

Part I: Atomistic / Chapter I

*Electronic Structure of the
Atom and the Periodic
Classification of Elements*



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Objectives:

By the end of this chapter, the learner will be able to:

- ✓ *Establish the ground-state electronic configuration of an atom or ion and represent it using conventional notations.*
- ✓ *Describe the valence shell of an atom or ion.*
- ✓ *Classify chemical elements within the periodic table.*



What is the Purpose of Atomic Theory?

Atomic theory aims to describe the distribution of electrons in all elements and to study the consequences of this distribution on their physicochemical properties.

I. Historical Development of Atomic Models:

1.1 Early Concept of the Atom:

- The term *atom* is derived from the Greek word “*atomos*”, meaning *indivisible*. This concept was first introduced by **Leucippus** (5th century BC) and later developed by his student **Democritus**.
- According to Democritus, matter is composed of tiny, indivisible particles characterized by:
 - ✓ Extremely small size (invisible to the naked eye)
 - ✓ Indivisibility
 - ✓ Absence of internal structure (solid particles)
 - ✓ Eternal and immutable nature
 - ✓ Constant motion in empty space
 - ✓ Infinite variety of shapes explaining the diversity of matter

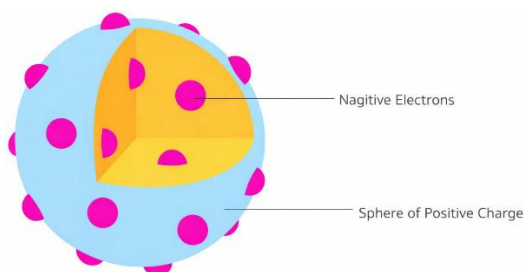
Although philosophical, this model laid the foundation for modern atomic theory.

1.2 Discovery of the Electron:

- In 1897, **J. J. Thomson** discovered the electron, the first identified subatomic particle, carrying a negative electric charge.
- He proposed the *plum pudding model* (1904), in which:
 - ✓ The atom is a positively charged sphere

- ✓ Electrons are embedded within this sphere

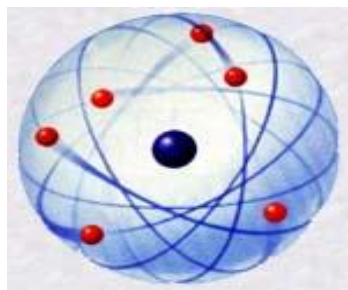
This model marked the first attempt to describe internal atomic structure.



Thomson's Atomic Model

1.3 Discovery of the Nucleus

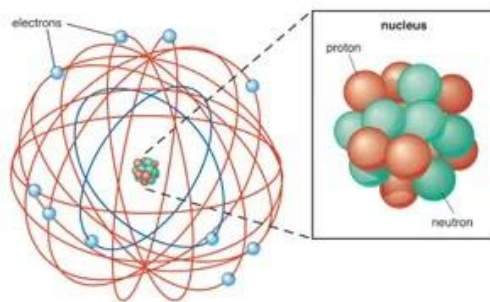
- In 1912, Ernest Rutherford (New Zealand physicist) discovered the atomic nucleus.
- His new atomic model revealed that the atom's positive electric charge, along with most of its mass, is concentrated in a nearly point-like nucleus.
- The atom's electrons orbit this nucleus like planets around the sun, with the attractive electric force (the electron's negative charge attracting the nucleus's positive charge) playing the role of gravitational force for planets—hence the name "planetary atomic model."
- Notably, unlike the Greek atom, Rutherford's atom is neither indivisible (being composite) nor solid, as it consists mostly of empty space: the nucleus-electron distance is 100,000 times greater than the nucleus diameter itself (nucleus diameter = 10^{-15} m = 1 femtometer).



Rutherford's Atomic Model

1.4 Discovery of Nucleons :

- Rutherford further established that the nucleus consists of:
- **Protons** (positively charged particles)
- **Neutrons** (neutral particles), discovered later in 1932 by **James Chadwick**
- These particles are collectively called **nucleons**.



Limitations of the Rutherford Model

According to classical physics:

- Accelerated charges (such as orbiting electrons) should emit energy
- Electrons would consequently spiral into the nucleus

This would result in an unstable atom, which contradicts experimental observations.

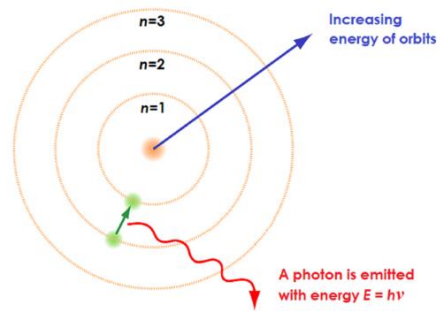
1.5 Bohr's Atomic Model:

To resolve the defects of Rutherford's model, **Niels Bohr** (1913) introduced a new model based on quantum ideas.

