Applied Chemistry in Nursing

Lecture one

Measurement

- **Measurement** is the comparison of a physical quantity to be measured with a unit of measurement ie, with a fixed standard of measurement. A unit is a scale or standard being used to represent a measurement.
- If you repeat measurement of a particular quantity the values changes slightly.
- The term **precision** refers to the closeness of the **set of values** obtained from identical measurements of a quantity.
- **Accuracy** is a related term; it refers to the closeness of a single measurement to its true value

Measurement

- The SI system(from the French Système international) is a worldwide measurement system based on the older metric system.
- SI is a decimal system with basic units for things like **mass**, **length**, and **volume** and prefixes that modify the basic units. For example;
- kilo- (k)means 1,000
- centi- (c)means 0.01
- milli- (m)means 0.001
- So a kilogram (kg) is 1,000 grams, and a kilometer (km) is 1,000 meters.
- A milligram (mg) is 0.001 grams — or you can say that there are 1,000 milligrams in a gram.

Measurements of Length, Volume, and Mass

- The fundamental SI unit of **length** is the **meter**, which is a little longer than a yard (1 meter = 39.37 inches).
- In the metric system fractions of a meter or multiples of a meter can be expressed by powers of 10, as summarized in Table below.

Unit	Symbol	Meter Equivalent
kilometer	km	1000 m or 10^3 m
meter	m	1 m
decimeter	dm	0.1 m or 10^{-1} m
centimeter	cm	0.01 m or 10^{-2} m
millimeter	mm	0.001 m or 10^{-3} m
micrometer	µm	0.000001 m or 10^{-6} m
nanometer	nm	0.000000001 m or 10^{-9} m

Measurement

- **Mass** is another important measurable quantity which can be defined as the quantity of matter present in an object.
- The fundamental SI unit of mass is the **kilogram**. The prefixes for the various mass units are based on the **gram**. In the laboratory we determine the mass of an object by using a balance. A balance compares the mass of the object to a set of standard.
- The commonly used metric unit of mass are summarized in the table

Unit	Symbol	Gram Equivalent
kilogram	kg	1000g = 10^3 g = 1kg
gram	g	1g
milligram	mg	0.001g = 10^{-3} g = 1mg

Unit	Symbol	Gram Equivalent
kilogram	kg	1000g = 10^3 g = 1kg
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- 1 kilogram = 1000 grams = 2.205 pounds(lb)
- 1 0unce(oz) = 28.35 grams 0.03527 oz = 1 g
- 1 pound(lb) = 453.59 grams = 0.45359 kilograms = 16 ounces
- 1 ton = 2000 pounds (lb) = 907.185 kilograms
- 1 metric ton = 1000 kilograms = 2 204.6 pounds(lb)

Trial

- Express the following quantities using an SI prefix and a base unit. For example, 1.6 x 10^{-6} m =1.6 μm or mcg. A quantity such as 0.000168 g could be written 0.168 mg or 168 μm.
- a. 1.84 x 10^{12} m
- c. 7.85 x 10^{-3} g
- d. 9.7 x 10^{3} m

Asignment

1. 0.000732 s
2. 0.000000000154 m
3. 5.67 x 10^{-6} g

- Find the meter equivalent of the following
- Femtometer
- Picometer
- decameter

Units of Measurement

Temperature

Kelvin Scale

Used in science.

Same temperature increment as Celsius scale.

Lowest temperature possible (absolute zero) is zero Kelvin.

Absolute zero: 0 K = -273.15^{o}C.

Celsius Scale

Also used in science.

Water freezes at 0^{o}C and boils at 100^{o}C.

To convert: K = ^{o}C + 273.15.

Fahrenheit Scale

Not generally used in science.

Water freezes at 32^{o}F and boils at 212^{o}F.

