

Chapter 6: Electronic Structure of Atoms



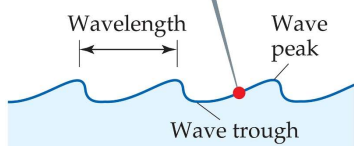
Learning Outcomes:

- Calculate the wavelength of electromagnetic radiation given its frequency or its frequency given its wavelength.
- Order the common kinds of radiation in the electromagnetic spectrum according to their wavelengths or energy.
- Explain what photons are and be able to calculate their energies given either their frequency or wavelength.
- Explain how line spectra relate to the idea of quantized energy states of electrons in atoms.
- Calculate the wavelength of a moving object.
- Explain how the uncertainty principle limits how precisely we can specify the position and the momentum of subatomic particles such as electrons.
- Relate the quantum numbers to the number and type of orbitals and recognize the different orbital shapes.
- Interpret radial probability function graphs for the orbitals.
- Explain how and why the energies of the orbitals are different in a many-electron atom from those in the hydrogen atom.
- Draw an energy-level diagram for the orbitals in a many-electron atom and describe how electrons populate the orbitals in the ground state of an atom, using the Pauli exclusion principle and Hund's rule.
- Use the periodic table to write condensed electron configurations and determine the number of unpaired electrons in an atom.

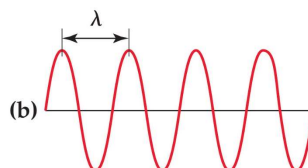
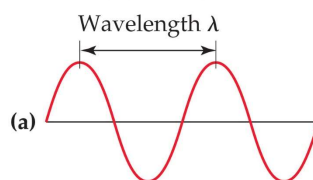
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The frequency is the number of complete waves passing any point per second.



Waves

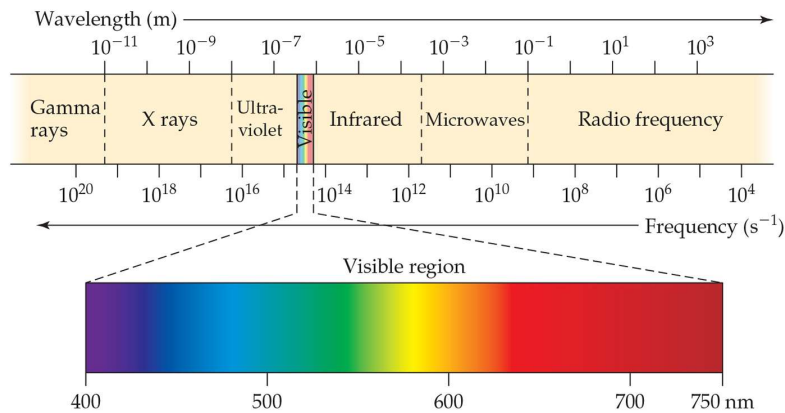


- To understand the electronic structure of atoms, one must understand the nature of electromagnetic radiation.
- The distance between corresponding points on adjacent waves is the **wavelength (λ)**.
- The number of waves passing a given point per unit of time is the **frequency (ν)**.
- For waves traveling at the same velocity, the longer the wavelength, the smaller the frequency.

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Electromagnetic Radiation

- All electromagnetic radiation travels at the same velocity in a vacuum: the speed of light (c), $c = 3.00 \times 10^8 \text{ m/s}$.
- The speed of a wave is the product of its wavelength (λ) and frequency (ν). $c = \lambda \nu$



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TABLE 6.1 Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Length (m)	Type of Radiation
Angstrom	Å	10^{-10}	X ray
Nanometer	nm	10^{-9}	Ultraviolet, visible
Micrometer	μm	10^{-6}	Infrared
Millimeter	mm	10^{-3}	Microwave
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	Television, radio
Kilometer	km	1000	Radio

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The Nature of Energy



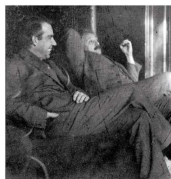
Potential energy of person walking up ramp increases in uniform, continuous manner



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

- The wave nature of light does not explain how an object can glow when its temperature increases.
- Max Planck explained it by assuming that energy comes in packets called **quanta**.
- These quanta were assumed to be absorbed or emitted by matter.

