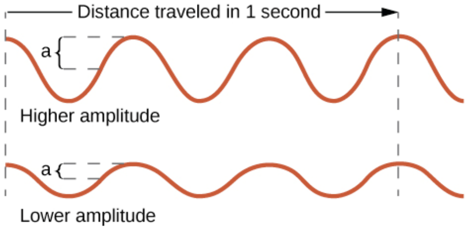
2) Frequency (ν)

- Number of successive wavelengths that pass a given point in a unit time.



3) Amplitude

- One half the distance between the peaks and troughs.



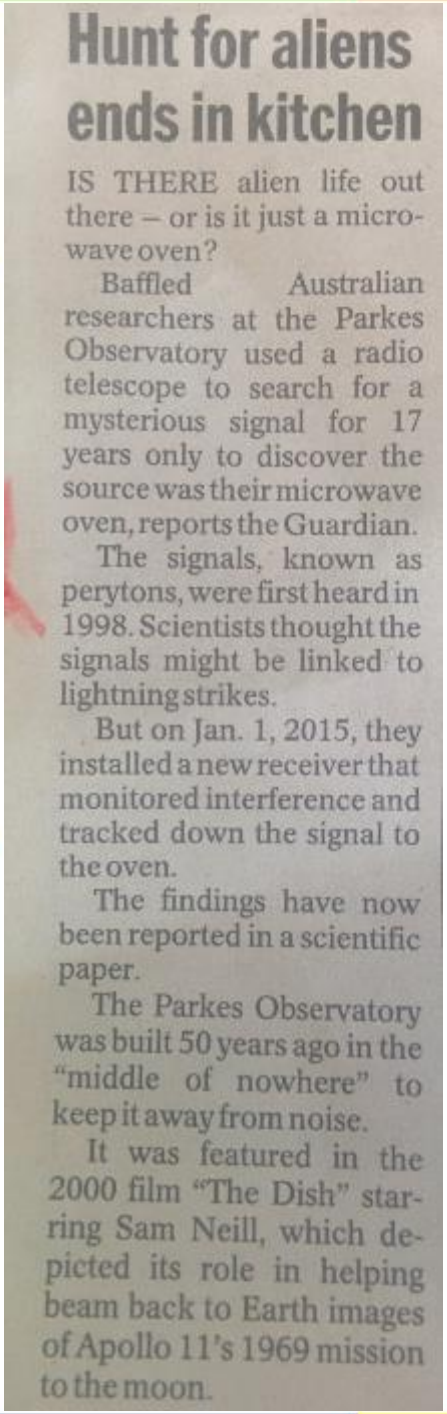
FREQUENCY

- The unit for frequency, expressed as cycles per second (s^{-1}), is the ***hertz (Hz).***

- Common multiples of the hertz are often used.
  - Megahertz, (1 MHz = 1×10^6 Hz)
  - Gigahertz (1 GHz = 1×10^9 Hz)

PERYTONS

- Daily News, 5/10/15, p.21
- 1-3 GHz (10^9 Hz)
- Monthly Notices of the Royal Astronomical Society, April 10, 2015
- http://arxiv.org/pdf/1504.02165v1.pdf



Hunt for aliens ends in kitchen

IS THERE alien life out there – or is it just a microwave oven?

Baffled Australian researchers at the Parkes Observatory used a radio telescope to search for a mysterious signal for 17 years only to discover the source was their microwave oven, reports the Guardian.

The signals, known as perytons, were first heard in 1998. Scientists thought the signals might be linked to lightning strikes.

But on Jan. 1, 2015, they installed a new receiver that monitored interference and tracked down the signal to the oven.

The findings have now been reported in a scientific paper.

The Parkes Observatory was built 50 years ago in the "middle of nowhere" to keep it away from noise.

It was featured in the 2000 film "The Dish" starring Sam Neill, which depicted its role in helping beam back to Earth images of Apollo 11's 1969 mission to the moon.

WAVELENGTH, FREQUENCY, AND SPEED

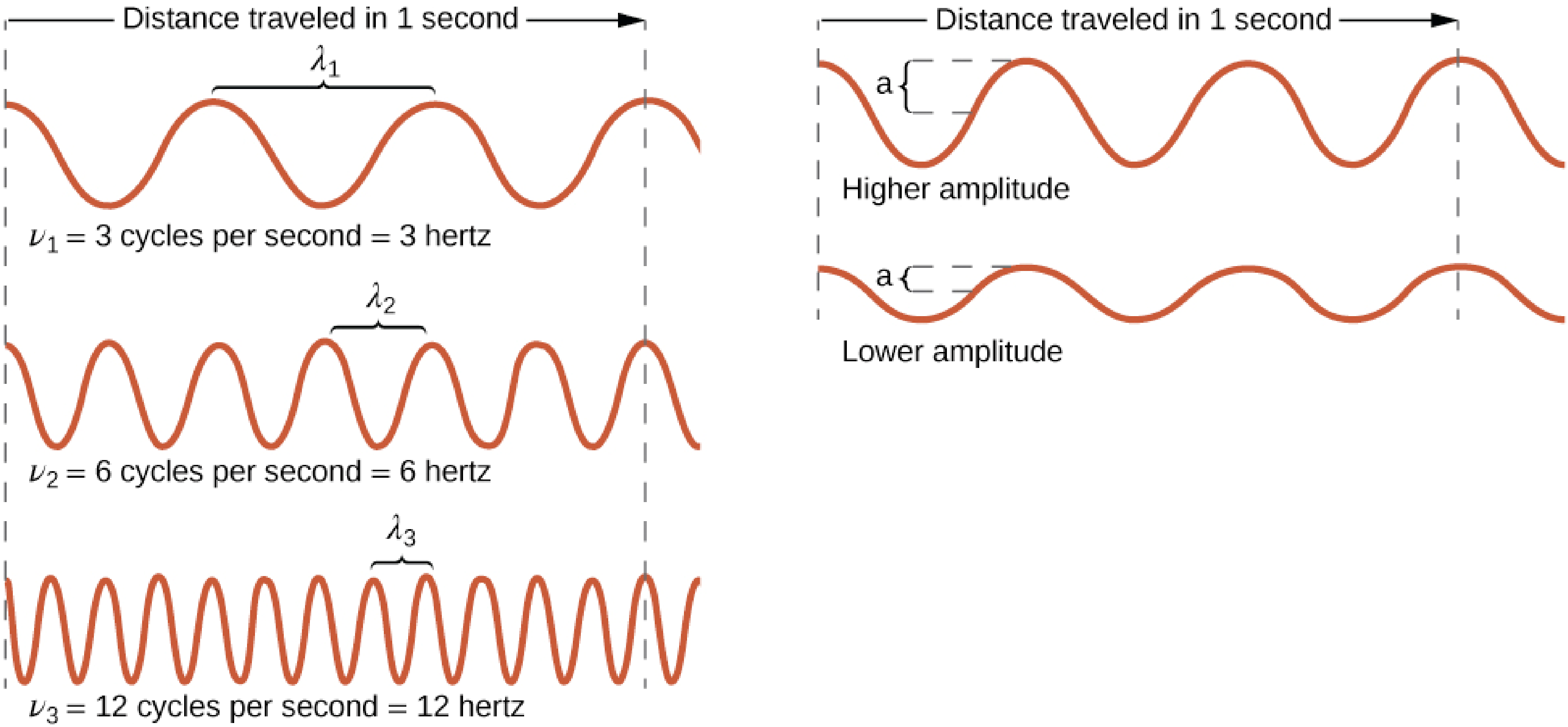
- The product of a wave's wavelength (λ) and its frequency (v), λv, is the speed of the wave.

- Thus, for electromagnetic radiation in a vacuum:

$$c = 2.998 \times 10^8 \text{ m/s} = \lambda v$$

- Wavelength and frequency are ***inversely proportional***:
  - As the wavelength increases, the frequency decreases and vice-versa.

FIGURE 6.2



One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

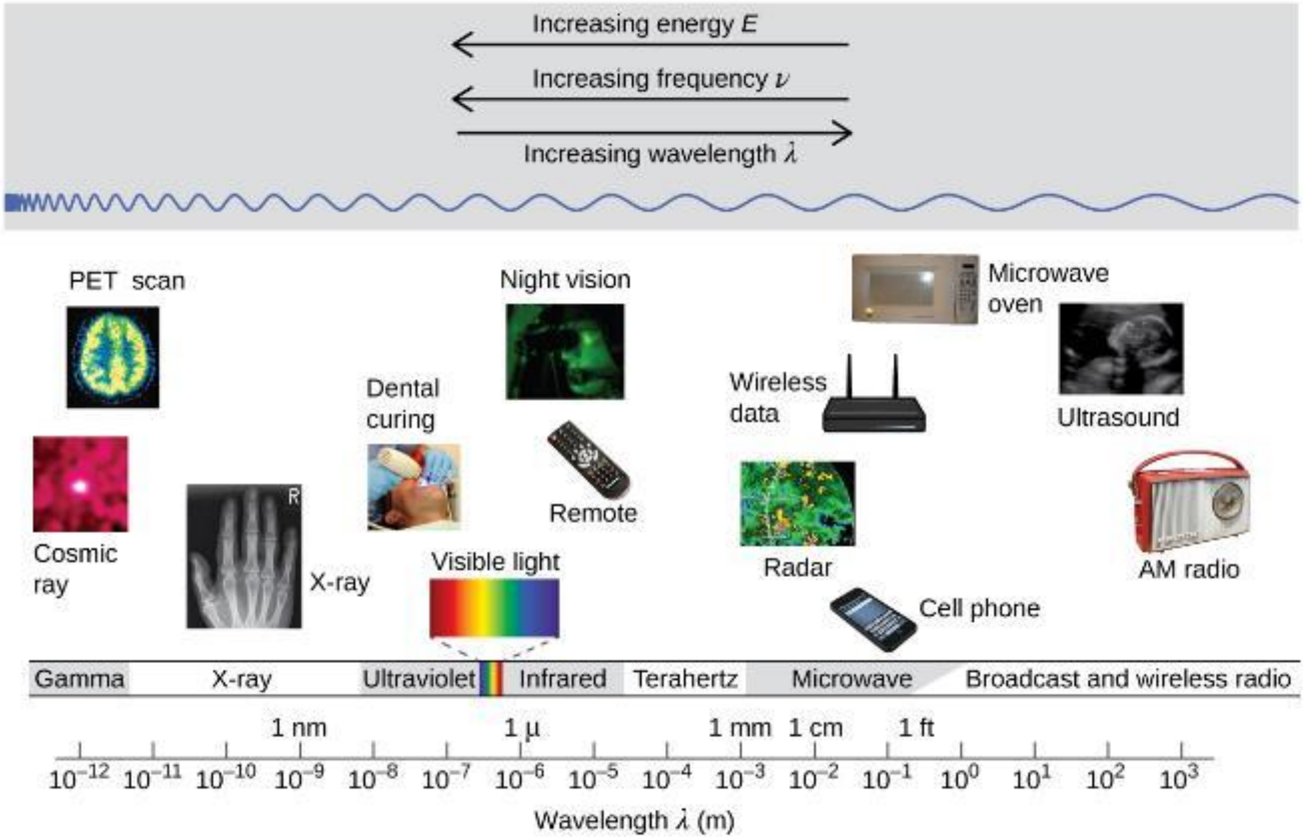
ELECTROMAGNETIC SPECTRUM

- The ***electromagnetic spectrum*** is the range of all types of electromagnetic radiation.

- Visible light makes up only a small portion of the electromagnetic spectrum.

- Each of the various colors of visible light has specific frequencies and wavelengths associated with them.

FIGURE 6.3



Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit “Cosmic ray”: modification of work by NASA; credit “PET scan": modification of work by the National Institute of Health; credit “X-ray”: modification of work by Dr. Jochen Lengerke; credit “Dental curing": modification of work by the Department of the Navy; credit “Night vision": modification of work by the Department of the Army; credit “Remote": modification of work by Emilian Robert Vicol; credit “Cell phone": modification of work by Brett Jordan; credit “Microwave oven”: modification of work by Billy Mabray; credit “Ultrasound": modification of work by Jane Whitney; credit “AM radio”: modification of work by Dave Clausen)

EXAMPLE 6.1

A sodium streetlight gives off yellow light that has a wavelength of 589 nm (1 nm = 1×10^{-9} m). What is the frequency of this light?

We can rearrange the equation $c = \lambda v$ to solve for the frequency:

$$n = \frac{c}{l}$$

EXAMPLE 6.1

Since *c* is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = \left(\frac{2.998\times10^{8}\ \cancel{m}s^{-1}}{589\ n\cancel{m}}\right)\left(\frac{1\times10^{9}\ n\cancel{m}}{1\ \cancel{m}}\right) = 5.09\times10^{14}\ s^{-1}$$

STANDING WAVES

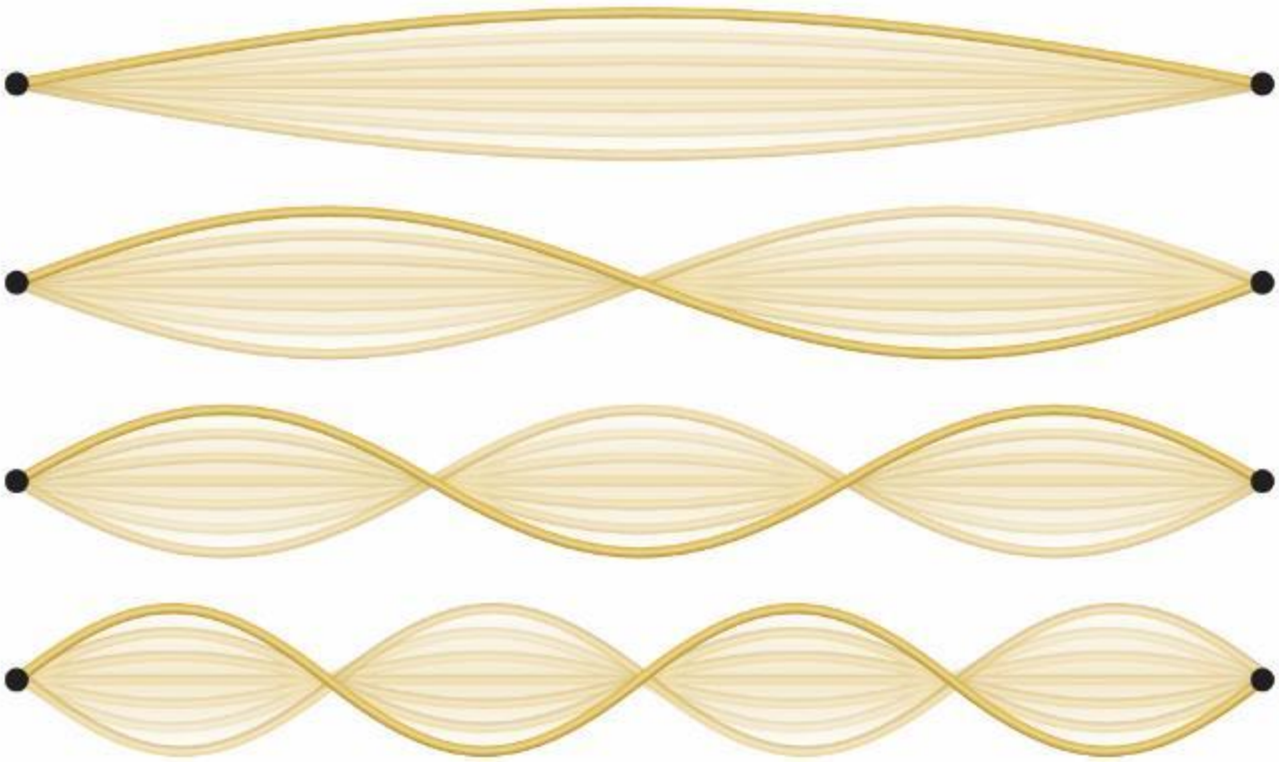
- Not all waves are travelling waves.

- ***Standing waves*** (also known as stationary waves) remain constrained within some region of space.

- Standing waves play an important role in our understanding of the electronic structure of atoms and molecules.

- A vibrating string that is held fixed at its two end points is an example of a ***one-dimensional standing wave.***

FIGURE 6.7



A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

STANDING WAVES

- ***Only those waves having an integer number, n, of half-wavelengths between the end points can form.***
- A system with fixed end points restricts the number and type of possible waveforms.
- This is an example of ***quantization***.
  - Only discrete values from a more general set of continuous values are observed.

STANDING WAVES

- Harmonic waves (those waves displaying more than one-half wavelength) all have one or more points between the two end points that are not in motion.

- These special points are ***nodes.***

BLACKBODY RADIATION AND THE ULTRAVIOLET CATASTROPHE

- ***Around 1900, Max Planck*** derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error).

- Planck developed his theoretical treatment on the premise that the atoms composing the oven vibrated.

- The atoms vibrated at increasing frequencies (or decreasing wavelengths), as the temperature increased.

