CHEM 103
CHEMISTRY I

CHAPTER 6
ELECTRONIC STRUCTURE OF ATOMS

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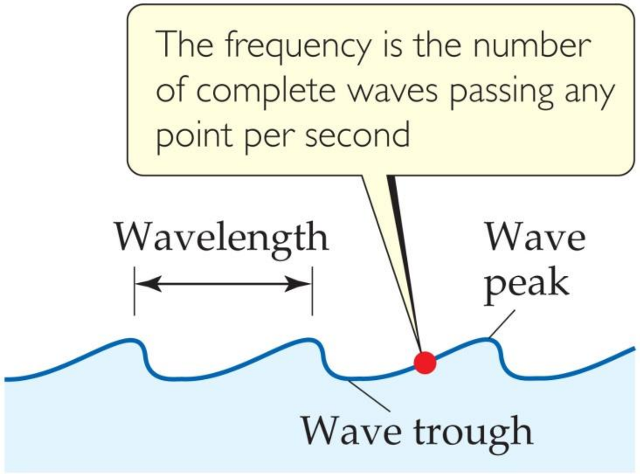
Electronic Structure

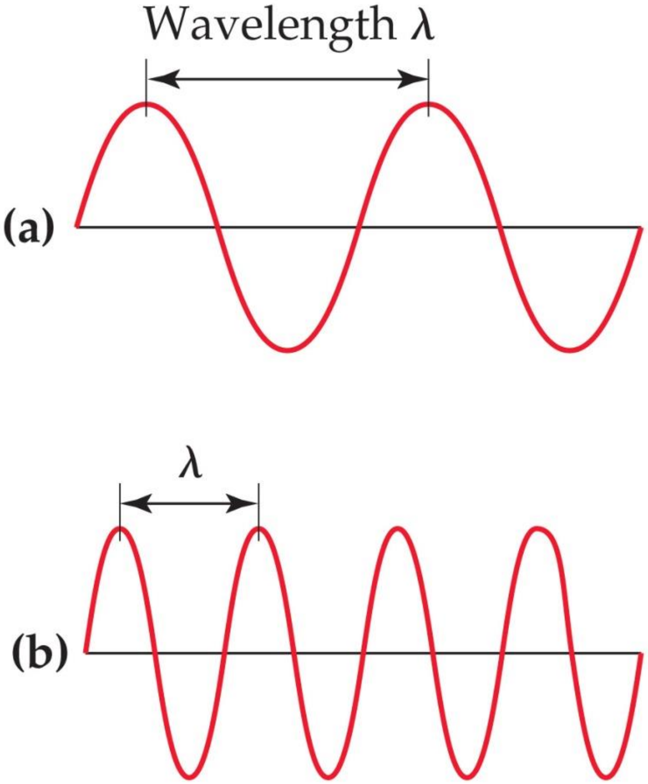
- This chapter is all about **electronic structure**—the arrangement and energy of electrons.
- It may seem odd to start by talking about **waves**. However, extremely small particles have properties that can only be explained in this manner!

Waves



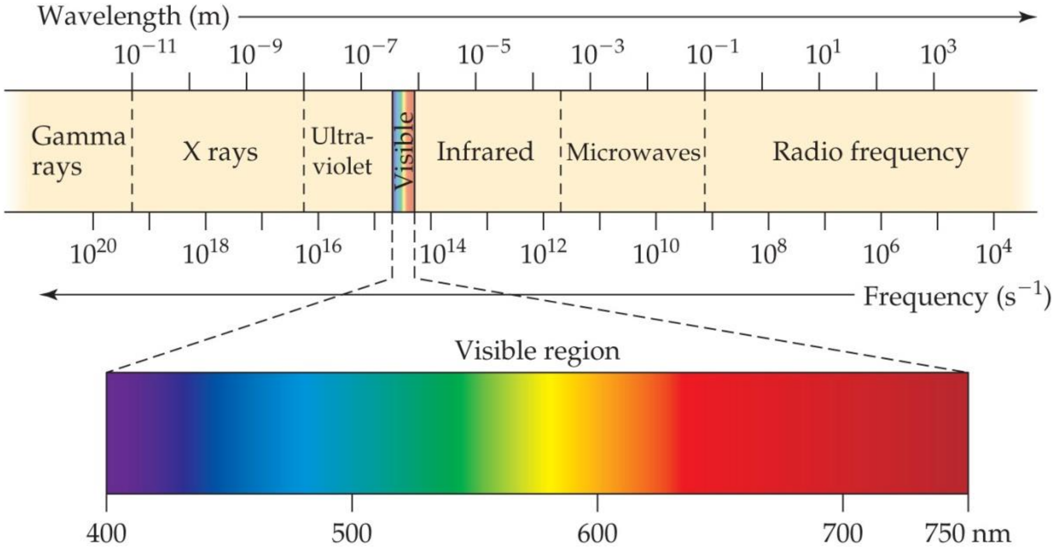
- To understand the electronic structure of atoms, one must understand the nature of electromagnetic radiation.
- The distance between corresponding points on adjacent waves is the **wavelength (λ)**.

Waves



- The number of waves passing a given point per unit of time is the **frequency (*ν*)**.
- For waves traveling at the same velocity, the longer the wavelength, the smaller the frequency.
- If the time associated with the lines to the left is one second, then the frequencies would be 2 s^{-1} and 4 s^{-1}, respectively.

Electromagnetic Radiation



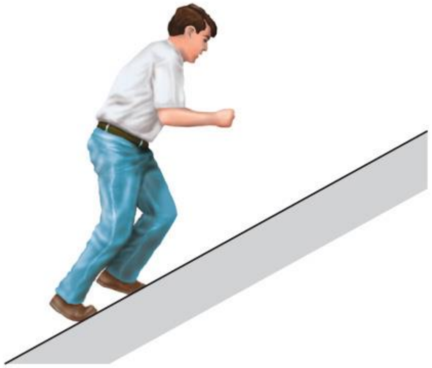
- All electromagnetic radiation travels at the same velocity: The speed of light (c) is 3.00×10^8 m/s.

$$c = \lambda \nu$$

The Nature of Energy

The wave nature of light does not explain how an object can glow when its temperature increases.