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The Nature of Energy

- Einstein used this assumption to explain the photoelectric effect.
- He concluded that energy is proportional to frequency:

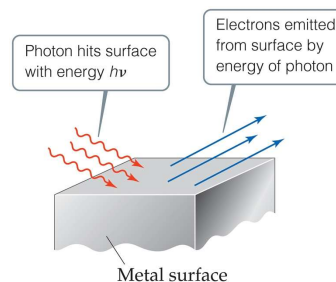
$$E = h\nu$$

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

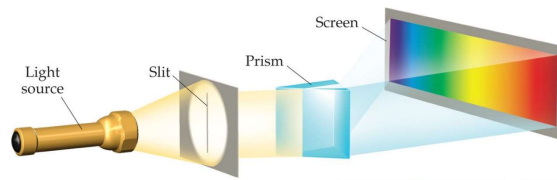
- Therefore, if one knows the wavelength of light, one can calculate the energy in one photon of that light:

$$c = \lambda\nu \quad \text{and} \quad E = h\nu$$

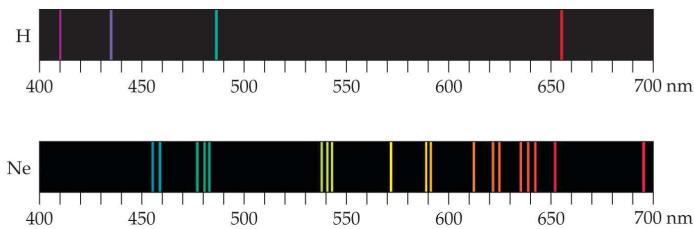
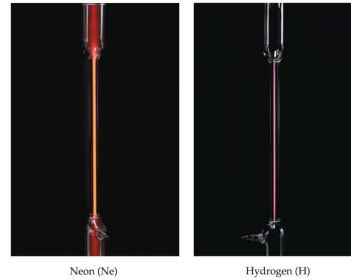
Photoelectric effect - the emission of electrons from metal surfaces on which light is shone



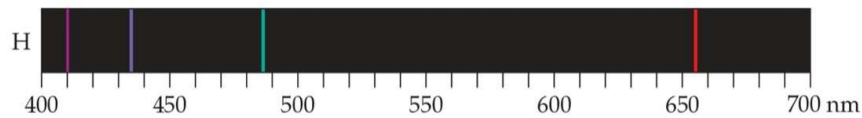
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- One does not observe a continuous spectrum, as one gets from a white light source.
- A **line spectrum** of discrete wavelengths is observed for elements.



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

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

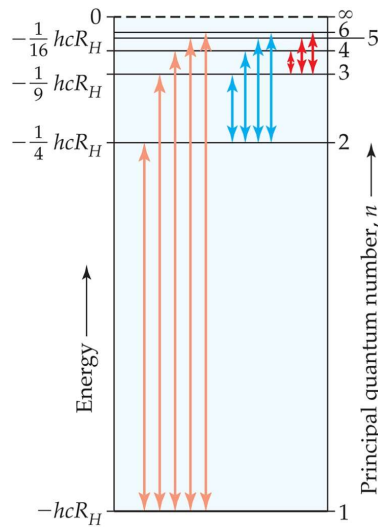
where $R_H = 1.096776 \times 10^7 \text{ m}^{-1}$

and n_2 is larger than n_1

- Neils Bohr explained why this mathematical relationship works.

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Energy Levels in the Bohr Model



Niels Bohr adopted Planck's assumption and explained these phenomena:

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

$$E = (-hcR_H) \left(\frac{1}{n^2} \right) = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{n^2} \right)$$