Bohr postulated that:

- Electrons move in **discrete circular orbits** called *stationary states*
- Each orbit corresponds to a specific energy level (**E**).
- Electrons do not emit radiation while in a stationary orbit (**E₀**)
- Radiation is emitted or absorbed only when an electron transitions between energy levels.
- The frequency " **ν** " of the emitted radiation is given by the equation: **$h \nu = E_1 - E_0$**

This model successfully explains the hydrogen atom spectrum but remains limited for multi-electron atoms.



Upon deeper study of the atom and its electrons, it became clear that the organization was not as simple as initially thought:

- Electron shells are **subdivided into subshells**.
- Electron trajectories are **not perfectly circular**.

These observations led to the development of **quantum mechanics**.

1.6 Quantum (Wave) Model:

- The Bohr model does not apply to atoms other than hydrogen, nor in the presence of electric or magnetic fields.
- Diffraction experiments demonstrate that the electron exhibits wave characteristics.
- The wavelength is determined by de Broglie's relation: $\lambda = \frac{h}{mv}$
- The electron is a particle with wave-like properties.
- The wave nature of the electron is described by a wave function ψ obtained from Schrödinger's equation: $H\psi = E\psi$

The electron does not possess a definite trajectory, only its probability density ψ^2 is measurable.

- The behavior of the hydrogen atom electron is described using four quantum numbers: ***n, l, m*** and ***S***.

II. Quantum Numbers

The state of an electron is defined by four quantum numbers.

II.1 Principal Quantum Number « n » :

- Defines the energy level (shell)
- Values : $n = 1, 2, 3, \dots$
- Determines the size and energy of the orbital

Maximum number of electrons per shell: $2n^2$

II.2 Le nombre quantique secondaire (azimutal) « l » :

- This second quantum number characterizes the subshell occupied by the electron.

It is an integer that can be zero.

- Its value depends on the principal quantum number n :

$$0 \leq l \leq n - 1 \text{ (yielding } n \text{ possible values)}$$

- The electronic subshell is conventionally designated by a lowercase letter instead of the numerical value of l .

Value of l	0	1	2	3	4	5
Subshell symbol	s	p	d	f	g	h

II.3 The Magnetic Quantum Number « m »:

- This third quantum number defines the possible orientations of the electron's angular momentum in the presence of an external magnetic field. It is an integer that can be zero.
- Its value depends on the secondary quantum number l :

$$-l \leq m \leq +l \text{ (yielding } 2l + 1 \text{ different values and thus the number of orbitals)}$$

To graphically represent this quantum number, a rectangle (quantum orbital) is used, which can hold 0, 1, or 2 electrons.



A number of rectangles equal to the possible values of m will be represented.

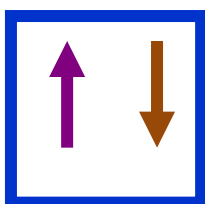
II.4 The Spin Quantum Number « S »:

Ce quatrième nombre quantique caractérise le mouvement de l'électron sur lui-même et peut prendre seulement deux valeurs différentes : $S = \pm 1/2$

Pour symboliser graphiquement ce nombre quantique de spin, on utilise :

- une flèche vers le haut (\uparrow) pour $s = +1/2$ ou vers le bas (\downarrow) pour $s = -1/2$.

L'habitude veut que l'électron de spin $+ 1/2$ (\uparrow) soit placé à gauche et l'électron de spin $- 1/2$ (\downarrow) à droite.



II.4 Representation of atomic orbitals (A.O):

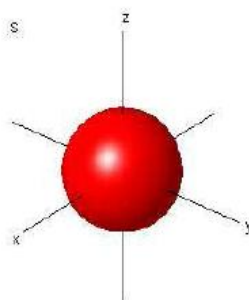
n	l	m	A.O. Notation	Energy
1	0	0	1s	$-13.6 Z^2$
2	→	4 degenerate A.O.		
	0	0	2s	$-13.6 Z^2/4$
	1	-1	2px	
		0	2pz	
		1	2py	
3	→	9 degenerate A.O.		
	0	0	3s	$-13.6 Z^2/9$
	1	-1	3px	
		0	3pz	
		1	3py	
	2	-2	3dxy	
		-1	3dyz	

n	l	m	A.O. Notation	Energy
		0	$3dz^2$	
		1	$3dxz$	
		2	$3dx^2-y^2$	

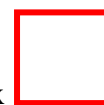
a) « s » Orbitals:

The s orbitals are characterized by $l = 0$ and $m = 0$.