Temperature

- The Fahrenheit scale is not used in scientific measurements.
- $^{o}F = 1.80\ (^{o}C\ ) + 32$
- $^{o}C = 0.56\ (^{o}F\ \ ) - 32$

Summary

Conversion of Temperature Units

- Celsius to Kelvin $\leftrightarrow$ $T_K = T_{^\circ C} + 273$
- Kelvin to Celsius $\Leftrightarrow$ $T_{^\circ C} = T_K - 273$
- Celsius to Fahrenheit $\Leftrightarrow$ $T_{^\circ F} = 1.80\,(T_{^\circ C}) + 32$
- Fahrenheit to Celsius $\Leftrightarrow$ $T_{^\circ C} = \frac{(T_{^\circ F})}{1.80} - 32$

Measurement

- The cube with a volume of 1dm^3 (1 liter) can in turn be broken into 1000 smaller cubes, each representing a volume of 1 cm^3. This means that each liter contains 1000 cm^3.
- One cubic centimeter is called a milliliter (abbreviated mL), a unit of volume used very commonly in chemistry. This relationship is summarized in Table below;

Relationship between liter and milliliter.

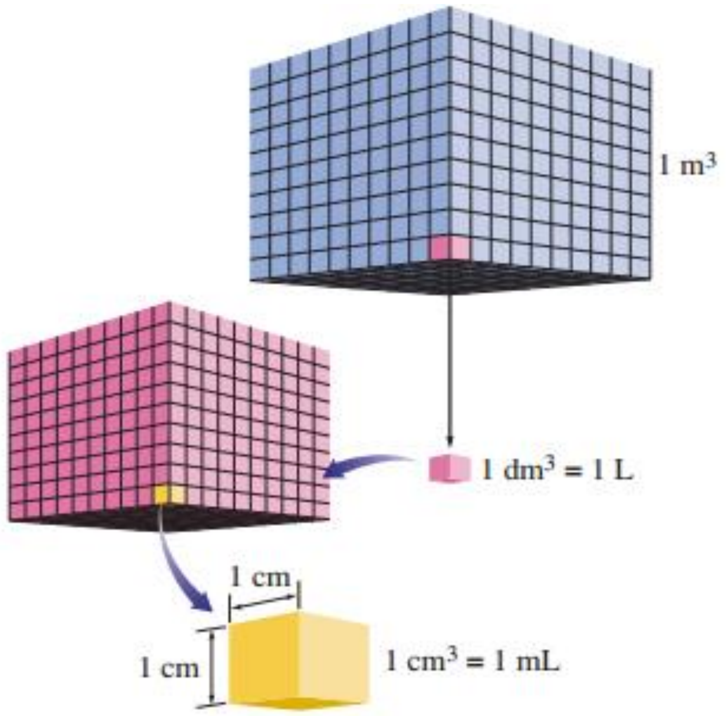
Unit	Symbol	Equivalent
Liter	L	1L=1000 mL
milliliter	mL	$= \frac{1}{1000} L = 10^{-3}$ L = 1mL

measurements

- Volume is the amount of three-dimensional space occupied by a substance. The fundamental unit of volume in the SI system is based on the volume of a cube that measures 1 meter in each of the three directions.
- That is, each edge of the cube is 1 meter in length. The volume of this cube is
- 1 m x1 m x1 m = $(1\mathbf{m})^3$ = $1\mathbf{m}^3$ or, in words, one cubic meter.
- In the figure below the cube is divided into 1000 smaller cubes. Each of these small cubes represents a volume of 1 $\mathbf{dm}^3$, which is commonly called the **liter** (rhymes with “meter” and is slightly larger than a quart) and abbreviated L.

Volume

- Measure of the amount of three dimensional space occupied by a substance.
- SI unit = cubic meter (m^3)
- Commonly measure solid volume in cm^3.
- 1 mL = 1 cm^3
- 1 L = 1 dm^3



Pressure

- SI Unit of pressure is pascal (Pa)
- 1 pascal = 1 $\mathbf{Nm}^{-2}$ = 1 $\mathbf{kgm}^{-1}\mathbf{s}^{-2}$
- 1 atmosphere = 101.325 kPa = 760 torr (mm Hg) = 14.70 pounds per square(Psi) inch
- 1 bar = 105 pascals (Pa)

Density

- A student wants to identify the main component in a commercial liquid cleaner. He finds that 35.8 mL of the cleaner weighs 28.1 g. Of the following possibilities, which is the main component of the cleaner?