2. Electrons in permitted orbits have specific, "allowed" energies; these energies will not be radiated from the atom.

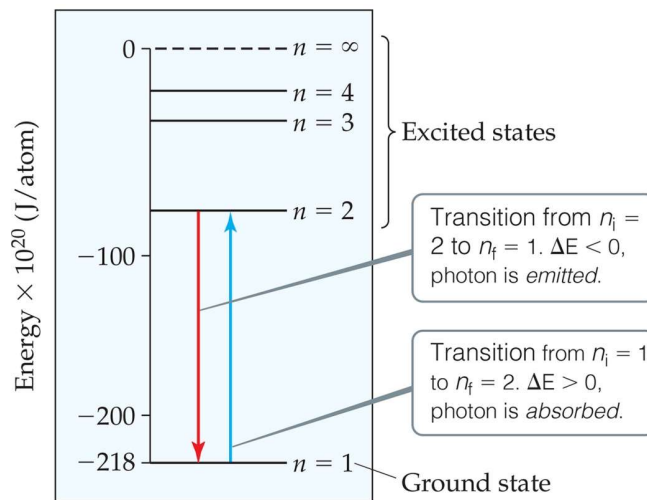
3. Energy is only absorbed or emitted in such a way as to move an electron from one "allowed" energy state to another; the energy is defined by: $E = h\nu$

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

$$\Delta E = E_f - E_i = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where n_i and n_f are the initial and final energy levels of the electron.

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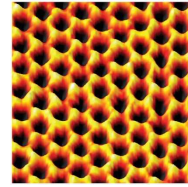


A positive ΔE means energy is absorbed. A photon is absorbed in this instance, when $n_f > n_i$.

A negative ΔE means energy is released. A photon is emitted in this instance, when $n_f < n_i$.

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The Wave Nature of Matter



- Louis de Broglie posited that if light can have material properties, matter should exhibit wave properties.
- He demonstrated that the relationship between mass and wavelength was $\lambda = \frac{h}{mv}$

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The Uncertainty Principle

- Heisenberg showed that the more precisely the momentum (mv) of a particle is known, the less precisely is its position (x) known:

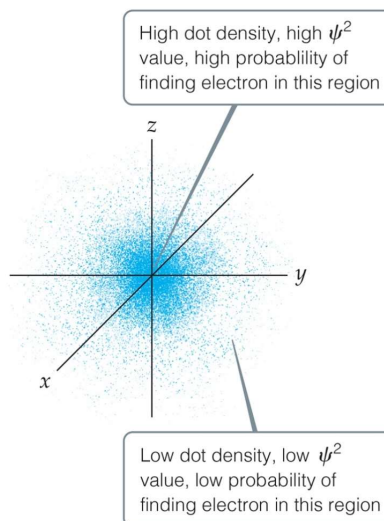
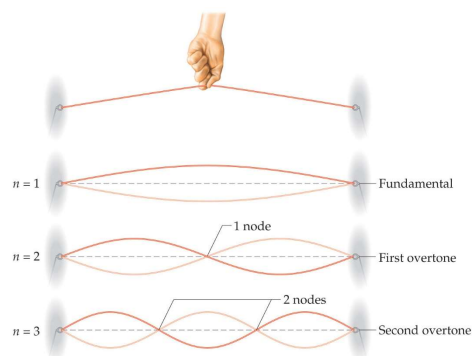
$$(\Delta x) (\Delta mv) \geq \frac{h}{4\pi}$$

$$1 \text{ J} = 1 \text{ kg m}^2 / \text{s}^2$$

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Quantum Mechanics

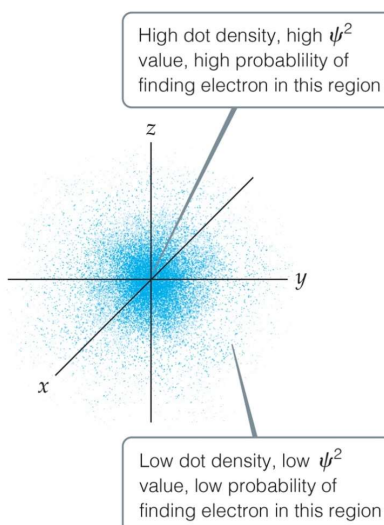
- Erwin Schrödinger developed a mathematical treatment into which both the wave and particle nature of matter could be incorporated.
- It is known as **quantum mechanics**.



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Quantum Mechanics

- The wave equation is designated with a lower case Greek *psi* (ψ).
- The square of the wave equation, ψ^2 , gives a probability density map of where an electron has a certain statistical likelihood of being at any given instant in time.
- Solving the Schroedinger 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**.
- A fourth quantum number describes the spin of the electron.



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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 .

Angular Momentum Quantum Number, l

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

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

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Magnetic Quantum Number, m_l

- Describes the three-dimensional orientation of the orbital. Values 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, etc.
- Orbitals with the same value of n form a **shell**.
- Different orbital types within a shell are **subshells**.

