Atomic Structure

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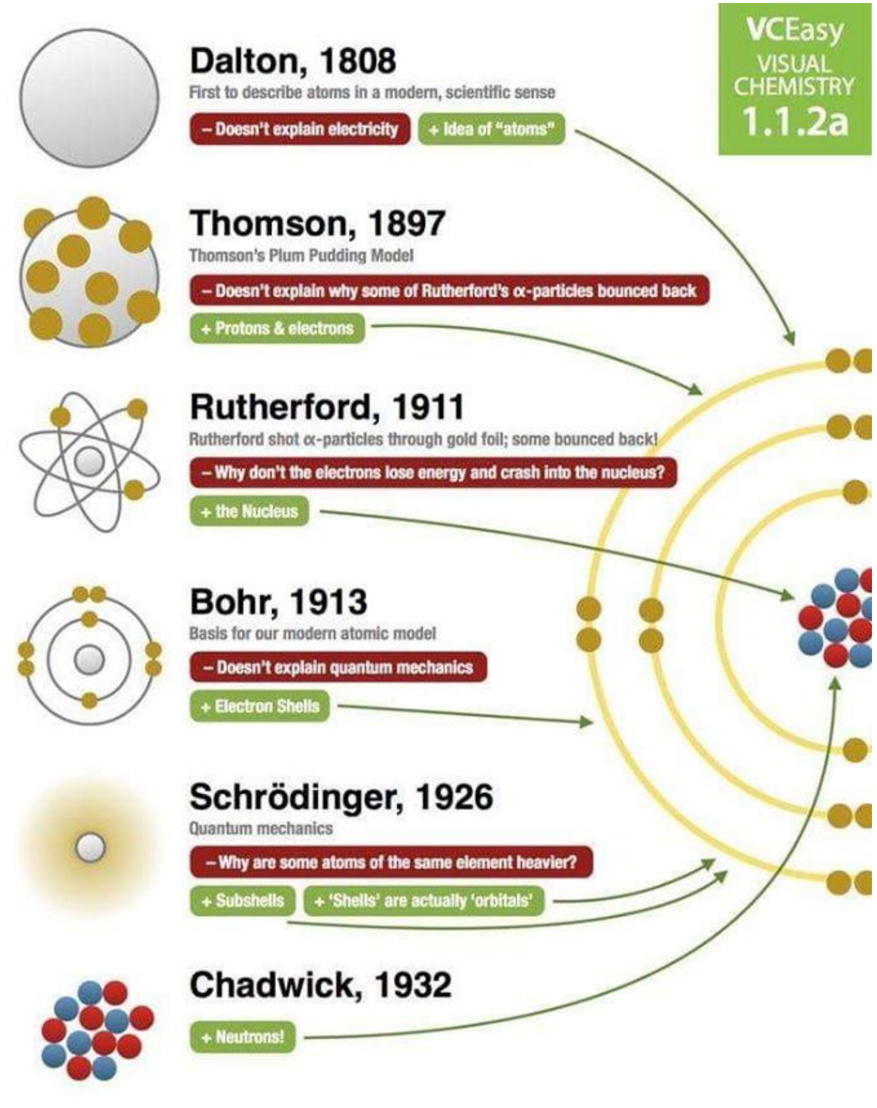
The contents of this presentation is made to give a brief idea about the topic, details will be discussed in the classes.
Contents have been collected from multiple textbooks and internet.

Theories for Atomic Structure in History

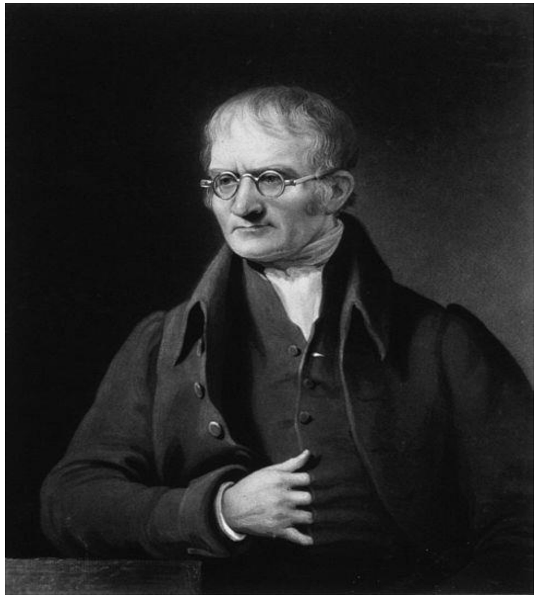
- **Dalton's**
- **Thomson's**
- **Rutherford's**
- **Bohr's**
- **Quantum Mechanical (QM)**
  - **Heisenberg; Schrodinger; Planck; Einstein, etc.**



atomic theory - historical development of the model of atomic theory with contributions from Dalton to Chadwick

John Dalton's Atomic Theory

- **Background:**
  - **- (1766-1844)**
  - **- Born in England**
  - **- Belonged to The Royal Society**
  - **- Is said to one of the top 50 most influential persons in history.**
- **Experiment-**
  - **- Measured Atomic Weight, and came up with The Atomic Theory.**



Postulates:

- **All matter is made of atoms. Atoms are indivisible and indestructible.**
- **All atoms of a given element are identical in mass and properties; atoms of different elements are different from each other.**
- **Compounds are formed by a combination of two or more different kinds of atoms in simple whole number ratios.**
- **A chemical reaction is a *rearrangement* of atoms.**

Limitations of Dalton's Atomic Theory

- It was proved that an atom is not indivisible. As an atom can be subdivided into electrons, protons and neutrons.

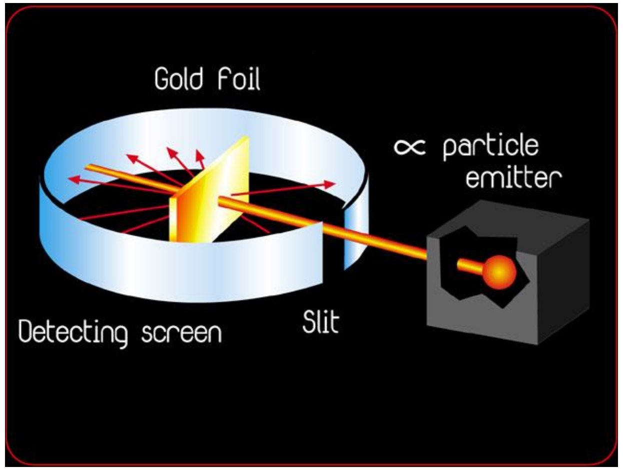
- According to Dalton Atomic Theory, atoms of an element are identical in mass, size and many other chemical or physical properties. But, practically we observe that atoms of several elements differ in their densities and masses. These atoms with the different masses are known as isotopes. For example, Chlorine (Cl) has 2 isotopes with the mass numbers of 35 and 37.

- According to Dalton Atomic Theory, when atoms of different elements (atoms of two or more elements) combine in simple whole number ratios, we get chemical compounds. But this is not true in case of complex organic compounds. For example, sucrose ($C_{12}H_{22}O_{11}$)

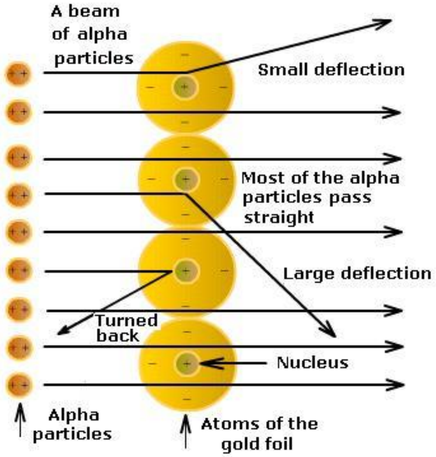
Earnest Rutherford's Atomic Theory

- **Background:**
  - (1871-1937)
  - Born In New Zealand
  - Nobel prize in Chemistry - 1908
  - Knighted – 1914
  - Rutherfordium (Rf) was named after him

- **Experiment-**
  - shot alpha particles at gold foil
  - noticed some went right through, and others came out at an angel or bounced directly back



Earnest Rutherford’s Atomic Theory



Rutherford’s Gold Foil Experiment

- **Major space in an atom is empty – A large fraction of α-particles passed through the gold sheet without getting deflected. Therefore, the major part of an atom must be empty.**

- **The positive charge in an atom is not distributed uniformly and it is concentrated in a very small volume.**

- **Very few α-particles had deflected at large angles or deflected back. Moreover, very few particles had deflected at 180^{o}. Therefore, he concluded that the positively charged particles covered a small volume of an atom in comparison to the total volume of an atom.**

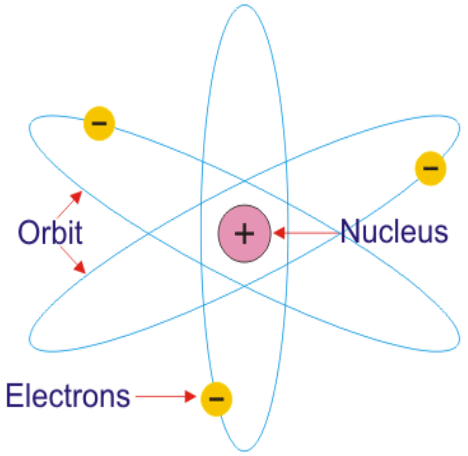
Earnest Rutherford's Atomic Theory

- An atom is composed of positively charged particles. Majority of the mass of an atom was concentrated in a very small region. This region of the atom was called as the nucleus of an atom.

- 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."

- An atom has no net charge or they are electrically neutral because electrons are negatively charged and the densely concentrated nucleus is positively charged.

