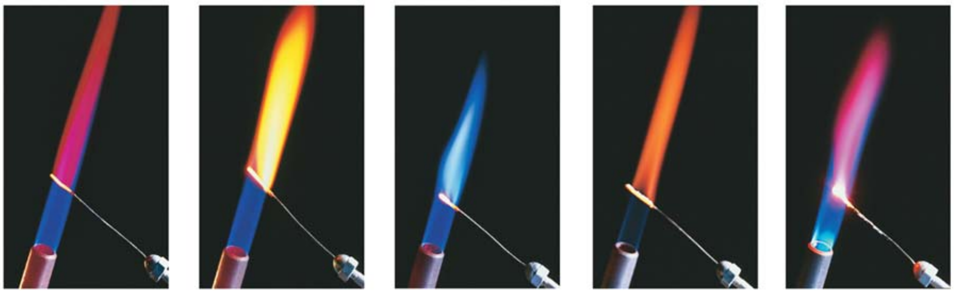
Lecture 2: Electronic Structure of Atoms

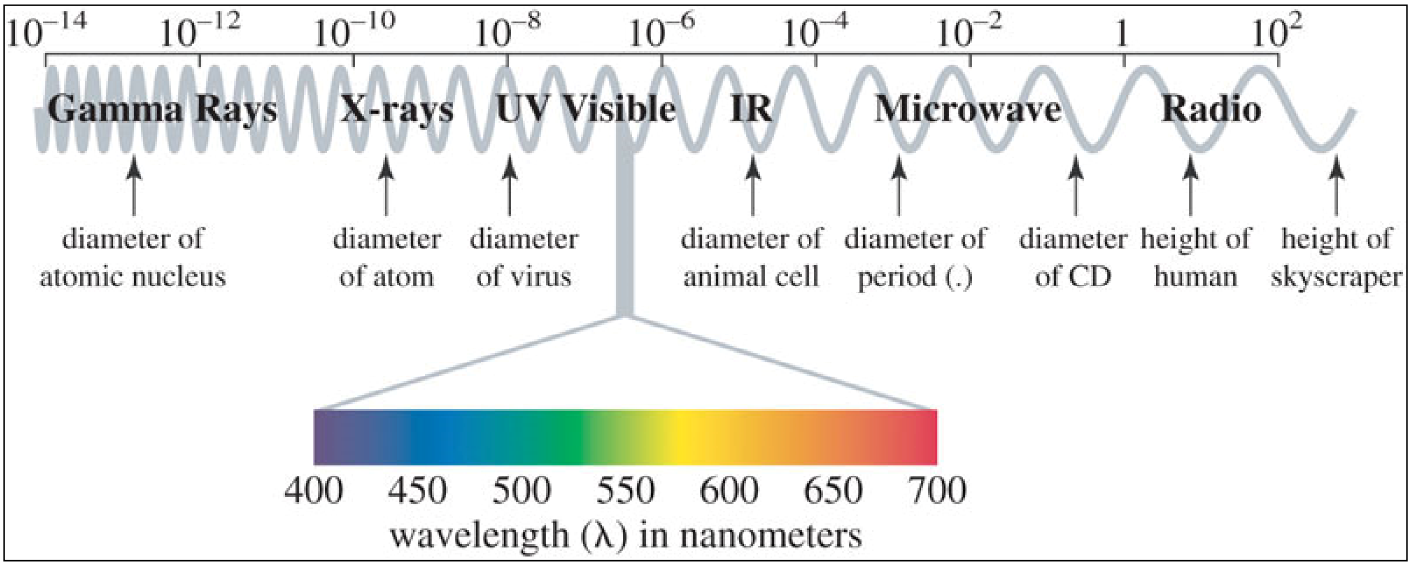
Certain elements can be identified by their characteristic colors emitted when their compounds are placed in a flame (**Flame Test**).

Different elements emit distinctive colors of light because the atoms of each element have unique *electronic structure*.



Lithium, Li | Sodium, Na | Potassium, K | Calcium, Ca | Strontium, Sr

Electromagnetic Radiation (Light)



- Visible light is a type of ***electromagnetic (EM) radiations***, which has both electric and magnetic components varying periodically in **wave-like** fashion.
- All EM radiations travel at the same velocity, $c = 2.998 \times 10^8$ m s^{-1} .
- Their properties are different because they have different wavelengths (λ) and frequencies (ν): $\boldsymbol{c = \lambda\nu}$

"Particles" of Light — Photons

*For a long time it was not possible to understand how **color** (which is **wave**) of an **object** (which is **particle**) can change when its temperature increases!*

Until………

- Max Planck and Albert Einstein suggested that lights do not only behave as ***waves***, but also as a stream of tiny ***particles***.
- These "particles" of light are named as ***photons***.
- The energy E of each photon of light with a frequency of ν is:

$$E = h\nu$$

where h is the Planck's constant, 6.626×10^{-34} J s.

The Nature of Light

- ***Light*** behaves as if it possesses both (1) ***wave-like*** and (2) ***particle-like*** properties.

(1) $c = \lambda\nu$

speed of light, c = 2.998×10^{8} m s^{-1}

(2) $E = h\nu$

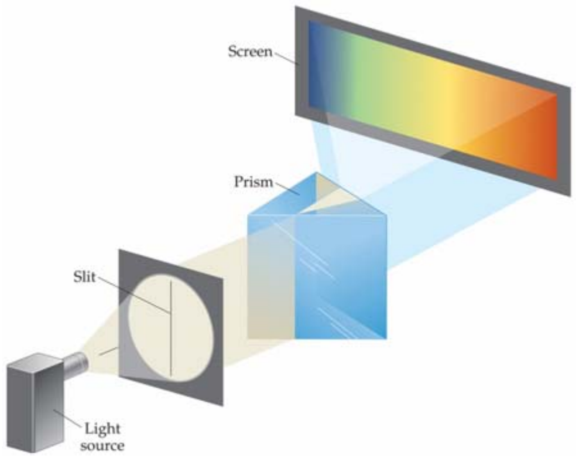
Planck constant, h = 6.626×10^{-34} J s

- The shorter the wavelength, the higher the frequency, and the higher the energy.