The Nature of Energy—Quanta

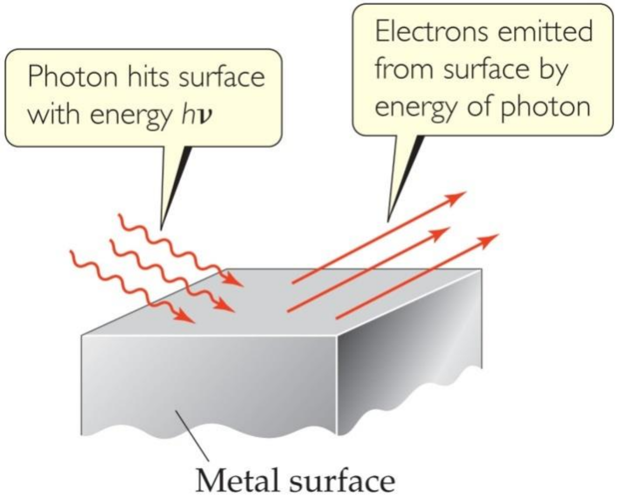


Potential energy of person walking up ramp increases in uniform, continuous manner

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

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

The Photoelectric Effect



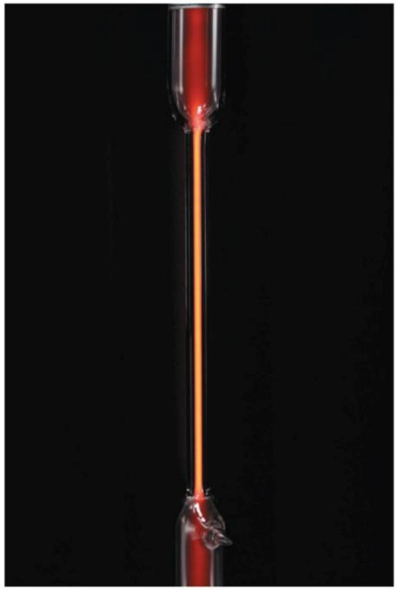
- Einstein used quanta to explain the photoelectric effect.
- Each metal has a different energy at which it ejects electrons. At lower energy, electrons are not emitted.
- He concluded that energy is proportional to frequency:

$$E = h\nu$$

where *h* is Planck’s constant, 6.626×10^{-34} J·s.

Atomic Emissions

Another mystery in the early twentieth century involved the emission spectra observed from energy emitted by atoms and molecules.

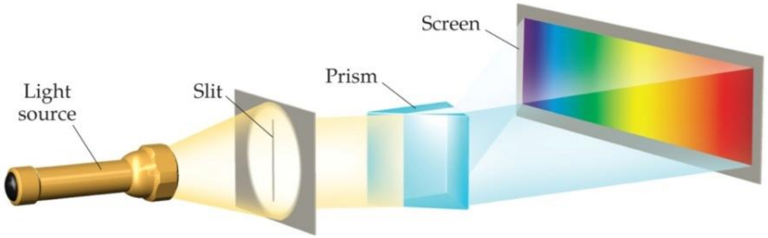


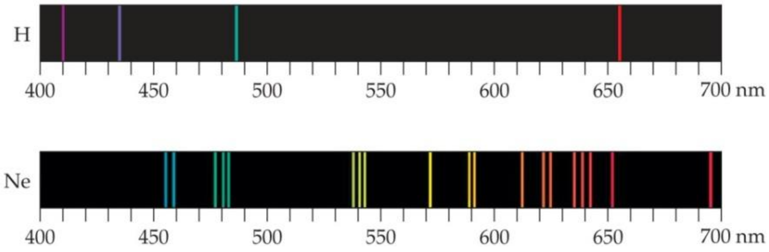
Neon (Ne)

Hydrogen (H)

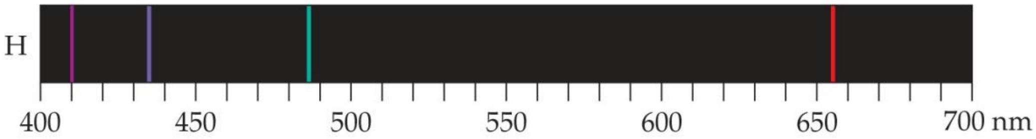
Continuous vs. Line Spectra

- For atoms and molecules, one does not observe a **continuous spectrum** (the “rainbow”), as one gets from a white light source.
- Only a **line spectrum** of discrete wavelengths is observed. Each element has a unique line spectrum.





The Hydrogen Spectrum

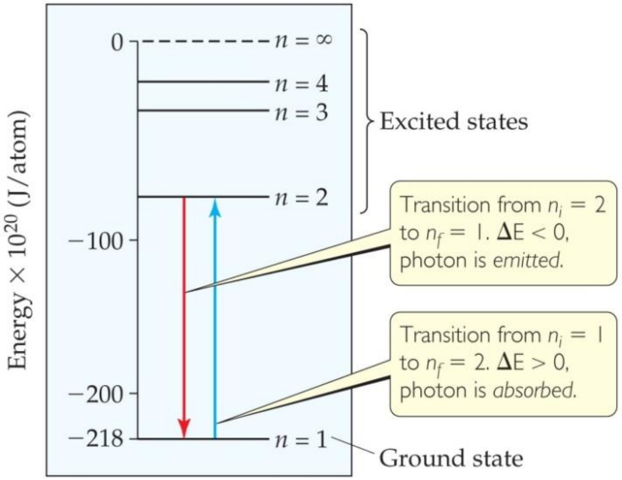


- Johann Balmer (1885) discovered a simple formula relating the four lines to integers.
- Johannes Rydberg advanced this formula.

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

- Neils Bohr explained *why* this mathematical relationship works.

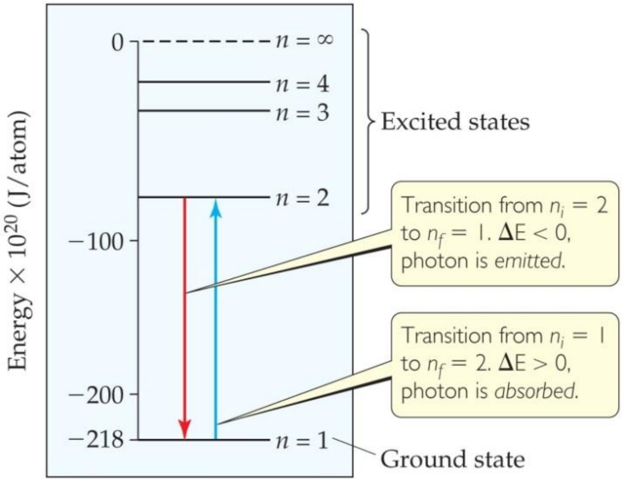
The Bohr Model



- Niels Bohr adopted Planck's assumption and explained these phenomena in this way:

  1. Electrons in an atom can only occupy certain orbits (corresponding to certain energies).

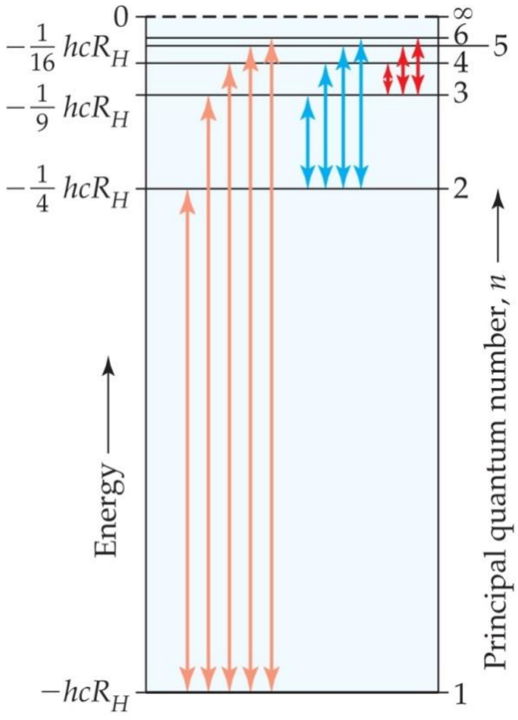
The Bohr Model



2. Electrons in permitted orbits have specific, “allowed” energies; these energies will not be radiated from the atom.
3. Energy is only absorbed or emitted in such a way as to move an electron from one “allowed” energy state to another; the energy is defined by

$$E = h\nu$$

The Bohr Model



The energy absorbed or emitted from the process of electron promotion or demotion can be calculated by the equation

$$\Delta E = -hcR_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

where R_H is the Rydberg constant, $1.097 \times 10^7\ \mathrm{m}^{-1}$, and n_i and n_f are the initial and final energy levels of the electron.

Limitations of the Bohr Model

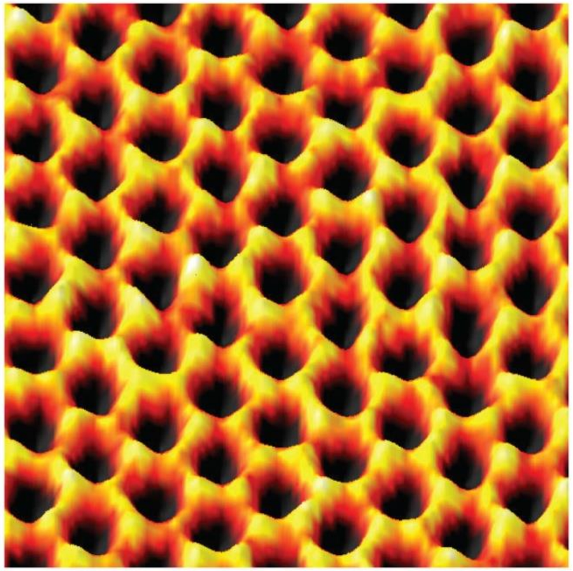
- It only works for hydrogen!
- Classical physics would result in an electron falling into the positively charged nucleus. Bohr simply assumed it would not!
- Circular motion is not wave-like in nature.

Important Ideas from the Bohr Model

- Points that are incorporated into the current atomic model include the following:

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

The Wave Nature of Matter



The wave nature of light is used to produce this electron micrograph.

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

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

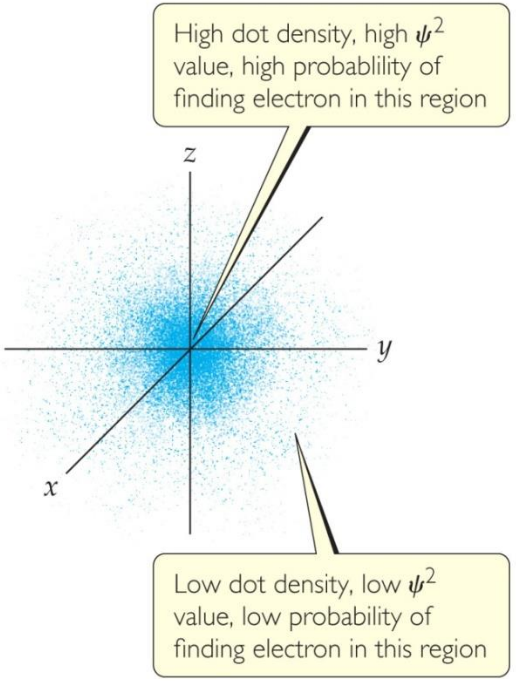
The Uncertainty Principle

Heisenberg showed that the more precisely the momentum of a particle is known, the less precisely is its position is known:

$$(\Delta x)\ (\Delta mv) \geq \frac{h}{4\pi}$$

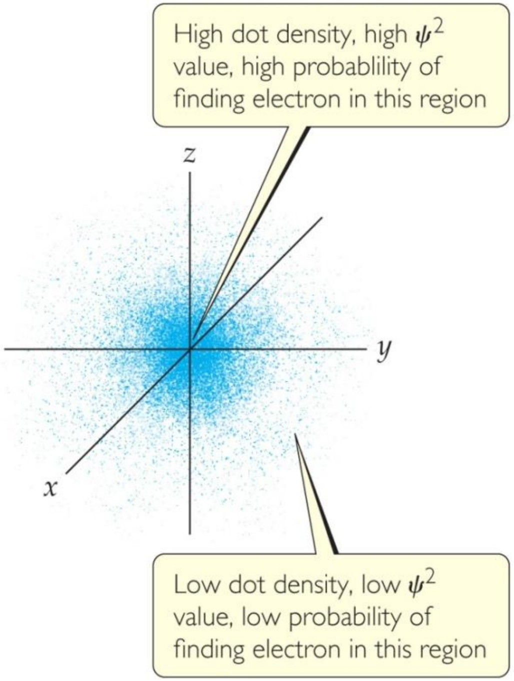
Quantum Mechanics

- Erwin Schrödinger developed a mathematical treatment into which both the wave and particle nature of matter could be incorporated.
- This is known as **quantum mechanics.**



Quantum Mechanics

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



Quantum Numbers

- Solving the wave equation gives a set of wave functions, or **orbitals**, and their corresponding energies.
- Each orbital describes a spatial distribution of electron density.
- An orbital is described by a set of three **quantum numbers**.