Substance	Density, g/cm3
chloroform	1.483
diethyl ether	0.714
isopropyl alcohol	**0.785. ans**
toluene	0.867

Density

- Density can be defined as the amount of matter present in a given volume of substance. That is, density is mass per unit volume, the ratio of the mass of an object to its volume:
- This is because lead has a much greater mass per unit volume a greater density.

$$\textbf{Density} = \frac{\textbf{mass}}{\textbf{volume}}$$

- Mercury has a density of 13.6 g/mL. What volume of mercury must be taken to obtain 225 g of the metal? **[16.54mL]**
- Suppose a student finds that 23.50 mL of a certain liquid weighs 35.062 g. What is the density of this liquid? **[1.49g/mL]**
- A gas cylinder having a volume of 10.5 L contains 36.8 g of gas. What is the density of the gas? [**0.35g/mL]**
- Using table 1.6 calculate the volume of 25.0 g of each of the following:

a. hydrogen gas (at 1 atmosphere pressure)

b. gold

c. iron

d. water

Density of selected substances

Table 2.8 Densities of Various Common Substances at 20 °C

Substance	Physical State	Density (g/cm^3)
oxygen	gas	0.00133*
hydrogen	gas	0.000084*
ethanol	liquid	0.785
benzene	liquid	0.880
water	liquid	1.000
magnesium	solid	1.74
salt (sodium chloride)	solid	2.16
aluminum	solid	2.70
iron	solid	7.87
copper	solid	8.96
silver	solid	10.5
lead	solid	11.34
mercury	liquid	13.6
gold	solid	19.32

*At 1 atmosphere pressure

Density

- A sample of a liquid solvent has a density of 0.915 g/mL. What is the mass of 85.5 mL of the liquid? **[78.23g]**
- An organic solvent has a density of 1.31 g/mL. What volume is occupied by 50.0 g of the liquid? **[38.17]**
- A certain mineral has a mass of 17.8 g and a volume of 2.35 cm3. What is the density of this mineral? **[7.57g/mL]**
- Suppose a student finds that 23.50 mL of a certain liquid weighs 35.062 g.What is the density of this liquid**?**

Assignment

- An ice cube measures 3.50 cm on each edge and weighs 39.45 g.

a. Calculate the density of the ice.

b. Calculate the mass of 400.4 mL of water in the ice cube

Solution ;

a. $$\textbf{Density} = \frac{39.45\textbf{g}}{42.88\textbf{cm}^3} = 0.92\textbf{gcm}^{-3}$$

mass= density x volume. **Volume of water is** $1\textbf{g}/\textbf{mL}$

Mass = 400.4mL x $1\textbf{g}/\textbf{mL}$= **400.4g**

Applications of Measurements and Conversion Factors in Medicine

- Quantity measurements are of great importance in clinical practice.
- Both doctors and nurses use measurements everyday while providing healthcare for people around the world.
- Medical professionals use measurements when drawing up statistical graphs of epidemics or success rates of treatments.
- If the weight of a patient is only known in pounds, it must be converted into kilograms and then find the amount of milligrams for the prescription.
- There is a very big difference between mg/kg and mg/lbs!

Applications of Measurements and Conversion Factors in Medicine

- Other routines nurses carry out in the ward which require knowledge of measurement and conversions are
- Temperature;
- Blood pressure; $\frac{120}{80}\,\mathbf{mmHg}$
- Body mass index (BMI), = $\frac{\mathbf{mass(kg)}}{\mathbf{(height)m^2}}$

Applications of Measurements and Conversion Factors in Medicine

- Suppose a patient takes a pill in the morning that has 50mg of a particular medicine.
- When the patient wakes up the next day, their body has washed out 40% of the medication.
- This means that 20mg have been washed out and only 30mg remain in the body.
- The patient continues to take their 50mg pill each morning.
- This means that on the morning of day two, the patient has the 30mg left over from day one, as well as another 50mg.