For example:

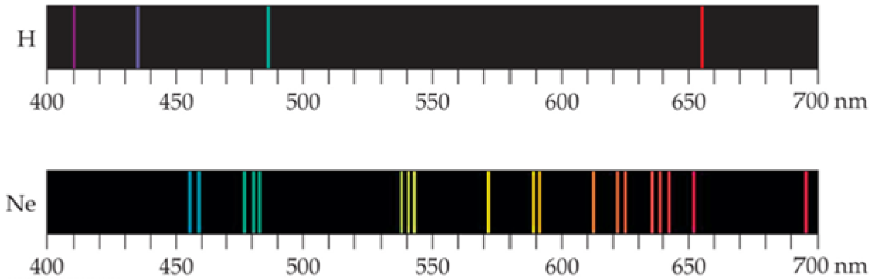
- *the frequency of a single red photon (wavelength λ = 725 nm) is 4.14×10^{14} s^{-1}.*
- *The energy E of this red photon is 2.74×10^{-19} J.*
- *<u>One mole</u> of such red photons contains 165 kJ mol^{-1} of energy.*

Atomic Spectrum



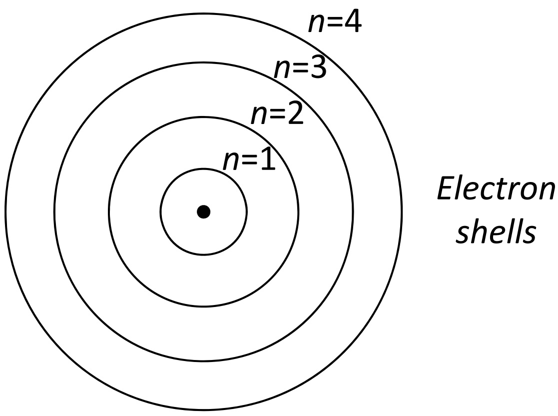
- A white-light source as shown on left-hand side gives a continuous spectrum.
- However, the light emitted from an atom (e.g. light from fireworks) contains photons of particular frequencies, giving a line spectrum.
- Niels Bohr tried to explain these phenomena with his atomic model (Bohr Model).

Neon (Ne) Hydrogen (H)



The line spectra of Ne and H atoms

Bohr's Atomic Model / 1



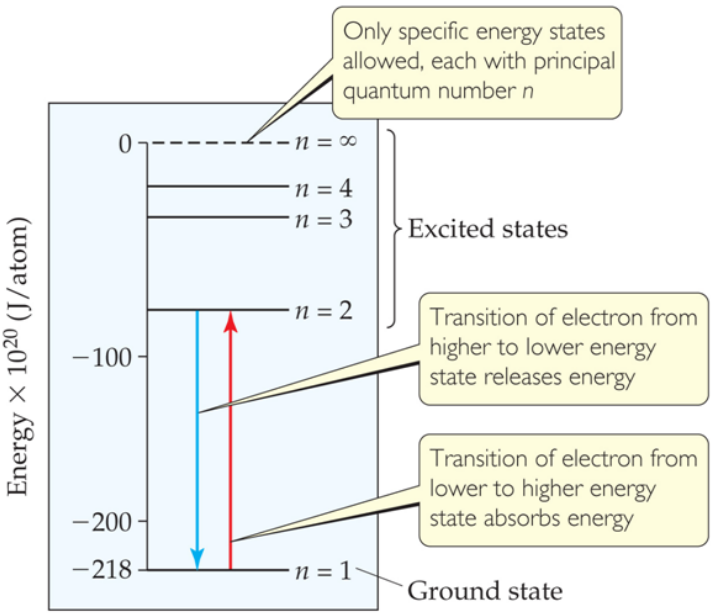
- Bohr's postulation for a **hydrogen** atom:

(1) the electron can be circling about the nucleus in some orbits of certain radii. Each orbit corresponds to a ***shell*** (***n***) with a specific energy.

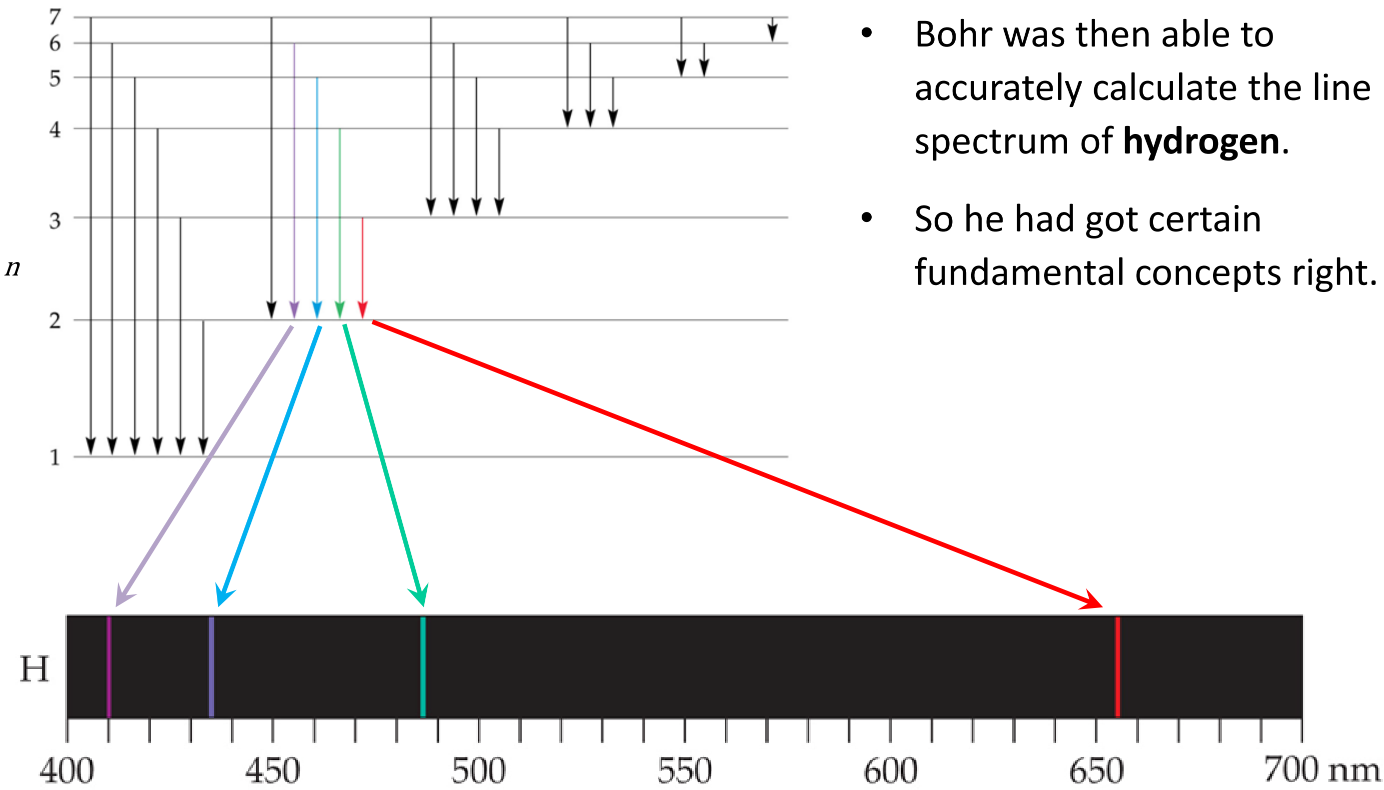
(2) the electron in a permitted orbit is in an ***allowed energy state***