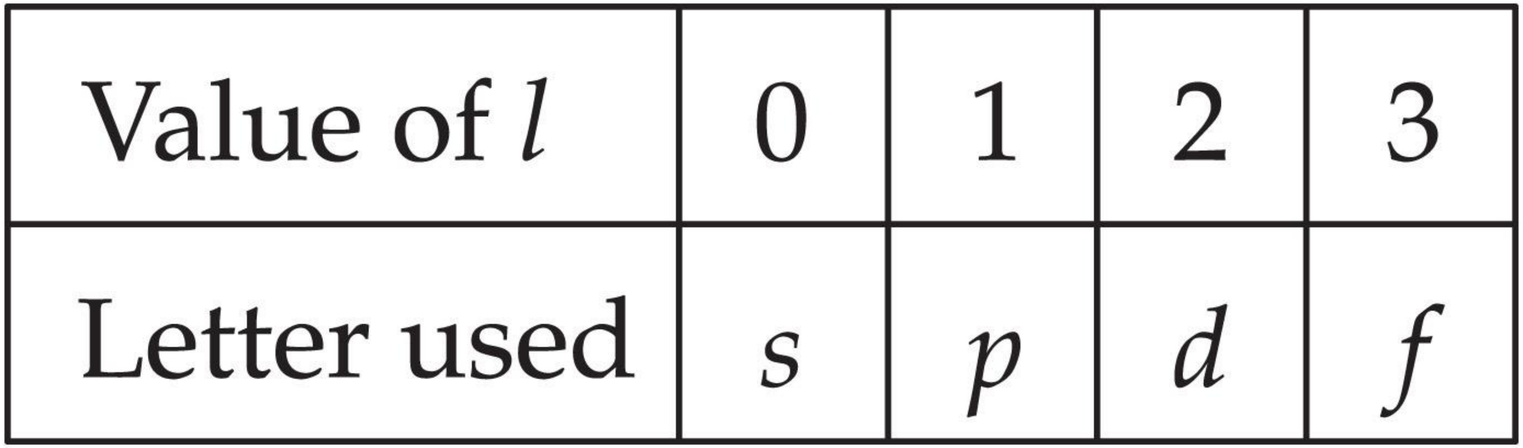
Principal Quantum Number (*n*)

- The principal quantum number, *n*, describes the energy level on which the orbital resides.
- The values of *n* are integers ≥ 1.
- These correspond to the values in the Bohr model.

Angular Momentum Quantum Number (*l*)

- This quantum number defines the shape of the orbital.
- Allowed values of *l* are integers ranging from 0 to $n - 1$.
- We use letter designations to communicate the different values of *l* and, therefore, the shapes and types of orbitals.

Angular Momentum Quantum Number (*l*)



Value of l	0	1	2	3
Letter used	s	p	d	f

Magnetic Quantum Number (m_l)

- The magnetic quantum number describes the three-dimensional orientation of the orbital.
- Allowed values of m_l are integers ranging from $-l$ to l:

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

- Therefore, on any given energy level, there can be up to 1 *s* orbital, 3 *p* orbitals, 5 *d* orbitals, 7 *f* orbitals, and so forth.

Magnetic Quantum Number (m_l)

- Orbitals with the same value of n form an **electron shell**.
- Different orbital types within a shell are **subshells**.

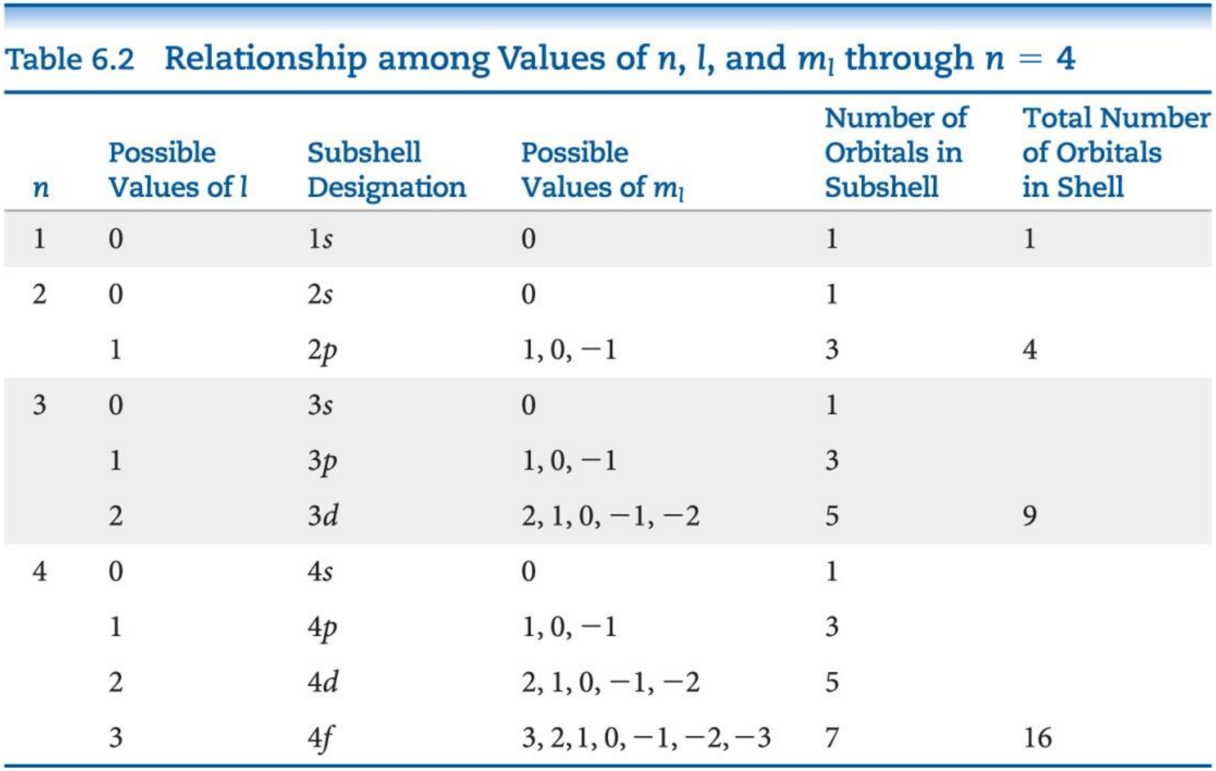
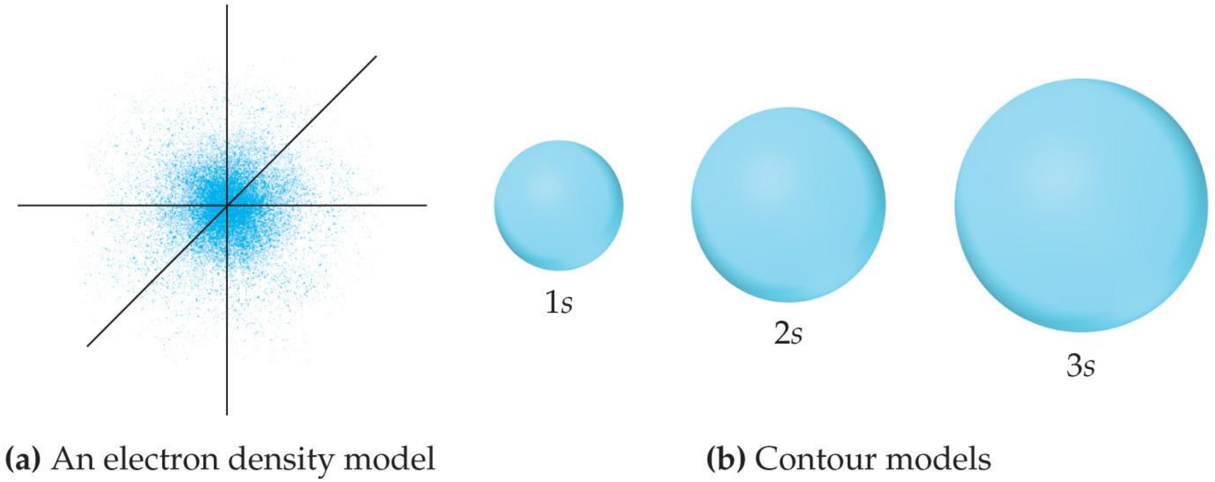