APPLICATIONS OF MEASUREMENTS AND CONVESION FACTORS IN MEDICINE

- Consider an order of 25mcg/kg/min. If the patient weighs 52kg, how many milligrams should he/she receive in one hour?
- If 1mcg = 0.001mg, then 1/0.001 = 25/x. Thus x = 0.025; implying that
- 25mcg = 0.025 mg.
- Thus a patient who weighs 52kg will receive 0.025mg x 52kg =1.3mg/min.
- Since 60s = 1 hour, so in one hour the patient receives 1.3mg x 60; making 78mg per hour.

The Atom

- The atomic structure consist of a central part called the **nucleus** and a hollow space surrounding it called **shell**.
- Most of the mass of the atom is in by the **nucleus**. The number of shells an atom has is determined by the number of electrons of the atom.
- The highest occupied electron shell is called the **valence shell**, and the electrons occupying this shell are called **valence electrons**.
- The atom is the smallest part of matter that represents a particular element. It is made up of three sub atomic particles namely; **protons neutrons** and **electrons.**
- An **element** is a substance composed of a single kind of atom

Atomic Symbols

The atomic symbol shows the mass number and atomic number

Give the symbol of the element.

mass number → $^{23}_{11}$**Na sodium-23**

atomic number →

Atomic Mass

Gives the mass of "average" atom of each element compared to ^{12}C

Atomic Number

An atom is neutral if its net charge is zero.

Number of protons = Number of electrons

Atomic number = Number of electrons

Isotopes

Atoms with the same number of protons, but different numbers of neutrons.