(3) the electron can change from one allowed energy state to another allowed energy state by **absorbing** or **releasing** energy in the form of light (i.e. photon)

$$\Delta E = h\nu.$$



Bohr's Atomic Model / 2



- Bohr was then able to accurately calculate the line spectrum of **hydrogen**.
- So he had got certain fundamental concepts right.

Energies released from these 4 electron transitions give out these corresponding wavelengths

Bohr's Atomic Model / 3

- However, his theory ***completely fails*** to account for the spectra ***of atoms containing more than one electron***---it fails even for helium, which contains only two electrons!

- *Bohr's atomic theory actually contains fundamental errors…*

  - Electrons are ***NOT*** classical particles.

  - They do ***NOT*** travel in well-defined orbits.

  - Our intuitive ideas about particles having definite trajectories through space are ***NOT*** applicable to electrons!

In fact, electrons, which were thought as particles, possess wave-like properties, too.

Wave-particle Duality of Matters

- Extending the concept of *wave-particle duality* of light (photon) to particles,

  Louis de Broglie proposed that an **electron** can be thought of moving around the nucleus **as a wave**, rather than as a particle.

Planck's constant (6.626×10^{-34} J s)

Wavelength of the electron → $$\lambda = \frac{h}{mv}$$

Momentum of the electron = (mass) x (velocity)

- For example,

Particle	*Mass (m)*	*Velocity (v)*	*Wavelength (λ)*
An electron	9×10^{-31} kg	6×10^{6} m s^{-1}	1×10^{-10} m (or 1 Å) (recall: what is the size of an atom?)

Can We Accurately Locate an Electron? — "No"

- We can locate an object by electromagnetic radiation.
- The position of an object cannot be determined with uncertainty that is smaller than the wavelength of the radiation used.
- Locating a tiny electron must use very short wavelength, which is too energetic and will change its momentum (mass × velocity).
- Werner Heisenberg's **Uncertainty Principle** states that for the dual nature of matter

  the more precisely the **position** is determined,

  the less precisely the **momentum** is known, or *vice versa*.

Uncertainty in momentum

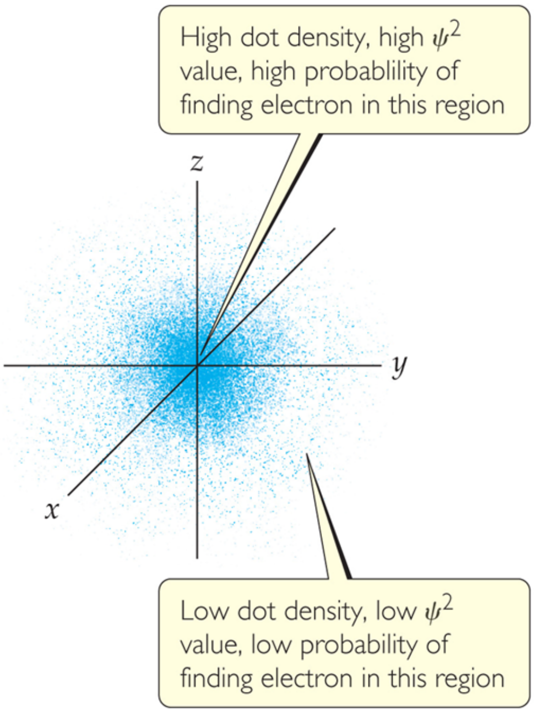
Uncertainty in position

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

Particle	*Mass (m)*	*Velocity (v)*	Δx (assuming $\Delta(mv)$ is 1%)
An electron	9×10^{-31} kg	6×10^{6} m s^{-1}	$\geq 1 \times 10^{-9}$ m (10 Å) (recall: what is the size of an atom?)

Quantum Mechanics and Atomic Orbitals

An Important Concept of Electron in Chemistry



- Erwin Schrödinger proposed a mathematical equation that incorporates both the wave and particle properties of the electron, which is the foundation of ***QUANTUM MECHANICS.***
- Solving this (initially) difficult equation leads to a series of *functions* ψ (known as **orbitals**).
- Each orbital has a characteristic energy.
- The position of an electron is represented by ψ^2, which is *the probability of finding an electron in a certain region of space at a given time* (or called ***electron density***), rather than its exact location.