PLANCK’S CONSTANT

- Planck had to assume that the the vibrating atoms required quantized energies, which he was unable to explain.

$$E = nh\nu \qquad\qquad n = 1, 2, 3, \ldots$$

- The quantity *h* is a constant now known as ***Planck's constant.***

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

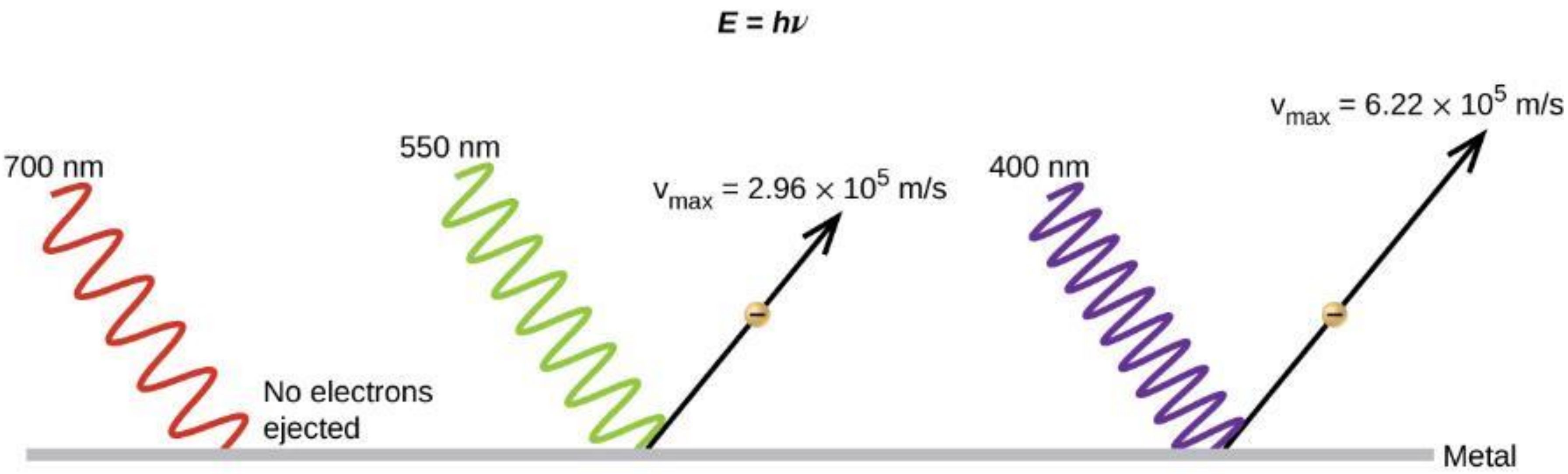
THE PHOTOELECTRIC EFFECT

- The next paradox in the classical theory to be resolved concerned the ***photoelectric effect.***

- It had been observed that electrons could be ejected from the surface of a metal.
  - The light had to have a frequency greater than some threshold frequency.

- Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light.

FIGURE 6.11



Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of ejected electron will be proportional to the energy of the incoming photon.

THE PHOTOELECTRIC EFFECT

- According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency.

- ***Albert Einstein*** was able to resolve the paradox by incorporating Planck's quantization findings into the particle view of light ***(Nobel prize).***

- Light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called ***photons***).

THE PHOTOELECTRIC EFFECT

- The energy of the photons depended on their frequency.

- According to Planck's formula:

$$E = hn$$

$$n = \frac{c}{l}$$

$$E = \frac{hc}{l}$$

THE PHOTOELECTRIC EFFECT

$$E = h\nu$$

- Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold).

- The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions.

- Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as ***wave-particle duality.***

EXAMPLE 6.2

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

We use the form of Planck's equation that includes the wavelength, *λ*, and convert units of nanometers to meters so that the units of *λ* and *c* are the same.

$$E = \frac{hc}{\lambda} = \frac{\left(6.626 \times 10^{-34}\ J \cdot \cancel{s}\right)\left(2.998 \times 10^{8}\ \cancel{m} \cdot \cancel{s^{-1}}\right)}{\left(640\ \cancel{nm}\right)\left(\dfrac{1\ \cancel{m}}{10^{9}\ \cancel{nm}}\right)}$$

$$E = 3.10 \times 10^{-19}\ J$$

LINE SPECTRA

- Scientists in the late nineteenth century struggled with understanding the light emitted from atoms and molecules.

- When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light.

- Photons produced in this manner have a range of energies, and thereby produce a ***continuous spectrum*** in which an unbroken series of wavelengths is present.

LINE SPECTRA

- In contrast to continuous spectra, light can also occur as discrete or ***line spectra*** having very narrow line widths interspersed throughout the spectral regions.

- Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra.

- Each element displays its own characteristic set of lines.

FIGURE 6.12

Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign show the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

LINE SPECTRA

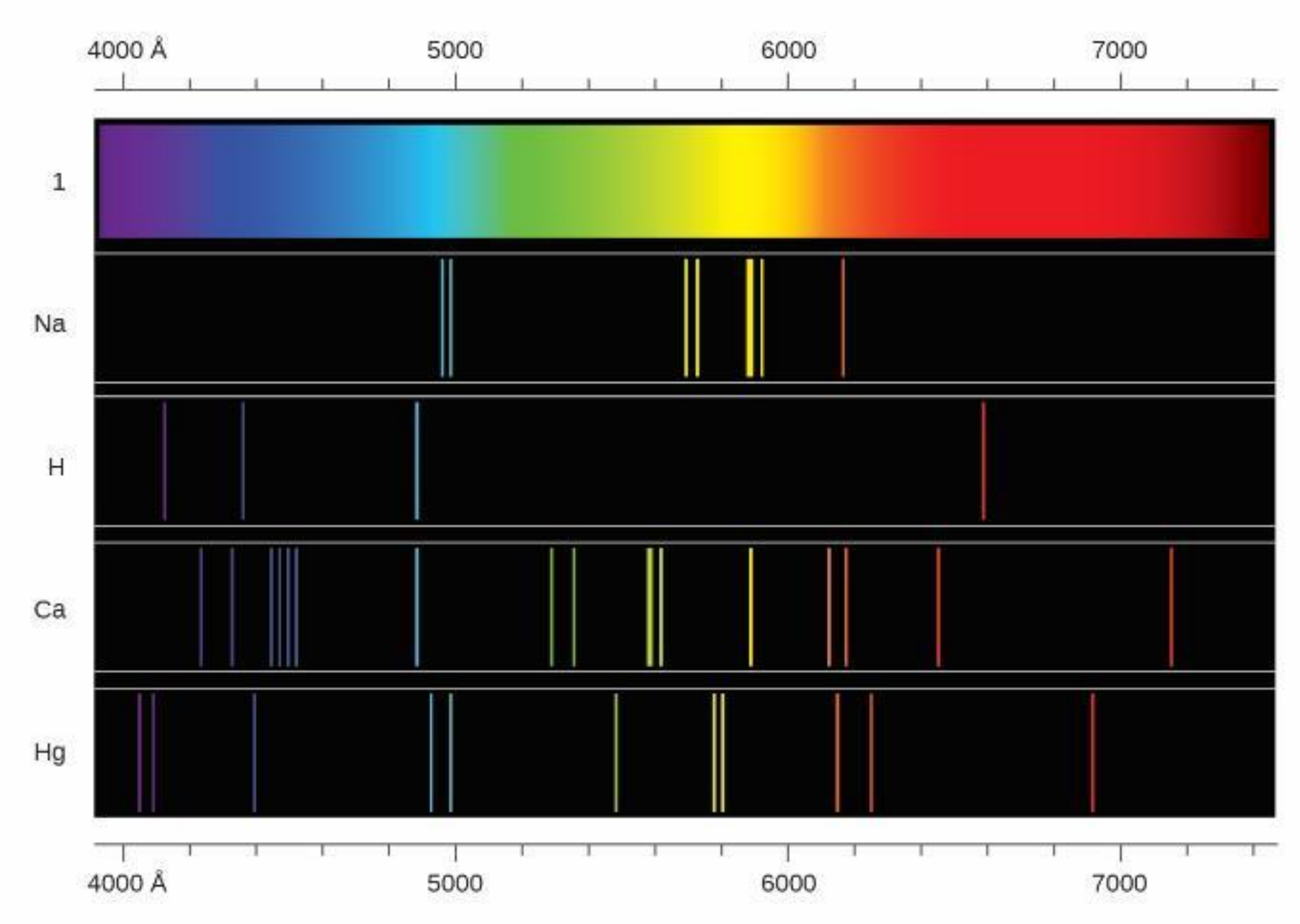
- Each emission line consists of a ***single wavelength of light***.

- This implies that the light emitted by a gas consists of a set of ***discrete energies.***

- The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists.

- According to classical electromagnetic theory, only continuous spectra should be observed.

FIGURE 6.13



Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

LINE SPECTRA

- ***In 1885, Johann Balmer*** was able to derive an empirical equation.

- The equation related the four visible wavelengths of light emitted by hydrogen atoms to whole integers.

$$\frac{1}{\lambda} = k\left(\frac{1}{4} - \frac{1}{n^2}\right), \quad n = 3, 4, 5, 6$$

- Other discrete lines for the hydrogen atom were found in the UV and IR regions.

LINE SPECTRA

- ***Johannes Rydberg*** generalized Balmer's work.

- He developed an empirical formula that predicted all of hydrogen's emission lines.

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

- n_1 and n_2 are integers
- $n_1 < n_2$
- R_{∞} is the ***Rydberg constant (1.097×10^7 m^{-1})***

6.2 BOHR MODEL

- The emission spectra for hydrogen was eventually explained by ***Neils Bohr in 1913.***

- Bohr’s work convinced scientists to abandon classical physics and spurred the development of modern ***quantum mechanics.***

ATOMIC MODEL PRIOR TO BOHR

- Atoms consisted of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus.

- This classical mechanical description of the atom is incomplete, since an electron moving in an elliptical orbit would be accelerating.

- According to classical electromagnetism, the electron should continuously emit electromagnetic radiation.

ATOMIC MODEL PRIOR TO BOHR

- This loss in orbital energy should result in the electron’s orbit getting continually smaller until it spirals into the nucleus.

- Neils Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism’s prediction that the orbiting electron in hydrogen would continuously emit light.

BOHR MODEL

- Bohr incorporated the following into the classical mechanics description of the atom.
  - Planck's ideas of quantization.
  - Einstein's finding that light consists of photons whose energy is proportional to their frequency.

- Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation.

- Rather the electron emits or absorbs a photon *if it moved to a different orbit*.

BOHR MODEL

- The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

$$|\Delta E| = |E_f - E_i| = h\nu = \frac{hc}{\lambda}$$

- E_i and E_f are the initial and final orbital energies.

- Bohr assumed only discrete values for the energy difference (ΔE) were possible.

BOHR MODEL

- Bohr’s expression for the quantized energies:

$$E_n = -\frac{k}{n^2} \qquad n = 1, 2, 3, \ldots$$

- *k* is a constant comprising fundamental constants such as the electron mass and charge and Planck’s constant.

BOHR MODEL

- Inserting the expression for the orbit energies into the equation for Δ*E* gives

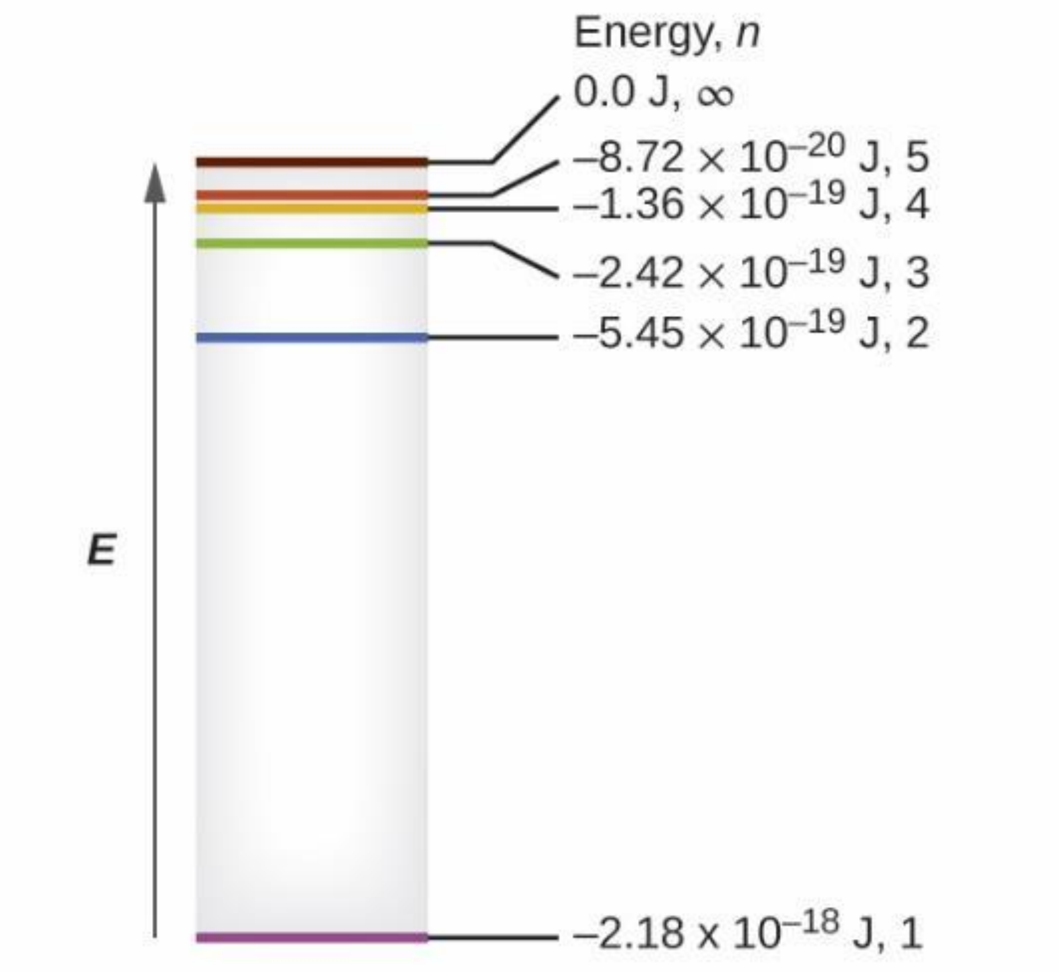
$$\Delta E = k\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{hc}{\lambda}$$

- *or*

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

- *which is identical to the Rydberg equation* for $R_\infty = \frac{k}{hc}$

FIGURE 6.14



Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

BOHR MODEL

- One of the fundamental laws of physics is that matter is most stable when it has the lowest possible energy.

- When the electron is in this lowest energy orbit (n = 1), the atom is said to be in its ***ground state.***

- If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher *n* value ***(excited state)***, which has a higher energy.

BOHR MODEL

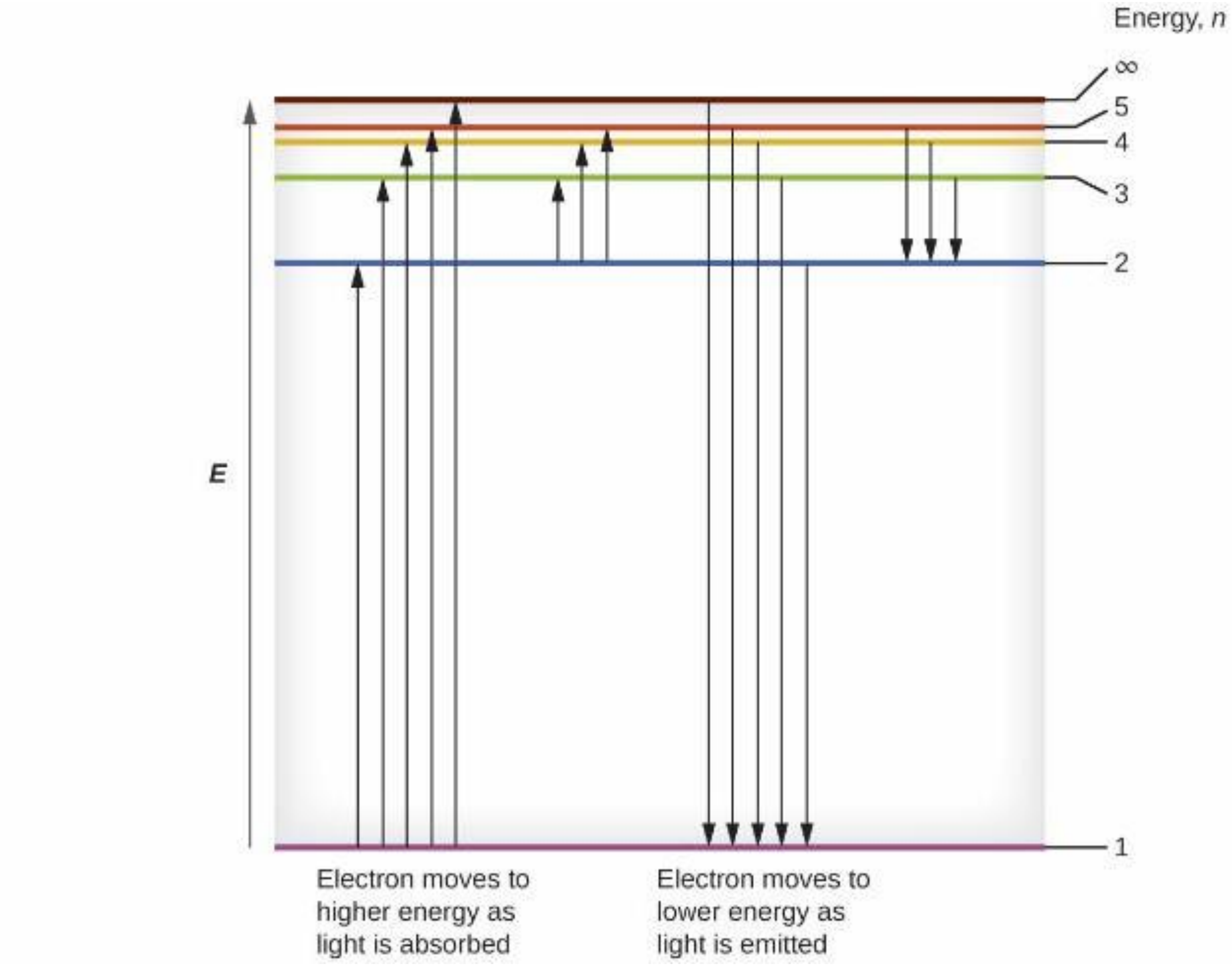
- When the atom ***absorbs energy as a photon,*** the electron moves from an orbit with a ***lower n to a higher n.***

- When an electron falls from an orbit with a ***higher n to a lower n, the atoms emits energy as a photon.***

- Since ΔE can only be discrete values, the ***photon absorbed or emitted can only have a wavelength with a discrete value*** (not continuous).