- The size of the nucleus of an atom is very small in comparison to the total size of an atom.

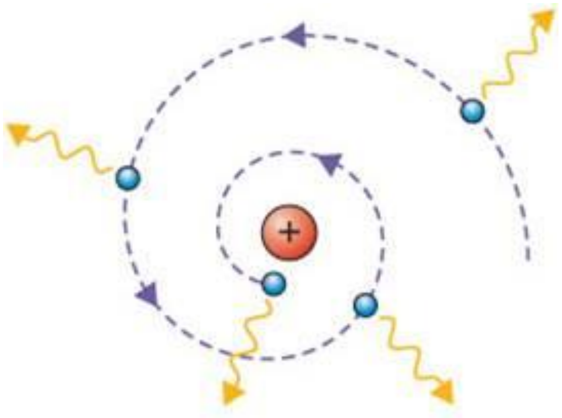


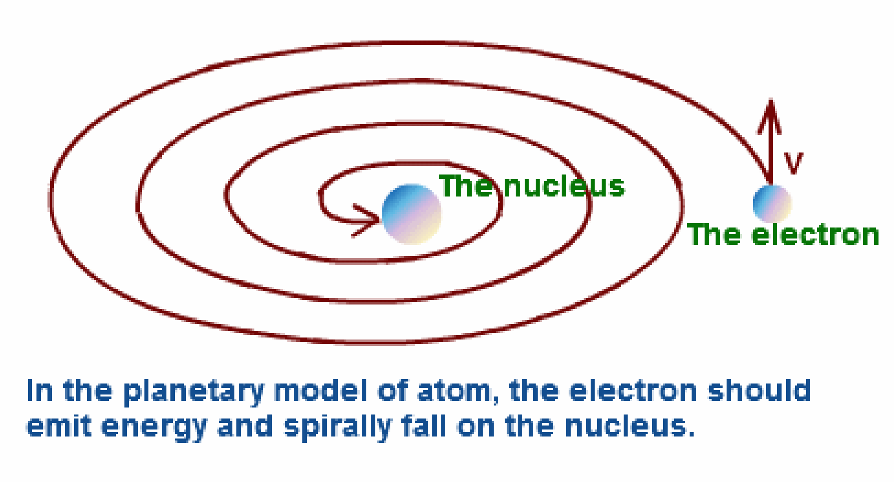
Rutherford's Atomic Model

Limitations of Rutherford Atomic Model

- According to Rutherford's postulate, electrons revolve at a very high speed around a nucleus of an atom in a fixed orbit. However, Maxwell explained accelerated charged particles release electromagnetic radiations. Therefore, electrons revolving around the nucleus will release electromagnetic radiation.

- The electromagnetic radiation will have energy from the electronic motion as a result of which the orbits will gradually shrink. Finally, the orbits will shrink and collapse in the nucleus of an atom.





Niels Bohr’s Atomic Theory

- **Background:**
  - (1885-1962)
  - Born In Denmark
  - Nobel prize in Physics - 1922
  - Founded the Institute of Theoretical Physics - 1920
  - Introduced The Quantum Theory

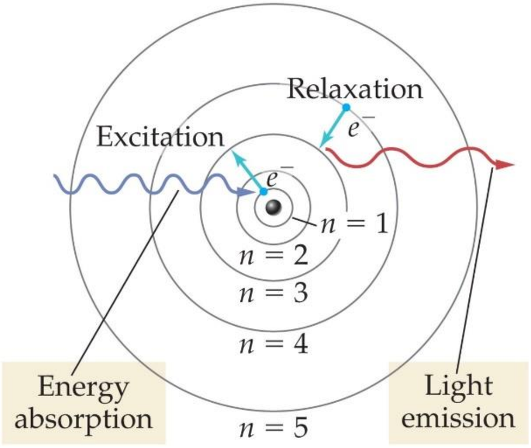
Bohr’s postulates

- **In an atom, electrons revolve around the positively charged nucleus in a definite circular path called as orbits or shells.**

- **The angular momentum of an electron revolving around the nucleus in an orbit is integer multiple of h/2π.**

$$mvr = nh/2\pi \qquad n = 1, 2, 3, 4, \ldots\ldots$$

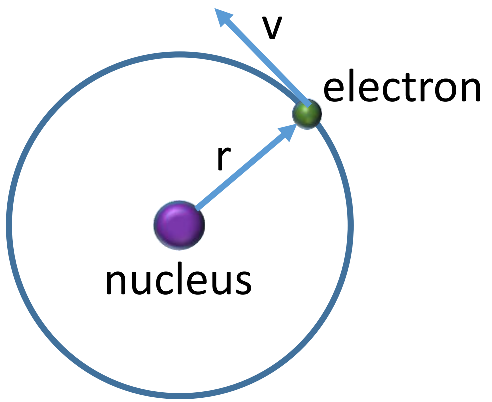
- **The electrons in an atom move from a lower energy level to a higher energy level by gaining the required energy and an electron moves from a higher energy level to lower energy level by losing energy.**



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

Niels Bohr's Atomic Theory

- **Radius of an orbit, and the energy of electron**



Charge of nucleus = Ze
Attraction force between electron and nucleus = $Ze.e/r^2 = Ze^2/r^2$

The attraction force is counterbalanced by the centrifugal force = mv^2/r

Therefore, $Ze^2/r^2 = mv^2/r$

or, $v^2 = Ze^2/mr$……………….(1)

According to Bohr's postulate,

$mvr = nh/2\pi$

or, $v^2 = n^2h^2/4\pi^2m^2r^2$………....(2)