Quantum Numbers

- Each ***atomic orbital*** in an atom is described by a unique set of integers called ***quantum numbers***.
- Three quantum numbers characterize orbitals' spatial properties:

n The principal quantum number **(determining orbitals' energy and size)**

Allowed values of ***n*** are positive integers **1, 2, 3, …… (shell)**

l The angular momentum quantum number **(determining orbitals' shape)**

Allowed values of ***l*** for a given *n* are integers from ***0*** to **(*n* – 1)** (**subshell**), each value of *l* is designated by a letter.

Value of *l*	0	1	2	3
Type of orbital	*s*	*p*	*d*	*f*

m_l The magnetic quantum number **(determining orbitals' spatial orientation)**

Allowed values of m_l are integers $-l \le m_l \le l$, ***including zero***

$-l\ ,\ (-l+1)\ ,\ (-l+2)\ ,\ \ldots\ ,\ 0\ ,\ \ldots.\ ,\ (l-2)\ ,\ (l-1)\ ,\ l$

Therefore, for each l, there are $(2l+1)$ values of m_l.

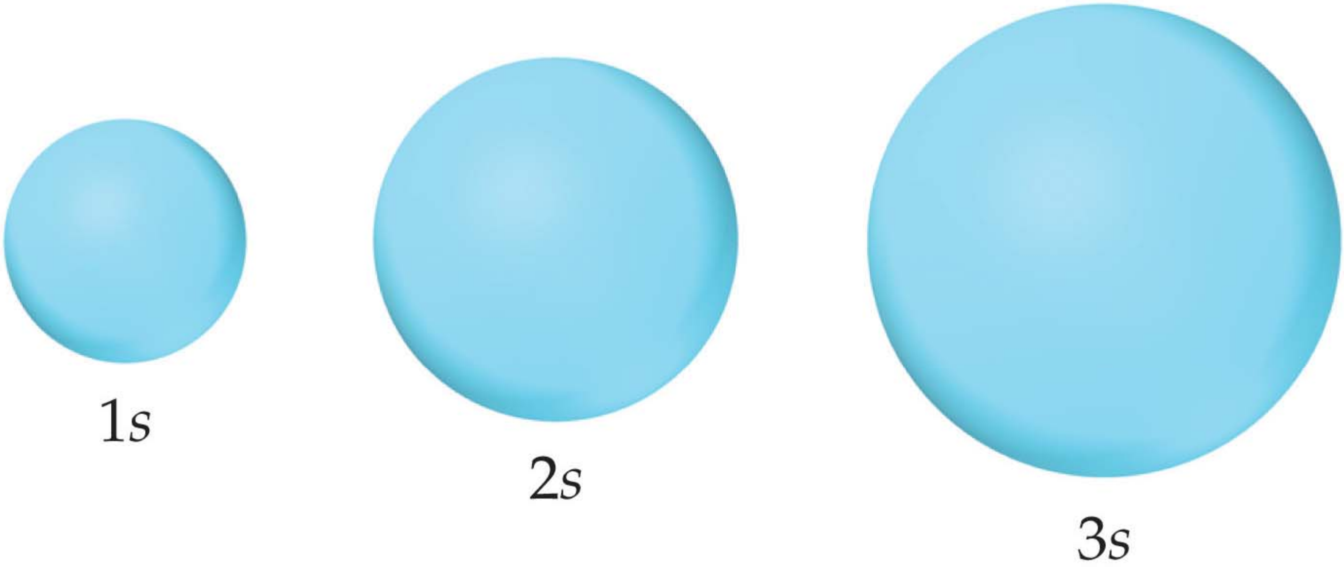
Quantum Numbers

A Summary of the Quantum Numbers of the Spatial Atomic Orbitals

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

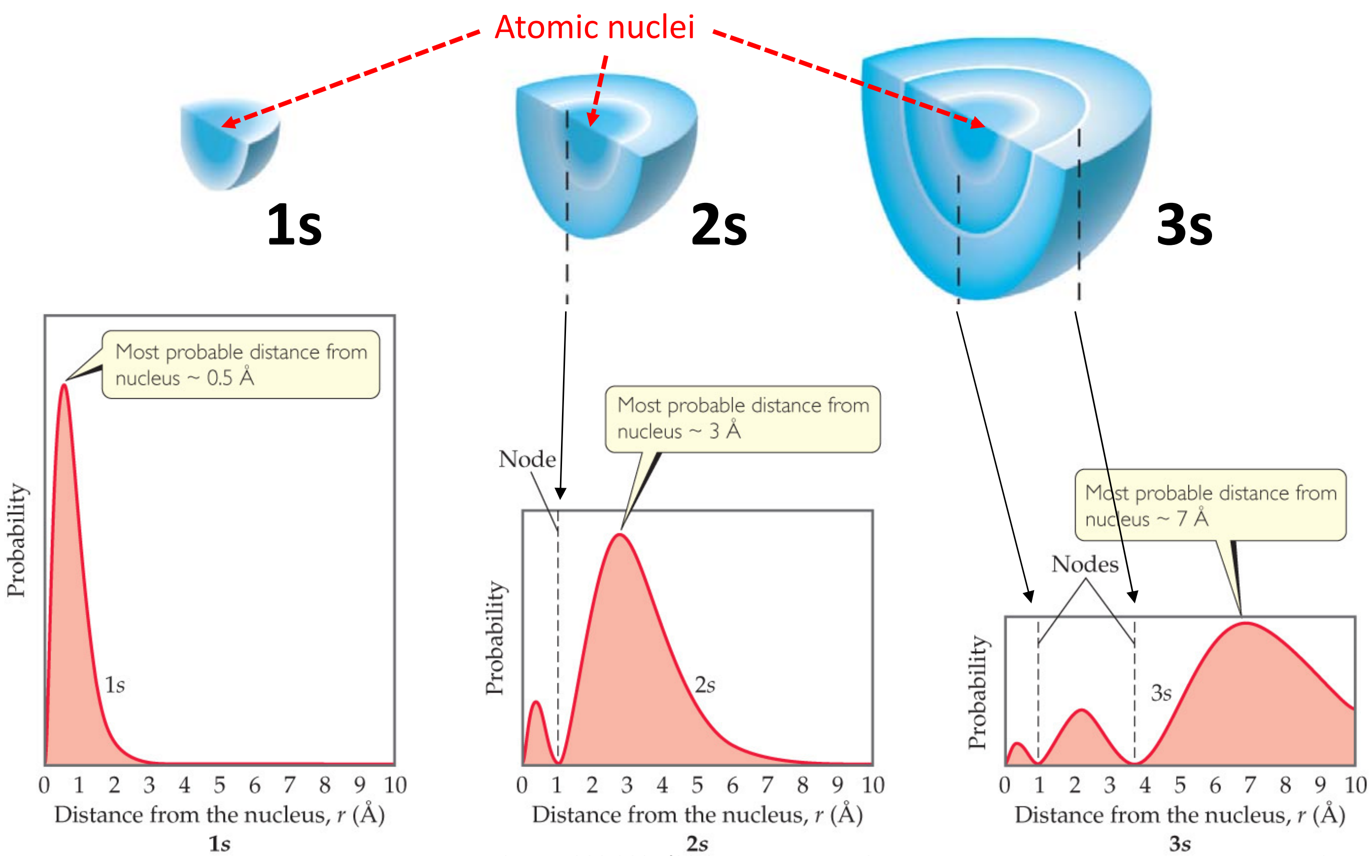
The *s* Orbitals (l = 0; m_l = 0)