Atoms of the same element (same atomic number) with different mass numbers

Isotopes of chlorine

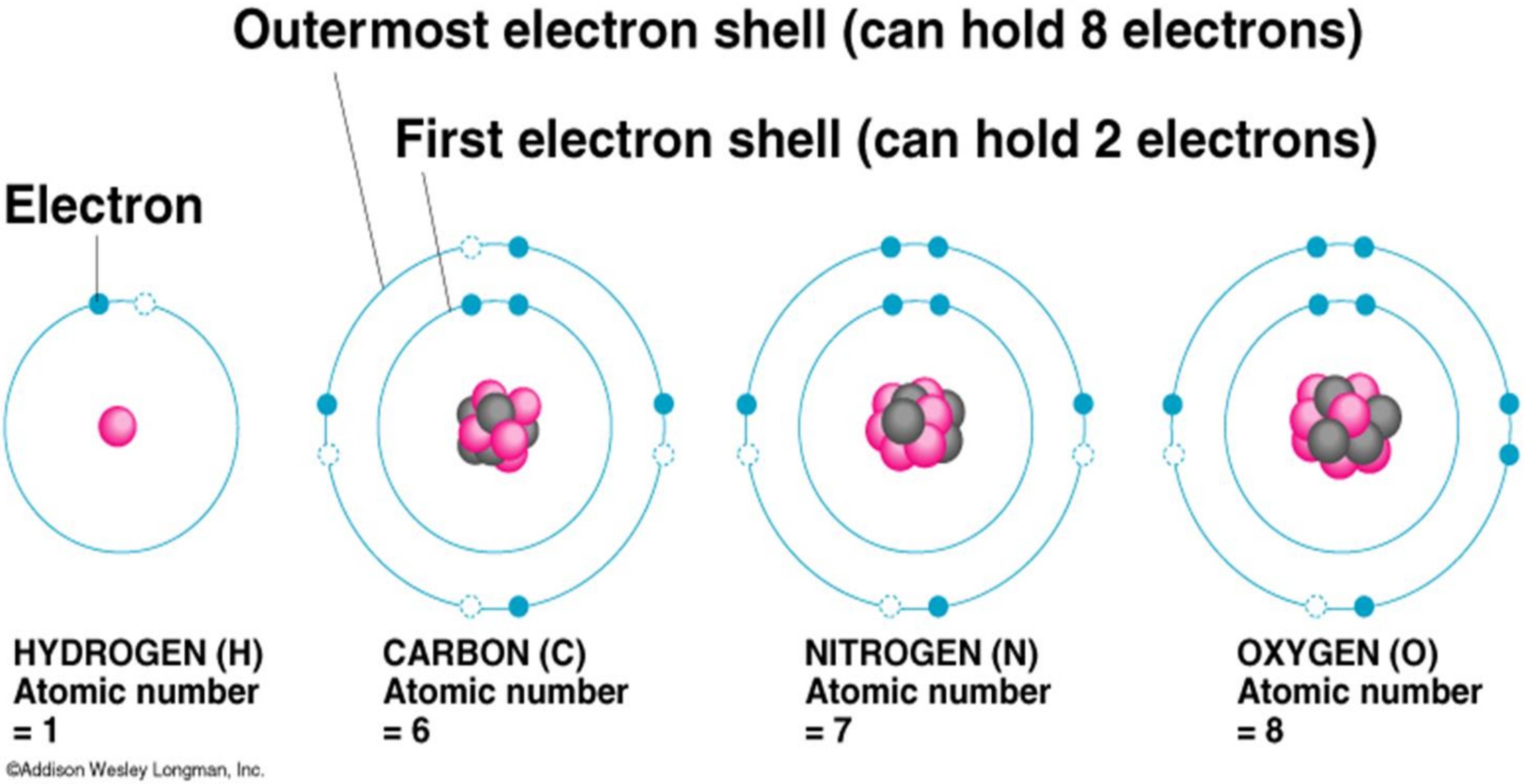
$^{35}_{17}Cl$ $^{37}_{17}Cl$

chlorine - 35 chlorine - 37

Electron Configurations and Orbital Diagrams

- The electronic configuration of an atom is a numeric representation of its electron orbitals.
- Electron orbitals are differently-shaped regions around the nucleus of an atom where electrons are mathematically likely to be located.
- An electron configuration can quickly and simply tell a reader how many electron orbitals an atom has as well as the number of electrons populating each of its orbitals.

Electron Configuration



Quantum Theory

- According to the quantum theory it is impossible to determine the exact position and momentum of an electron at the same time.
- Scientist therefore used the quantum mechanical model to represent the structure of the atom.
- Quantum numbers were used to describe the characteristics of electrons and their orbitals.
- **Quantum numbers**
- Principal Quantum Number n
- Angular Momentum Quantum Number **(*l*)**
- Magnetic Quantum Number **(m*l*)**
- Electron Spin Quantum Number (m*s*)

Quantum Numbers

Symbol	Values	Description
n (principal)	1, 2, 3, ..	Orbital size and energy of the electron
l (angular)	0, 1, 2, .. n-1	Orbital shape or type (subshell)
m_l (magnetic)	-l..0..+l	Orbital orientation in space
m*s* (Electron Spin)	-1/2 or +1/2	Direction of spins: clockwise or anti-clockwise

Principal Quantum Number n

- n determines the size of the orbital and as well the energy of the electron. The higher the n value the higher the energy of the electron. n also determines the distance of an electron from the nucleus; the higher the n value the greater the electron from the nucleus
- For n = 1, l = 0 and m_l = 0

There is only one subshell and that subshell has a single orbital

(m_l has a single value ---> 1 orbital)

This subshell is labeled **s** and we call this orbital **1s**

Each shell has 1 orbital labeled s. It is **spherica**l in shape.