From equation (1) and (2),

$$\mathbf{r = n^2h^2/4\pi^2mZe^2}$$

Total energy E of an electron in any orbit,

$E = K.E. + P.E.$

$= \frac{1}{2} mv^2 + (-Ze^2/r)$

We know, $mv^2/r = Ze^2/r^2$

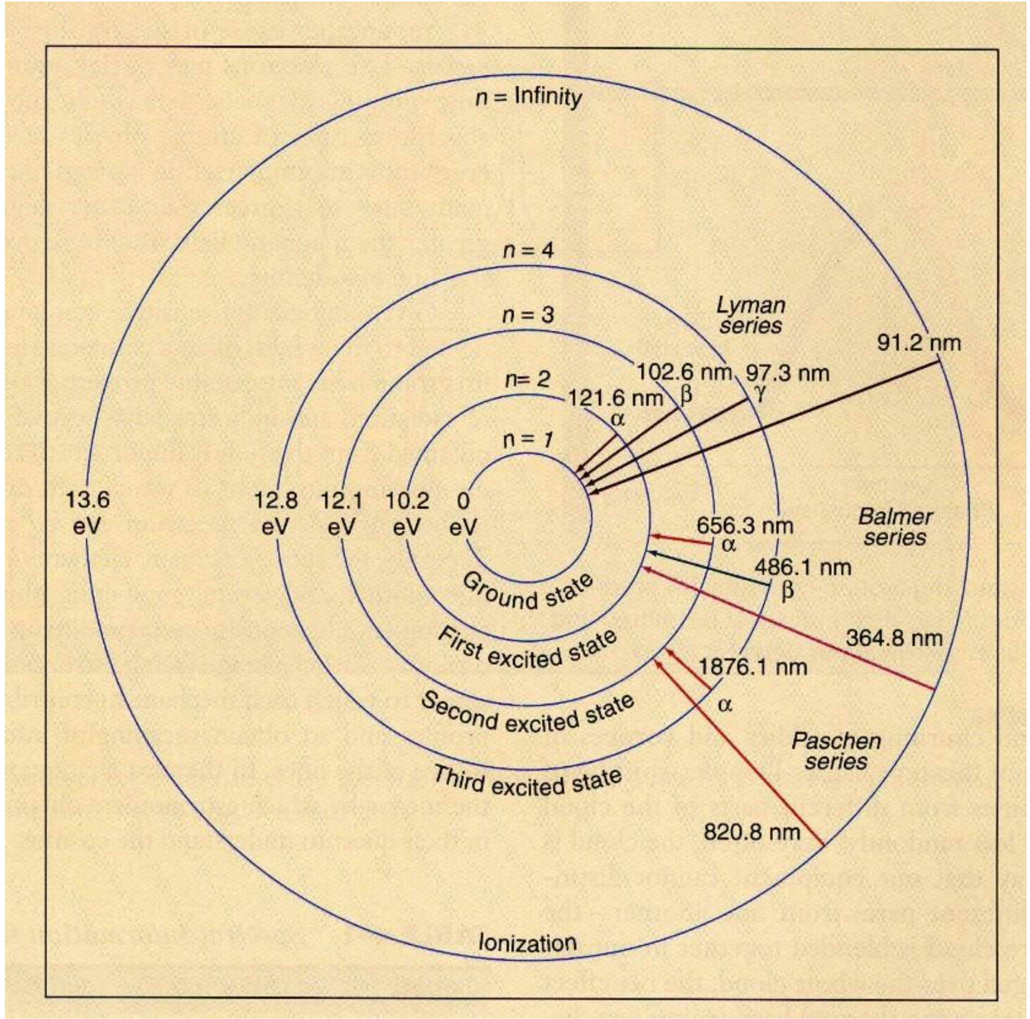
Therefore, $E = Ze^2/2r - Ze^2/r$

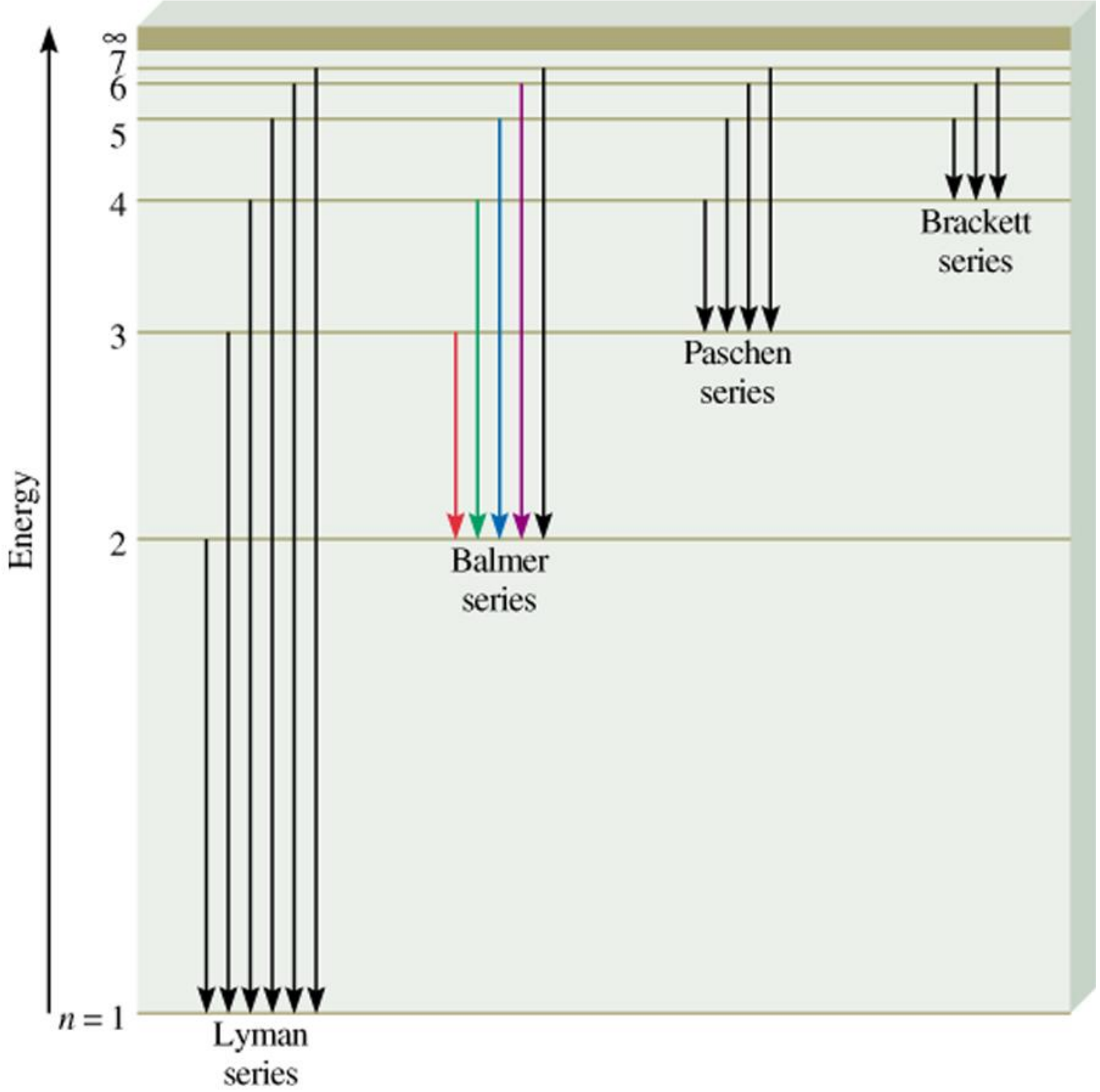
$= - Ze^2/2r$

Substituting the value of r,

$$\mathbf{E = - 2\pi^2mZ^2e^4/n^2h^2}$$

Niels Bohr’s Atomic Theory





Limitations of Bohr’s Atomic Theory

- **It could not explain the spectra obtained from larger atoms.**

- **It violates the Heisenberg Uncertainty Principle.**

- **Failed to explain the Zeeman Effect (effect of magnetic field on the spectra of atoms) and Stark effect (effect of electric field on the spectra of atoms).**

Wave nature of electrons

An electron moving in a close orbit is considered as a stationary or standing wave.

Therefore, according to Planck's equation,

$E = h\nu$;h is Planck's constant, ν is frequency

Using Einstein's equation,
$E = mc^2$;m is the mass, c is velocity

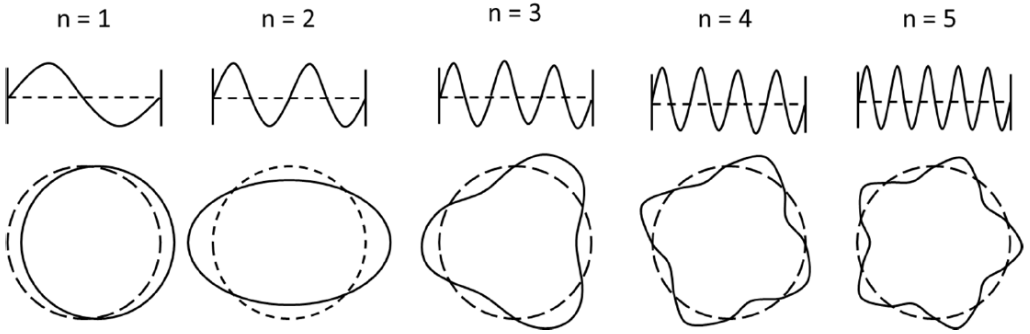
Therefore,

$mc^2 = h\nu$

or, $mc = h\nu/c = h/\lambda$

or, $\lambda = h/mc$

or, $\lambda = h/mv$………….. (1) ;For electron, velocity c = v



If r is the radius of orbit, and n is the number of wave

Therefore, the circumference,

$2\pi r = n\lambda$

or, $\lambda = 2\pi r/n$…………… (2)

From equation (1) and (2),

$2\pi r/n = h/mv$

or, $\mathbf{mvr = nh/2\pi}$

Quantum Mechanical Model of Atomic Structure

- ***De Broglie:*** **suggested that electrons have characteristics similar to those of waves.**

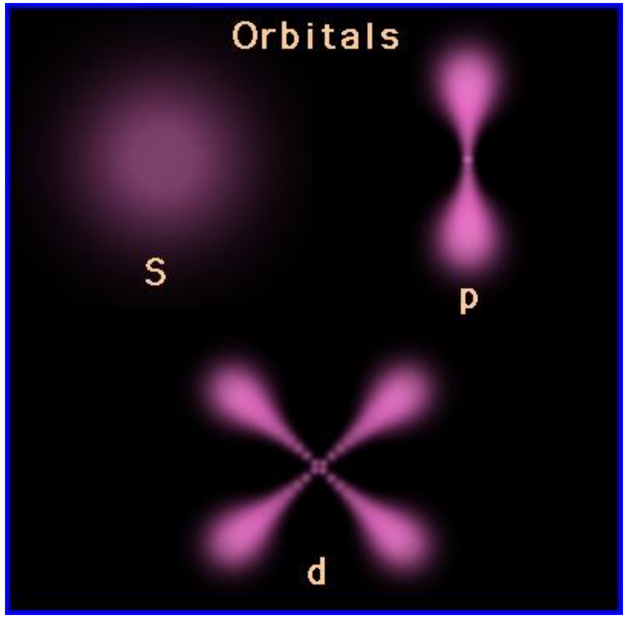
- ***The Heisenberg Uncertainty Principle:*** **it is impossible to precisely know both the position and velocity of electron at the same time.**

- ***The Schrödinger Wave Equation:*** **the atomic model in which electrons are treated as waves is known as the wave mechanical model or the quantum mechanical model of the atom**

Schrödinger's Quantum mechanical model

Key points:

- **Electrons do not follow fixed paths**
- **They move randomly in areas of probability (orbitals)**
- **There are specific energies associated with each orbital**

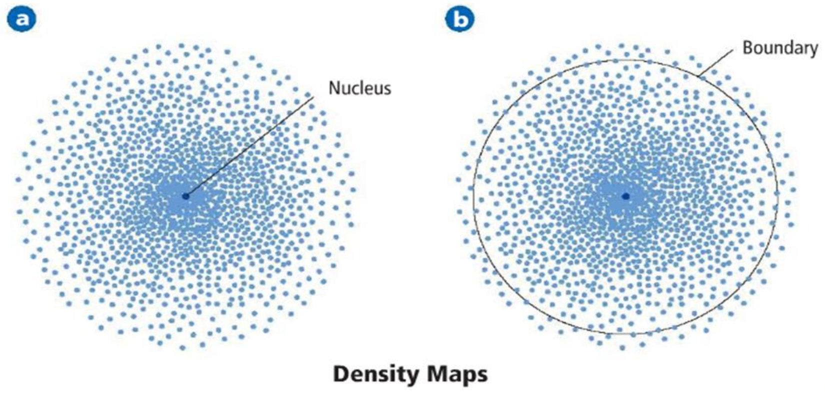


Quantum mechanical model

- **The only quantity that can be known is the probability for an electron to occupy a certain region around the nucleus.**