All s orbitals (ns) exhibit spherical symmetry because the electron probability density varies identically in all directions around the nucleus.



The s atomic orbital (A.O.) is represented by a single quantum box



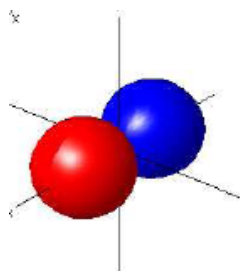
b) « p » Orbitals :

Pour $l = 1 \Rightarrow m = -1, 0$ ou $1 \Rightarrow 3$ orbitales p

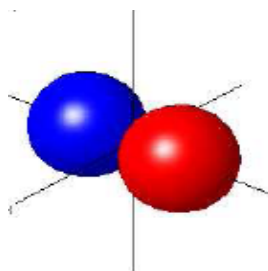
On For $l = 1 \Rightarrow m = -1, 0, \text{ or } 1 \Rightarrow 3p$ orbitals

The p_x , p_y , and p_z orbitals have identical shapes but are each elongated along one of the three perpendicular axes.

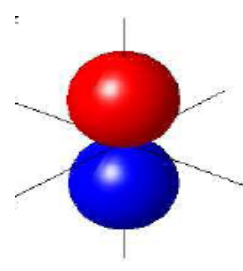
A p orbital possesses a **nodal plane**, where the probability of finding the electron is zero. This plane passes through the nucleus.



P_x



P_y



P_z

The p atomic orbitals (A.O.) with the same energy are represented by three quantum boxes.

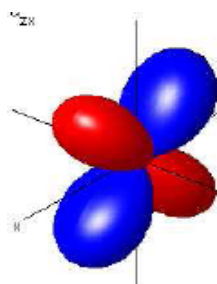


c) « d » Orbitals :

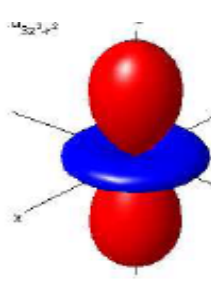
For $l = 2 \Rightarrow m = -2, -1, 0, +1, +2 \Rightarrow 5d$ orbitals

The five d orbitals (d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$, d_{z^2}) have complex cloverleaf or double-dumbbell shapes with four lobes each.

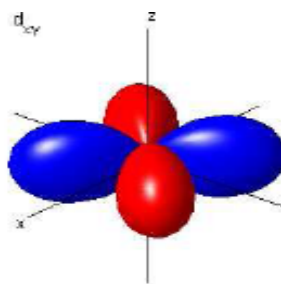
Each d orbital contains **two nodal planes** passing through the nucleus.



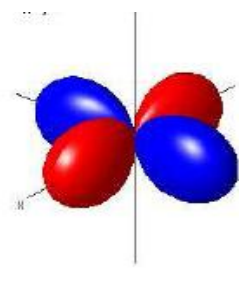
D_{xz}



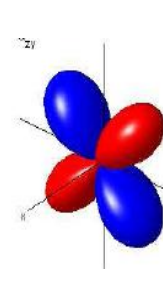
d_{z²}



d_{xy}



d_{x²-y²}



d_{zy}

The d atomic orbitals (A.O.) with the same energy are represented by five quantum boxes.



III. Electronic Structure of Atoms :

The general organization into energy levels is identical for all atoms.

The goal is to place Z electrons (neutral atom) across the different levels, yielding the **electronic configuration**.

The electronic configuration of an atom represents the distribution of its Z electrons in the ground state across atomic orbitals.

This filling of atomic orbitals follows three fundamental rules:

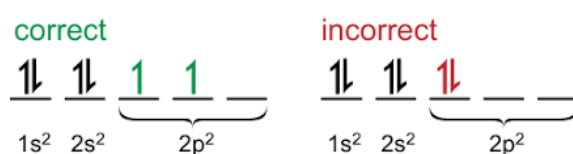
- **Pauli Exclusion Principle**
- **Hund's Rule**
- **Klechkowski's Rule**

a) Pauli exclusion principle:

- No two electrons have identical four quantum numbers
- Maximum of two electrons per orbital with opposite spins

b) Hund's Rule :

- Electrons occupy degenerate orbitals singly first.
- Spins are parallel before pairing occurs.



c) KLECHKOVSKI's Rule :