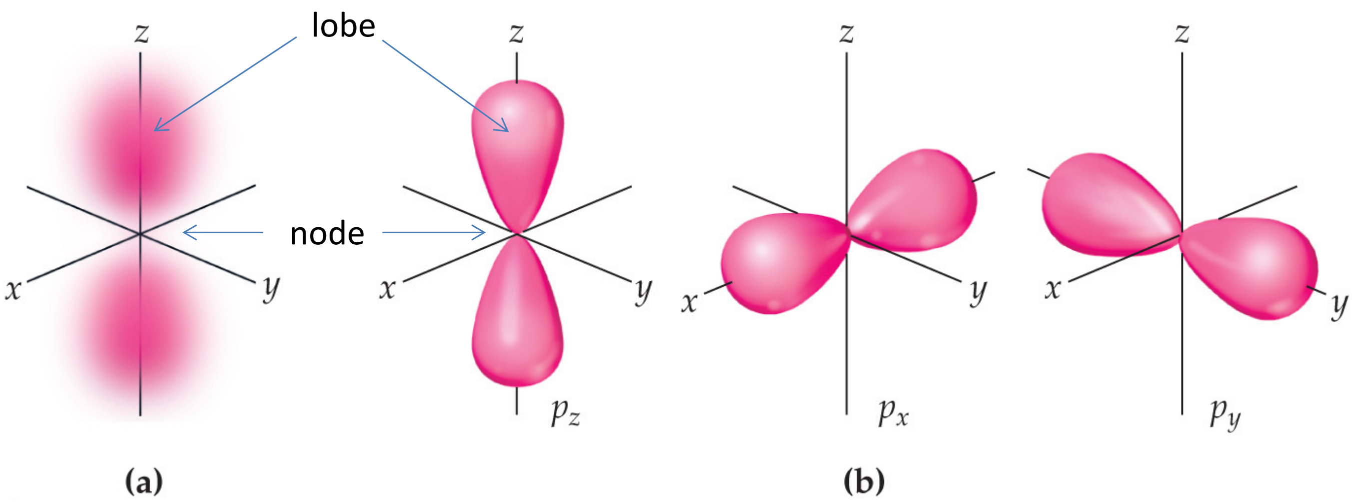
- The ***s*** orbitals are spherically in shape.
- As the principal quantum number (***n***) ***increases***,
  - the orbital becomes ***larger***, and
  - the electron has ***higher*** energy and is ***less tightly bound*** to the nucleus.

Radial Probability of 1s, 2s and 3s Orbitals

The electron distribution from the atomic center (i.e. the nucleus)



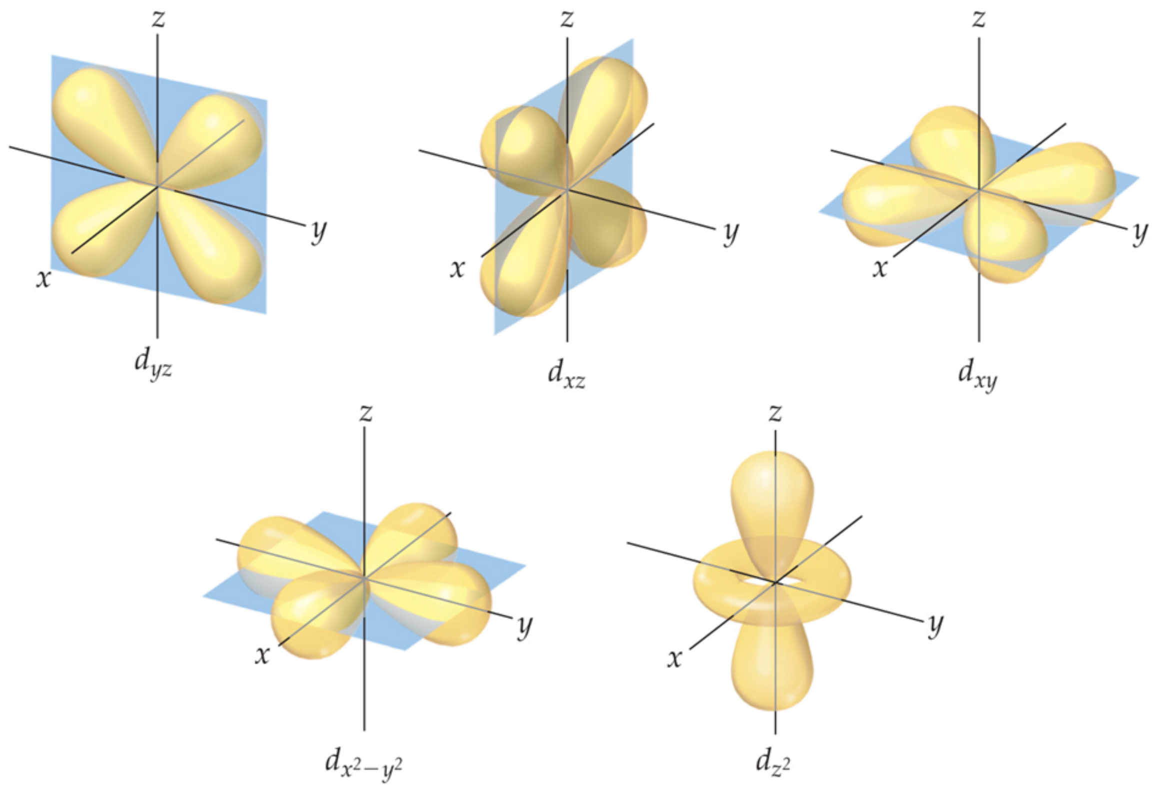
The *p* Orbitals (l = 1; m_l = –1, 0, 1)