- ***This explained the line spectra for the hydrogen atom.***

FIGURE 6.15



The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

EXAMPLE 6.5

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with $n = 4$ to the orbit with $n = 6$? In what part of the electromagnetic spectrum do we find this radiation?

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression where $k = 2.179 \times 10^{-18}$ J:

$$\Delta E = k\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

EXAMPLE 6.5

$$\Delta E = 2.179 \times 10^{-18}\ J\left(\frac{1}{4^2} - \frac{1}{6^2}\right) = 7.566 \times 10^{-20}\ J$$

This energy difference is positive, indicating a photon enters the system (is absorbed) to excite the electron from the *n* = 4 orbit up to the *n* = 6 orbit. The wavelength of a photon with this energy is found by the expression:

$$\Delta E = \frac{hc}{\lambda}$$

EXAMPLE 6.5

Rearrangement gives:

$$\lambda = \frac{hc}{\Delta E} = \frac{\left(6.626 \times 10^{-34}\ \cancel{J}\cdot \cancel{s}\right)\left(2.998 \times 10^{8}\ m\cdot \cancel{s}^{-1}\right)}{7.566 \times 10^{-20}\ \cancel{J}}$$

$$= 2.626 \times 10^{-6}\ m$$

This wavelength is found in the infrared portion of the electromagnetic spectrum.

LIMITATIONS OF THE BOHR MODEL

- Bohr was unable to extend his theory to the next simplest atom, He, which only has two electrons.

- It is does not account for electron–electron interactions in atoms with more than one electron.

- Bohr’s model was severely flawed, since it was still based on the classical mechanics notion of precise orbits.

THE BOHR MODEL

- The Bohr model does introduce several important features of all models used to describe the distribution of electrons in an atom.
  - The energies of electrons (energy levels) in an atom are quantized, described by ***quantum numbers***: integer numbers having only specific allowed values and used to characterize the arrangement of electrons in an atom.
  - An electron’s energy increases with increasing distance from the nucleus.
  - The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

MOVING FORWARD

- Bohr won a Nobel Prize in Physics for his contributions.

- It became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules.

- A proper model of quantum mechanics was later developed to supersede classical mechanics.

6.3 DEVELOPMENT OF QUANTUM THEORY

- Particles and waves are very different phenomena in the macroscopic realm.

- By the 1920s it became increasingly clear that very small pieces of matter follow a different set of rules from those we observe for large objects.

- The unquestionable separation of waves and particles was no longer the case for the microscopic world.

LOUIS DE BROGLIE

- ***If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character?***

- In 1925 ***Louis de Broglie*** extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles.

DE BROGLIE WAVELENGTH

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

- h = Planck's constant
- m = particle mass
- v = particle velocity
- p = particle momentum
- λ = de Broglie wavelength

- The ***de Broglie wavelength*** is a characteristic of particles, not electromagnetic radiation.

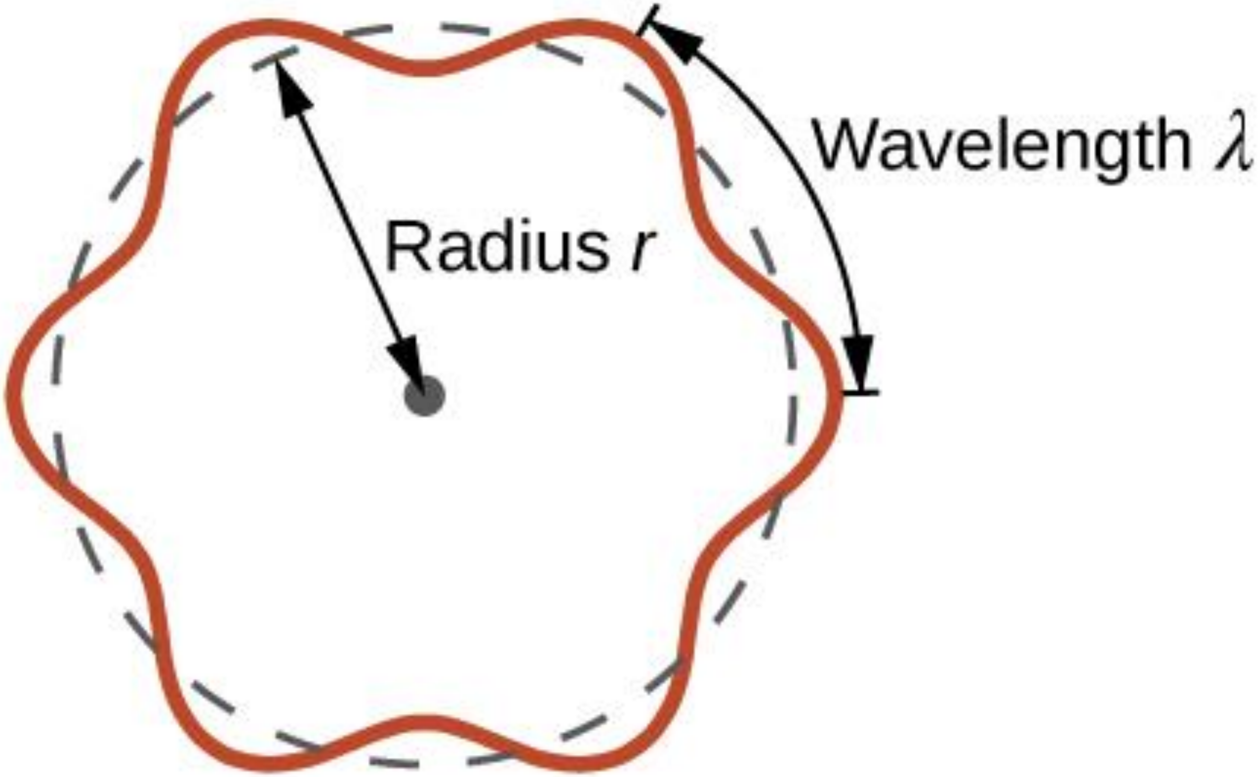
DE BROGLIE WAVELENGTH

- Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits.

- de Broglie argued that Bohr’s assumption of quantization can be explained if the electron is considered a circular standing wave.

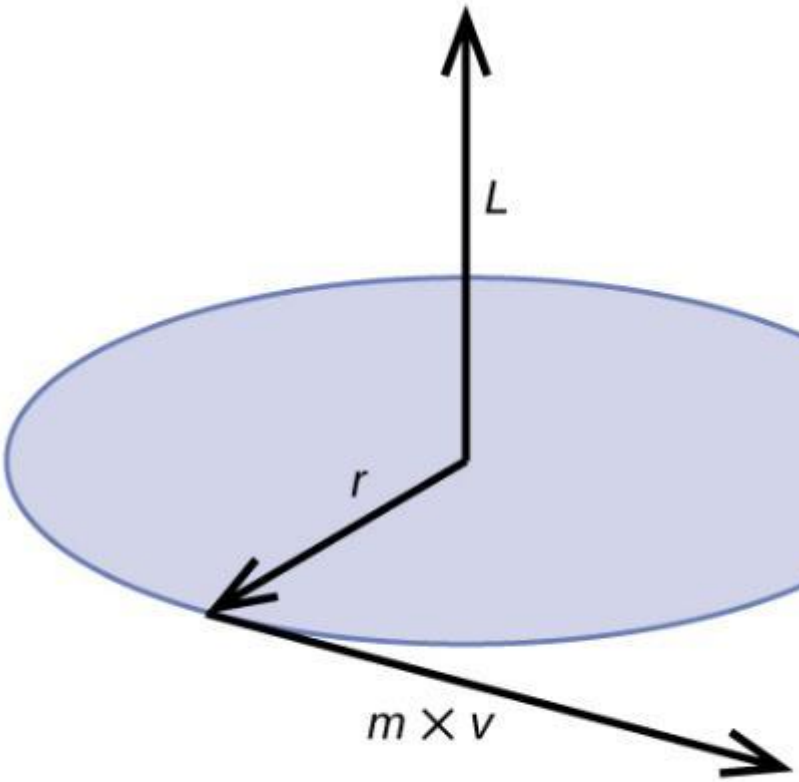
- Only an integer number of wavelengths can fit exactly within the orbit.

FIGURE 6.17



If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.

FIGURE 6.18



The diagram shows angular momentum for a circular motion.

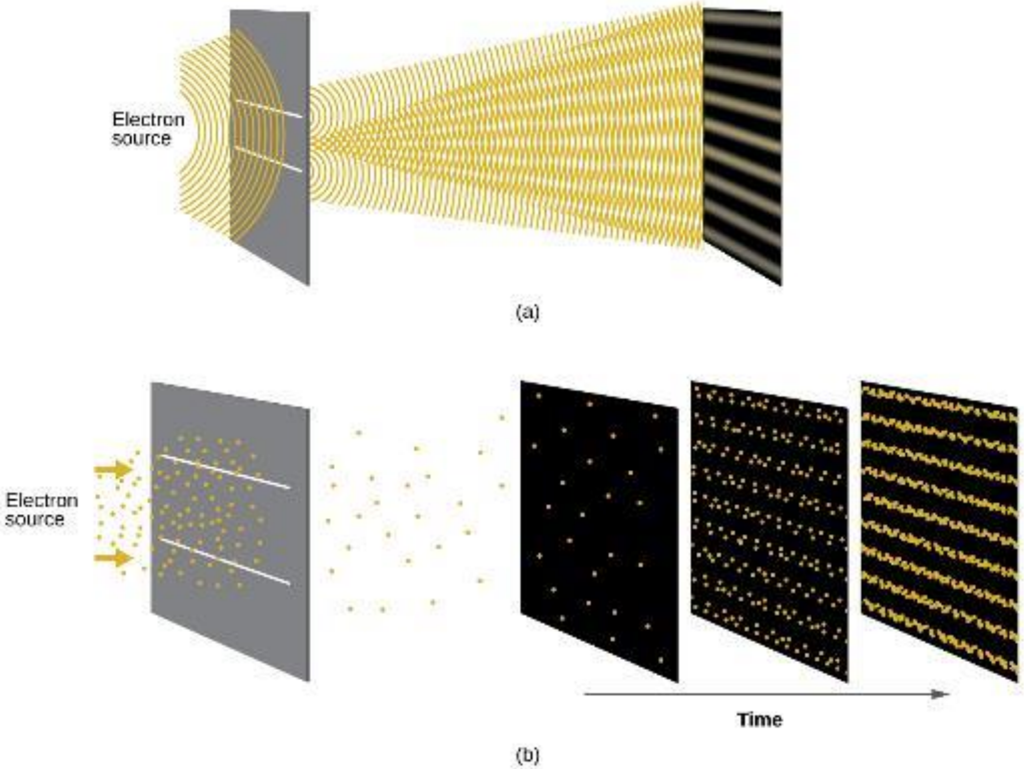
WAVE NATURE OF ELECTRONS

- C. J. Davisson and L. H. Germer, demonstrated experimentally that ***electrons can exhibit wavelike behavior.***

- They showed that electrons travelling through a regular atomic pattern in a crystal produced an interference pattern.

- The interference pattern is strikingly similar to the interference patterns for light.

FIGURE 6.19



(a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior.

(b) The experimental results illustrated here demonstrate the wave–particle duality in electrons. The electrons pass through very closely spaced slits, forming an interference pattern, with increasing numbers of electrons being recorded from the left image to the right. With only a few electrons recorded, it is clear that the electrons arrive as individual localized “particles,” but in a seemingly random pattern. As more electrons arrive, a wavelike interference pattern begins to emerge. Note that the probability of the final electron location is still governed by the wave-type distribution, even for a single electron, but it can be observed more easily if many electron collisions have been recorded.

WAVE-PARTICLE DUALITY

- Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics.

- Instead some type of wave equation governs a probability distribution for an electron’s motion.

- Thus the ***wave–particle duality*** first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.

HEISENBERG UNCERTAINTY PRINCIPLE

- ***Werner Heisenberg*** determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously.

- The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa.

- ***Heisenberg Uncertainty Principle:*** *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle*.

HEISENBERG UNCERTAINTY PRINCIPLE

$$(\Delta x)(\Delta p_x) \geq \frac{\hbar}{2}$$

- Δx = uncertainty in the position of the particle

- Δp_x = uncertainty in the momentum of the particle in the x-direction.

THE QUANTUM-MECHANICAL MODEL OF AN ATOM

- ***Erwin Schrödinger*** extended de Broglie’s work by incorporating the de Broglie relation into a wave equation.

- Today this equation is know as the ***Schrödinger equation.***

- Schrödinger properly thought of the electron in terms of a three-dimensional stationary wave, or ***wavefunction***, represented by the Greek letter psi, ***ψ.***

THE QUANTUM-MECHANICAL MODEL OF AN ATOM

- A few years later, ***Max Born:*** *Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes.*

- The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space.

- Wavefunctions can be used to determine the distribution of the electron’s density with respect to the nucleus in an atom.

THE SCHRÖDINGER EQUATION

- In the most general form, the ***Schrödinger equation*** can be written as:

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

- ***Ĥ is the Hamiltonian operator***, a set of mathematical operations representing the total energy of the quantum particle.

- ***ψ is the wavefunction*** of the particle.

- ***E is the total energy*** of the particle.

QUANTUM MECHANICS

- Schrödinger’s work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as ***quantum mechanics.***

UNDERSTANDING QUANTUM THEORY OF ELECTRONS IN ATOMS

- Electrons in atoms can exist only in discrete energy levels but not between them.

- The energy of an electron in an atom is quantized.

- The energy can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

PRINCIPAL QUANTUM NUMBER

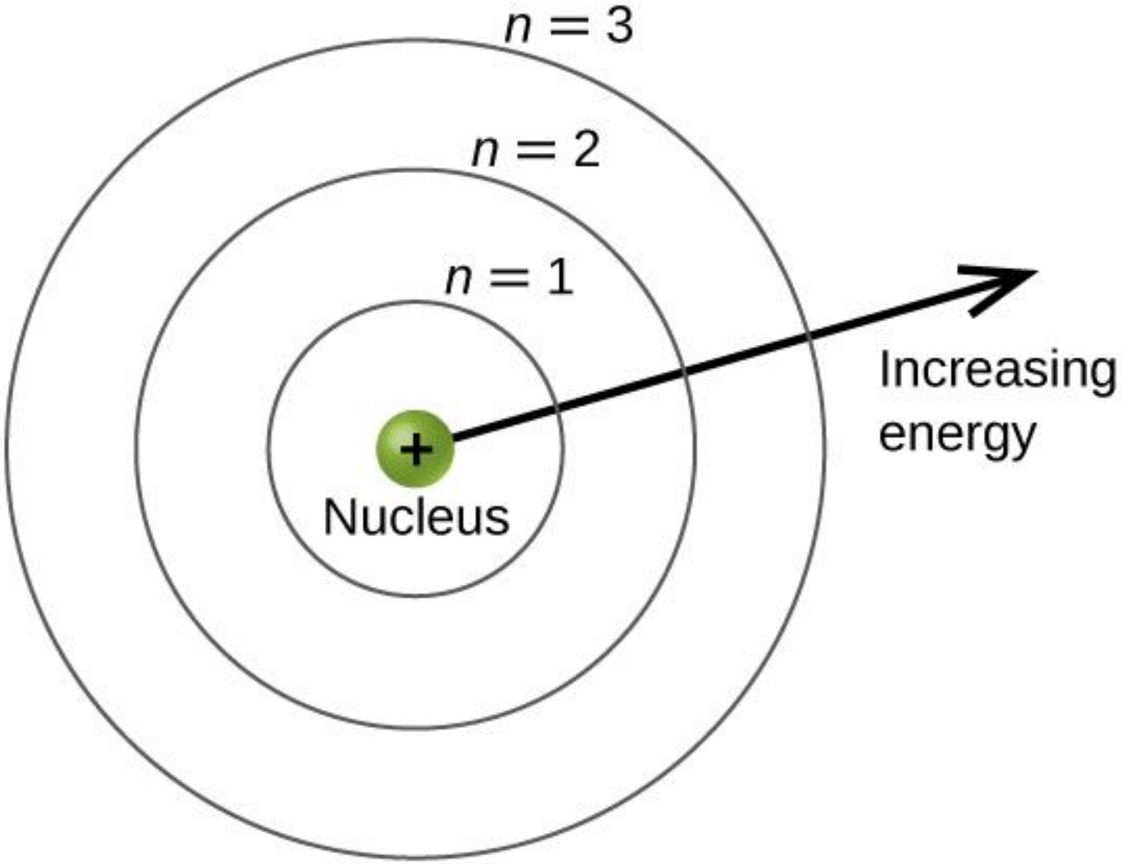
- The energy levels are labeled with an ***n* value**, where *n* = 1, 2, 3, ….