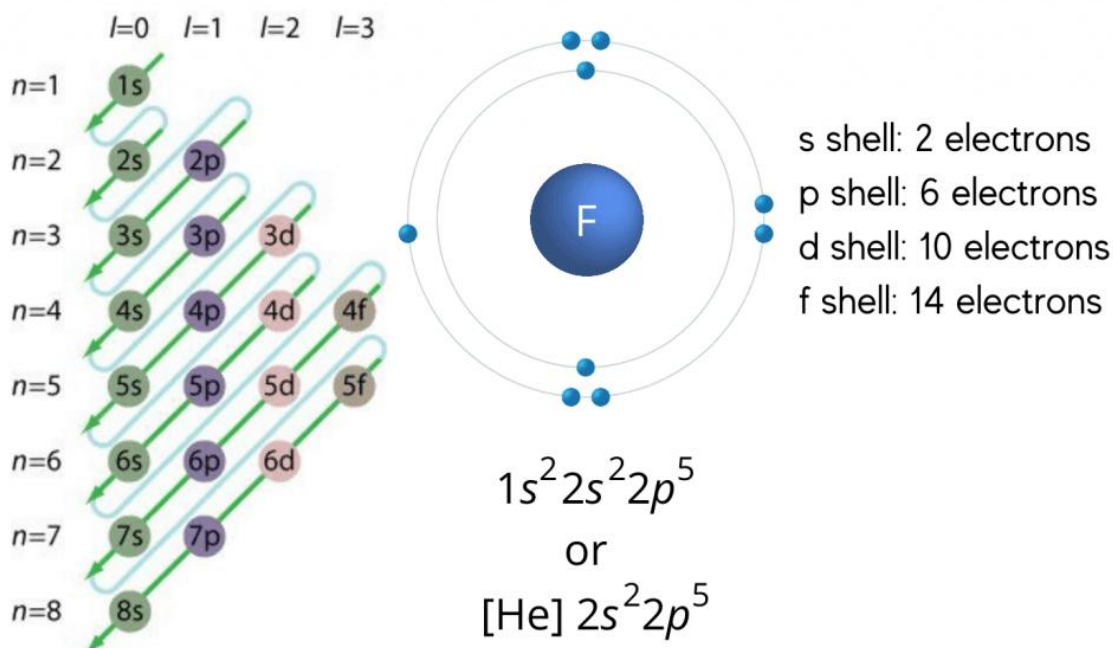
Klechkowski's Rule is an empirical method for determining the order of electron filling in orbitals. This method applies to electrically neutral atoms in their ground state.

It is crucial for understanding atomic electronic structure and chemical behavior.

The rule relies on a simple criterion: the secondary quantum number (l) and principal quantum number (n). In summary:

- Add $n + l$ for each orbital.
- Fill orbitals in order of **increasing** $n + l$.
- When $n + l$ values are equal, fill the orbital with the **lowest** n first.

Electron Configuration



How to Determine an Atom's Electronic Configuration?

Step 1: Identify the atomic number Z (number of electrons in a neutral atom).

Step 2: List orbitals in Klechkowski's order (1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, etc.).

Step 3: Fill orbitals respecting the three rules:

- Pauli: Maximum 2 electrons per orbital (opposite spins)
- Hund: Single electrons in degenerate orbitals first (parallel spins)
- Klechkowski: Order of increasing $n + l$, then lowest n

Notation: $1s^2 2s^2 2p^6 3s^1$ (superscript = number of electrons).



Applying Klechkowski's Rule, we first determine the **electronic structure** (also called **electron cloud**), which differs from the **electronic configuration** for elements with d and f subshells.

Key Distinction (for $Z > 20$):

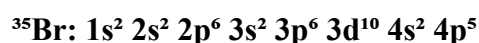
- **electron cloud:** Full distribution including all orbitals (e.g., Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$)
- **Electronic configuration:** Noble gas core + valence electrons (e.g., Fe: $[\text{Ar}] 4s^2 3d^6$)

The cortège shows complete filling order per Klechkowski, while configuration prioritizes chemical reactivity via valence electrons.

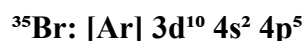
c).1 Simplified Electronic Configuration:

The simplified electronic configuration uses the configuration of the preceding noble gas to abbreviate the inner shells, detailing only the valence electrons and the outermost subshell.

For example, for bromine (Br), whose complete electronic configuration is:



The simplified configuration is written:



This uses the electronic configuration of argon (Ar), the preceding noble gas, to represent the inner shells, then describes only the outermost subshells containing the valence electrons.

c).2. Core and Valence Electrons:

- **Core electrons:** inner shells
- **Valence electrons:** outermost shell

IV. Periodic classification of elements :

The periodic classification arranges **118 elements** by increasing **atomic number (Z)** into **7 periods** (rows) and **18 groups** (columns), revealing repeating chemical properties.

