

Rutherford's atomic model (alpha particle scattering experiment)

This model is put forward by Ernest Rutherford in 1911 with the help of an alpha particle scattering experiment. In this experiment, he bombarded a thin sheet of gold foil with alpha particles (positive particles equal to helium ion) which were obtained from a radioactive substance. The scattered alpha particles were observed on the surface of the circular zinc sulphide screen. Lead can absorb alpha particles. So lead plate with a slit was used to obtain a beam of alpha particles.

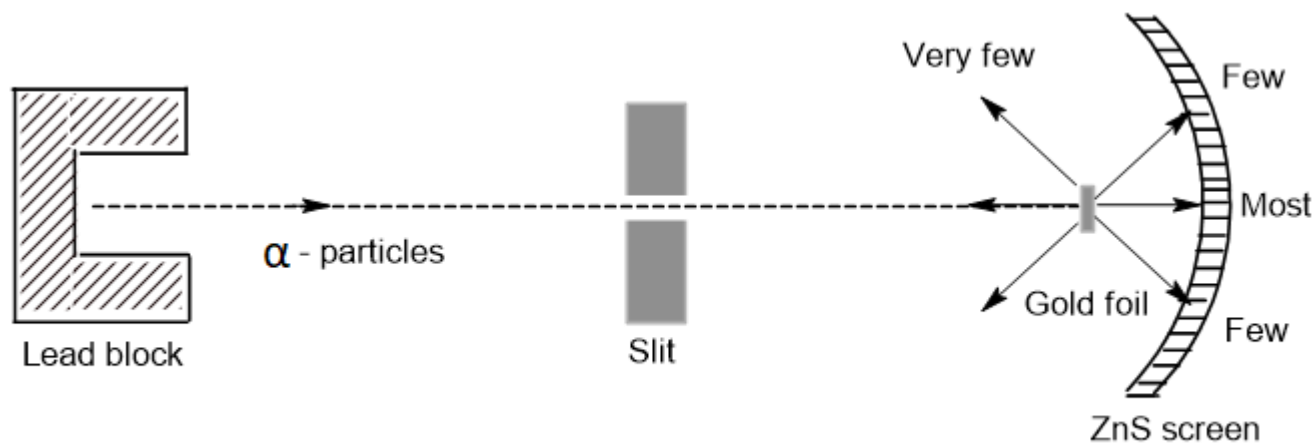


Fig: Rutherford's α - particle scattering experiment

Observations

1. Most of the alpha particles passed through the gold foil without deflection.
2. Some of the alpha particles deflected through small angles.
3. Very few alpha particles were deflected through angles more than 90° or bounced back.

Inference

1. Most of the space inside the atom is empty.
2. There is a presence of a heavy positively charged body at the centre of the atom.
3. There is a close encounter of alpha particles with a positively charged body.