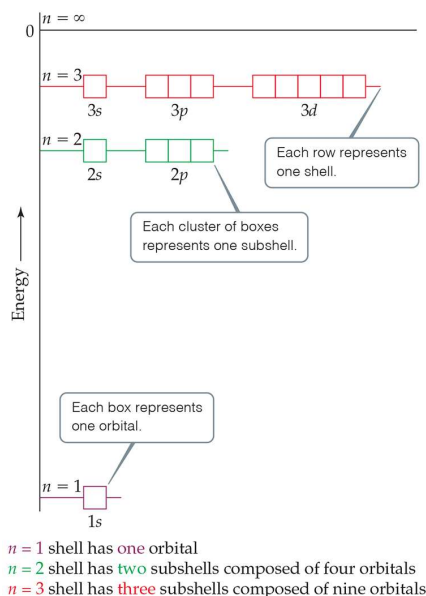
TABLE 6.2 Relationship among Values of n , l , and m_l through $n = 4$

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	1s	0	1	1
2	0	2s	0	1	4
	1	2p	1, 0, -1	3	
3	0	3s	0	1	9
	1	3p	1, 0, -1	3	
	2	3d	2, 1, 0, -1, -2	5	
4	0	4s	0	1	16
	1	4p	1, 0, -1	3	
	2	4d	2, 1, 0, -1, -2	5	
	3	4f	3, 2, 1, 0, -1, -2, -3	7	

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Energies of Orbitals

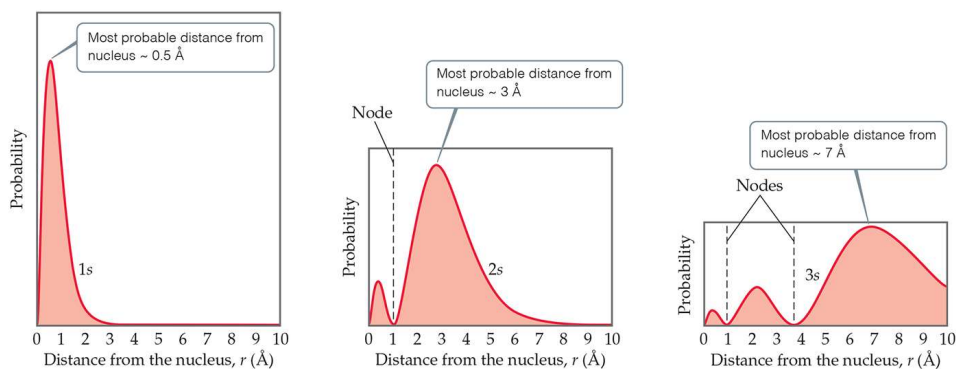
- For a one-electron hydrogen atom, orbitals with the same n have the same energy. That is, they are **degenerate**.
- As the number of electrons increases, though, so does the repulsion between them.
- Therefore, in many-electron atoms, orbitals on the same n are no longer degenerate.



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Radial probability functions

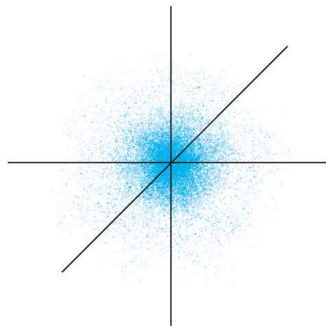
- Show the probability of finding the electron as a function of the distance from the nucleus.
- As n increases, so does the most likely distance at which to find the electron.



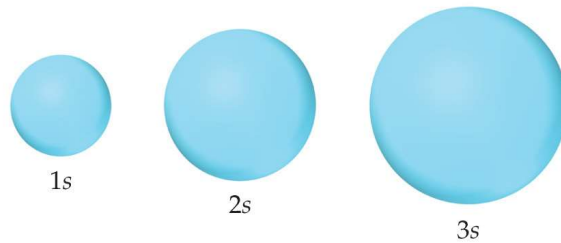
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s Orbitals

- Value of $l = 0$.
- Spherical in shape.
- Radius of sphere increases with increasing value of n .