Table 6.2 Relationship among Values of n, l, and m_l through $n = 4$

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

s Orbitals

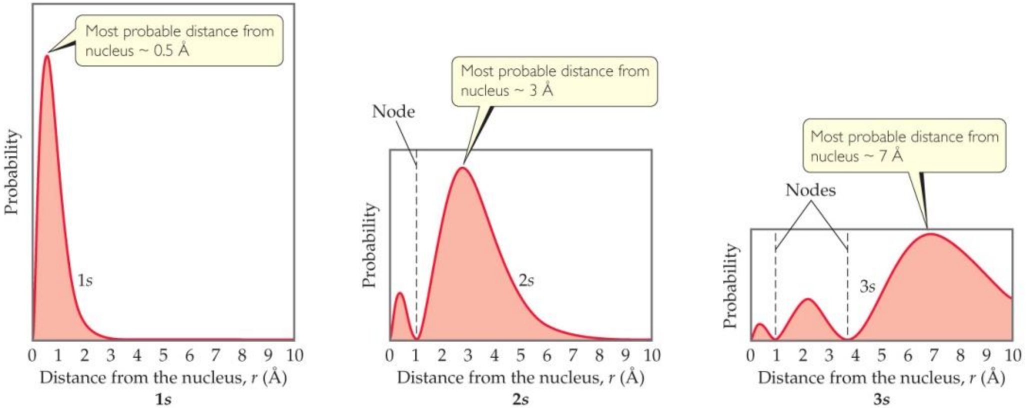


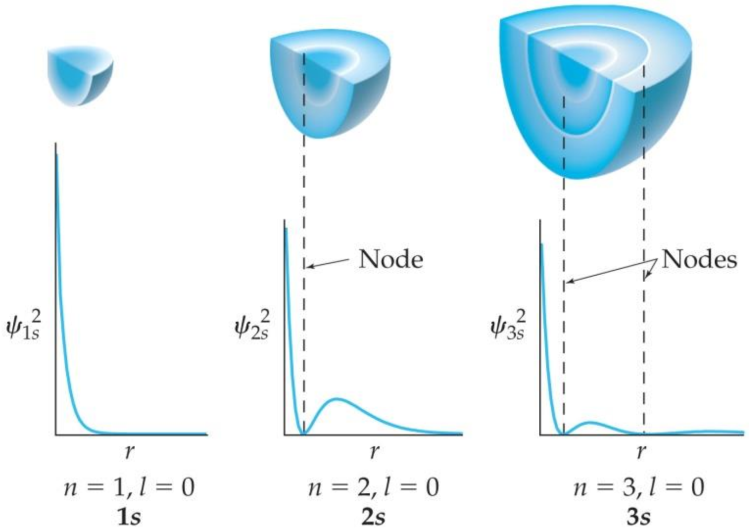
(a) An electron density model

(b) Contour models

- The value of *l* for *s* orbitals is 0.
- They are spherical in shape.
- The radius of the sphere increases with the value of *n.*