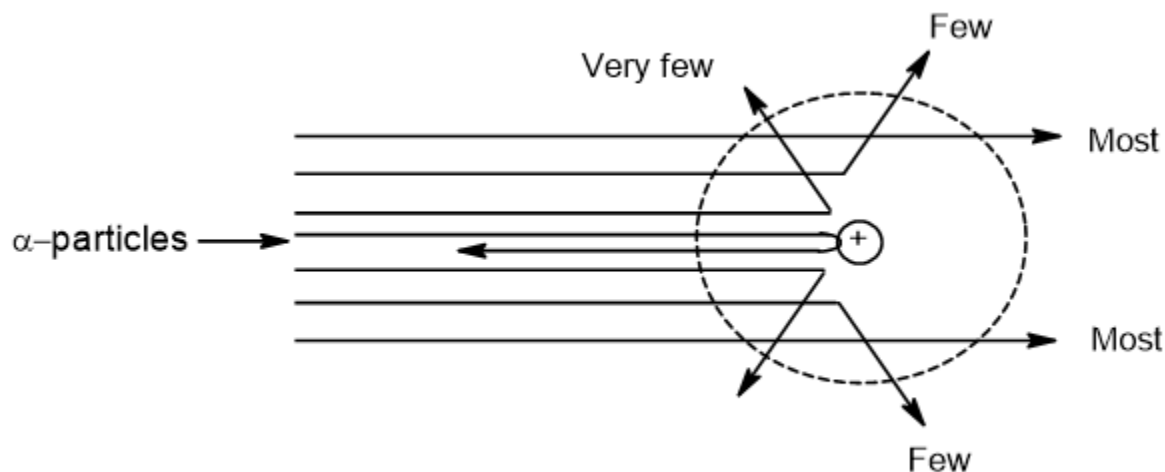


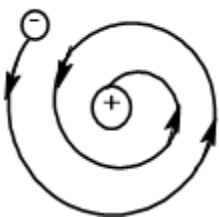
Fig: Scattering of alpha particles by a single atom

Postulates of Rutherfords atomic model:

1. An atom consists of a positively charged nucleus at which the entire mass is concentrated and its size is extremely small as compared to the size of the atom.
2. The space between the nucleus and revolving electron is empty.
3. An atom has no net charge or they are **electrically neutral** because electrons are negatively charged and the densely concentrated nucleus is positively charged. A strong electrostatic force of attractions holds together the nucleus and electrons.
4. Atoms nucleus is surrounded by negatively charged particles called **electrons**. The electrons revolve around the nucleus in a fixed circular path at very high speed. These fixed circular paths were termed as "**orbits.**"

Limitations

1. It could not explain the stability of an atom:
According to the law of thermodynamics, any accelerated charged particles must emit radiation. Charged particles such as an electron in motion lose energy continuously and their energy should decrease gradually. Then electron should ultimately fall into the nucleus and should collapse. But this could not happen.



Bohr's atomic model

In 1913, Neil Bohr proposed an atomic model to overcome the limitations of Rutherford's atomic model of the atom. The postulates of Bohr's atomic model are:

1. Electrons revolve around the nucleus in a defined circular path called orbits. The electrostatic force of attraction between the revolving electron and nucleus is equal to the centrifugal force acting on the electron.
2. As long as the electron remains in a particular orbit, it will neither gain nor lose energy and hence the energy of the electron in a particular orbit remains constant. This means these orbits are non-radiating and thus called stationary state or energy level and designated as K, L, M, N, etc.
3. Only those orbits are permitted in an atom whose angular momentum of the electron is equal to the whole number multiple of $h/2\pi$ where h is Planck's constant.

$$\text{Angular momentum } (mvr) = \frac{nh}{2\pi}$$

where, m = mass of electron

v = velocity of electron

r = radius of orbit

$n = 1, 2, 3, \dots$

h = Planck's constant = $6.67 \times 10^{-27} \text{ erg sec}$

4. Energy is emitted or absorbed by the electron in the form of a photon only when it jumps from one energy level to another. The quantum or photon of energy absorbed or emitted is the difference between the higher and lower energy level.

$$\Delta E = E_2 - E_1 = h\nu$$

ΔE = energy emitted or absorbed

E_2 = higher energy level

E_1 = lower energy level

h = Planck's constant

ν = frequency of radiation

Energy is absorbed when an electron jumps from lower to higher energy level and energy is emitted when an electron jumps from higher to lower energy level.

Origin of hydrogen spectrum

When hydrogen gas is taken in a discharge tube and high voltage is applied, then there is the dissociation of hydrogen molecule into hydrogen atoms. Although hydrogen consists of only one electron, it produces

different types of spectra. When energy is supplied, the electron of the hydrogen atom absorbs energy and jumps to a high energy level. The electrons in high energy level (excited state) are unstable and jump to lower energy level with the emission of electromagnetic radiation which give rise to line spectra called spectral series. When electron absorb the energy and jumps to the higher energy level, the absorption spectra are produced and when electron loses energy and jumps to lower energy level, the emission spectra are produced.

The equation to calculate the wavelength of different spectral series is:

$$\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where, λ = wavelength

R = Rydberg constant

n_1 and n_2 are energy level.