- Generally speaking, the energy of an electron in an atom is greater for larger values of *n*.

- *n* is referred to as the ***principal quantum number or shell number.***

- The principal quantum number defines the ***location of the energy level*** and is similar in concept to the Bohr model.

FIGURE 6.20



Different shells are numbered by principle quantum numbers.

ATOMIC ORBITALS

- The principal quantum number is one of three quantum numbers used to characterize an ***orbital.***

- An ***atomic orbital*** is a general region in an atom that an electron is most probable to reside.

- An atomic orbital is distinct from an *orbit*.

- The quantum mechanical model specifies the probability of finding an electron in a three-dimensional space around the nucleus.

ANGULAR MOMENTUM QUANTUM NUMBER

- The ***angular momentum quantum number (ℓ)*** is an integer that defines the ***shape of the orbital.***

- ℓ takes on the values, ℓ = 0, 1, 2, …, *n* – 1.

- For an orbital with *n* = 1; ℓ = 0

- For an orbital with *n* = 2; ℓ = 0 and 1

- Orbitals with the same value of ℓ form a **subshell.**

ANGULAR MOMENTUM QUANTUM NUMBER

- Instead of using numbers, the angular momentum quantum number is often designated by letters.
    - For ℓ = 0: ***s orbital***
    - For ℓ = 1: ***p orbital***
    - For ℓ= 2: ***d orbital***
    - For ℓ = 3: ***f orbital***

RADIAL NODES

- There are certain distances from the nucleus at which the probability density of finding an electron located in a particular orbital is zero.

- The value of the wavefunction ψ is zero at this distance for this orbital.

- Such a value of radius r is called a ***radial node.***

RADIAL NODES

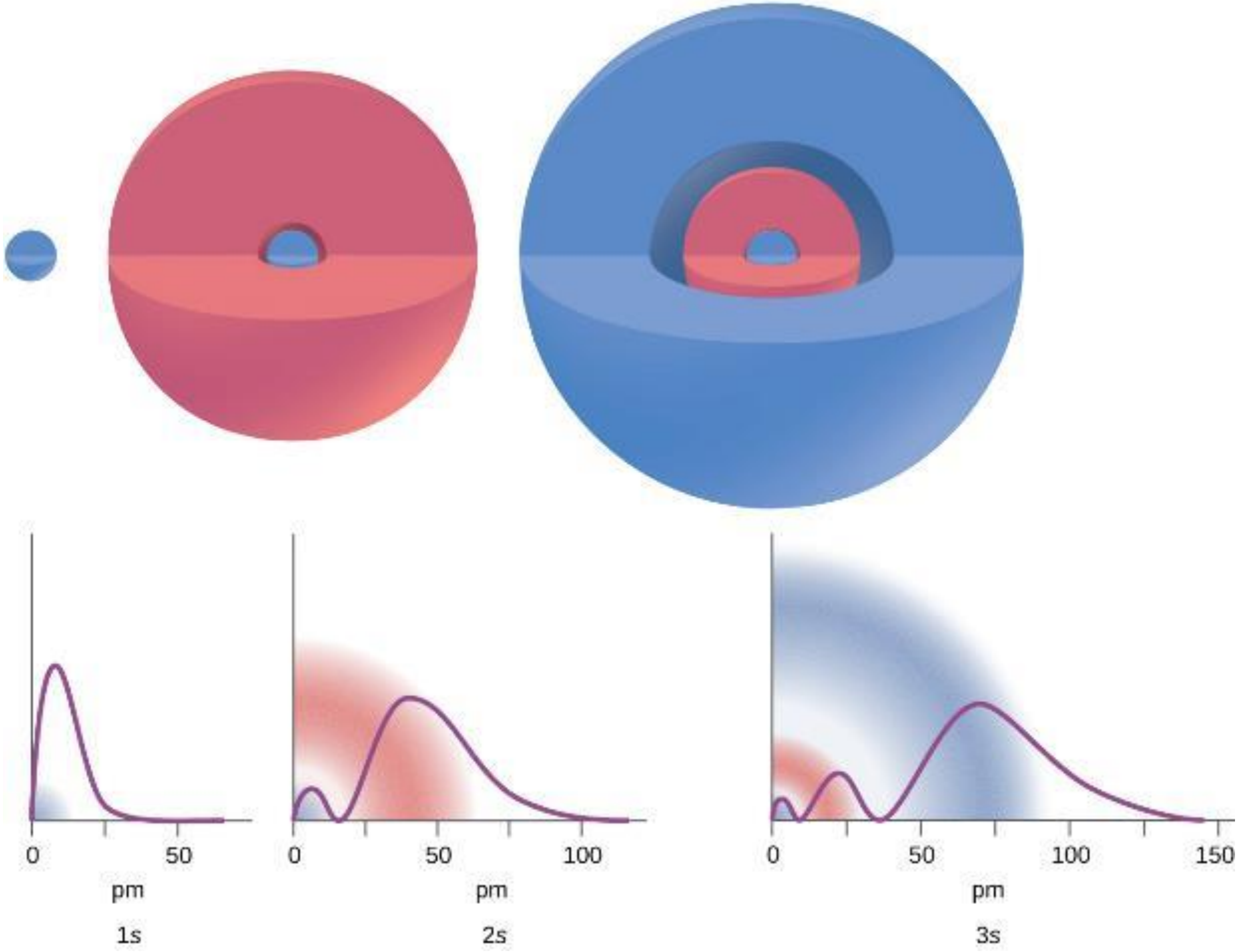
- The number of radial nodes in an orbital is $n - \ell - 1$.

- For a 1s orbital ($n = 1$, $\ell = 0$)
  - The number of nodes = $1 - 0 - 1 = 0$

- For a 2s orbital ($n = 2$, $\ell = 0$)
  - The number of nodes = $2 - 0 - 1 = 1$

- For a 3s orbital ($n = 3$, $\ell = 0$)
  - The number of nodes = $3 - 0 - 1 = 2$

FIGURE 6.21

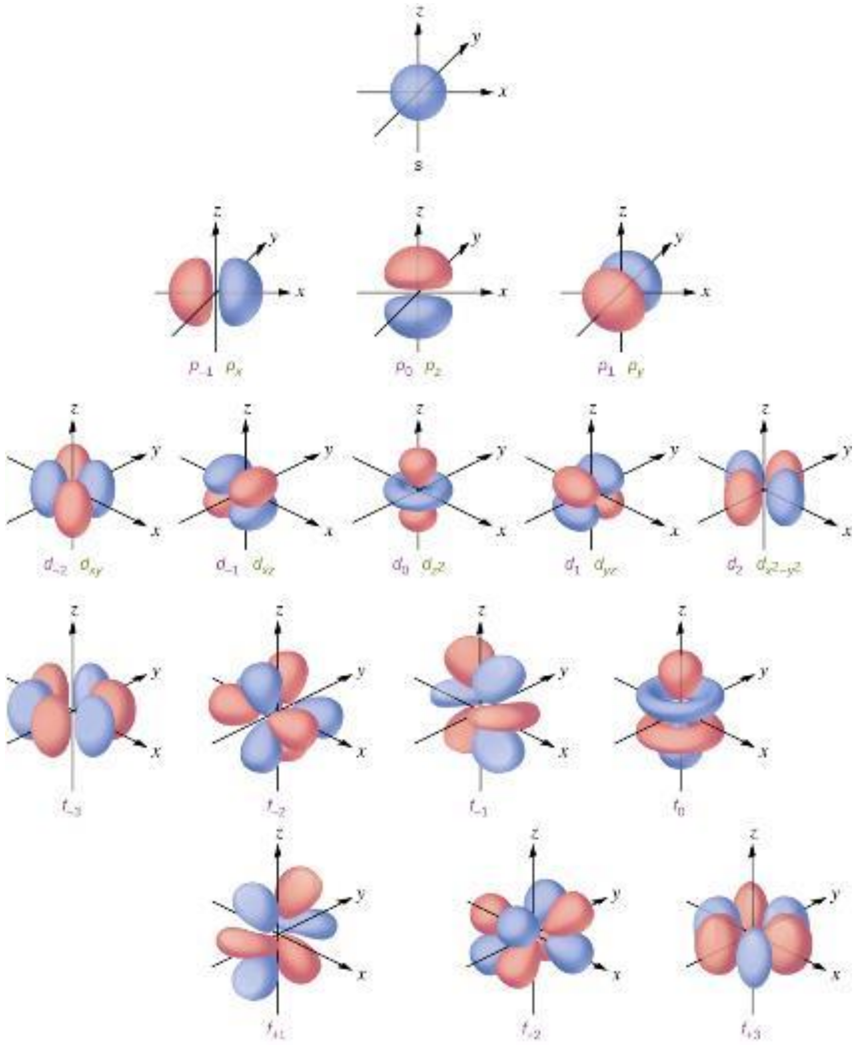


The graphs show the probability (*y* axis) of finding an electron for the 1*s*, 2*s*, 3*s* orbitals as a function of distance from the nucleus.

ORBITAL SHAPES

- The ***s subshell*** has a ***spherical*** shape.
- The ***p subshell*** has a ***dumbbell*** shape.
- The ***d and f orbitals*** are more ***complex.***
- These shapes represent the *three-dimensional regions where the electron is likely to be found*.

FIGURE 6.22



Shapes of *s*, *p*, *d*, and *f* orbitals. They can be constructed and described by (a) the values of the magnetic quantum number or (b) with the axis that defines their orientation.

MAGNETIC QUANTUM NUMBER

- If an orbital has an angular momentum ($\ell \neq 0$), then this orbital can point in different directions.

- The ***magnetic quantum number, m_l,*** specifies the orientation of the orbital in space.

MAGNETIC QUANTUM NUMBER

- The value of **m_ℓ** depends on the value of **ℓ.**

- **$m_\ell = -\ell \ldots -1, 0, +1, \ldots +\ell$**

- There are $2\ell + 1$ orbitals with the same ℓ value.
  - One *s*-orbital for $\ell = 0$
  - Three *p*-orbitals for $\ell = 1$
  - Five *d*-orbitals for $\ell = 2$
  - Seven *f*-orbitals for $\ell = 3$

ORBITAL RELATIVE ENERGIES

- When referring to an orbital, usually both the **n** value and and the letter designation for **ℓ** are reported.
  - Examples: 2s, 3p

- In the case of a hydrogen atom, energies of all the orbitals with the same *n* are the same.
  - This is called a ***degeneracy,*** and the energy levels with the same principal quantum number, *n*, are called ***degenerate energy levels.***

ORBITAL RELATIVE ENERGIES

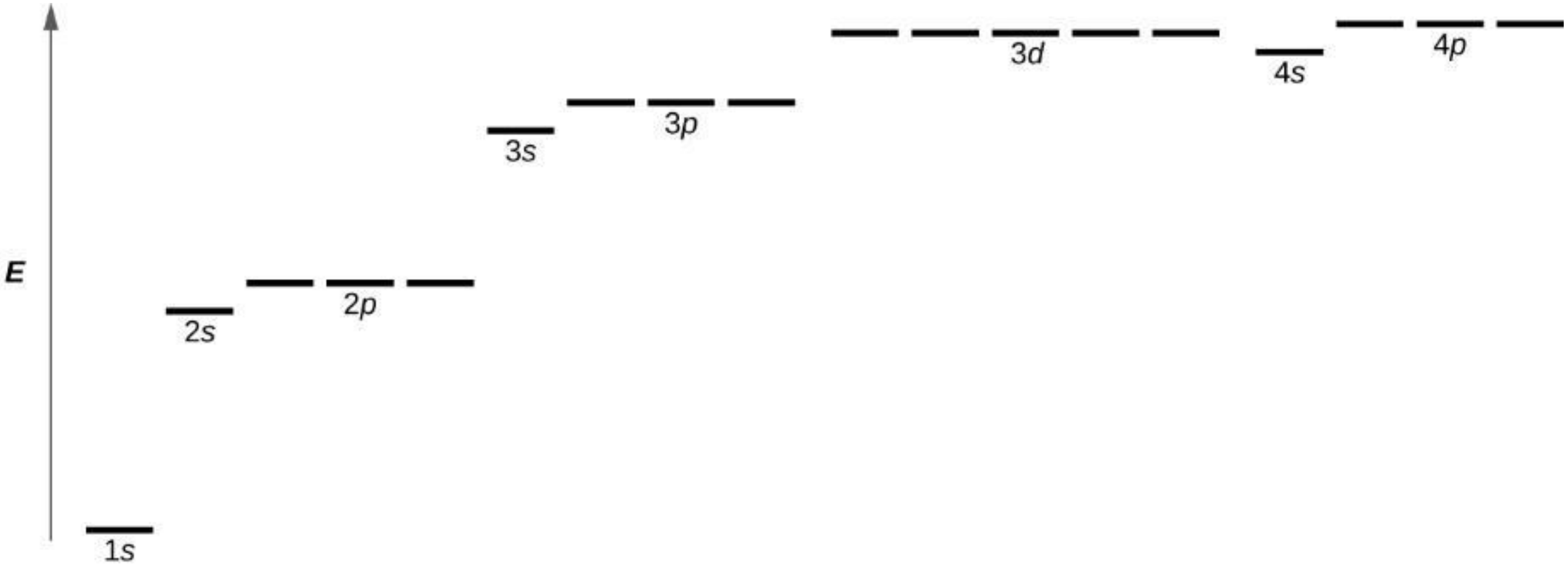
- However, in atoms with more than one electron, this degeneracy is eliminated by electron–electron interactions.

  - Orbitals that belong to different subshells have different energies.

  - Orbitals within the same subshell are still ***degenerate*** and have the same energy.

FIGURE 6.23

Energies of electron orbitals in a **multi-electron** atom.



SPIN QUANTUM NUMBER

- The first three quantum numbers, *n*, *l*, and m_l, define the region of space where an electron is most likely to be located.

- The electron spin is a different kind of property.

- Electron spin describes an intrinsic electron “rotation” or “spinning”.

- An electron can only “spin” in one of two quantized states.

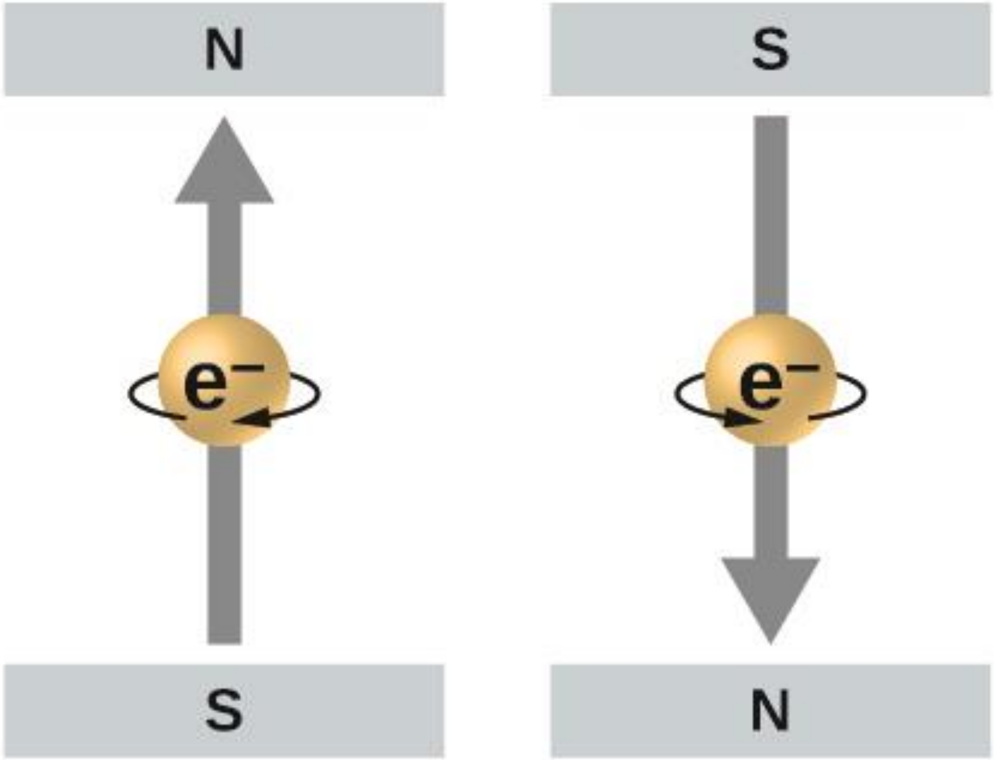
SPIN QUANTUM NUMBER

- The ***spin quantum number, m_s,*** describes the two possible states.