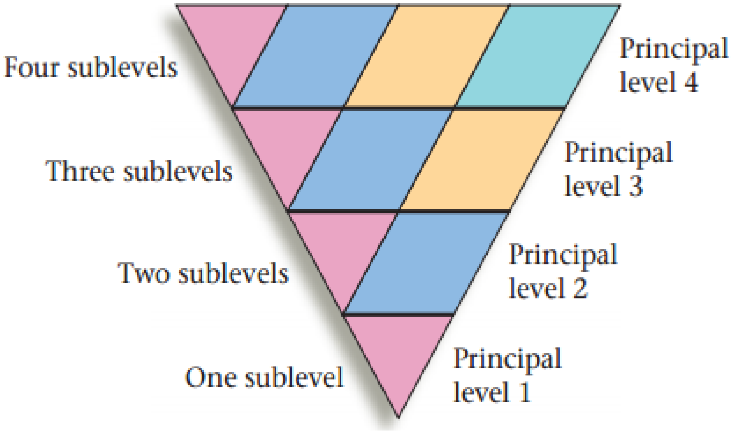
Angular Momentum Quantum Number (l)

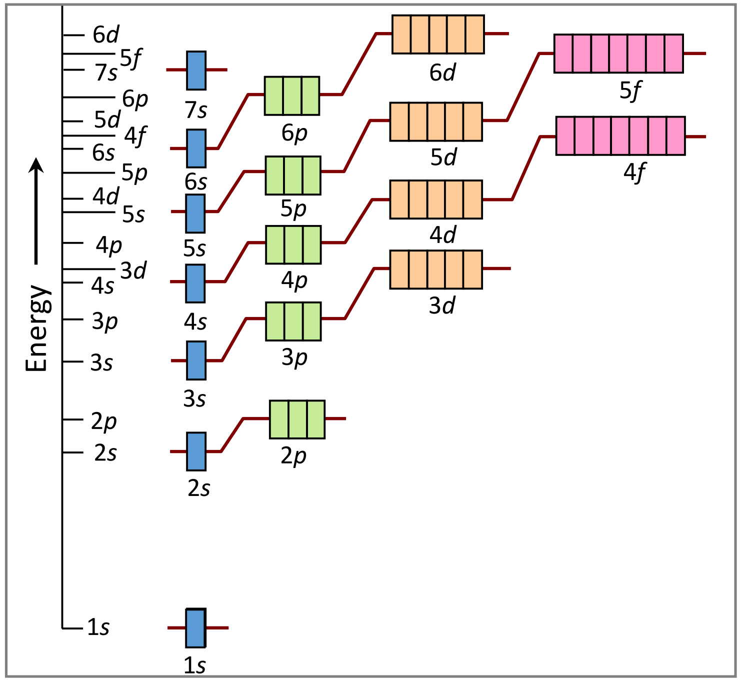
- l determines the shape of the orbital. It depends on the value of n. it gives the number of subshells an orbital has
- For example
- If n = 2; l = 0, 1
- n = 3; l = 0, 1, 2.
- Values of l are generally designated by the letters *s*, *p*, *d*, *f*. corresponding to n=1, n =2, n=3, n=4…….