Different types of spectral series are given below:

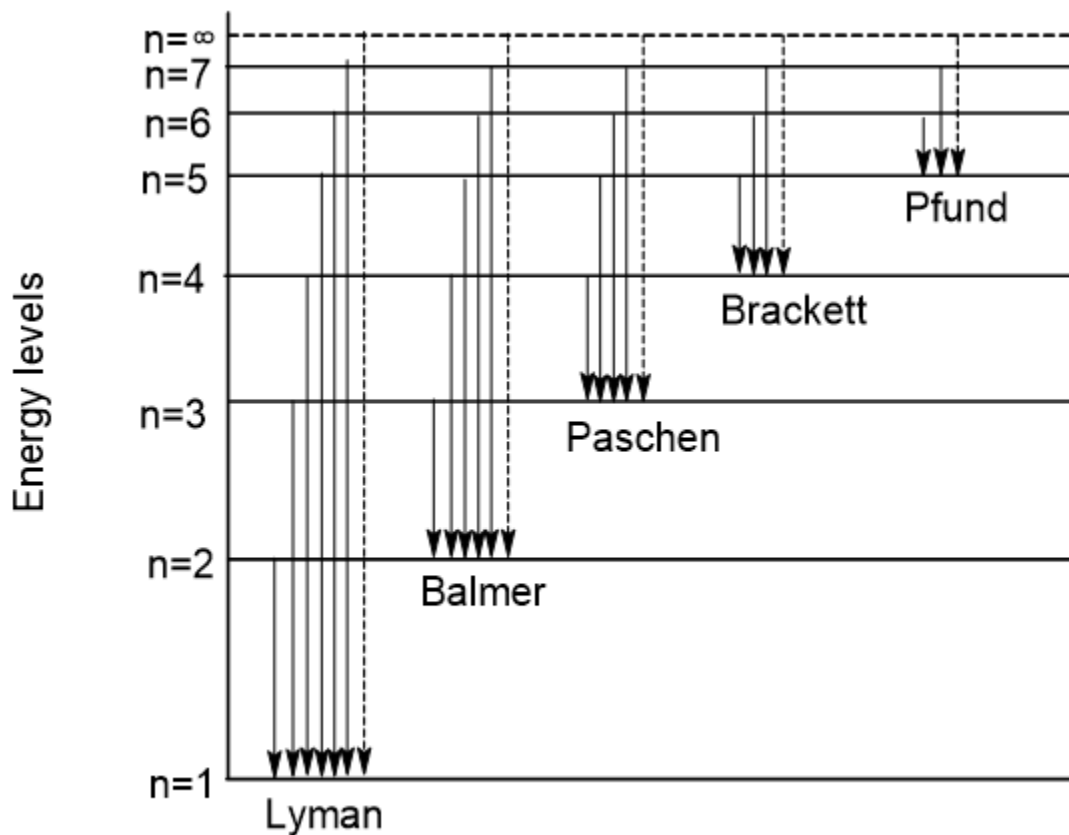


Fig: Hydrogen spectra

1. Lyman series (92-120 nm):
It is observed when an electron jumps from a higher energy level ($n=2,3,4\dots$) to the first energy level ($n=1$). It lies in the ultraviolet region.
2. Balmer series (400-650 nm):
It is observed when an electron jumps from a higher energy level ($n=3,4,5\dots$) to a second energy level ($n=2$). It lies in the visible region.
3. Paschen series (950-1875 nm):
It is observed when an electron jumps from a higher energy level ($4,5,6\dots$) to a third energy level ($n=3$). It lies in the infrared region.
4. Brackett series (1945-4050 nm):
It is observed when an electron jumps from a higher energy level ($5,6,7\dots$) to a fourth energy level ($n=4$). It lies in the infrared region.
5. Pfund series (above 4050 nm):
It is observed when an electron jumps from a higher energy level ($6,7\dots$) to a fifth energy level ($n=5$). It lies in the infrared region.

Significances of Bohr's atomic model

1. It explains the stability of the atom.
2. It explains the origin of line spectra of the hydrogen atom.
3. The energy of an electron in an orbit and radius of stationary orbit can be calculated.