- $m_s = +½$ or $–½$

- Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the ***spin quantum number.***

FIGURE 6.24



Electrons with spin values ±½ in an external magnetic field.

THE PAULI EXCLUSION PRINCIPLE

- An electron in an atom is completely described by four quantum numbers: n, l, m_l, and m_s.

- Wolfgang Pauli, an Austrian physicist, formulated a general principle.

- ***The Pauli Exclusion Principle:*** *No two electrons in the same atom can have exactly the same set of all four quantum numbers.*

THE PAULI EXCLUSION PRINCIPLE

- Electrons can share the same orbital (the same set of quantum numbers n, l, and m_l).

- But only if they have different m_s numbers.

- Since the spin quantum number can only have two values (± ½), ***no more than two electrons can occupy the same orbital.***

- ***If two electrons are located in the same orbital, they must have opposite spins.***

SUMMARY OF QUANTUM NUMBERS

Name	**Symbol**	**Allowed values**	**Physical meaning**
principal quantum number	n	1, 2, 3, 4, ….	shell, the general region for the value of energy for an electron in the orbital
angular momentum quantum number	ℓ	$0, 1, 2, \ldots, n - 1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-\ell \ldots -1, 0, +1, \ldots +\ell$	orientation of the orbital
spin quantum number	m_s	$+\frac{1}{2}$, $-\frac{1}{2}$	direction of the intrinsic quantum “spin” of the electron

6.4 ELECTRONIC STRUCTURE OF ATOMS (ELECTRON CONFIGURATIONS)

- The energy of atomic orbitals increases as the principal quantum number, *n*, increases.

- As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus.

- Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized).

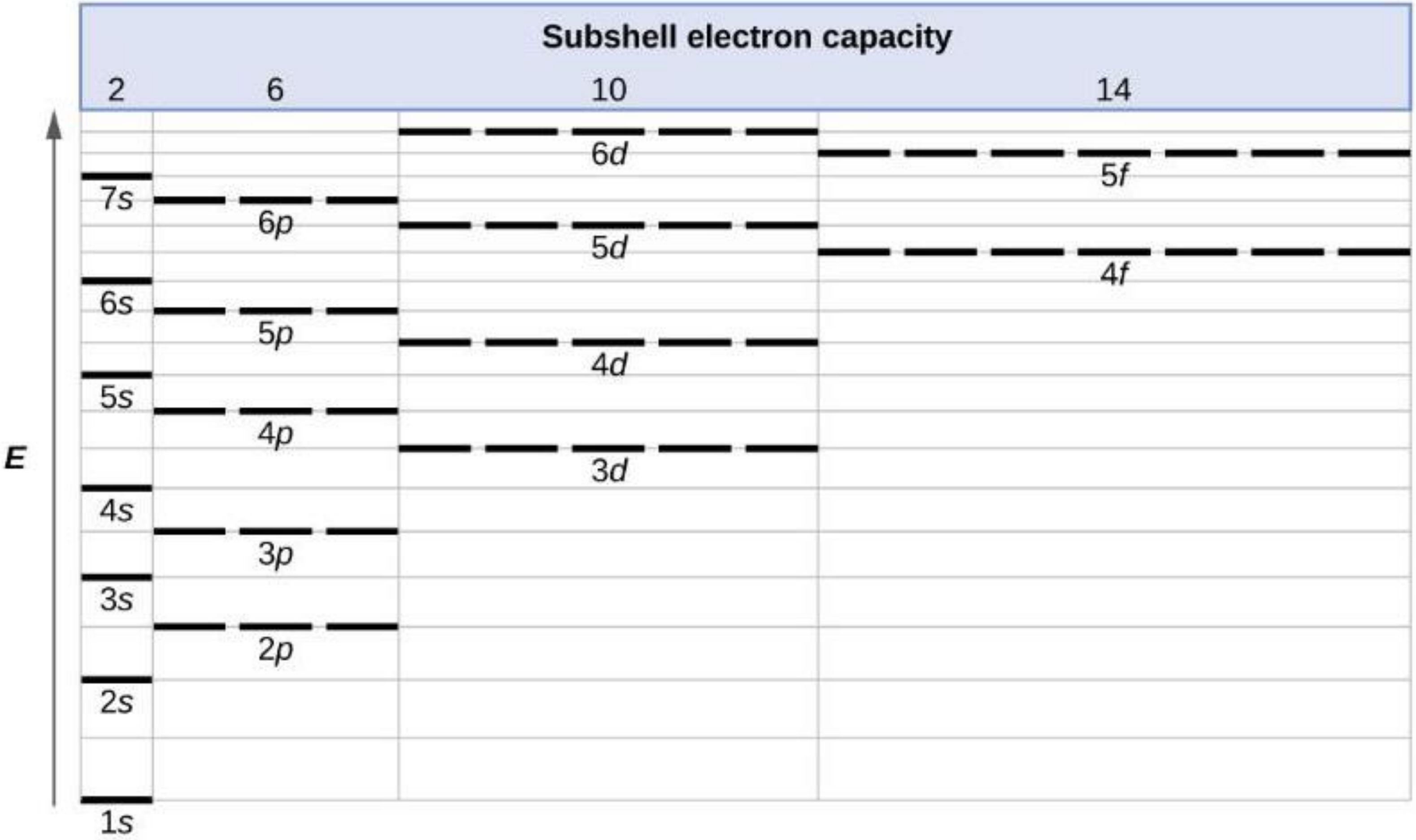
ORBITAL ENERGIES AND ATOMIC STRUCTURE

- In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of *l* differ.

- The energy of the orbitals increases within a shell in the order *s* < *p* < *d* < *f.*

- Electrons in atoms tend to fill low-energy orbitals first.

FIGURE 6.25



Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

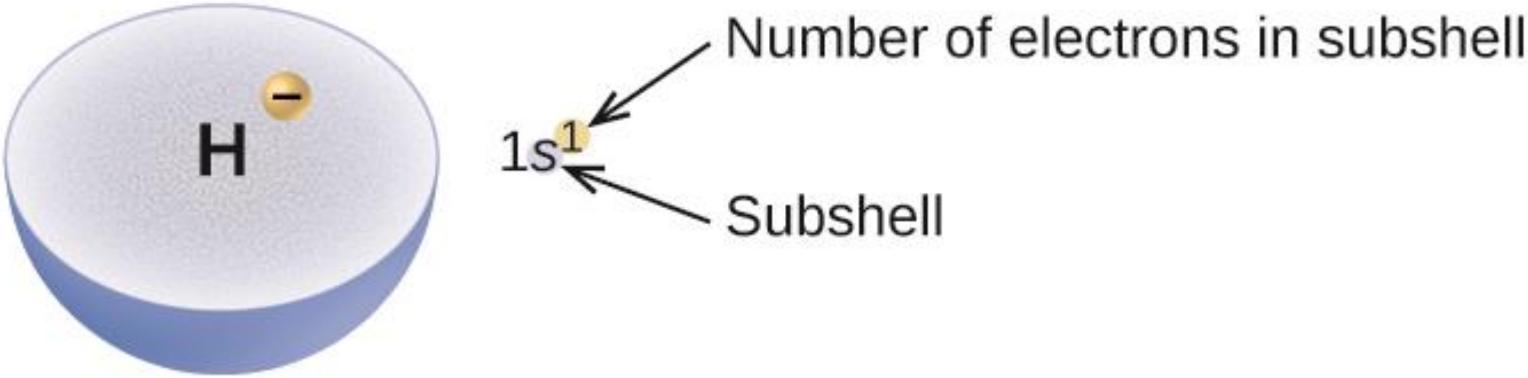
ELECTRON CONFIGURATION

- The arrangement of electrons in the orbitals of an atom is called the ***electron configuration*** of the atom.

- An ***electron configuration*** consists of symbols that contain three pieces of information:

  1) The principal quantum shell, *n*.
  2) The letter that designates the orbital type (*l*).
  3) A superscript number that designates the number of electrons in that particular subshell.

FIGURE 6.26



The diagram of an electron configuration specifies the subshell (*n* and *l* value, with letter symbol) and superscript number of electrons.

THE AUFBAU PRINCIPLE

- To determine the electron configuration for an atom we add a number of electrons equal to its atomic number.

- Beginning with hydrogen, and continuing across the periods of the periodic table, we add one electron to the subshell of lowest available energy.

- This procedure is called the ***Aufbau principle***, from the German word *Aufbau* (“to build up”).

- When writing electron configurations and orbital diagrams keep in mind the Pauli Exclusion principle.

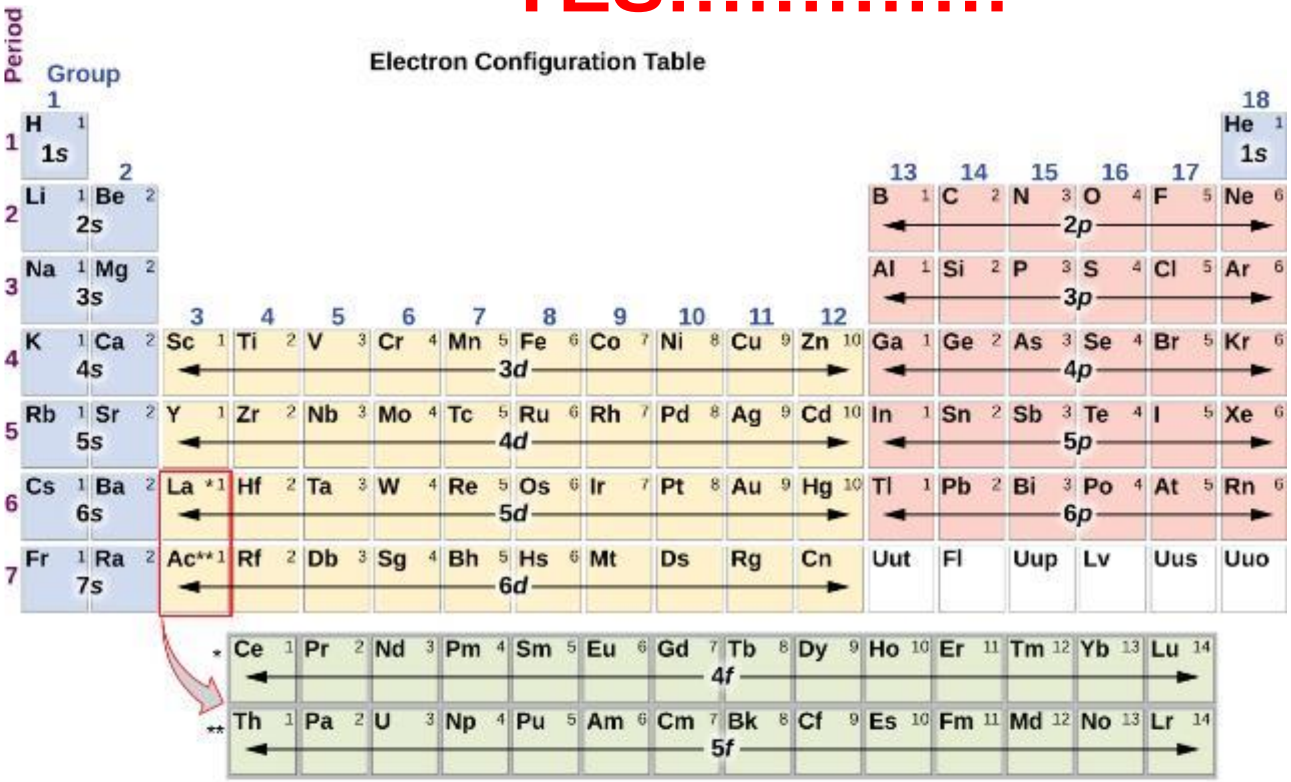
FIGURE 6.27

FOR THE LOVE OF GOD, NO!!!!!!!!!!!!!!!

The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the *s* orbitals with each *n* shell on a separate row. Repeat for *p*, *d*, and *f*. Be sure to only include orbitals allowed by the quantum numbers (no 1*p* or 2*d*, and so forth). Finally, draw diagonal lines from top to bottom as shown.

FIGURE 6.28

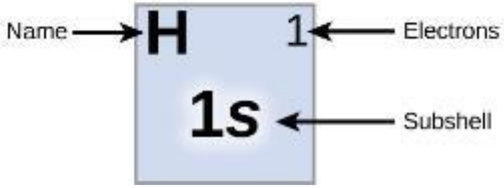
YES!!!!!!!!!!!!!



Electron Configuration Table

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1 1s																	He 1 1s
2	Li 1	Be 2 2s											B 1	C 2	N 3	O 4 2p	F 5	Ne 6
3	Na 1	Mg 2 3s											Al 1	Si 2	P 3	S 4 3p	Cl 5	Ar 6
4	K 1	Ca 2 4s	Sc 1	Ti 2	V 3	Cr 4	Mn 5	Fe 6 3d	Co 7	Ni 8	Cu 9	Zn 10	Ga 1	Ge 2	As 3	Se 4 4p	Br 5	Kr 6
5	Rb 1	Sr 2 5s	Y 1	Zr 2	Nb 3	Mo 4	Tc 5	Ru 6 4d	Rh 7	Pd 8	Ag 9	Cd 10	In 1	Sn 2	Sb 3	Te 4 5p	I 5	Xe 6
6	Cs 1	Ba 2 6s	La *1	Hf 2	Ta 3	W 4	Re 5	Os 6 5d	Ir 7	Pt 8	Au 9	Hg 10	Tl 1	Pb 2	Bi 3	Po 4 6p	At 5	Rn 6
7	Fr 1	Ra 2 7s	Ac** 1	Rf 2	Db 3	Sg 4	Bh 5	Hs 6 6d	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

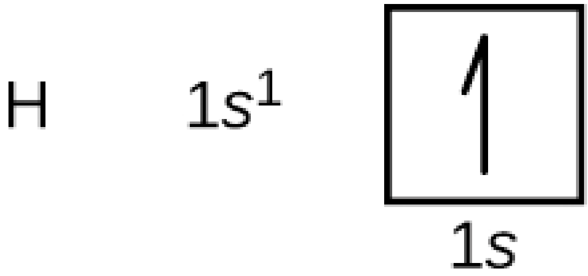
*	Ce 1	Pr 2	Nd 3	Pm 4	Sm 5	Eu 6	Gd 7	Tb 8 4f	Dy 9	Ho 10	Er 11	Tm 12	Yb 13	Lu 14
**	Th 1	Pa 2	U 3	Np 4	Pu 5	Am 6	Cm 7	Bk 8 5f	Cf 9	Es 10	Fm 11	Md 12	No 13	Lr 14



This periodic table shows the electron configuration for each subshell. By “building up” from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

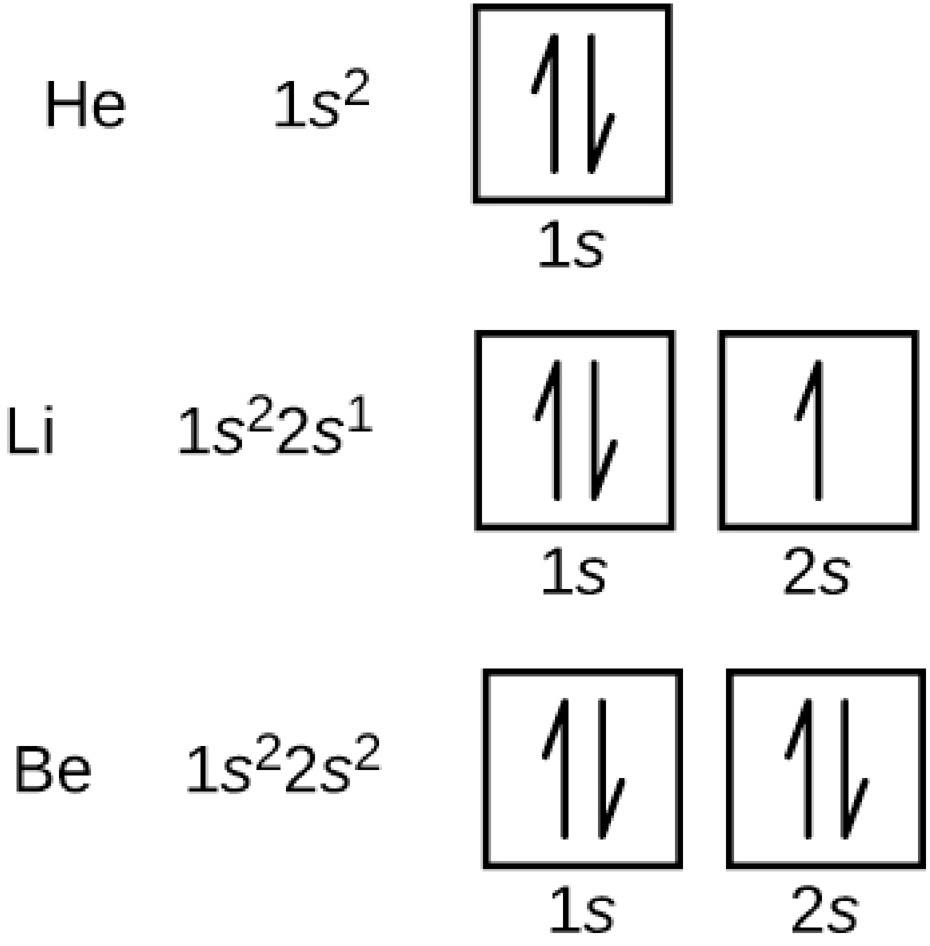
ELECTRON CONFIGURATIONS AND ORBITAL DIAGRAMS

- ***Orbital diagrams*** are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons.