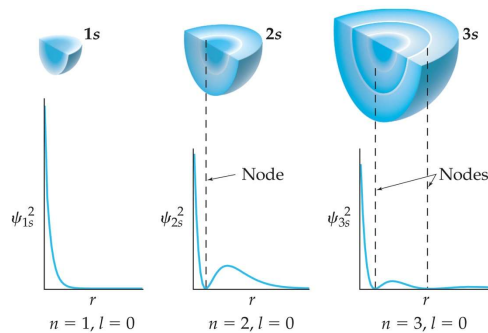
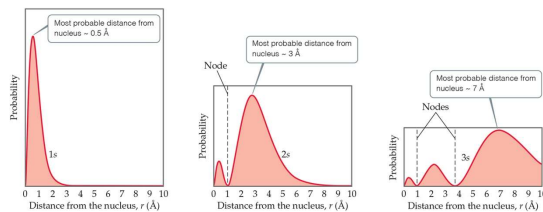
(a) An electron density model



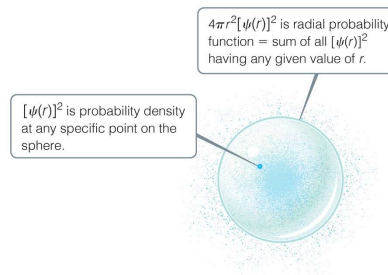
(b) Contour models

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s Orbitals



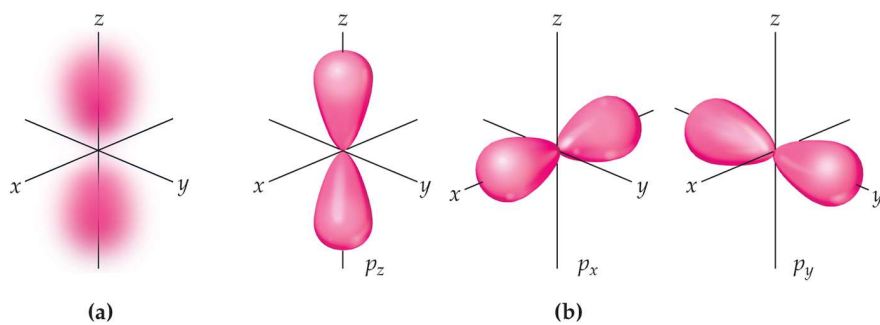
Observing a graph of probabilities of finding an electron versus distance from the nucleus, we see that s orbitals possess $n-1$ nodes, or regions where there is 0 probability of finding an electron.



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p Orbitals

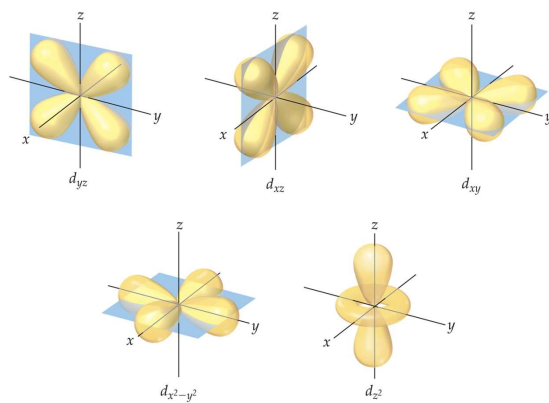
- Value of $l = 1$.
- Have two lobes with a node between them.
- The subscript denotes axis along which the orbital is aligned



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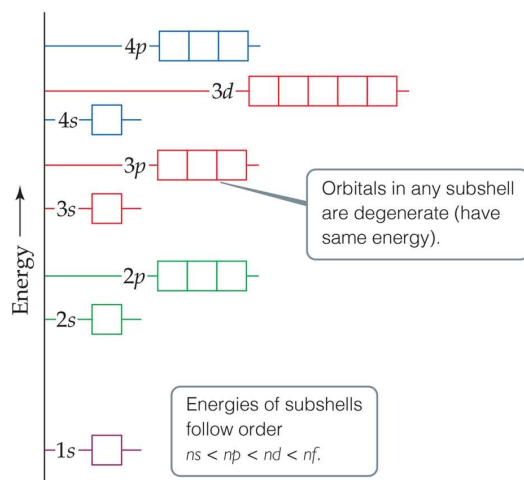
d Orbitals

- Value of l is 2.
- Four of the five orbitals have 4 lobes; the other resembles a p orbital with a torus around the center.