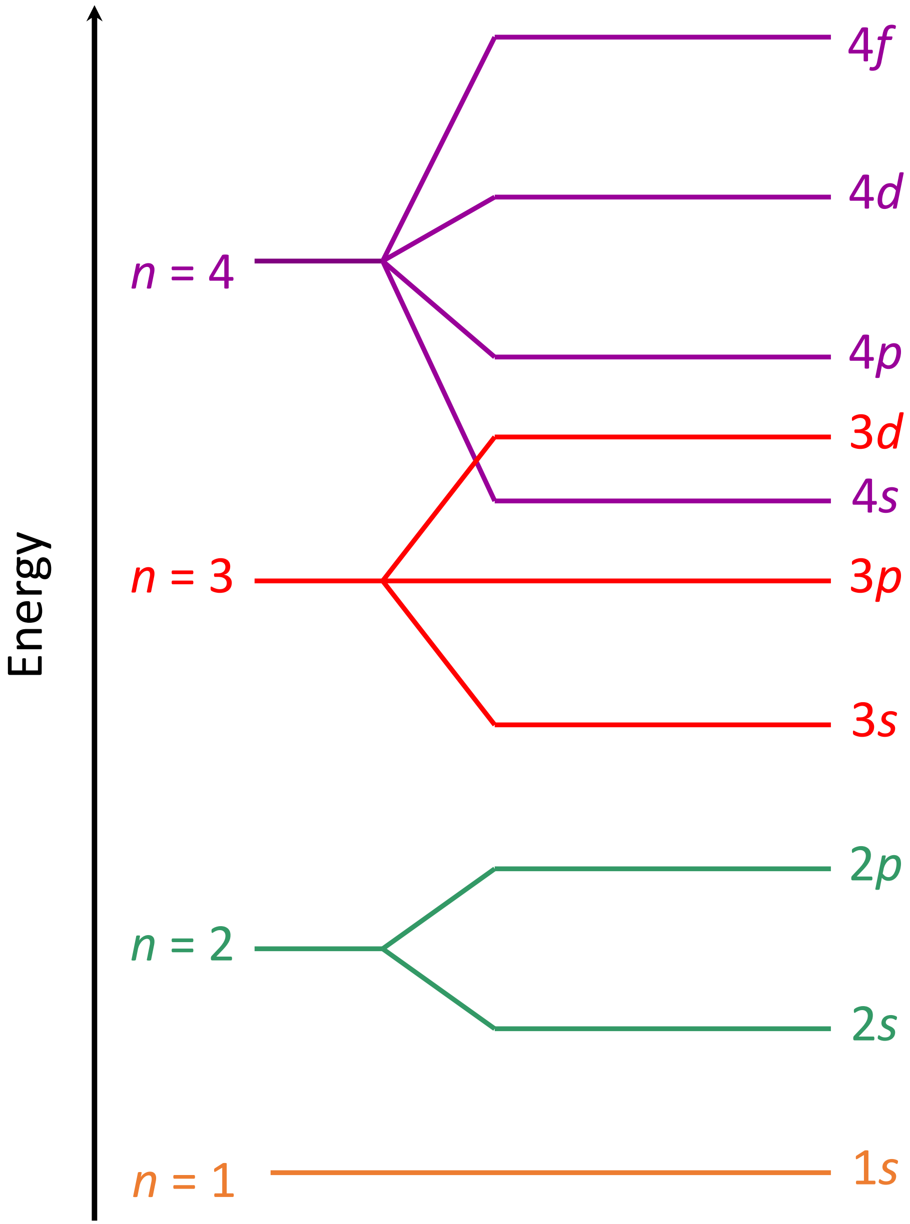
Magnetic Quantum Number (m_l)

- It describes the orientation of the orbital in space.
- Within a sub-shell, the value of m_l depends on the value of the angular momentum quantum number *l*.

- Values of m*l* are given by (2*l*+1). Hence
- If $l = 0$, then $m_l = 0$.
- If $l = 1$, then there are [(2 x 1) + 1] or three values of m_l namely, -1, 0, 1.
- If $l = 2$, m*l* has five values ie five positions


Four sublevels
Three sublevels
Two sublevels
One sublevel
Principal level 4
Principal level 3
Principal level 2
Principal level 1