- An upwards arrow represents and electron with $m_s = + ½$.
- A downwards arrow represents and electron with $m_s = - ½$.

ELECTRON CONFIGURATIONS AND ORBITAL DIAGRAMS



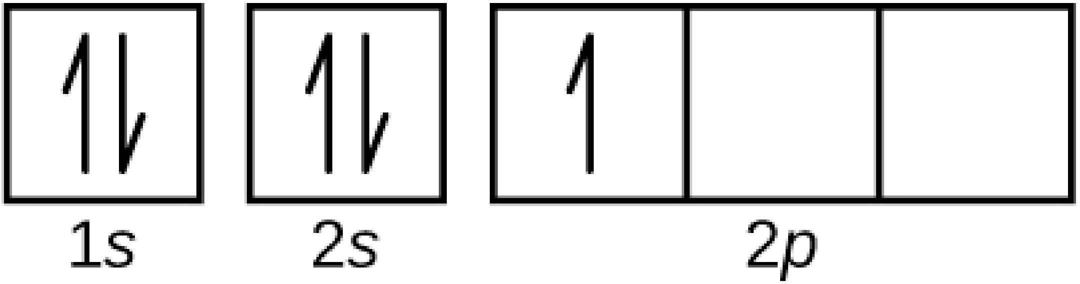
He $1s^2$

Li $1s^22s^1$

Be $1s^22s^2$

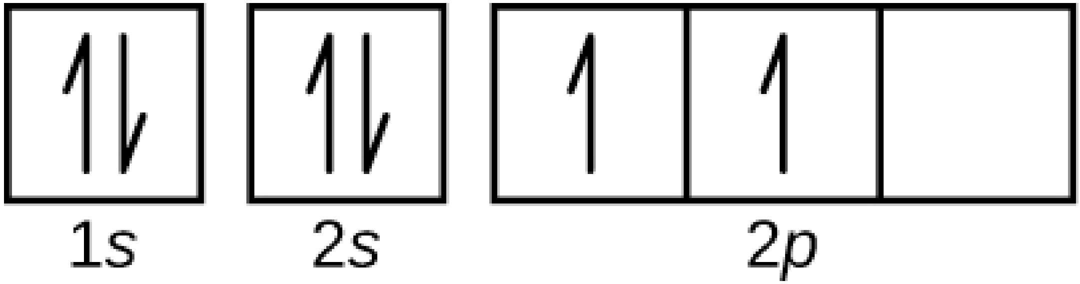
ELECTRON CONFIGURATIONS AND ORBITAL DIAGRAMS

B $1s^22s^22p^1$

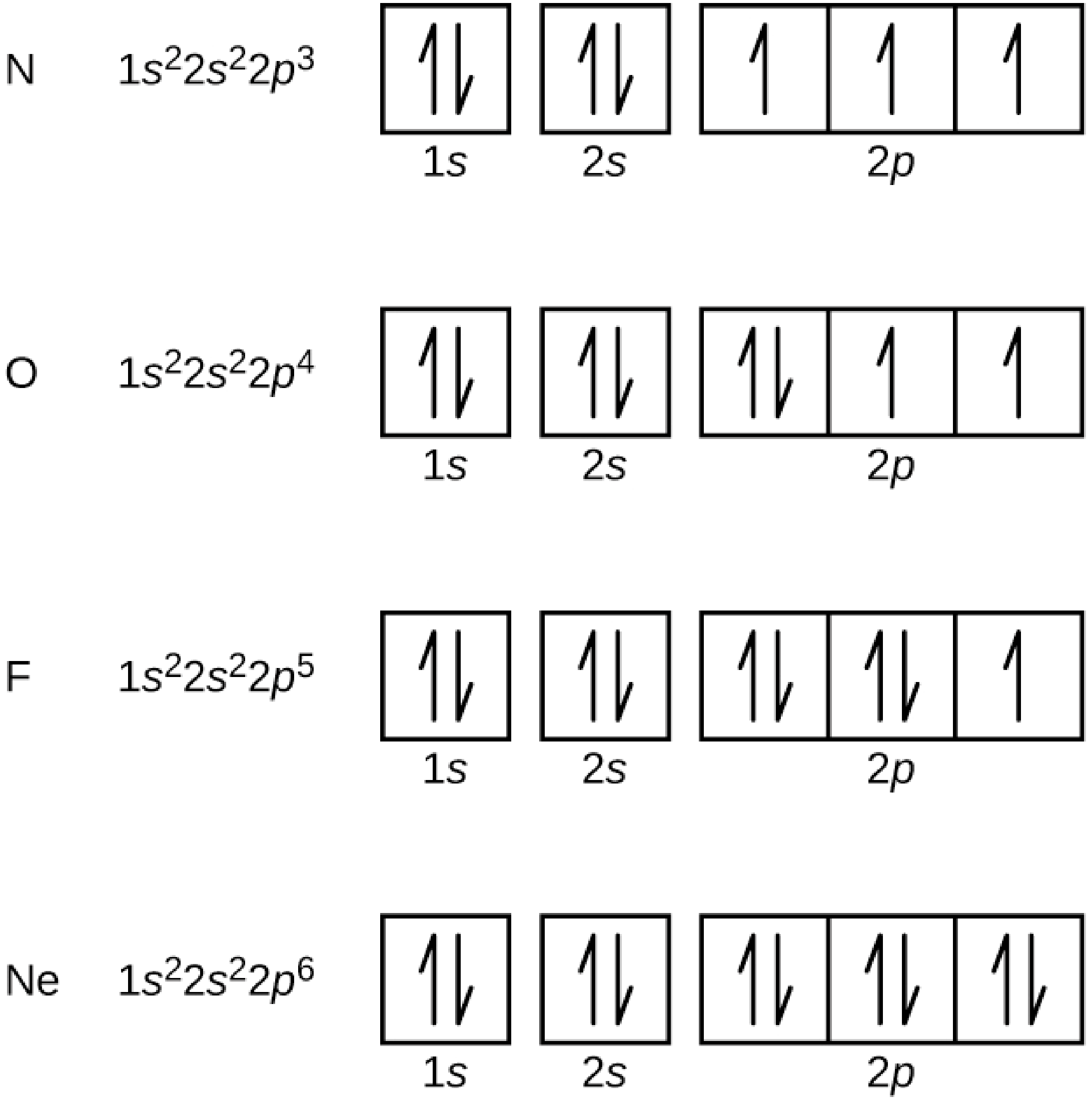


- ***Hund's rule:*** the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons.

C $1s^22s^22p^2$



ELECTRON CONFIGURATIONS AND ORBITAL DIAGRAMS



N $1s^2 2s^2 2p^3$

O $1s^2 2s^2 2p^4$

F $1s^2 2s^2 2p^5$

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

VALENCE AND CORE ELECTRONS

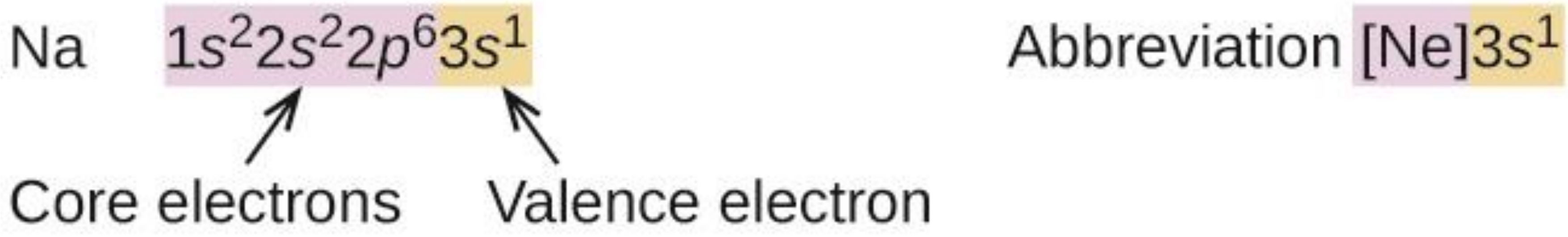
- The electrons occupying the orbital(s) in the outermost shell (highest value of *n*) are called ***valence electrons.***

- The electrons occupying the inner shell orbitals are called ***core electrons.***

- The core electrons represent ***noble gas electron configurations.***

- Electron configurations can be expressed in an abbreviated format by writing the noble gas that matches the core electron configuration, along with the valence electrons.

FIGURE 6.29



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

Abbreviation $[\text{Ne}]3s^1$

Core electrons

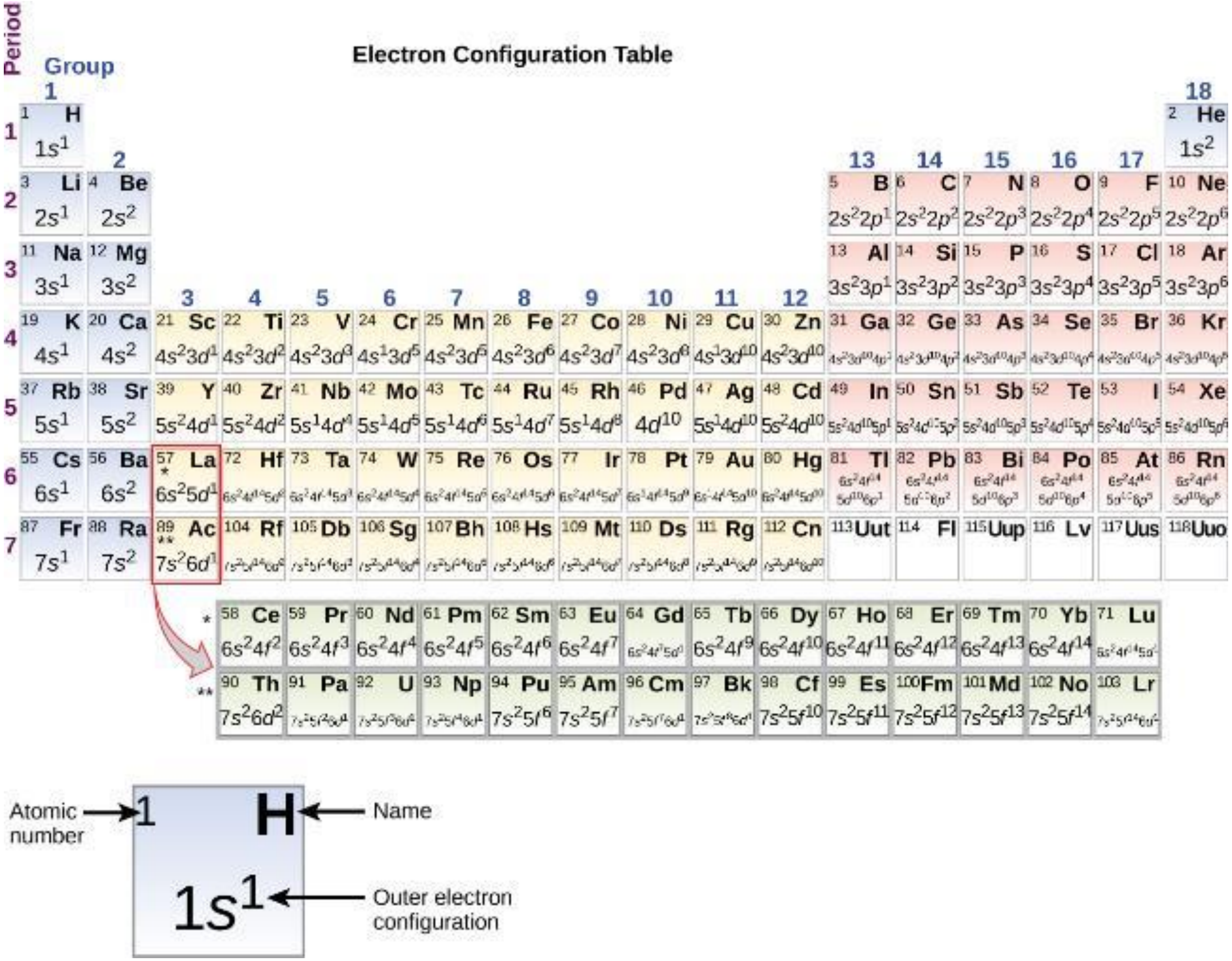
Valence electron

A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

ABBREVIATED ELECTRON CONFIGURATIONS

- Abbreviated electron configurations emphasize the similarity of the configurations of elements in the same group.
- ***Group 1:***
  - Li: [He]$2s^1$
  - Na: [Ne]$3s^1$
  - K: [Ar]$4s^1$
- ***Group 2:***
  - Be: [He]$2s^2$
  - Mg: [Ne]$3s^2$
  - Ca: [Ar]$4s^2$

FIGURE 6.30



Electron Configuration Table

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											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 $2s^22p^6$
3	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 $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^23d^1$	22 Ti $4s^23d^2$	23 V $4s^23d^3$	24 Cr $4s^13d^5$	25 Mn $4s^23d^5$	26 Fe $4s^23d^6$	27 Co $4s^23d^7$	28 Ni $4s^23d^8$	29 Cu $4s^13d^{10}$	30 Zn $4s^23d^{10}$	31 Ga $4s^23d^{10}4p^1$	32 Ge $4s^23d^{10}4p^2$	33 As $4s^23d^{10}4p^3$	34 Se $4s^23d^{10}4p^4$	35 Br $4s^23d^{10}4p^5$	36 Kr $4s^23d^{10}4p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^24d^1$	40 Zr $5s^24d^2$	41 Nb $5s^14d^4$	42 Mo $5s^14d^5$	43 Tc $5s^14d^6$	44 Ru $5s^14d^7$	45 Rh $5s^14d^8$	46 Pd $4d^{10}$	47 Ag $5s^14d^{10}$	48 Cd $5s^24d^{10}$	49 In $5s^24d^{10}5p^1$	50 Sn $5s^24d^{10}5p^2$	51 Sb $5s^24d^{10}5p^3$	52 Te $5s^24d^{10}5p^4$	53 I $5s^24d^{10}5p^5$	54 Xe $5s^24d^{10}5p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La * $6s^25d^1$	72 Hf $6s^24f^{14}5d^2$	73 Ta $6s^24f^{14}5d^3$	74 W $6s^24f^{14}5d^4$	75 Re $6s^24f^{14}5d^5$	76 Os $6s^24f^{14}5d^6$	77 Ir $6s^24f^{14}5d^7$	78 Pt $6s^14f^{14}5d^9$	79 Au $6s^14f^{14}5d^{10}$	80 Hg $6s^24f^{14}5d^{10}$	81 Tl $6s^24f^{14}5d^{10}6p^1$	82 Pb $6s^24f^{14}5d^{10}6p^2$	83 Bi $6s^24f^{14}5d^{10}6p^3$	84 Po $6s^24f^{14}5d^{10}6p^4$	85 At $6s^24f^{14}5d^{10}6p^5$	86 Rn $6s^24f^{14}5d^{10}6p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac ** $7s^26d^1$	104 Rf $7s^25f^{14}6d^2$	105 Db $7s^25f^{14}6d^3$	106 Sg $7s^25f^{14}6d^4$	107 Bh $7s^25f^{14}6d^5$	108 Hs $7s^25f^{14}6d^6$	109 Mt $7s^25f^{14}6d^7$	110 Ds $7s^25f^{14}6d^8$	111 Rg $7s^25f^{14}6d^9$	112 Cn $7s^25f^{14}6d^{10}$	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

*	58 Ce $6s^24f^2$	59 Pr $6s^24f^3$	60 Nd $6s^24f^4$	61 Pm $6s^24f^5$	62 Sm $6s^24f^6$	63 Eu $6s^24f^7$	64 Gd $6s^24f^75d^1$	65 Tb $6s^24f^9$	66 Dy $6s^24f^{10}$	67 Ho $6s^24f^{11}$	68 Er $6s^24f^{12}$	69 Tm $6s^24f^{13}$	70 Yb $6s^24f^{14}$	71 Lu $6s^24f^{14}5d^1$
**	90 Th $7s^26d^2$	91 Pa $7s^25f^26d^1$	92 U $7s^25f^36d^1$	93 Np $7s^25f^46d^1$	94 Pu $7s^25f^6$	95 Am $7s^25f^7$	96 Cm $7s^25f^76d^1$	97 Bk $7s^25f^86d^1$	98 Cf $7s^25f^{10}$	99 Es $7s^25f^{11}$	100 Fm $7s^25f^{12}$	101 Md $7s^25f^{13}$	102 No $7s^25f^{14}$	103 Lr $7s^25f^{14}6d^1$

This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

ELECTRON CONFIGURATIONS

- Beginning with the ***transition metal*** scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell.