Limitations of Bohr's atomic model

1. **No explanation for the multi-electron system:**
This model only explained the origin of spectra of the hydrogen atom and hydrogen-like ions like He^+ , Li^{++} , etc. but it doesn't explain the origin of the spectra of the multielectron system.
2. **No explanation of the hyperfine structure of spectra:**
When the hydrogen spectra are observed with the help of a spectroscope of high resolving power, it is found that the individual spectral lines are not really single but consists of several closely packed lines called hyperfine lines. These fine lines cannot be explained by this model. Such structure means that in a given orbit, there are several orbits called sub orbits having different energies.
3. **No explanation of Zeeman and Stark effect:**
The splitting of spectral lines in presence of a magnetic field is called the Zeeman effect and the splitting of spectral lines in presence of an electric field is called the Stark effect. Bohr's atomic model didn't explain such effects.
4. **No explanation for the dual nature of electron:**
This model has treated electron as a particle of a certain mass revolving around the nucleus in a

fixed orbit. But de-Broglie suggested that electron has a dual nature i. e. electron behaves as a particle as well as wave nature.

Dual nature of matter (de-Broglie equation)

In 1905, Einstein suggested the dual nature of light. According to this, light possesses a wave and particle nature. In 1924, de-Broglie advanced the idea that not only photons or light but also matter like electron shows the dual nature. The wave associated with matter is the matter wave or de-Broglie wave. So, the electron is a subatomic particle that can behave sometimes as a particle and sometimes as a wave. The wave particle duality of matter led de-Broglie to derive the equation $\lambda = h/P$ which indicates the wave and particle nature of the matter in motion.

Derivation

According to Planck's quantum theory,

$$E = h\nu \text{ --- (i) } \quad E = \text{energy of photon,} \quad h = \text{Planck's constant} \quad \nu = \text{frequency}$$

According to Einstein equation,

$$E = mc^2 \text{ --- (ii)}$$

m=mass, c=velocity of light

Combining eqn (i) and (ii),

$$\begin{aligned} h\nu &= mc^2 \\ \text{or, } h\frac{c}{\lambda} &= mc^2 \quad (\nu = c/\lambda \text{ and } \lambda = \text{wavelength}) \\ \text{or, } \lambda &= \frac{h}{mv} \\ \lambda &= \frac{h}{P} \quad (P \text{ is momentum and } P = mv) \end{aligned}$$

It is de-Broglie wave equation. It shows that the momentum of a particle in motion is inversely proportional to its wavelength.

Significance

- i. It shows the relation between particle and wave character of matter.
- ii. It is applicable for all matter but more significant for microscopic particles like electron.
- iii. It helps to deduce Bohr's condition for quantization of angular momentum.

Heisenberg uncertainty principle

It states that “It is impossible to determine the position and momentum of microscopic particles like an electron simultaneously and accurately”.

Mathematically,

$$\Delta x \cdot \Delta y \geq \frac{h}{4\pi}$$

$\Delta x = \text{uncertainty in position}$

$\Delta y = \text{uncertainty in momentum}$

Uncertainty means

- i. If we measure the position more accurately, then the uncertainty in momentum occurs.
- ii. If we measure the momentum more accurately, then the uncertainty in position occurs.

Concept of orbital

The space around the nucleus where the probability of finding the electron is maximum is called orbital.

Differences between orbit and orbital

Orbit	Orbital
It is the well defined circular path where the electron revolves around the nucleus.	It is the space around the nucleus where the probability of finding the electron is maximum.
Orbits are circular in shape.	Orbitals have a different shape.
Orbit uses a two-dimensional concept.	Orbitals use three-dimensional concept.
Orbits don't have directional characteristics.	Orbitals have directional characteristics except for s-orbitals.
One orbit can accommodate a maximum of $2n^2$ number of electron where n is the principal quantum number.	One orbital can accommodate a maximum of two electrons.
Orbit concept can't explain the geometry of a molecule.	The orbital concept explains the geometry of a molecule.
It is developed by Bohr's atomic model.	It is developed by the Heisenberg uncertainty principle.

Shape of s and p orbital

s-orbitals are spherical in shape and p-orbitals are dumb-bell shape consisting of two lobes. The two lobes are separated by a nodal plane. There are three orientations of P orbitals. And they are designated as p_x , p_y and p_z .