s Orbitals

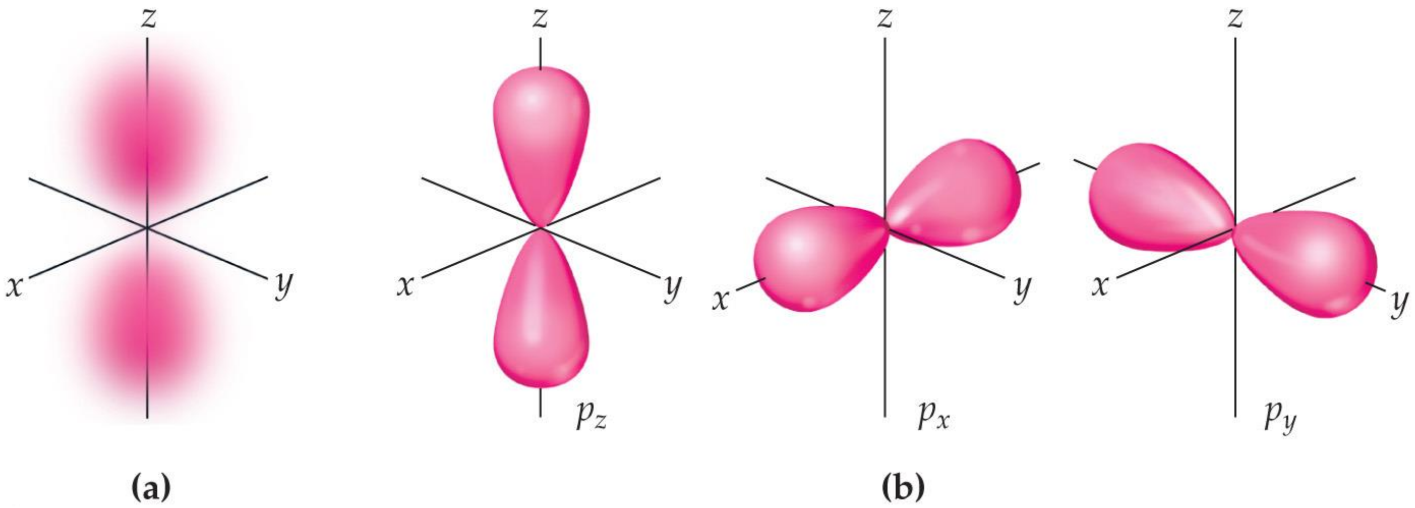




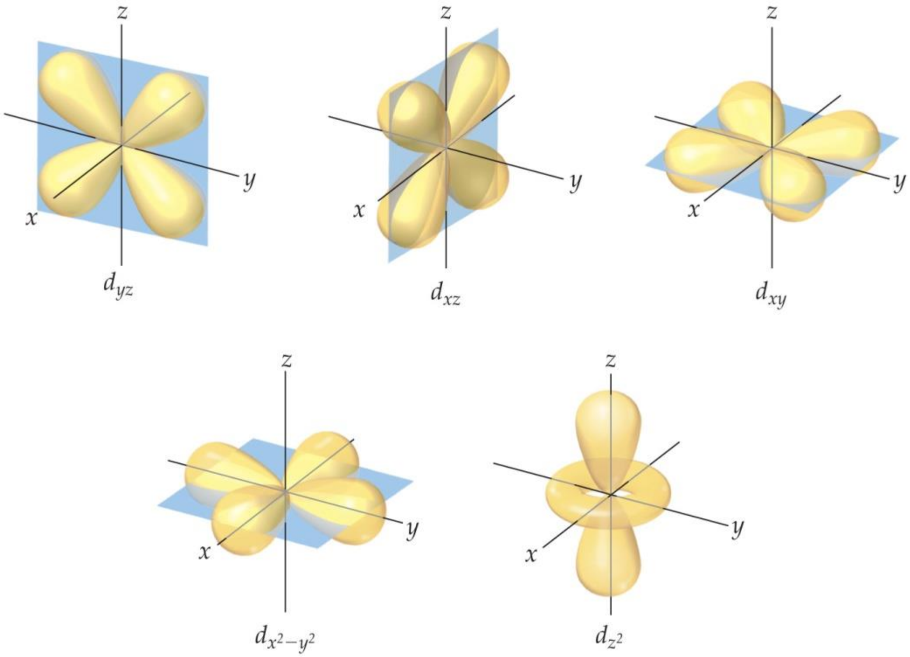
- For an *ns* orbital, the number of peaks is *n*.
- For an *ns* orbital, the number of nodes (where there is zero probability of finding an electron) is *n – 1*.
- As *n* increases, the electron density is more spread out and there is a greater probability of finding an electron further from the nucleus.

p Orbitals

- The value of *l* for *p* orbitals is 1.
- They have two lobes with a node between them.



d Orbitals



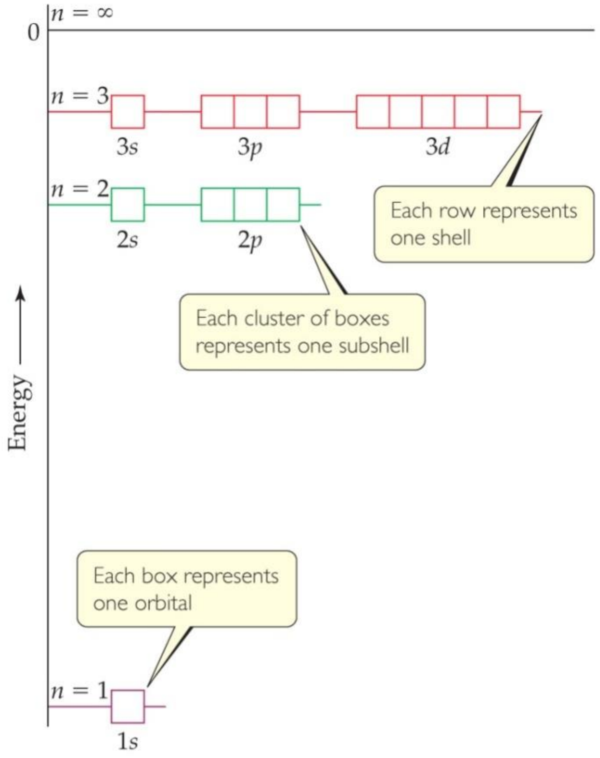
- The value of *l* for a *d* orbital is 2.
- Four of the five *d* orbitals have four lobes; the other resembles a *p* orbital with a doughnut around the center.

f Orbitals

- Very complicated shapes (not shown in text)
- Seven equivalent orbitals in a sublevel
- *l* = 3

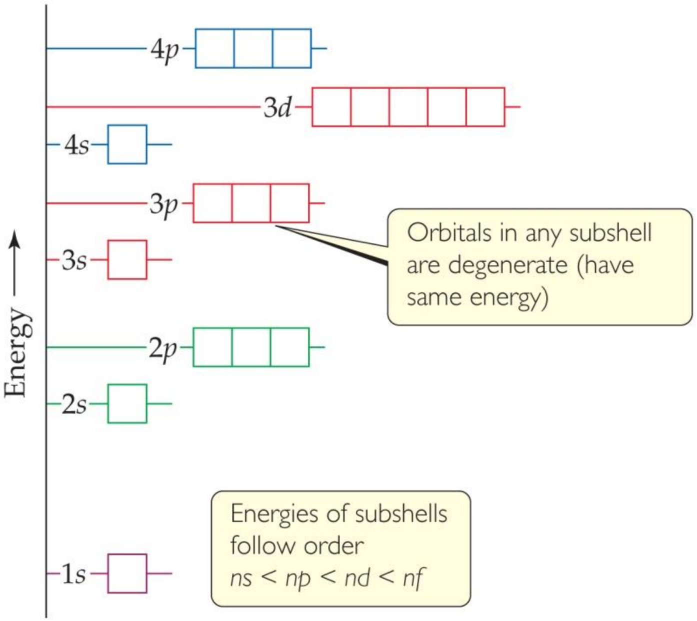
Energies of Orbitals—Hydrogen

- For a one-electron hydrogen atom, orbitals on the same energy level have the same energy.
- Chemists call them **degenerate** orbitals.



$n = 1$ shell has one orbital
$n = 2$ shell has two subshells composed of four orbitals
$n = 3$ shell has three subshells composed of nine orbitals

Energies of Orbitals—Many-electron Atoms



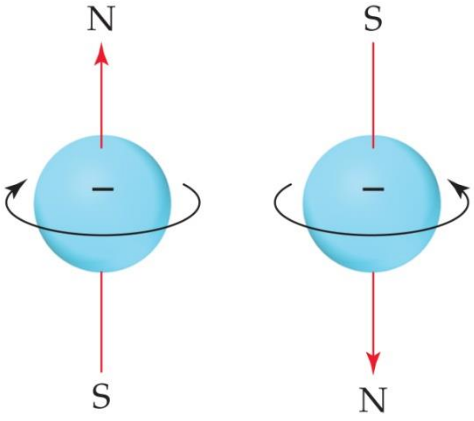
Orbitals in any subshell are degenerate (have same energy)

Energies of subshells follow order *ns* < *np* < *nd* < *nf*

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

Spin Quantum Number, m_s

- In the 1920s, it was discovered that two electrons in the same orbital do not have exactly the same energy.
- The “spin” of an electron describes its magnetic field, which affects its energy.
- This led to the spin quantum number, m_s.
- The spin quantum number has only two allowed values, +½ and –½.