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General energy ordering of orbitals for a *many-electron* atom.



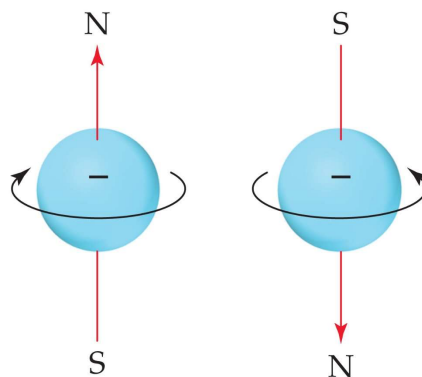
Transition metals fill the 4s by followed by filling 3d in the 4th period.

Each orbital box can hold up to two electrons.

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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 a fourth quantum number, the spin quantum number, m_s .
- The spin quantum number has only 2 allowed values: $+1/2$ and $-1/2$.



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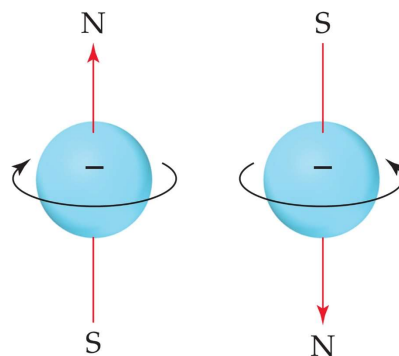
Quantum Numbers

	name	values	description
n	principle	1, 2, 3...	SHELL: distance, energy E_n
l	angular momentum	0, 1, 2... n-1	SUBSHELL orbital shape
m_l	magnetic	-l,...-1, 0, +1, ...+l	orbital orientation
m_s	electron spin	$+\frac{1}{2}$, $-\frac{1}{2}$	electron spin

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Pauli Exclusion Principle

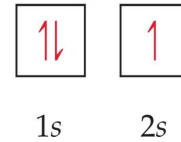
- No two electrons in the same atom can have exactly the same energy.
- No two electrons in the same atom can have identical set of four quantum numbers n , l , m_l , and m_s .



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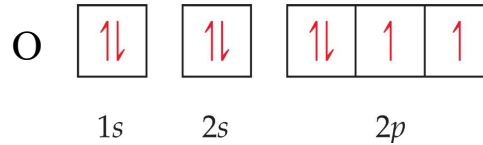
Orbital Diagrams

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



Hund's Rule

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

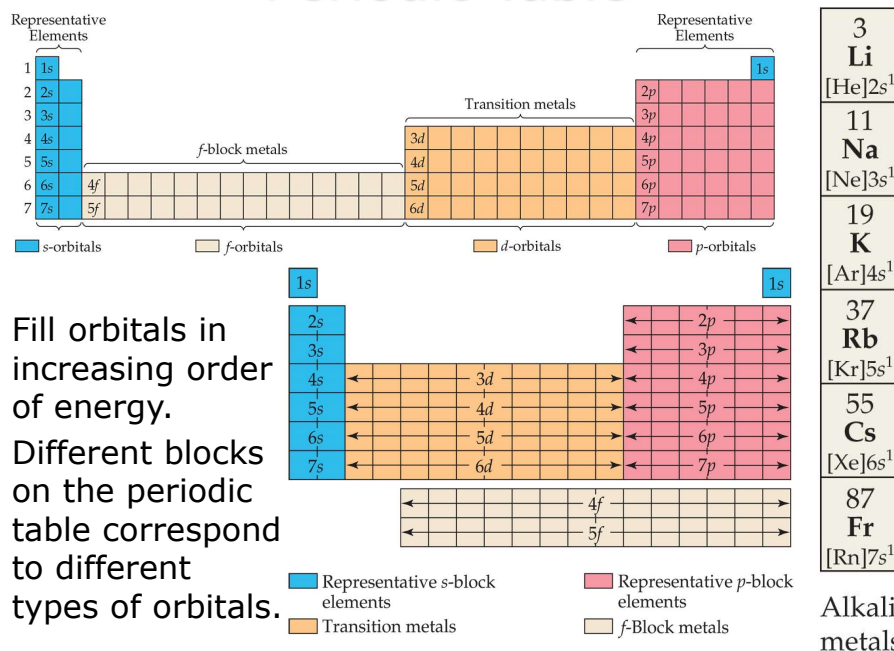


Aufbau Principle

Electrons are added to the lowest energy orbitals available.