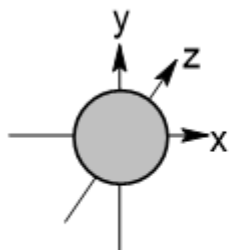


Fig: Shape of s-orbital

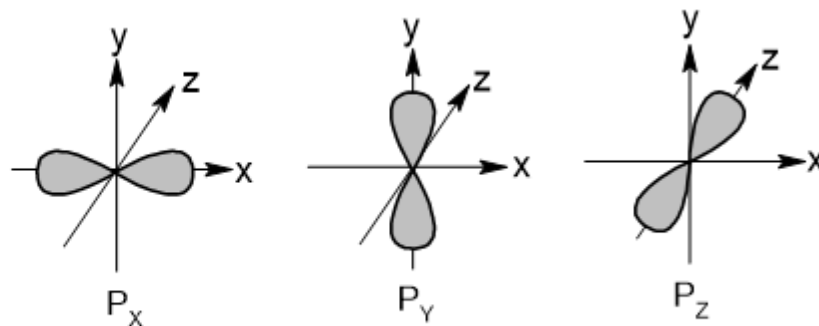


Fig: Shape of p-orbital

Quantum numbers

The quantum mechanical parameters which tell us about the location and motion of an electron in an atom are called quantum numbers. It gives complete information of a particular electron relating to its energy level, shape and orientation of orbital with its spin. The quantum numbers are as follows:

1. Principal quantum number (n)

It represents the number of shells or orbit or energy level in an atom. One orbit can accommodate a maximum of $2n^2$ number of electrons where n is principal quantum number (given by Bohr-Bury rule).

It indicates about the number of subshells (by n) and the number of orbitals in a shell (by $2n^2$).

Value of n	Shell	Number of electrons
1	K	2
2	L	8
3	M	18
4	N	32

2. Azimuthal quantum number (l)

It describes the sub-shell or sub-energy level. Its value lies from 0 to (n-1) for the value of n. It is also called a subsidiary quantum number.

n	l	Number of sub-shells
1	0 (s-sub shell)	1
2	0 (s-sub shell) 1 (p-sub shell)	2
3	0 (s-sub shell) 1 (p-sub shell) 2 (d-sub shell)	3

3. Magnetic quantum number (m)

It gives information about spatial arrangement of orbital with respect to the standard coordinate axis.

It gives information about the number of orbitals in a sub-shell. For the value of l, there are (2l+1) number of orbitals(m) with the value of m from -l to +l.

n	l	m
1	0 (s-sub shell)	0 (s-orbital)
2	0 (s-sub shell)	0 (s-orbital)
	1 (p-sub shell)	-1(px-orbital) 0 (py-orbital) +1(pz-orbital)
3	0 (s-sub shell)	0 (s-orbital)
	1 (p-sub shell)	-1(Px-orbital) 0 (Py-orbital) +1(Pz-orbital)
	2(d-sub shell)	-2 (dxy-orbital) -1 (dyz-orbital) 0 (dxz-orbital) +1 (dx ² -y ² -orbital) +2(dz ² -orbital)

4. Spin quantum number Spin Quantum Number represents the [direction](#) of the spin of the electrons. This can either be in the direction of clockwise or even anti-clockwise. Spin Quantum Number is denoted by the symbol s. It can have about only two values i.e. +1/2 or -1/2.

Arrangement of electron in atomic orbitals

1. Pauli's exclusion principle

It states that "No two electrons in an atom can have identical set of four quantum numbers".or

Only two electrons may exist in the same orbital and these electrons must have opposite spin.

The two electrons present in same orbital can have same n, l and m quantum number but s value must be opposite.

n	l	m	s
1	0	0	+1/2
1	0	0	-1/2
2	0	0	+1/2
2	0	0	-1/2
2	1	-1	+1/2
2	1	-1	-1/2
2	1	0	+1/2
2	1	0	-1/2
2	1	+1	+1/2
2	1	+1	-1/2

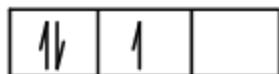
Here, all electrons have different(unique)set of quantum numbers.This justifies paulis exclusion principle.