- *d* subshells are filled to capacity with 10 electrons.
  - For $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l.
  - Five *d* orbitals have a combined capacity of 10 electrons.

- After the 3*d* subshell is filled, electrons are next added to the 4*p* subshell.

ELECTRON CONFIGURATIONS

- For the two periods of ***inner transition metals***, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr).
  - Electrons are added to an *f* subshell.
  - For $l = 3$ [*f* orbitals], there are $2l + 1 = 7$ values of m_l.
  - Seven *f* orbitals have a combined capacity of 14 electrons.

ELECTRON CONFIGURATION EXCEPTIONS

- There are some exceptions to the order of filling subshells.

- Examples: Cu and Cr
  - There is stability associated with a ***half-filled or fully filled (d) subshell.***
  - An electron shifts from the 4*s* into the 3*d* subshell to achieve this stability.
  - Cu:
    - Expect: $[Ar]4s^2 3d^9$
    - Actual: $[Ar]4s^1 3d^{10}$
  - Cr
    - Expect: $[Ar]4s^2 3d^4$
    - Actual: $[Ar]4s^1 3d^5$

ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

- The periodic table arranges atoms so that elements with the same chemical and physical properties are in the same group.

- ***Elements in the same group have similar valence electron configurations.***

- Valence electrons play the most important role in chemical reactions.

- This describes why elements in the same group have similar chemical reactivity.

ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

- ***Main group elements or representative elements*** are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell.

  - The valence electrons for main group elements are those with the highest *n* level.

  - **Example Gallium (Ga):** [Ar]$4s^2 3d^{10} 4p^1$
    - Ga has three valence electrons ($4s^2$ and $4p^1$).

    - The completely filled *3d* orbitals count as core, not valence electrons.

ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

- ***Transition elements or transition metals*** are metallic elements in which the last electron added enters a *d* orbital.
  - The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and (*n* – 1)*d* electrons.
  - **Example Vanadium (V):** [Ar]$4s^2 3d^3$
    - V has five valence electrons ($4s^2$ and $3d^3$).

ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

- ***Inner transition elements*** are metallic elements in which the last electron added occupies an *f* orbital.
  - The valence electrons (those added after the last noble gas configuration) in these elements include the *ns*, (n – 2)*f*, and if present the (n – 1)*d* subshells.
  - **Example Promethium (Pm):** [Ar]$6s^2 4f^5$
    - Pm has seven valence electrons ($6s^2$ and $4f^5$).

ELECTRON CONFIGURATIONS OF IONS

- Recall, ions are formed when atoms gain or lose electrons.

- A ***cation*** (positively charged ion) forms when one or more ***electrons are removed*** from an atom.
  - For ***main group elements***, the electrons that were added last are the first electrons removed.
  - For ***transition metals and inner transition metals,*** the highest *ns* electrons are lost first, and then the (n – 1)*d* or (n – 2)*f* electrons are removed.

ELECTRON CONFIGURATIONS OF IONS

- An ***anion*** (negatively charged ion) forms when one or more ***electrons are added*** to a parent atom.
    - The electrons are added in the order predicted by the Aufbau principle.

EXAMPLE 6.11

Predicting Electron Configurations of Ions

What is the electron configuration of:

(a) Na^+

(b) P^{3-}

(c) Al^{2+}

(d) Fe^{2+}

(e) Sm^{3+}

First, write out the electron configuration for the parent atom, and then add or remove the appropriate number of electrons from the correct orbital(s).

EXAMPLE 6.11

(a) Na: $1s^2 2s^2 2p^6 3s^1$. Sodium loses one electron.
Na^+: $1s^2 2s^2 2p^6$

(b) P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus gains three electrons.
P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$

(c) Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum loses two electrons.
Al^{2+}: $1s^2 2s^2 2p^6 3s^1$

EXAMPLE 6.11

(d) Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital.

Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

(e) Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital.

Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$

6.5 PERIODIC VARIATIONS IN ELEMENT PROPERTIES

- Many properties of the elements vary periodically as the electronic structure of the elements changes.

- These properties govern the chemical behavior of elements.

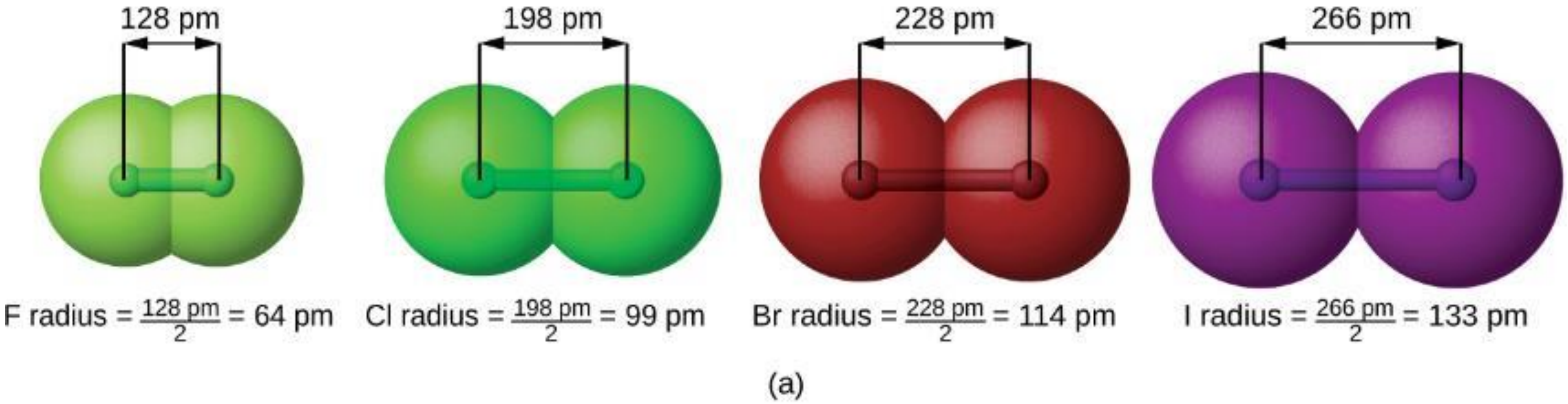
- **These periodic properties include:**
  1) Size (radius) of atoms and ions
  2) Ionization energies
  3) Electron affinities

VARIATIONS IN COVALENT RADII

- The ***covalent radius*** is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond.

- ***Down a group:***
  - The principal quantum number, *n*, increases by one for each element.
  - The electrons are added to a region of space that is increasingly farther from the nucleus.
  - ***The size of the atom (and its covalent radius) increases down a group.***

FIGURE 6.31(A)



(a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as *n* increases.

EFFECTIVE NUCLEAR CHARGE

- ***Effective nuclear charge, Z_{eff},*** is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions.

- For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal.

- For all other atoms, the electron of interest are partially ***shielded*** from the pull of the nucleus by the other electron(s) present.

EFFECTIVE NUCLEAR CHARGE

- Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently.

- Each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly due to electrons being added only to the valence shell.

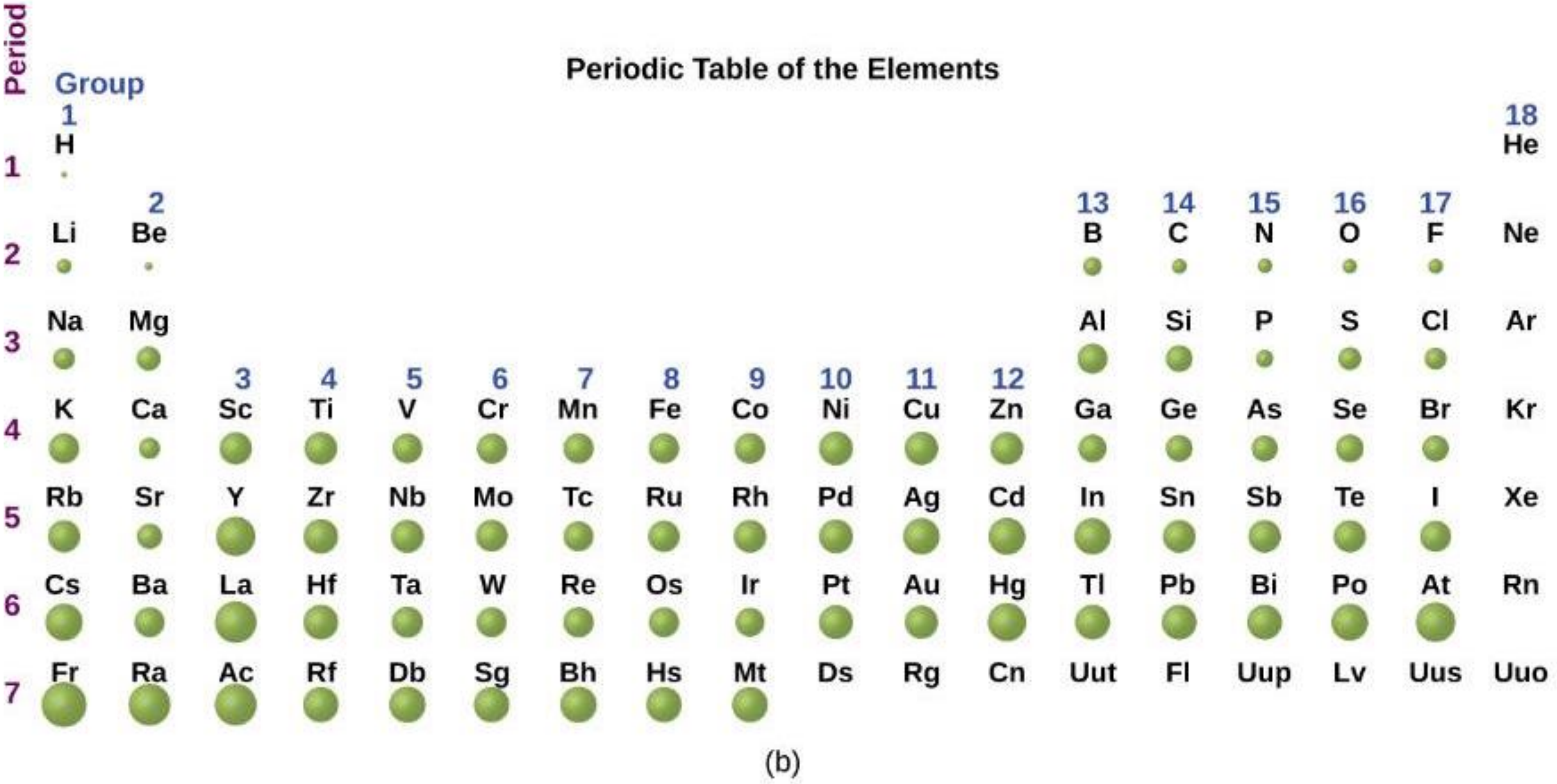
- ***Z_{eff} increases as we move from left to right across a period.***

VARIATIONS IN COVALENT RADII

- ***Across a period:***
  - A stronger pull (higher effective nuclear charge) is experienced by the outermost electrons, drawing them closer to the nucleus.

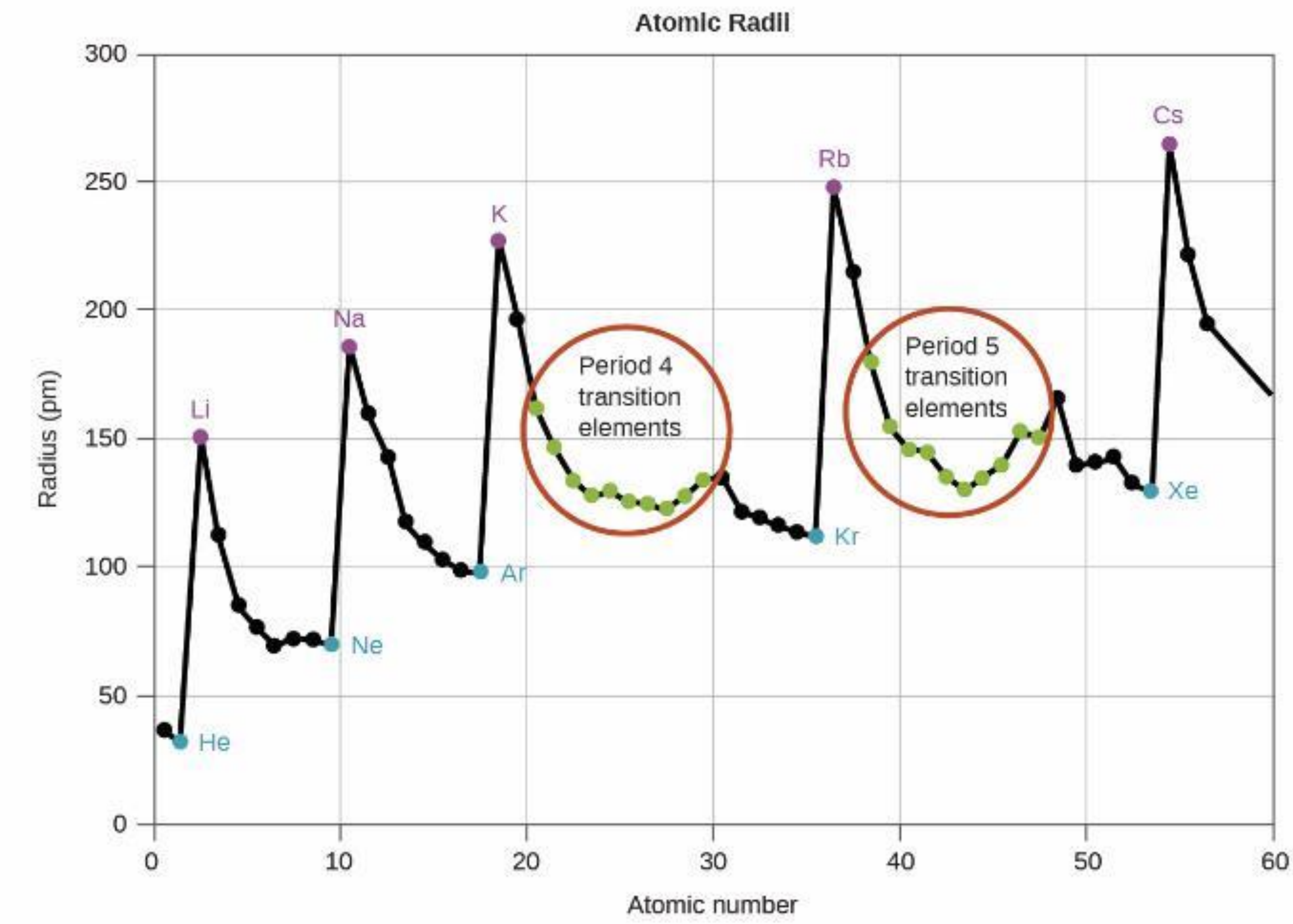
  - ***The size of the atom (and its covalent radius) decreases across a period.***

FIGURE 6.31(B)



(a) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

FIGURE 6.32



Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

VARIATIONS IN IONIC RADII

- ***Ionic radius*** is the measure used to describe the size of an ion.

- A cation always has fewer electrons and the same number of protons as the parent atom.

- As electrons are removed from the outer valence shell, the remaining electrons experience a greater Z_{eff} charge and are drawn even closer to the nucleus.

- ***A cation is always smaller than the atom from which it is derived.***

VARIATIONS IN IONIC RADII

- An anion always has more electrons and the same number of protons as the parent atom.

- This results in a greater repulsion among the electrons and a decrease in Z_{eff}.

- This causes the valence electrons to be farther from the nucleus.

- ***An anion is always larger than the atom from which it is derived.***

FIGURE 6.33

The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

ISOELECTRONIC

- Atoms and ions that have the same electron configuration are said to be ***isoelectronic***.

- **Examples of isoelectronic species:**
  - N^{3-}, O^{2-}, F^{-}, Ne, Na^{+}, Mg^{2+}, and Al^{3+} ($1s^2 2s^2 2p^6$).
  - P^{3-}, S^{2-}, Cl^{-}, Ar, K^{+}, Ca^{2+}, and Sc^{3+} ($[Ne]3s^2 3p^6$).

- For atoms or ions that are isoelectronic, the number of protons determines the size.

- ***The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.***

IONIZATION ENERGY

- The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its ***first ionization energy (IE_1)***.

$$X(g) \longrightarrow X^+(g) + e^- \qquad IE_1$$

- The energy required to remove the second most loosely bound electron is called the ***second ionization energy (IE_2)***.

$$X^+(g) \longrightarrow X^{2+}(g) + e^- \qquad IE_2$$

- The energy required to remove the third electron is the third ionization energy, and so on.