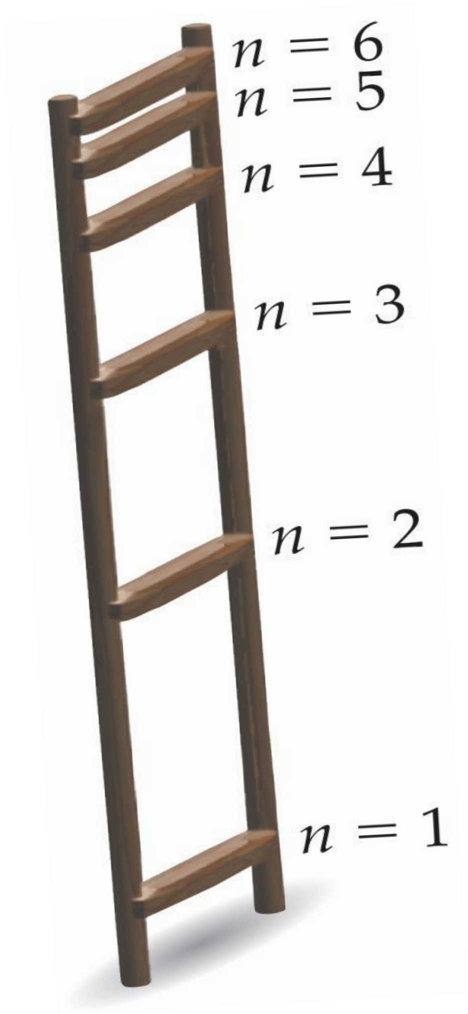
- **Schrödinger's equation applied equally well to elements other than hydrogen (unlike Bohr's model).**

- **Bohr orbits were replaced with quantum-mechanical orbitals.**



Quantum mechanical model

➢ **Each electron is described by Four Quantum numbers (QM)**



❑Principal QM (*n*) :

- **indicates the relative size and energy of atomic orbitals.**
- **n = 1, 2, 3,….**

✓ **This quantum number is the one on which the energy of an electron in an atom primarily depends. The smaller the value of *n*, the lower the energy and the smaller the orbital.**

✓ **Orbitals with the same value for *n* are said to be in the same shell.**

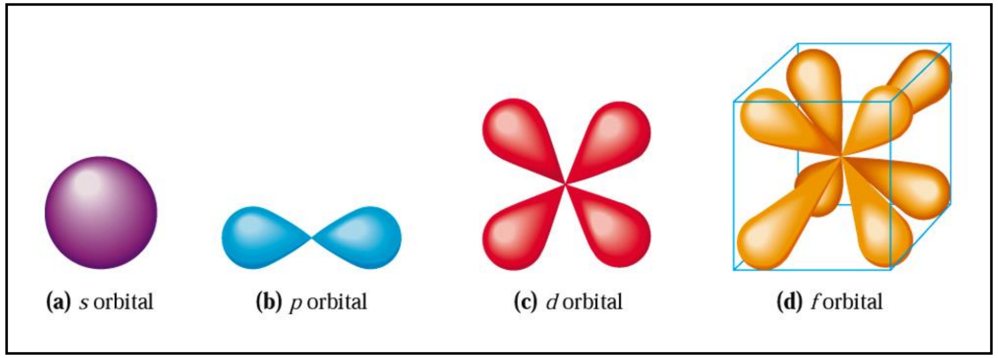
✓ **Shells are sometimes designated by uppercase letters:**

Letter	***K***	***L***	***M***	***N***	**. . .**
n	**1**	**2**	**3**	**4**	

❑Azimuthal QM/Subsidiary QM/Angular momentum QM (*l*)

- ✓ This quantum number distinguishes orbitals of a given *n* (shell) having different shapes.
- ✓ It can have values from 0, 1, 2, 3, . . . to a maximum of (*n* – 1).
- ✓ For a given *n*, there will be *n* different values of *l*, or *n* types of subshells (denoted by *s, p, d or f*).
- ✓ Orbitals with the same values for *n* and *l* are said to be in the same shell and subshell.

An *s* orbital has spherical shape; a *p* orbital has two lobes; a *d* orbital has four lobes; and an *f* orbital has eight lobes.



n	1	2	3	4
l	0	1	2	3
Letter	*s*	*p*	*d*	*f*

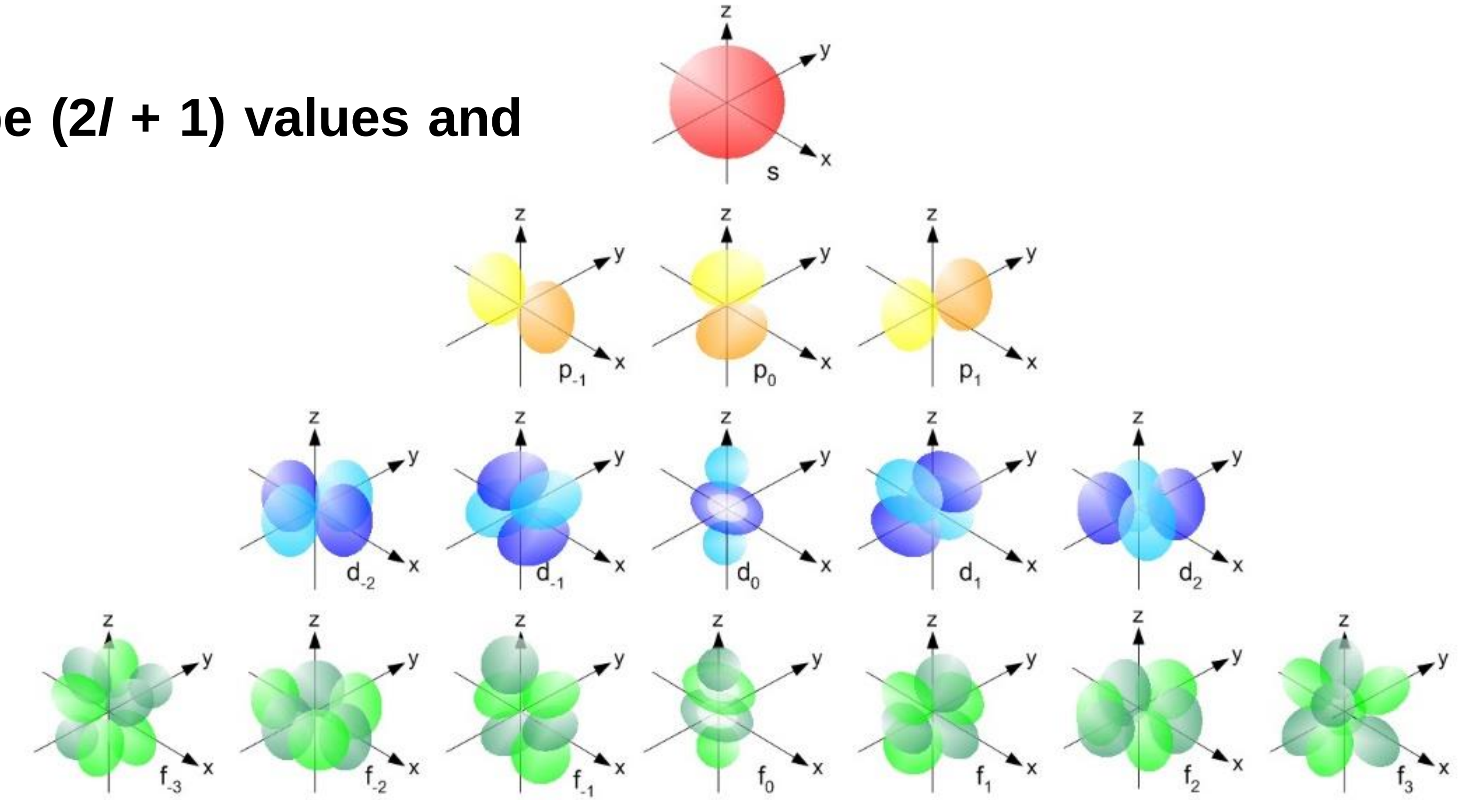
Not every subshell type exists in every shell.

❑Magnetic Quantum Number, *m*

- **This quantum number distinguishes orbitals of a given *n* and *l* - that is, of a given energy and shape but having different orientations.**

- **The magnetic quantum number depends on the value of *l* and can have any integer value from –*l* to 0 to +*l*.**

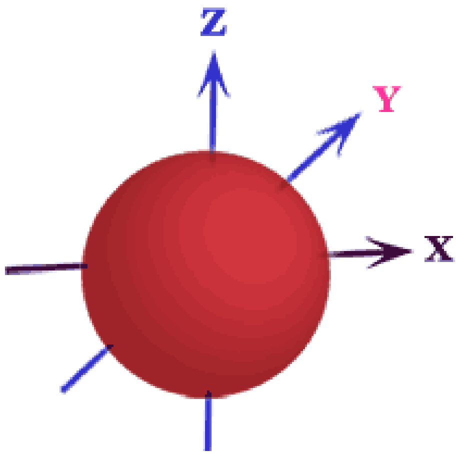
- **For a given subshell, there will be (2*l* + 1) values and therefore (2*l* + 1) orbitals.**