Pauli Exclusion Principle

- No two electrons in the same atom can have exactly the same energy.
- Therefore, no two electrons in the same atom can have identical sets of quantum numbers.
- This means that every electron in an atom must differ by at least one of the four quantum number values: n, l, m_l, and m_s.

Electron Configurations

$4p^5$

- The way electrons are distributed in an atom is called its **electron configuration**.
- The most stable organization is the lowest possible energy, called the **ground state**.
- Each component consists of
  - a number denoting the energy level;

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Electron Configurations

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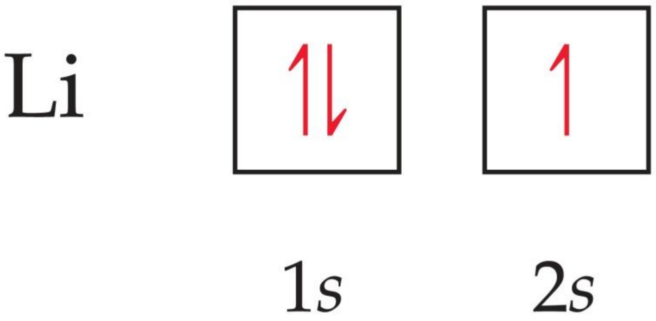
  - a letter denoting the type of orbital;
  - a superscript denoting the number of electrons in those orbitals.

Orbital Diagrams

- Each box in the diagram represents one orbital.
- Half-arrows represent the electrons.
- The direction of the arrow represents the relative spin of the electron.



Hund’s Rule

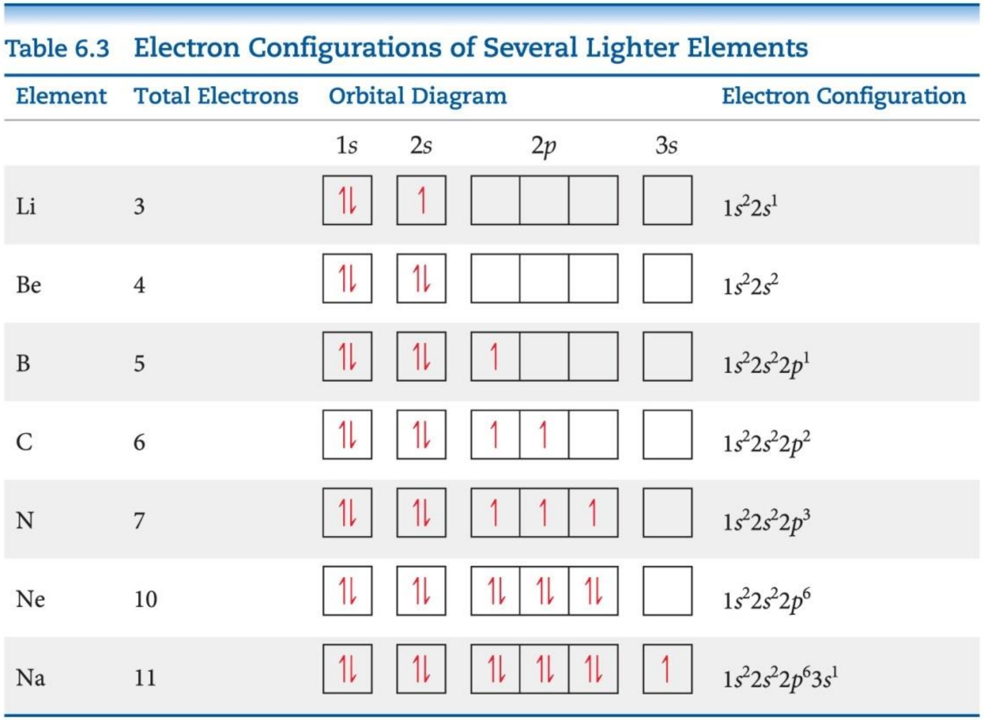


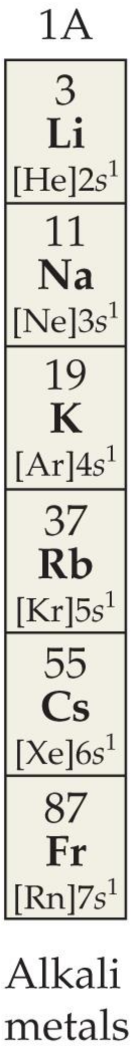
Table 6.3 Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram				Electron Configuration
		1*s*	2*s*	2*p*	3*s*	
Li	3	↑↓	↑	☐ ☐ ☐	☐	$1s^22s^1$
Be	4	↑↓	↑↓	☐ ☐ ☐	☐	$1s^22s^2$
B	5	↑↓	↑↓	↑ ☐ ☐	☐	$1s^22s^22p^1$
C	6	↑↓	↑↓	↑ ↑ ☐	☐	$1s^22s^22p^2$
N	7	↑↓	↑↓	↑ ↑ ↑	☐	$1s^22s^22p^3$
Ne	10	↑↓	↑↓	↑↓ ↑↓ ↑↓	☐	$1s^22s^22p^6$
Na	11	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	$1s^22s^22p^63s^1$

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

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

Condensed Electron Configurations



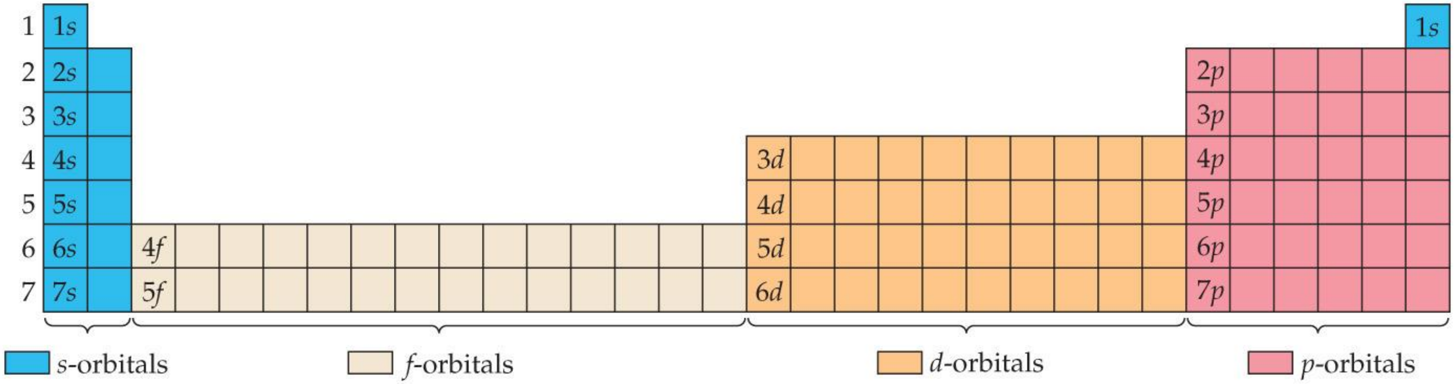
1A
3 **Li** [He]$2s^1$
11 **Na** [Ne]$3s^1$
19 **K** [Ar]$4s^1$
37 **Rb** [Kr]$5s^1$
55 **Cs** [Xe]$6s^1$
87 **Fr** [Rn]$7s^1$