- Each of the <u>three</u> *p* orbitals has **two lobes** and **one node** between them.

- The *p* orbitals having the same ***n*** have the same size and shape, but differ from one another in spatial orientation.

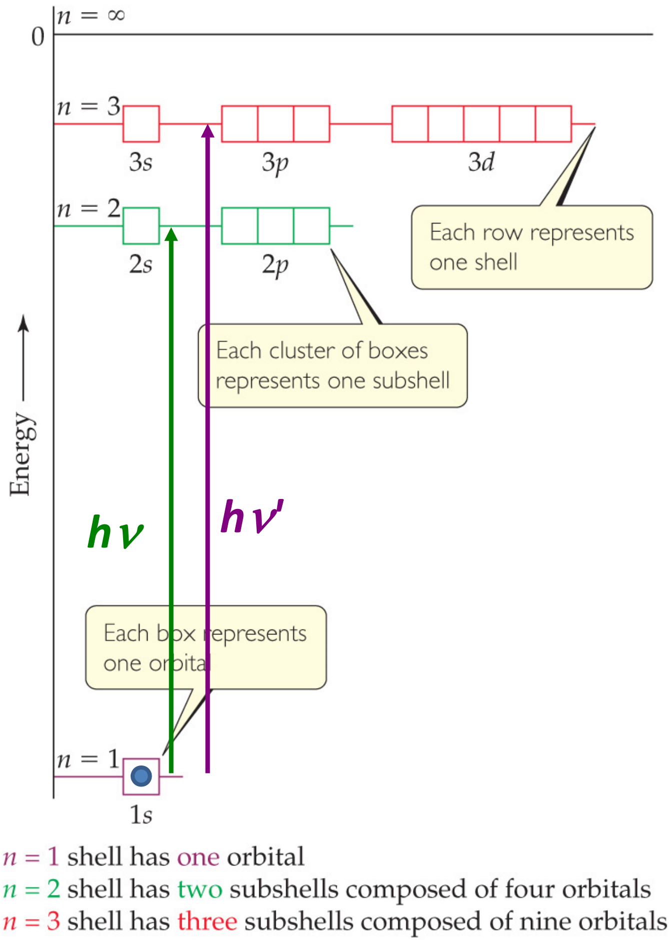
The *d* Orbitals (l = 2 ; m_l = –2, –1, 0, 1, 2)



- Four of the <u>five</u> *d* orbitals have 4 lobes.
- The fifth one resembles a *p* orbital with a “ring” around the center.

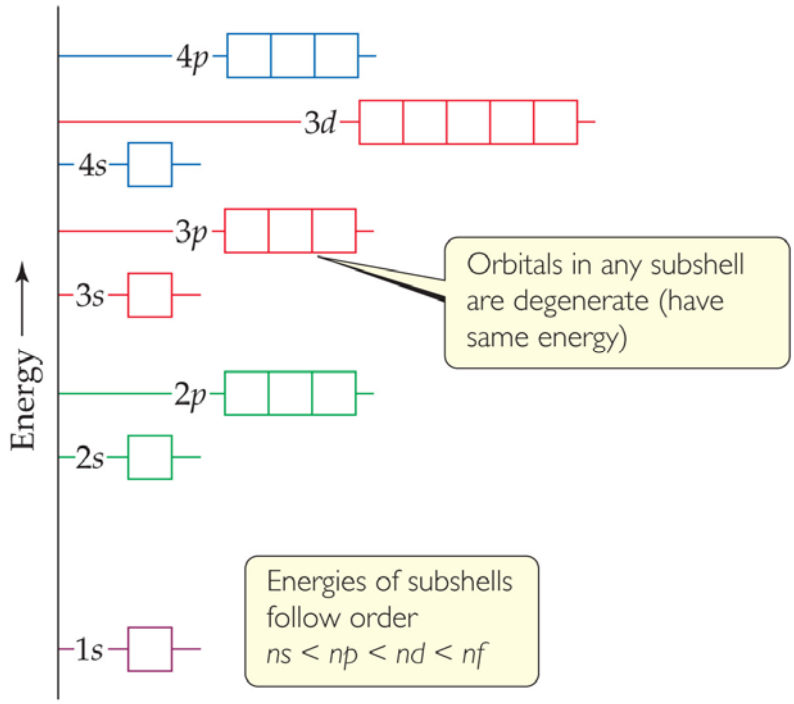
Energies of Atomic Orbitals for Hydrogen Atom

- For the **<u>hydrogen atom</u>**, the orbitals in a given shell *n* are ***degenerate*** (*lie at the same energy*).
- The H atom is in its ***ground state*** when the electron occupies the ***lowest energy orbital*** (1*s*).
- An ***excited state*** of a H atom is formed when the electron occupies any other orbitals promoted by ***electronic excitation***.
- The electron can be excited by absorbing a photon of appropriate energy $h\nu$.
- The excited H atom can be relaxed back to the ground state by emitting a photon with this same amount of energy.