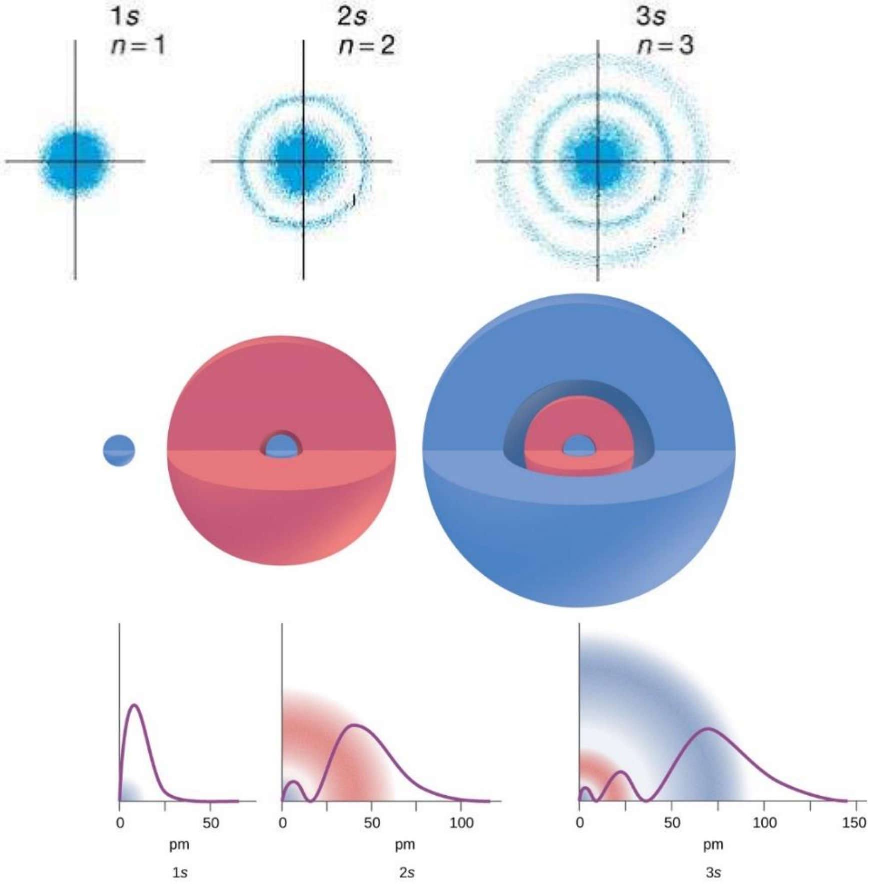
❑Magnetic Quantum Number, *m*

When *n* = 1, *l* has only one value, 0; therefore, *m* has only one value, 0.

So the first shell (*n* = 1) has one subshell, an *s*-subshell, 1*s.* That subshell, in turn, has one orbital.



1s orbital

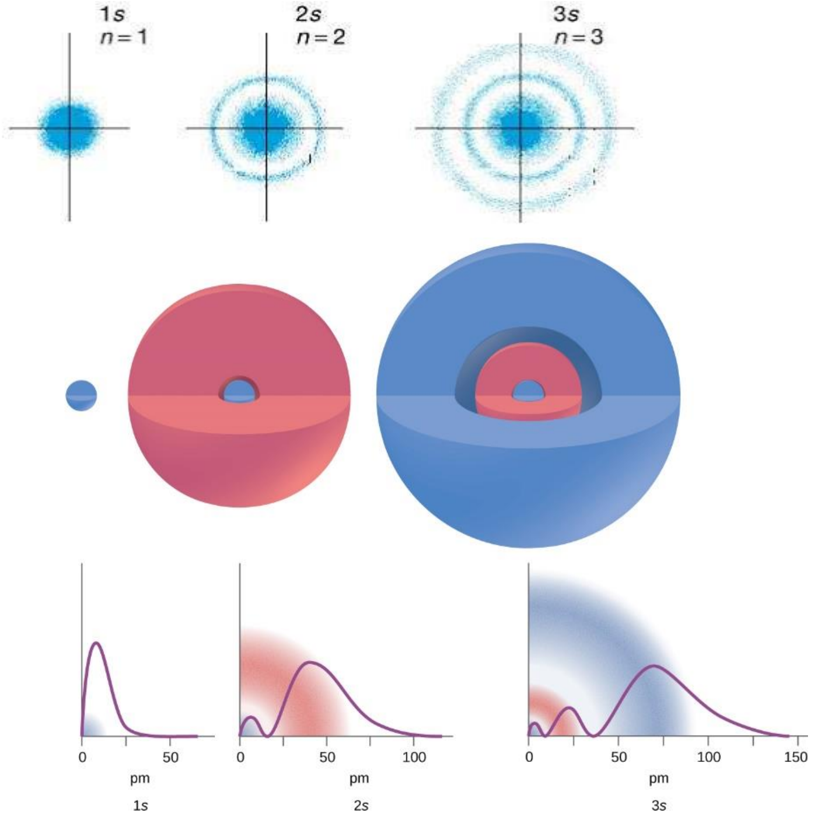


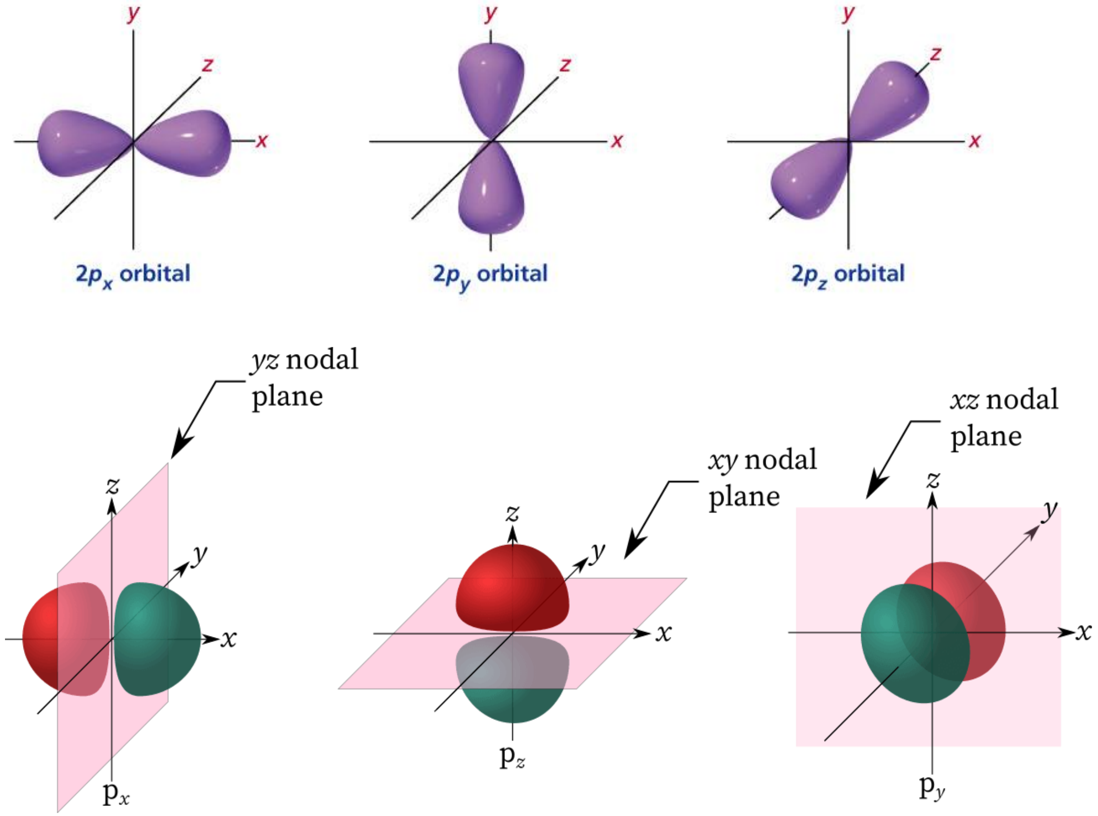
❑Magnetic Quantum Number, *m*

When *n* = 2, *l* has two values, 0 and 1.

When *l* = 0, m_l has only one value, 0. So there is a 2*s* subshell with one orbital.

When *l* = 1, m_l has only three values, -1, 0, 1. So there is a 2*p* subshell with three orbitals.





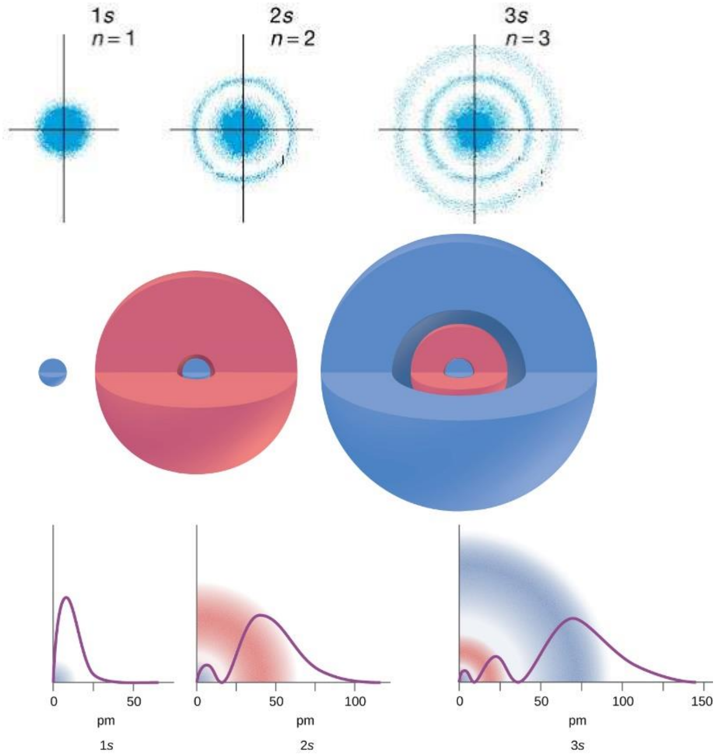
❑Magnetic Quantum Number, *m*

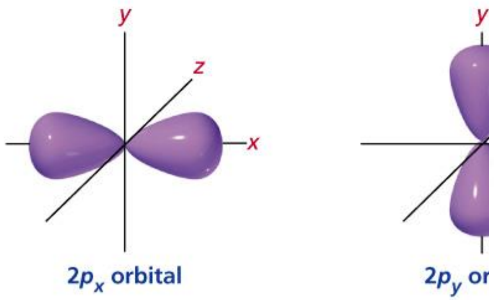
When n = 3, l has three values, 0, 1, and 2.