Key Features

- **Periods:** Horizontal rows (2-32 elements) – electrons fill new shells
- **Groups:** Vertical columns – same valence electron configuration, similar reactivity
- **Blocks:** s, p, d, f based on outermost orbital type

Properties repeat predictably due to electronic structure, enabling Mendeleev's predictions and modern chemistry.

VI. 2. Important families:

- Noble Gases Family :

Located in the last column (Group 18: He, Ne, Ar, Kr, ...), characterized by exceptional stability. These elements are highly unreactive, explained by the **octet rule**: all have their outermost shell filled with 8 electrons (2 for helium).

- Alkali Metals Family:

Elements in the first column (Group 1: H, Li, Na, K, ...) tend to form +1 cations (H^+ , Li^+ , Na^+ , K^+ , ...) by losing their single valence electron.

- Halogens Family:

Elements in the second-to-last column (Group 17: F, Cl, Br, I, ...) tend to form -1 anions (F^- , Cl^- , Br^- , I^- , ...) by gaining one electron to complete their octet.

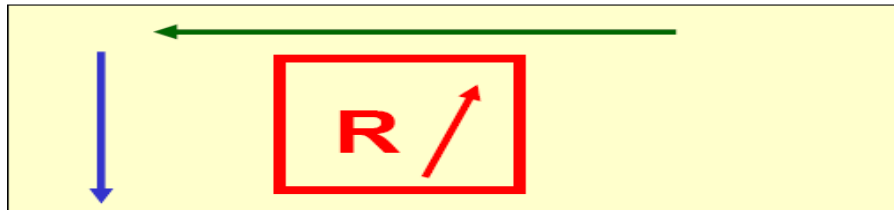
IV.3 Chemical properties of atoms :

The chemical properties of atoms depend primarily on their **outermost electronic configuration**, specifically the electrons in the valence shell. Key properties that indicate chemical behavior include:

- **Tendency to lose or gain electrons** (determines cation/anion formation)
- **Electron cloud deformability** (affects bonding and molecular geometry)

a) Atomic Radius

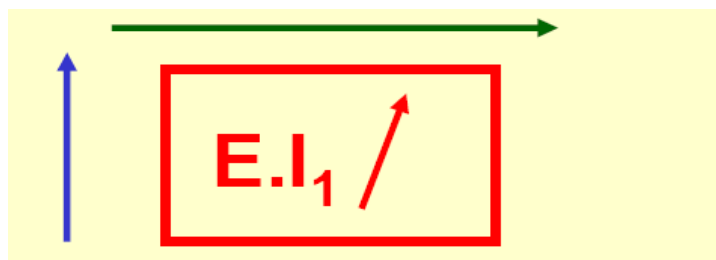
- Decreases across a period
- Increases down a group



b) Ionization Energy (I.E.)

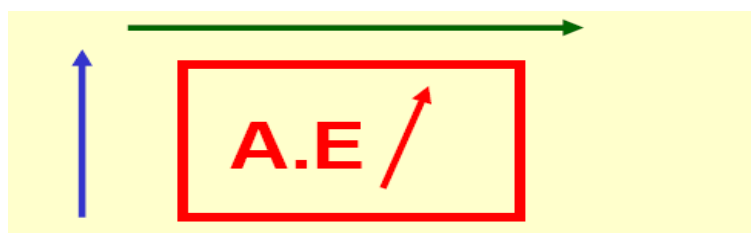
Energy required to remove an electron:

- Increases across a period
- Decreases down a group



c) Electron Affinity (E.A.)

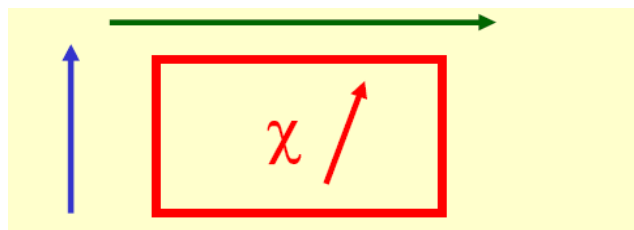
Energy released when gaining an electron.



d) Electronegativity (χ)

Ability to attract electrons:

- Increases across a period
- Decreases down a group



Periodic Table of the Elements

1 1A 11A																	18 VIII 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.09	35 Br Bromine 79.904	36 Kr Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [288]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

57 Lanthanide Series La Lanthanum 138.905	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.965	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
89 Actinide Series Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal	Alkaline Earth	Transition Metal	Semimetal	Nonmetal	Basic Metal	Halogen	Noble Gas	Lanthanide	Actinide
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