Energies of Atomic Orbitals (Except Hydrogen)

- For **<u>all other types of atom</u>** (i.e. non-hydrogen atoms), *electron-electron repulsions* cause the different subshells to be ***non-degenerate*** (lie at *different energies*).
- For a given *n*, the orbitals increase in energy in this order: ***ns < np < nd < nf***

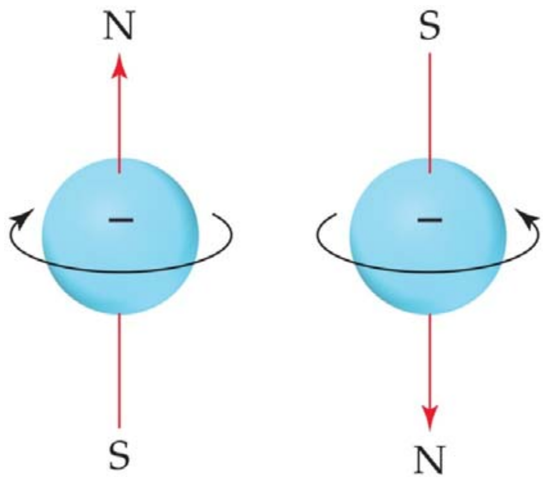


For atoms with more than one electron, what are the rules that determine how electrons are distributed among the available orbitals?
Before we answer this question, we need to know one more quantum number
– ***Spin Magnetic Quantum Number***.

The Spin Magnetic Quantum Number (m_s)

- An electron may be thought of as a particle again, which is spinning about its own axis in either one of **TWO** possible directions.

- The two spin directions create oppositely directed magnetic fields.



- Electron spin is also **quantized** and described by the ***spin magnetic quantum number m_s***.

- The two allowed values for m_s are: +½ or –½

Pauli Exclusion Principle

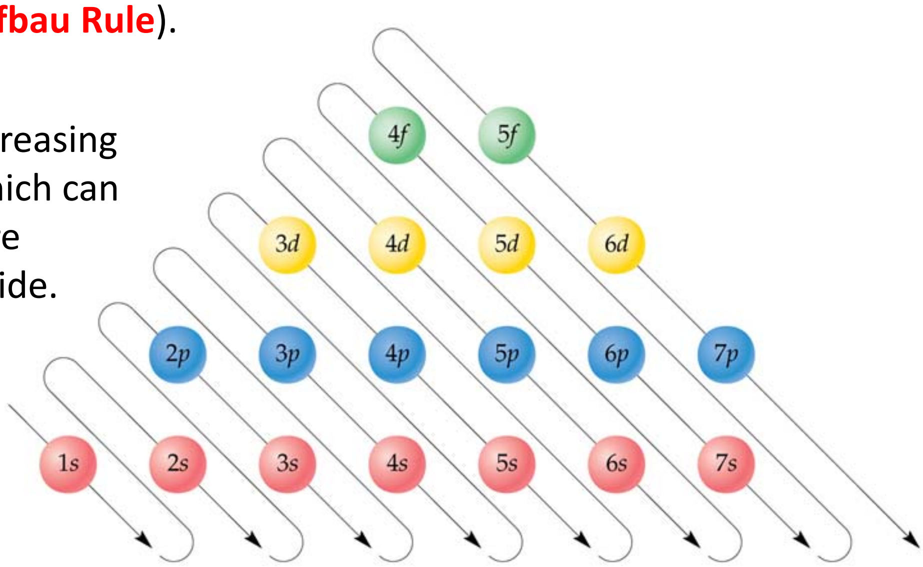
- Wolfgang Pauli demonstrated theoretically that ***no two electrons in a single atom can have identical set of the four quantum numbers (n , l , m_l, m_s)***.

- What does Pauli's theory imply? Let's consider the 3s orbital as an example:

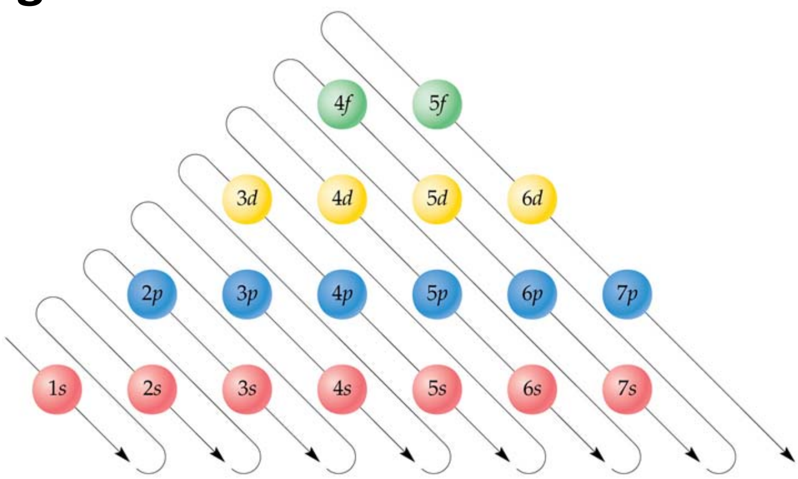
- Pauli Exclusion Principle implies that each orbital can hold a maximum of **TWO** electrons (***an electron pair***), which must have **opposite spins**.

Electron Configurations

- The arrangement of electrons among various orbitals of an atom is called the ***electron configuration***.
- The most stable (lowest energy) electron configuration of an atom defines its ***ground state.***
- The atomic ground state corresponds to electrons arranged in the lowest possible energy levels (**Aufbau Rule**).
- So, orbitals are filled in increasing order of orbital energy, which can be illustrated by the picture shown on the right-hand side.
- Any other possible configurations refer to ***atomic excited states***.