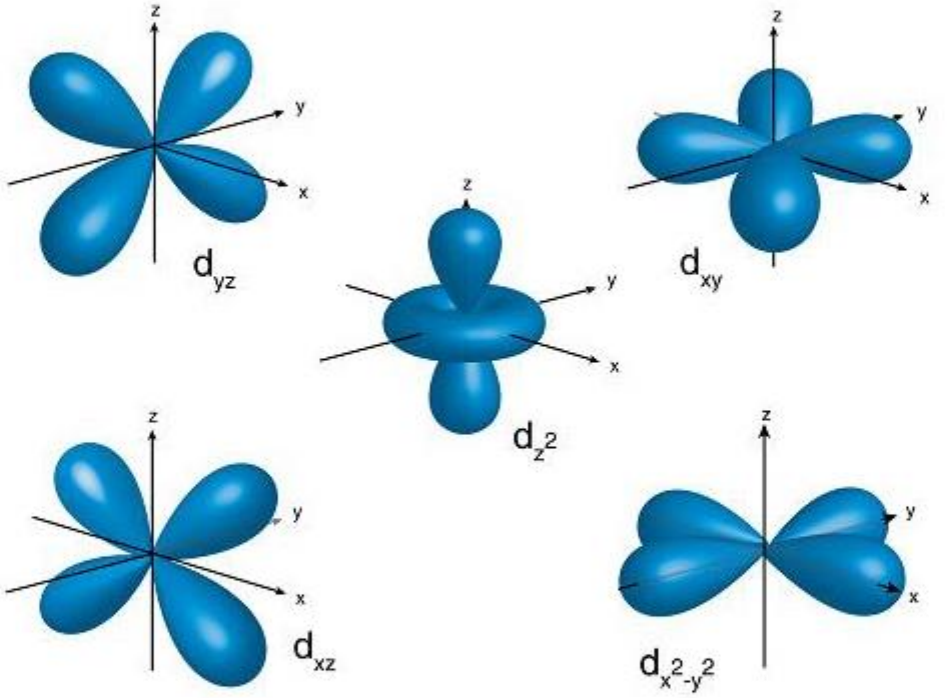
When l = 0, m_l has only one value, 0. So there is a 3*s* subshell with one orbital.

When l = 1, m_l has only three values, -1, 0, 1. So there is a 3*p* subshell with three orbitals.

When l = 2, m_l has only five values, -2, -1, 0, 1, 2. So there is a 3*d* subshell with five orbitals

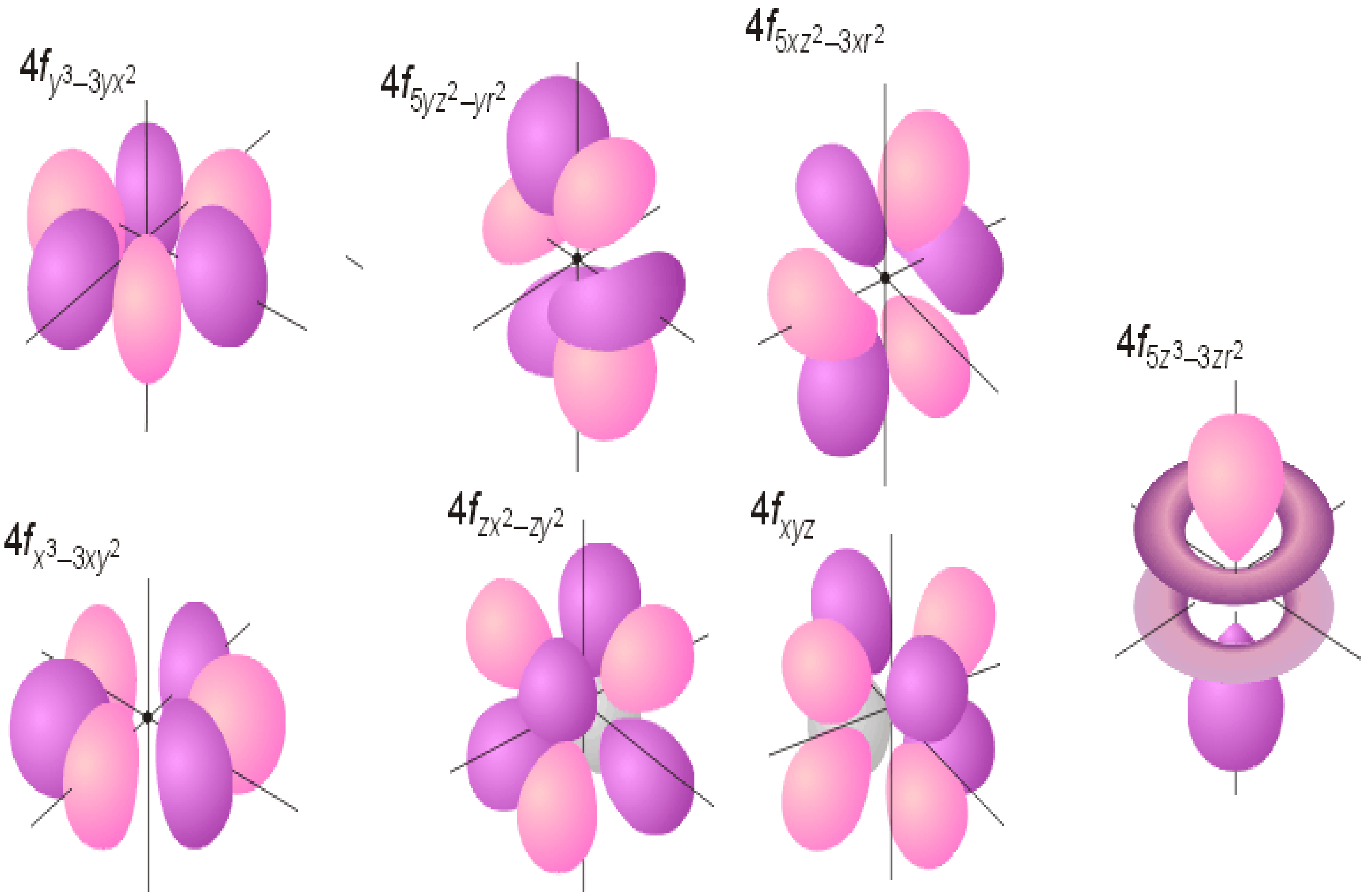






❑ Magnetic Quantum Number, *m*

***f* orbitals**



Spin Quantum Number (s):

- defines the direction of spin on an axis of each electron (one axis, therefore 2 spins possible)

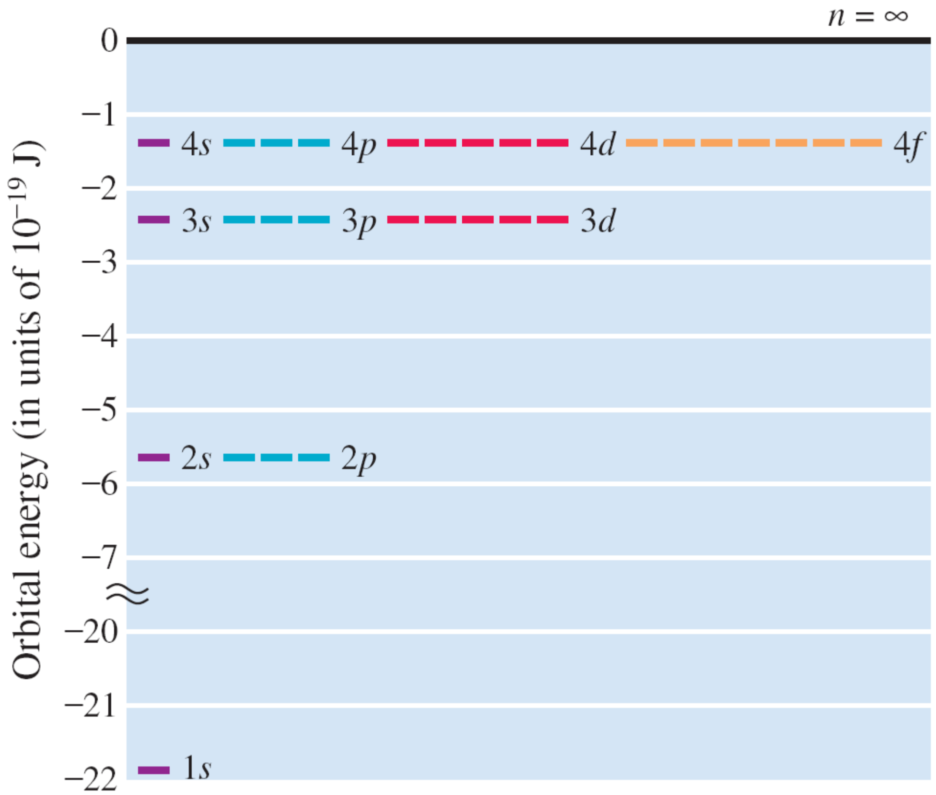
Clockwise (+1/2)

Counterclockwise (-1/2)