2. Hund's rule for maximum multiplicity

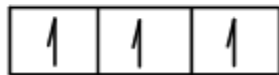
It states that "In an orbital of the same sub-shell, electrons are filled singly first before pairing starts".

Pairing of electrons in orbitals belonging to same subshell doesnot takes place until each orbitals belonging to that subshell is singly occupied,

Illustration: Let us take an example of the filling of electrons in a nitrogen atom. The electronic configuration of nitrogen is $1s^2 2s^2 2p^3$. There are the following possibilities in filling the electrons in $2p$.



One paired electron (incorrect)



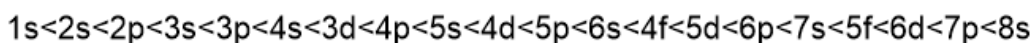
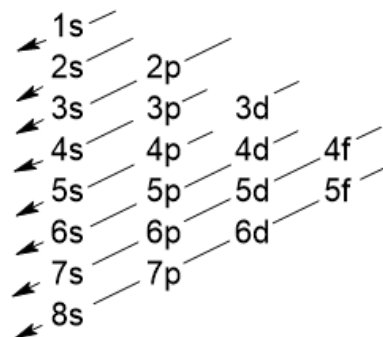
Three unpaired electron (correct)

3. Aufbau principle

It states that "The orbitals are filled up with electrons in the increasing order of their energy".

Electrons first occupies the lowest energy orbital available to them and enter into higher energy orbitals only after filling lower energy orbitals.

The order of filling electrons can be remembered as following diagram. The fundamental basis of aufbau principle lies on $(n+l)$ rule. Higher the $(n+l)$ value of orbitals, higher will be the energy.



The above sequence can also be satisfied by the Madelung rule which is also called the $(n+l)$ rule. According to the rule:

1. The orbitals with lower $(n+l)$ value has lower energy than the orbitals of higher $(n+l)$ value.
For 4s orbital, $n = 4, l = 0, n+l=4$
For 3d orbital, $n = 3, l = 2, n+l=5$
2. When two orbitals have the same $(n+l)$ value, the orbitals with a lower value of n has lower energy.
For 3d orbital, $n = 3, l = 2, n+l=5$
For 4p orbital, $n = 4, l = 1, n+l=5$
3d orbitals have less value of n . so it is filled first.

Limitations of Aufbau principle

Exactly half filled and full filled orbitals have greater stability than other due to following reasons:

1. Symmetry: Half filled and full filled orbitals are more symmetrical than any other and symmetry lead to stability.
2. Exchange energy: The electrons present in different orbitals of the same subshell can exchange their position. Each such exchange leads to a decrease in energy known as exchange energy. Greater the number of exchanges, the greater the exchange energy and the greater the stability.

Electronic configuration of elements in ground state

Atomic number	Name	Symbol	Electronic configuration
1	Hydrogen	H	$1s^1$
2	Helium	He	$1s^2$
3	Lithium	Li	$1s^2 2s^1$
4	Beryllium	Be	$1s^2 2s^2$
5	Boron	B	$1s^2 2s^2 2p^1$
6	Carbon	C	$1s^2 2s^2 2p^2$
7	Nitrogen	N	$1s^2 2s^2 2p^3$
8	Oxygen	O	$1s^2 2s^2 2p^4$
9	Fluorine	F	$1s^2 2s^2 2p^5$
10	Neon	Ne	$1s^2 2s^2 2p^6$
11	Sodium	Na	$1s^2 2s^2 2p^6 3s^1$
12	Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
13	Aluminium	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$
14	Silicon	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$
15	Phosphorous	P	$1s^2 2s^2 2p^6 3s^2 3p^3$
16	Sulphur	S	$1s^2 2s^2 2p^6 3s^2 3p^4$
17	Chlorine	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$
18	Argon	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
19	Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
20	Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
21	Scandium	Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
22	Titanium	Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
23	Vanadium	V	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
24	Chromium	Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
25	Manganese	Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
26	Iron	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
27	Cobalt	Co	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
28	Nickel	Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
29	Copper	Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Electronic configuration of some ions

$$\text{Fe}^{++} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^6$$

$$\text{Fe}^{+++} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$$