Examples: Electron Configurations of the First 21 Elements



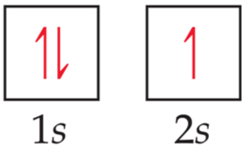
Electron Configurations and Orbital Diagrams

For example: The electron configuration of a lithium atom is **$1s^2 2s^1$**.

Each component of the electron configuration consists of

- a **number** denoting the energy level, *n*
- a **letter** denoting the type of orbital, *l*
- a **superscript** denoting the number of electrons in each orbital.

- The electron configurations do not show the spin of the electrons.
- These information can be represented using **orbital diagrams**.

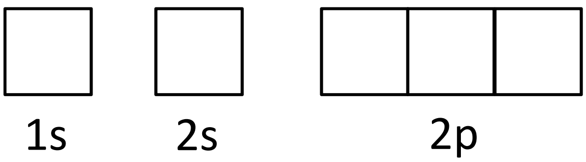


- The two electrons in the 1s orbital are ***paired*** with opposite spins.
- The electron in the 2s orbital is ***unpaired***.

- Each box in the diagram represents one orbital.
- Half-arrows represent the electrons.
- Direction of the arrow (up or down) represents the spin of the electron.

Electron Configurations and Orbital Diagrams

Example: Boron $_5B$ ($1s^2$ $2s^2$ $2p^1$)



Hund's Rule

Table 6.3 Electron Configurations of Several Lighter Elements

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

The three 2*p* orbitals are degenerate. Each of them tends to be filled with a single electron (i.e. **half-filled** or **singly occupied**).

Pairs of electrons (i.e. **full-filled** or **doubly occupied**).

For degenerate orbitals, the lowest energy is attained when the number of electrons with the **same (parallel) spin is maximized**. Because electron-electron **repulsions are minimized** and the magnetic fields of each electron all **point to the same direction**.

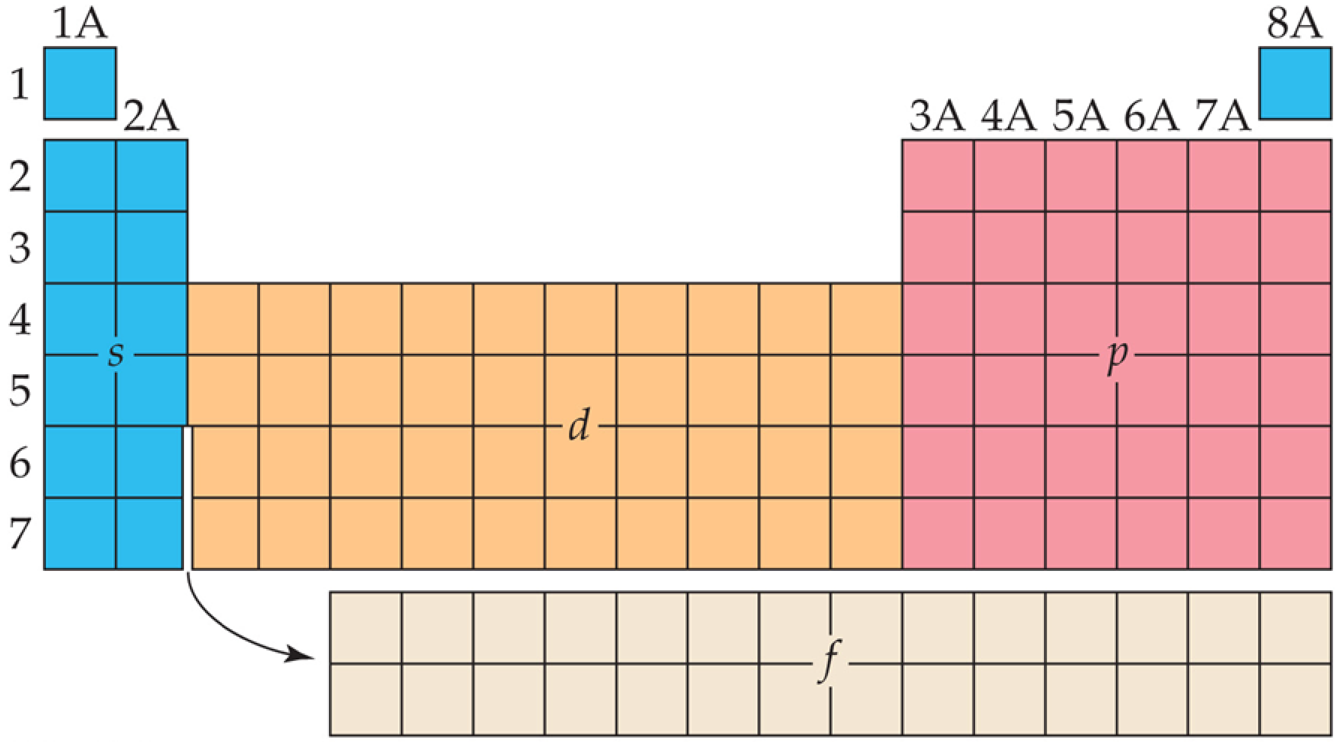
Condensed Electron Configurations

- Condensed electron configurations show only the ***outer-shell (valence) electrons*** and represent the ***inner-shell (core) electrons*** by the chemical symbol of the *preceding noble gas element* in brackets ([He], [Ne], [Ar], etc.)

Examples:

Element	Full electron configuration	Condensed electron configuration
Lithium $_{3}Li$	$1s^2 2s^1$	$[He]2s^1$ where [He] represents the electron configuration of helium.
Sulfur $_{16}S$	$1s^2 2s^2 2p^6 3s^2 3p^4$	$[Ne]3s^2 3p^4$ where [Ne] represents the electron configuration of neon.
Bromine $_{35}Br$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$	$[Ar]4s^2 3d^{10} 4p^5$ where [Ar] represents the electron configuration of argon.

Electron Configurations and Periodic Table



- Structure of the periodic table shows the sequence in which the orbitals are filled.
- Different blocks (*s*-, *p*-, *d*- or *f*-block) on the periodic table correspond to different types of orbitals.