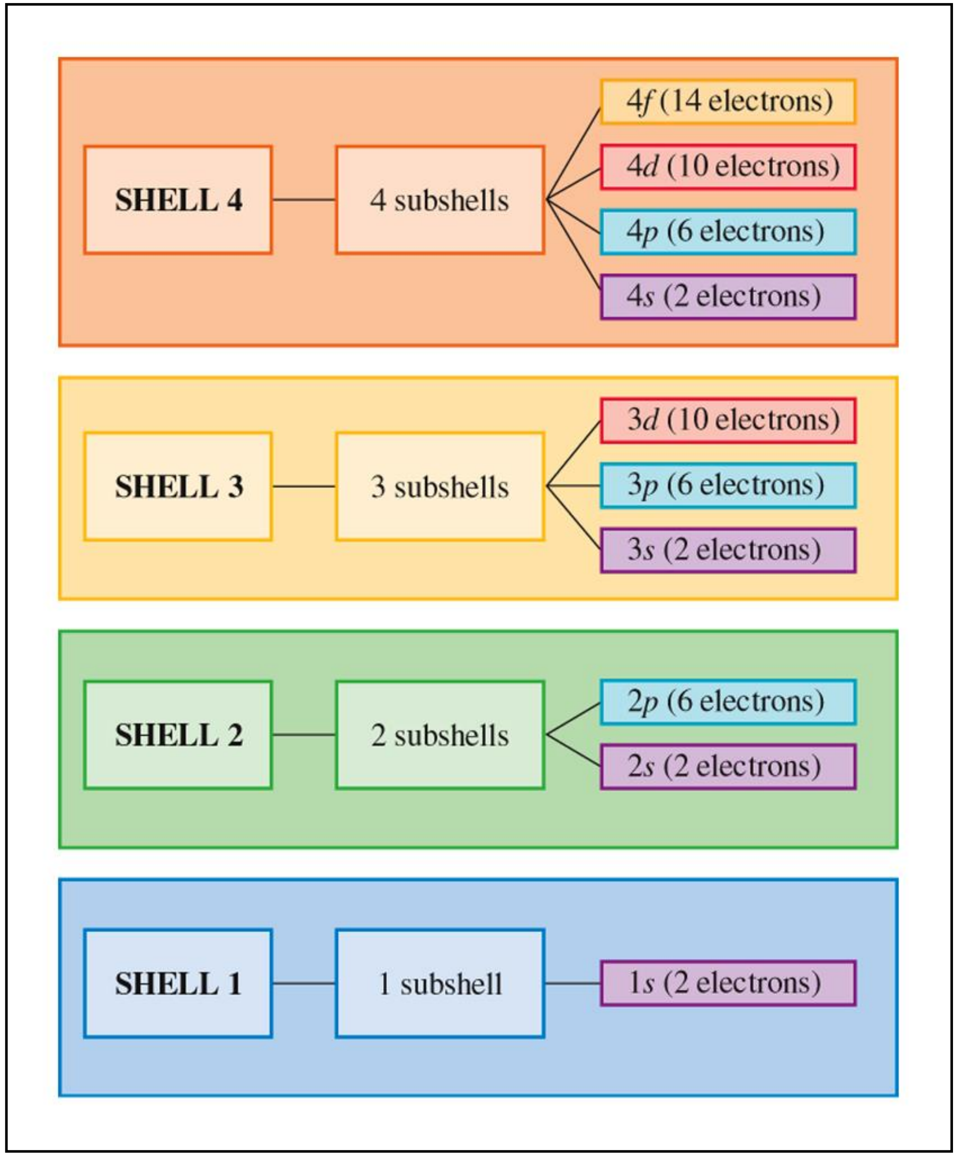
Quantum Numbers and Atomic Orbitals

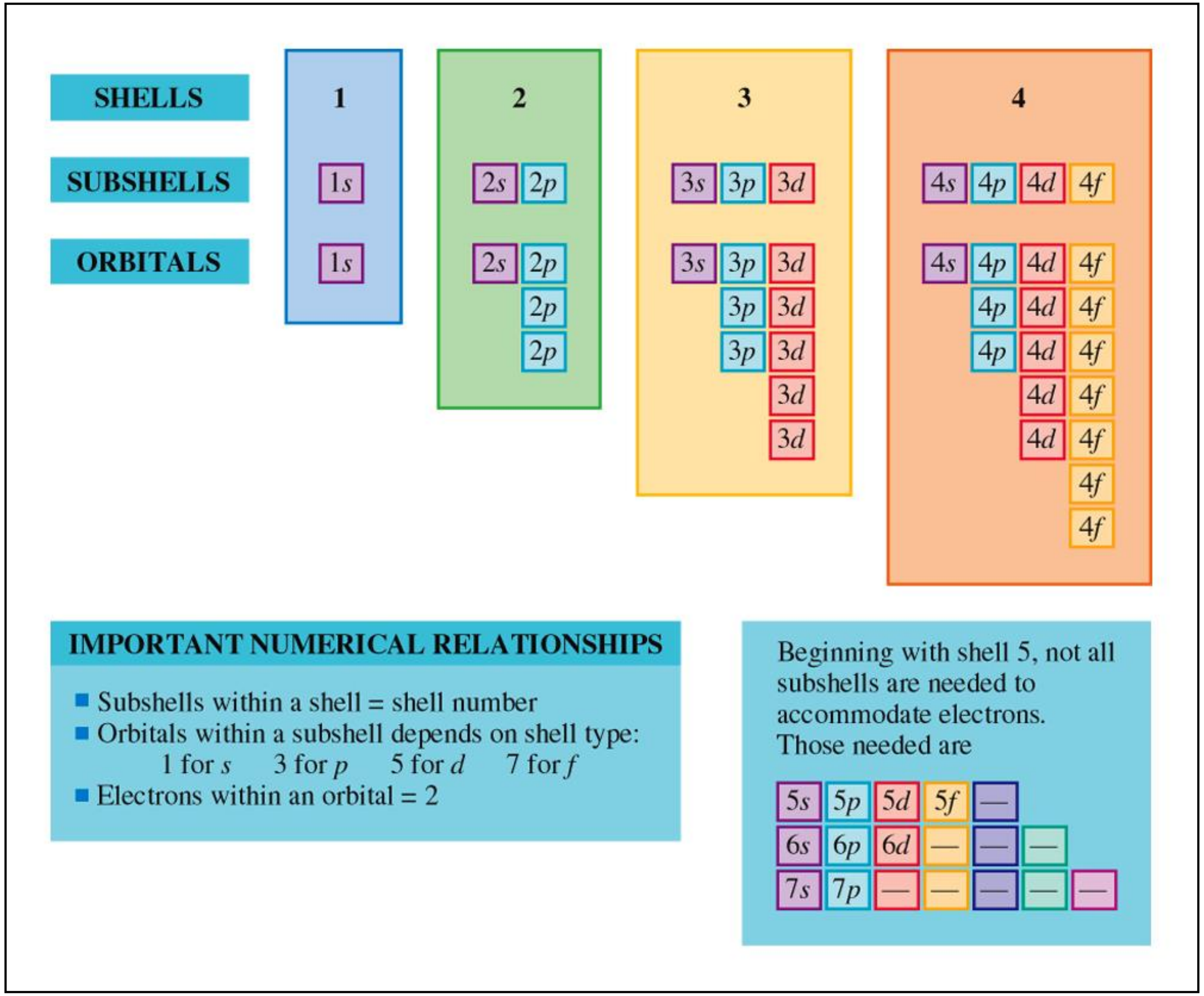
n	l	m_l*	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1s	1
2	0	0	2s	1
2	1	−1, 0, +1	2p	3
3	0	0	3s	1
3	1	−1, 0, +1	3p	3
3	2	−2, −1, 0, +1, +2	3d	5
4	0	0	4s	1
4	1	−1, 0, +1	4p	3
4	2	−2, −1, 0, +1, +2	4d	5
4	3	−3, −2, −1, 0, +1, +2, +3	4f	7

*Any one of the m_l quantum numbers may be associated with the n and l quantum numbers on the same line.