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Periodic Table



- Fill orbitals in increasing order of energy.
- Different blocks on the periodic table correspond to different types of orbitals.

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TABLE 6.3 Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram						Electron Configuration
		1s	2s	2p			3s	
Li	3	<div>↑↓</div>	<div>↑</div>	<div></div>	<div></div>	<div></div>	<div></div>	1s ² 2s ¹
Be	4	<div>↑↓</div>	<div>↑↓</div>	<div></div>	<div></div>	<div></div>	<div></div>	1s ² 2s ²
B	5	<div>↑↓</div>	<div>↑↓</div>	<div>↑</div>	<div></div>	<div></div>	<div></div>	1s ² 2s ² 2p ¹
C	6	<div>↑↓</div>	<div>↑↓</div>	<div>↑</div>	<div>↑</div>	<div></div>	<div></div>	1s ² 2s ² 2p ²
N	7	<div>↑↓</div>	<div>↑↓</div>	<div>↑</div>	<div>↑</div>	<div>↑</div>	<div></div>	1s ² 2s ² 2p ³
Ne	10	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div></div>	1s ² 2s ² 2p ⁶
Na	11	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑</div>	1s ² 2s ² 2p ⁶ 3s ¹

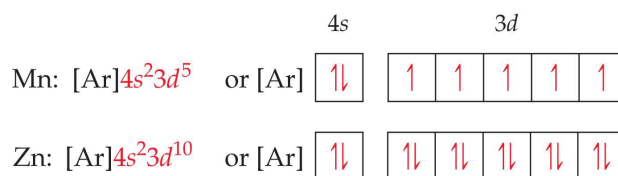
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Writing Atomic Electron Configurations

- 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;

Mn, atomic number = 25, the complete electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$. The condensed electron configuration is $[\text{Ar}]4s^2 3d^5$

core e⁻ valence e⁻



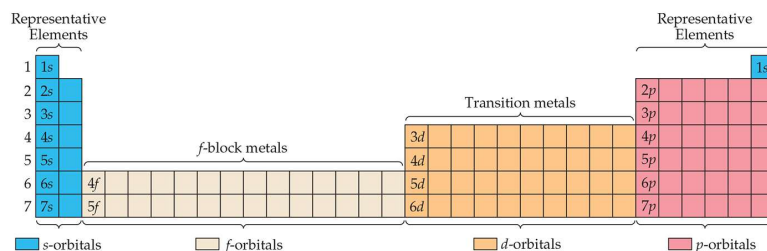
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Diagram illustrating the filling order of atomic orbitals (s, p, d, f) across the periodic table, showing the sequence of orbitals filled (1s, 2s, 3s, 4s, 5s, 6s, 7s, 3d, 4d, 5d, 6d, 2p, 3p, 4p, 5p, 6p, 4f, 5f).

Legend:

- s-block elements
- d-block elements (transition metals)
- p-block elements
- f-block elements: lanthanides (4f) and actinides (5f)

Group 2A	
Be	[He] $2s^2$
Mg	[Ne] $3s^2$
Ca	[Ar] $4s^2$
Sr	[Kr] $5s^2$
Ba	[Xe] $6s^2$
Ra	[Rn] $7s^2$
Group 3A	
B	[He] $2s^2 2p^1$
Al	[Ne] $3s^2 3p^1$
Ga	[Ar] $3d^{10} 4s^2 4p^1$
In	[Kr] $4d^{10} 5s^2 5p^1$
Tl	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$



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[illegible]

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Anomalies

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

- **Electron configuration for chromium (Cr):**

[Ar] $4s^1 3d^5$ rather than [Ar] $4s^2 3d^4$.

- **Electron configuration for copper (Cu):**

[Ar] $4s^1 3d^{10}$ rather than [Ar] $4s^2 3d^9$.

- **Others:**

Mo [Kr] $5s^1 4d^5$

Ag [Kr] $5s^1 4d^{10}$

Au [Xe] $4f^{14} 6s^1 5d^{10}$

La [Xe] $6s^2 5d^1$

Ce [Xe] $6s^2 4f^1 5d^1$