VARIATIONS IN IONIZATION ENERGIES

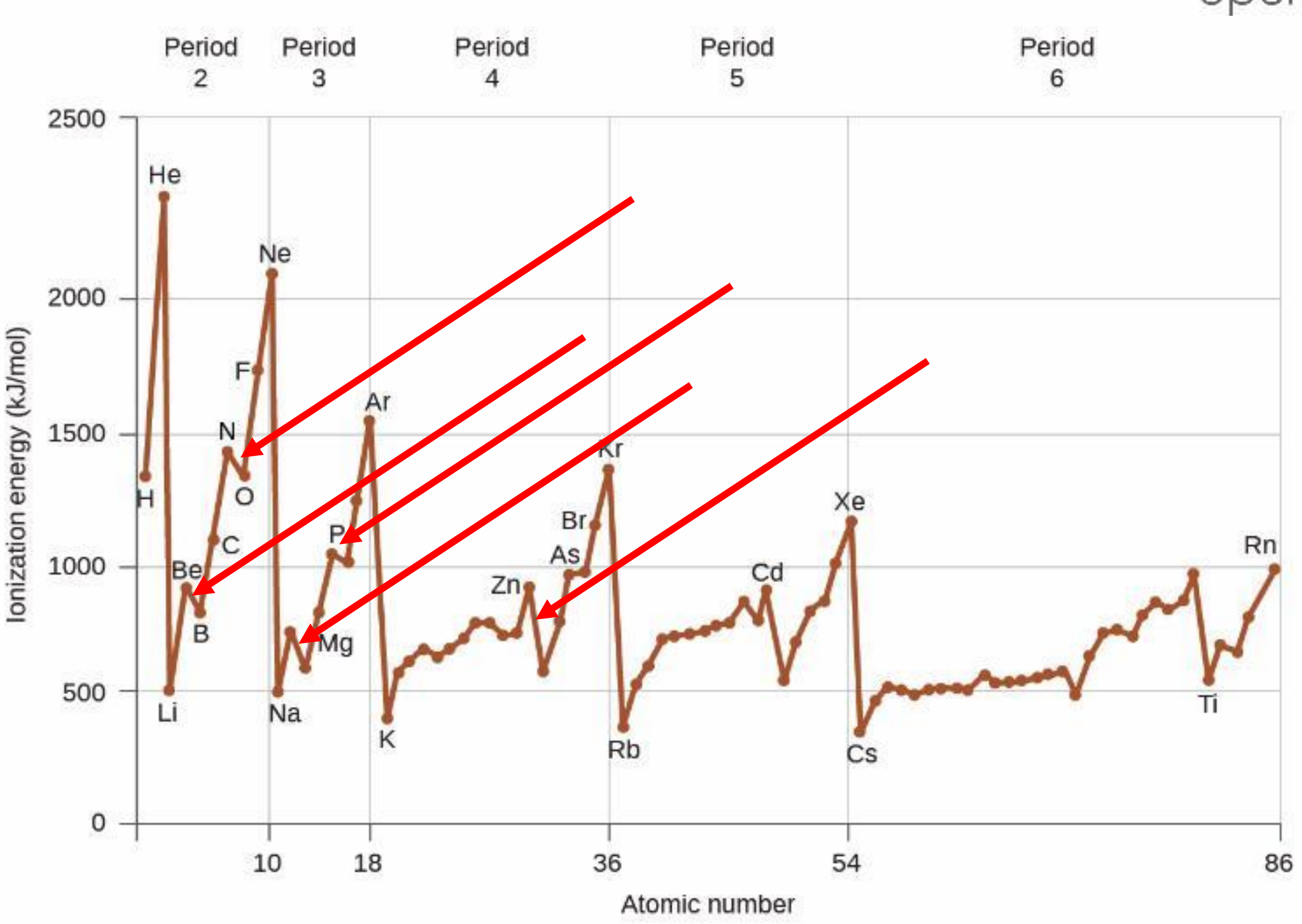
- Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive.

- As size (atomic radius) increases, the ionization energy decreases.

- ***First ionization energies:***
  - ***Decrease down a group***
  - ***Increase across a period***

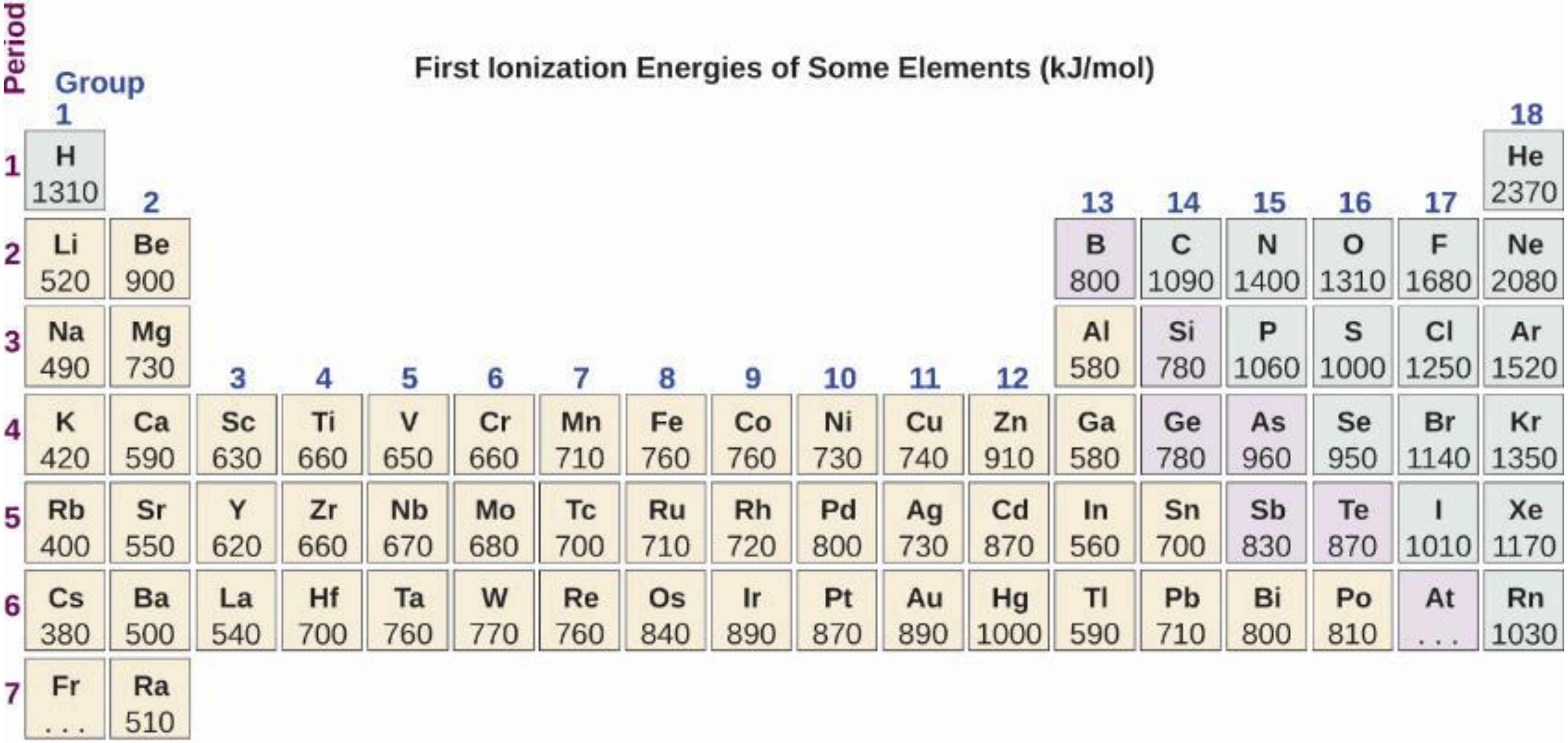
- There are some deviations from this trend.

FIGURE 6.34



The first ionization energy of the elements in the first five periods are plotted against their atomic number.

FIGURE 6.35



First Ionization Energies of Some Elements (kJ/mol)

Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1310																	He 2370
2	Li 520	Be 900											B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 490	Mg 730											Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520
4	K 420	Ca 590	Sc 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	Co 760	Ni 730	Cu 740	Zn 910	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350
5	Rb 400	Sr 550	Y 620	Zr 660	Nb 670	Mo 680	Tc 700	Ru 710	Rh 720	Pd 800	Ag 730	Cd 870	In 560	Sn 700	Sb 830	Te 870	I 1010	Xe 1170
6	Cs 380	Ba 500	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At . . .	Rn 1030
7	Fr . . .	Ra 510																

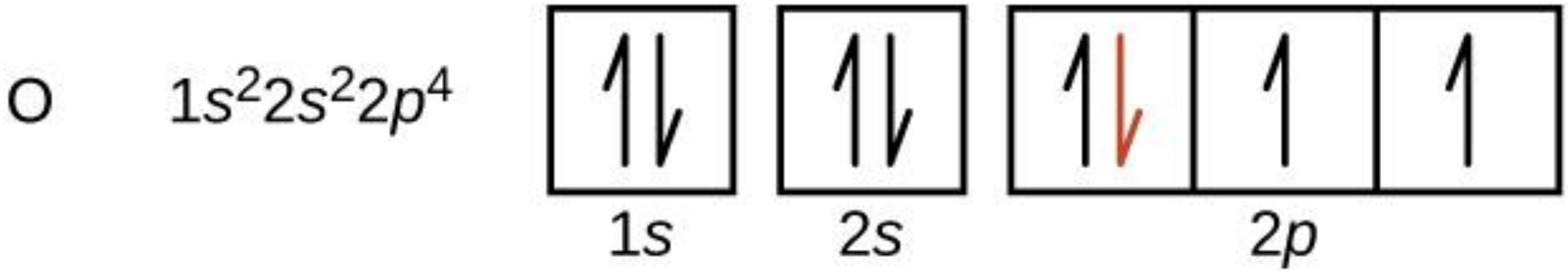
This version of the periodic table shows the first ionization energy (IE_1), in kJ/mol, of selected elements.

DEVIATIONS IN IONIZATION ENERGY TREND

- ***Deviation:*** Beryllium (Be) has a higher IE_1 than Boron (B).
  - The electron removed during the ionization of beryllium ([He]2s^2) is an *s* electron.
  - The electron removed during the ionization of boron ([He]2$s^2$2p^1) is a *p* electron.
  - The energy of a subshell increases as *l* increases.
  - This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell.

DEVIATIONS IN IONIZATION ENERGY TREND

- ***Deviation:*** Oxygen (O) has a lower IE_1 than nitrogen (N).
  - Removing one electron from O will eliminate the electron–electron repulsion caused by pairing the electrons in the 2*p* orbital.



  - This means that removing an electron from O is more energetically favorable than removing an electron from N.

SUCCESSIVE IONIZATION ENERGIES

- Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation.

- Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge.

- ***Thus, successive ionization energies for an element always increase.***

SUCCESSIVE IONIZATION ENERGIES FOR SELECTED ELEMENTS (KJ/MOL)

Element	IE$_1$	IE$_2$	IE$_3$	IE$_4$	IE$_5$	IE$_6$	IE$_7$
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4		
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	

SUCCESSIVE IONIZATION ENERGIES

- At some point, there is always a large increase in successive ionization energies for an element.

- ***This large increase corresponds to the removal of core electrons,*** which are harder to remove than the valence electrons.

- **Example:**
  - Sc and Ga both have three valence electrons.
  - The large increase in ionization energy occurs after the third ionization.

ELECTRON AFFINITY

- The ***electron affinity (EA)*** is the energy change for the process of adding an electron to a gaseous atom to form an anion.

$$X(g) \quad + \quad e^- \quad \longrightarrow \quad X^-(g) \qquad EA_1$$

- This process can be either endothermic or exothermic, depending on the element.
  - For some elements ***energy is released*** when the gaseous atom accepts an electron ***(negative EA).***
  - For other elements ***energy is required*** for the gaseous atom to accept an electron ***(positive EA).***

VARIATIONS IN ELECTRON AFFINITIES

- It becomes easier to add an electron as the effective nuclear charge of the atoms increases.

- ***Electron Affinities becomes more negative across a period.***

- ***There are some deviations from this trend.***

DEVIATIONS IN ELECTRON AFFINITY TREND

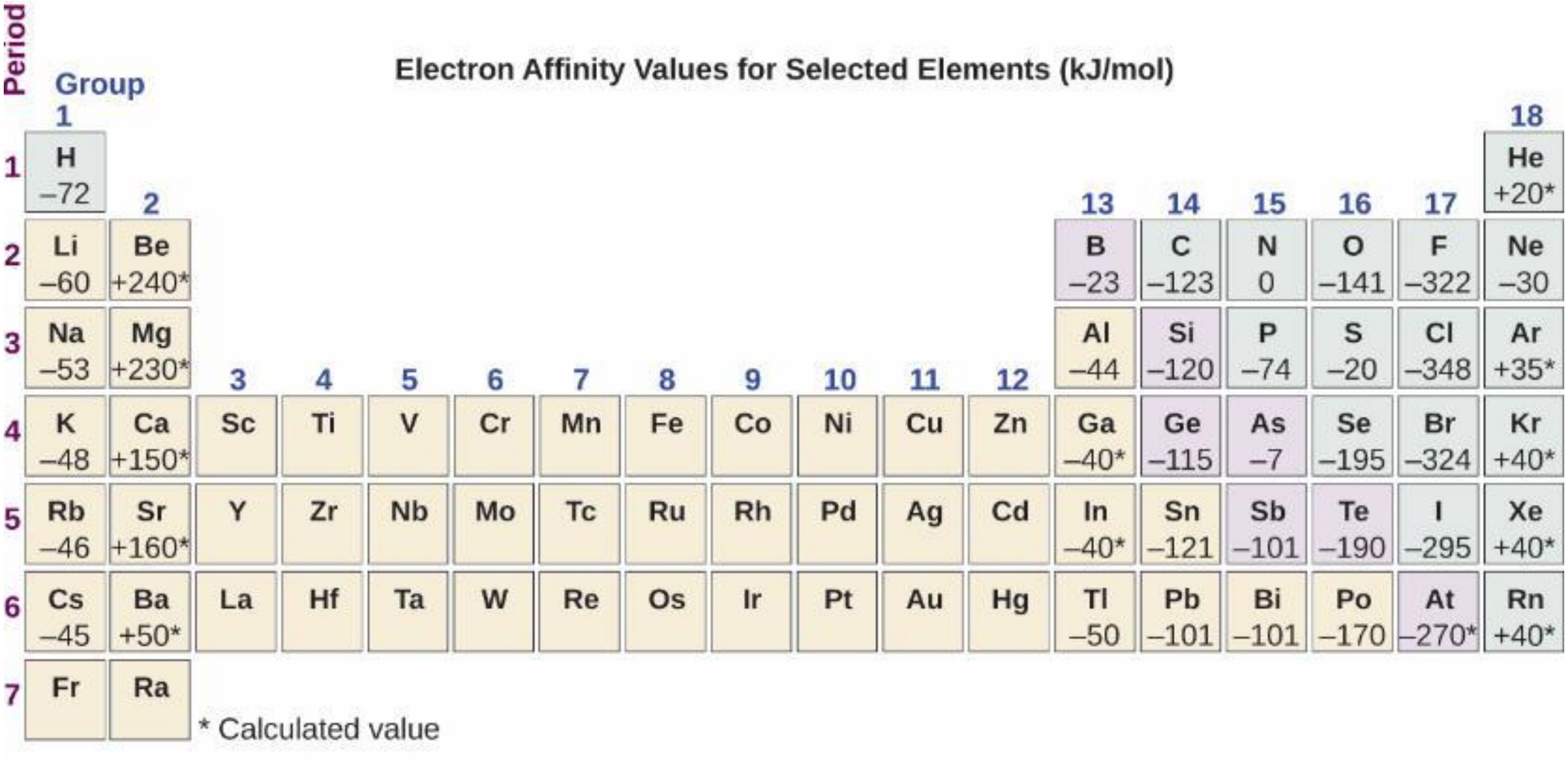
- ***The noble gases, group 18***, have a completely filled shell and the incoming electron must be added to a higher energy *n* level.

- ***Group 2*** has a filled *ns* subshell, and so the next electron added goes into the higher energy *np* subshell.

- ***Group 15*** has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron.

- In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

FIGURE 6.36



Electron Affinity Values for Selected Elements (kJ/mol)

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H –72																	He +20*
2	Li –60	Be +240*											B –23	C –123	N 0	O –141	F –322	Ne –30
3	Na –53	Mg +230*											Al –44	Si –120	P –74	S –20	Cl –348	Ar +35*
4	K –48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga –40*	Ge –115	As –7	Se –195	Br –324	Kr +40*
5	Rb –46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In –40*	Sn –121	Sb –101	Te –190	I –295	Xe +40*
6	Cs –45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl –50	Pb –101	Bi –101	Po –170	At –270*	Rn +40*
7	Fr	Ra																

* Calculated value

This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

HW problems: 9, 11, 27, 35, 45, 49, 53, 61, 67, 71, 77