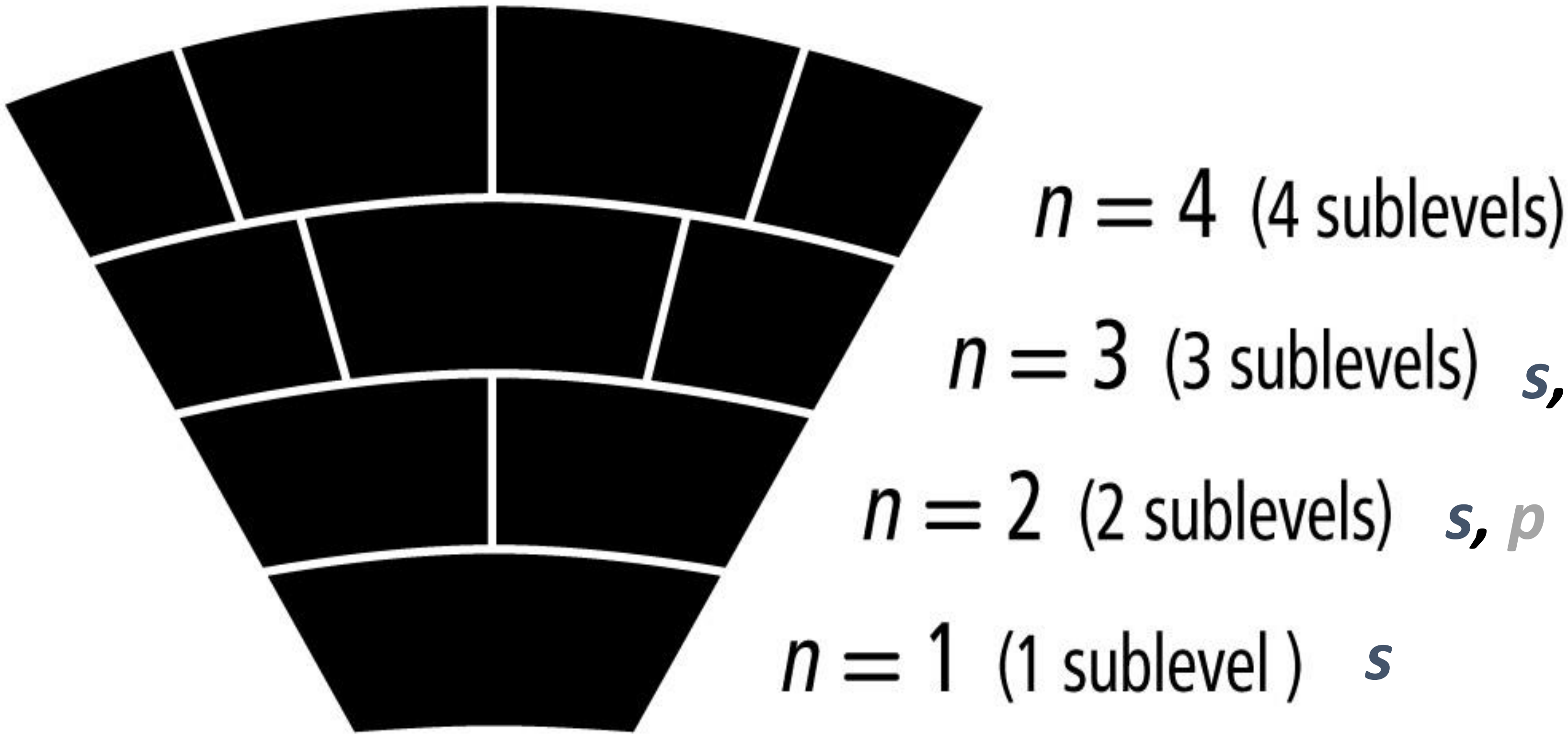


Subshell arrangement





- **Energy sublevels** are contained within the principal energy levels.
    - Each energy sublevel relates to orbitals of different shape.



s, ***p***, ***d***, ***f***

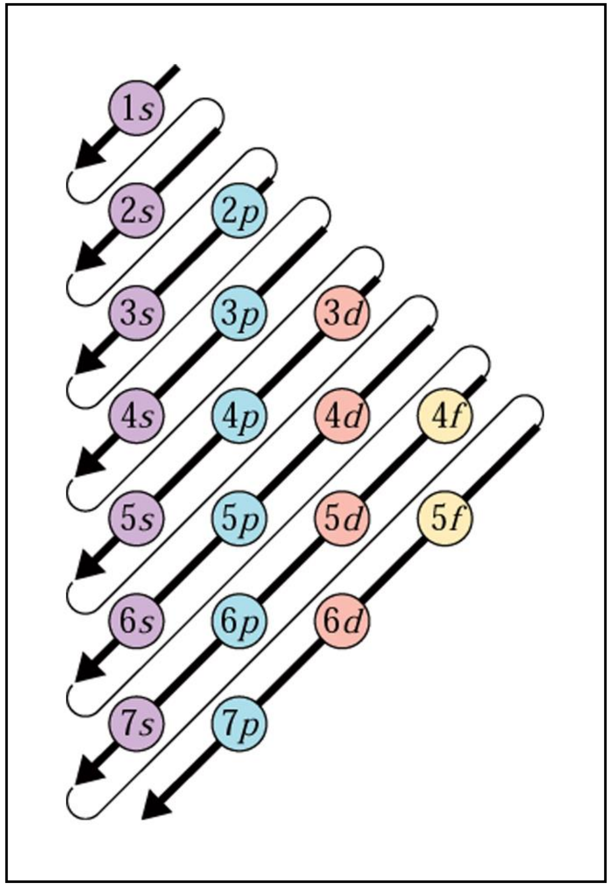
s, ***p***, ***d***

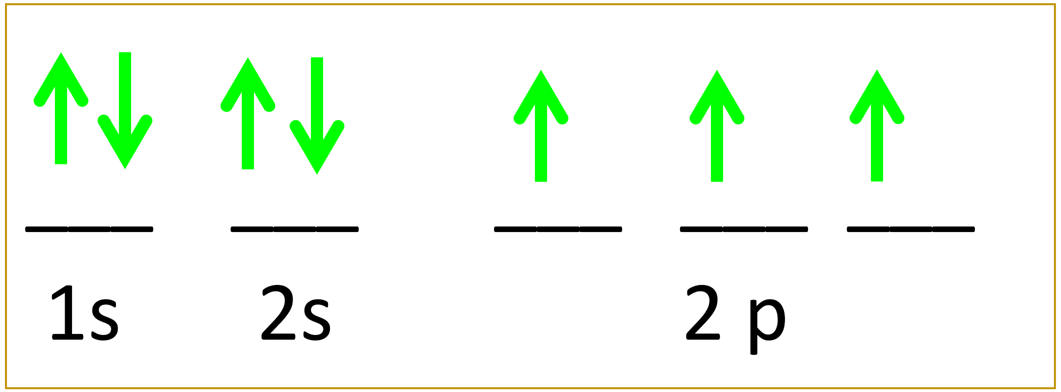
s, ***p***

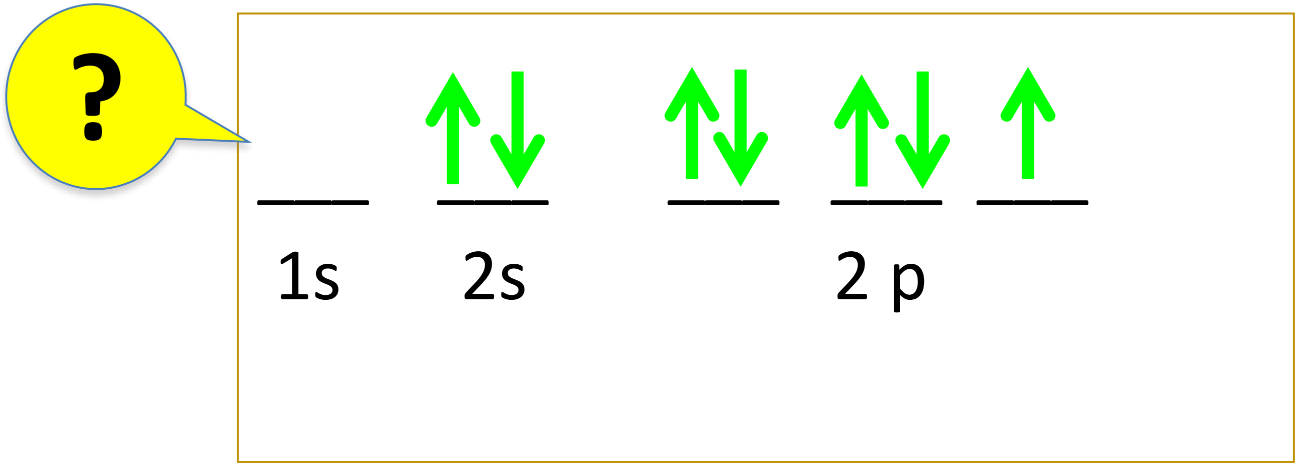
s

❑ Aufbau Principle

- **Electrons go into the subshell having the lowest possible energy.**







Exceptions to the Aufbau Rule

Cr [Ar] $3\,d^4 4s^2$

Cu [Ar] $3\,d^9 4s^2$

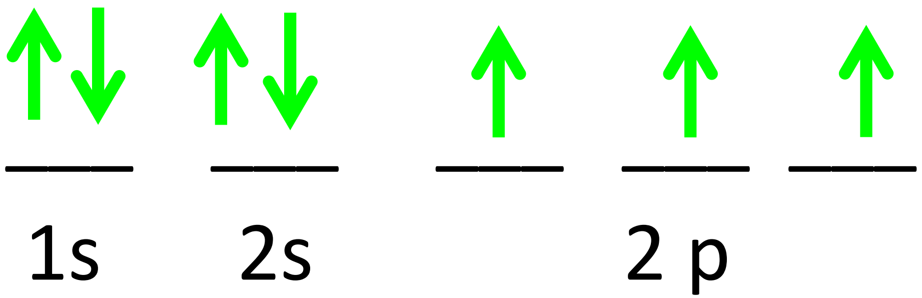
However, the actual electron configuration, determined experimentally, are:

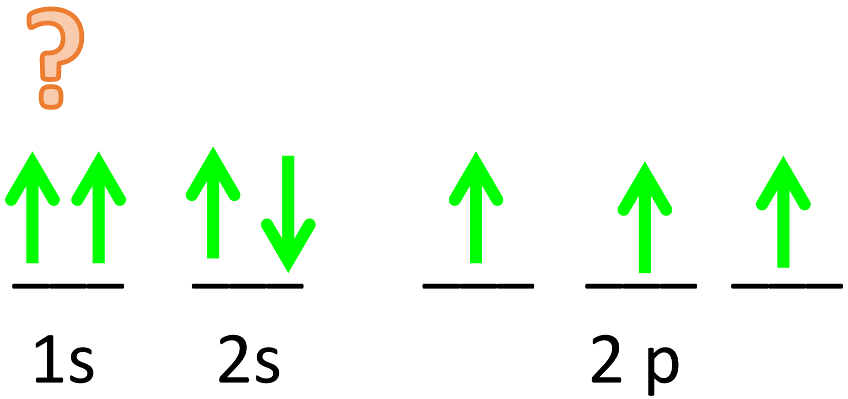
Cr [Ar] $\boxed{3d^5 4s^1}$

Cu [Ar] $\boxed{3d^{10} 4s^1}$

❑ Pauli’s exclusion Principle

No two electrons in an atom have the same four quantum numbers





❑ Hund's Rule

- **Every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.**