Alkali metals

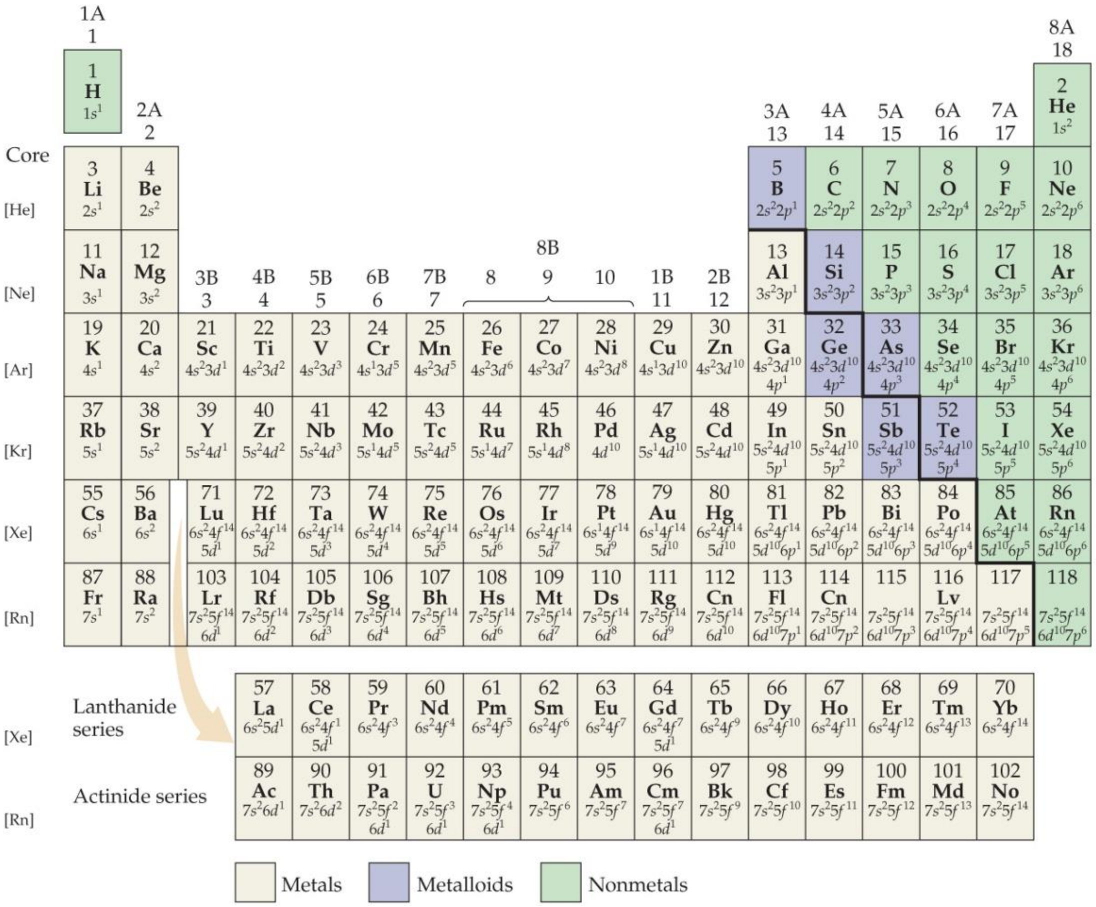
- Elements in the same group of the periodic table have the same number of electrons in the outer most shell. These are the **valence electrons**.
- The filled inner shell electrons are called **core electrons**. These include completely filled *d* or *f* sublevels.
- We write a shortened version of an electron configuration using brackets around a noble gas symbol and listing only valence electrons.

Periodic Table

- We fill orbitals in increasing order of energy.
- Different blocks on the periodic table correspond to different types of orbitals: *s* = blue, *p* = pink (*s* and *p* are representative elements); *d* = orange (transition elements); *f* = tan (lanthanides and actinides, or inner transition elements)



Some Anomalies



Core	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1 **H** $1s^1$																	2 **He** $1s^2$
[He]	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** $2s^22p^6$
[Ne]	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** $3s^23p^6$
[Ar]	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** $4s^23d^{10}4p^6$
[Kr]	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^24d^1$	40 **Zr** $5s^24d^2$	41 **Nb** $5s^24d^3$	42 **Mo** $5s^14d^5$	43 **Tc** $5s^24d^5$	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** $5s^24d^{10}5p^6$
[Xe]	55 **Cs** $6s^1$	56 **Ba** $6s^2$	71 **Lu** $6s^24f^{14}5d^1$	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** $6s^24f^{14}5d^{10}6p^6$
[Rn]	87 **Fr** $7s^1$	88 **Ra** $7s^2$	103 **Lr** $7s^25f^{14}6d^1$	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 **Fl** $7s^25f^{14}6d^{10}7p^1$	114 **Cn** $7s^25f^{14}6d^{10}7p^2$	115 $7s^25f^{14}6d^{10}7p^3$	116 **Lv** $7s^25f^{14}6d^{10}7p^4$	117 $7s^25f^{14}6d^{10}7p^5$	118 $7s^25f^{14}6d^{10}7p^6$

[Xe]	Lanthanide series	57 **La** $6s^25d^1$	58 **Ce** $6s^24f^15d^1$	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** $6s^24f^{14}$
[Rn]	Actinide series	89 **Ac** $7s^26d^1$	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** $7s^25f^9$	98 **Cf** $7s^25f^{10}$	99 **Es** $7s^25f^{11}$	100 **Fm** $7s^25f^{12}$	101 **Md** $7s^25f^{13}$	102 **No** $7s^25f^{14}$

⬜ Metals 🟪 Metalloids 🟩 Nonmetals

- Some irregularities occur when there are enough electrons to half-fill *s* and *d* orbitals on a given row.

Chromium as an Anomaly

- For instance, the electron configuration for chromium is

  $[\mathrm{Ar}]\ 4s^1\ 3d^5$

  rather than the expected

  $[\mathrm{Ar}]\ 4s^2\ 3d^4$.
- This occurs because the 4*s* and 3*d* orbitals are very close in energy.
- These anomalies occur in *f*-block atoms with *f* and *d* orbitals, as well.