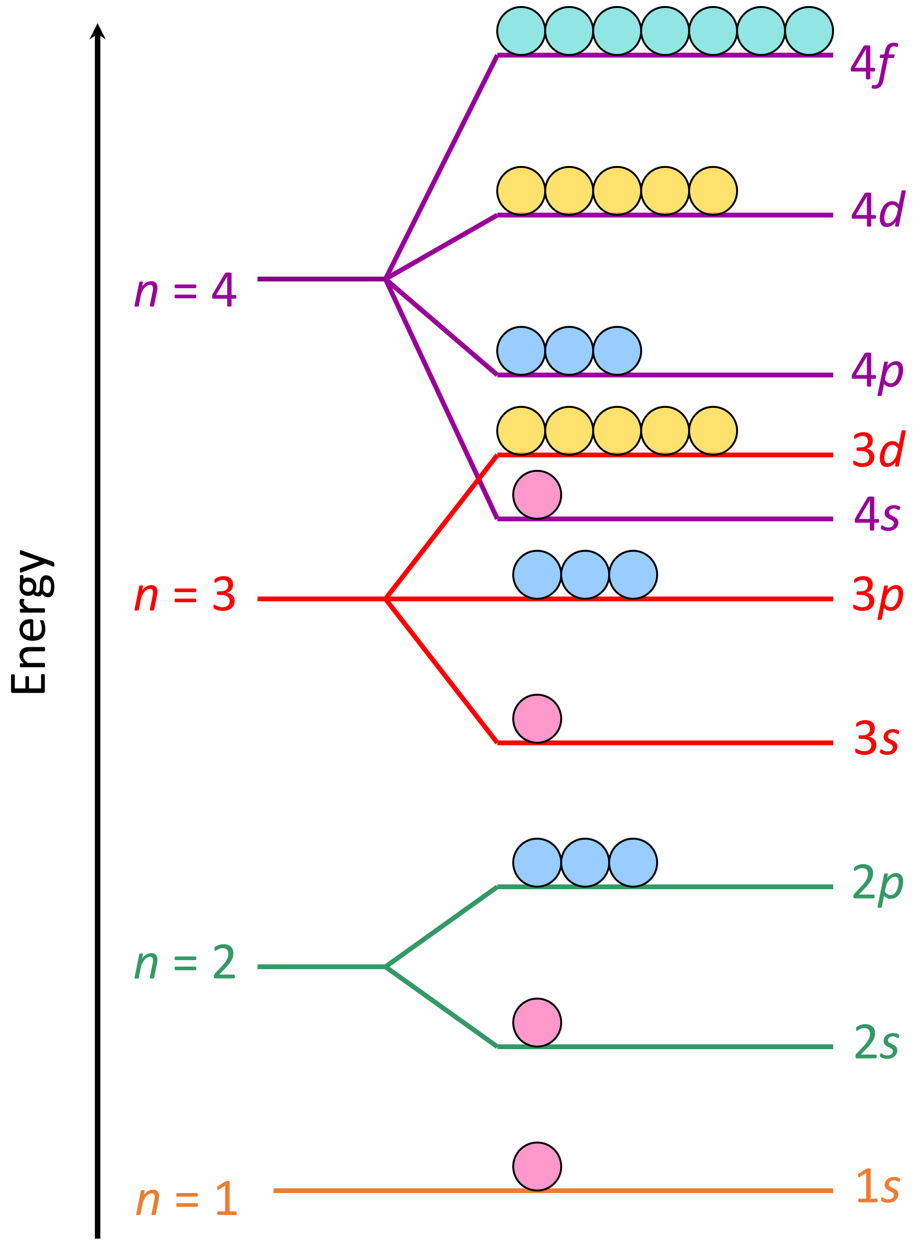

Energy
6d
7s
5f
6p
5d
4f
6s
5p
4d
5s
4p
4s
3d
3p
3s
2p
2s
1s


Energy
n = 4
n = 3
n = 2
n = 1
4f
4d
4p
3d
4s
3p
3s
2p
2s
1s

Sublevels

s p d f
s p d
s p
s

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$…



Maximum Number of Electrons in the various Subshells

The maximum no of electrons in the various subshells is given as follows

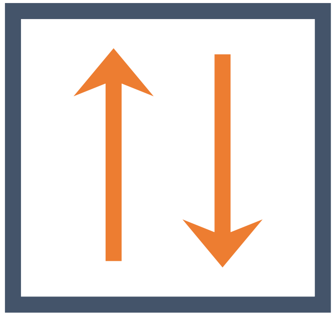
Subshell	Number of Orbitals	Maximum Number of Electrons
s(l=0)	1	2
p(l=1)	3	6
d(l=2)	5	10
f(l=3)	7	14

Principles Determine the Arrangement of Electron in the Orbitals.

- **Pauli Exclusion Principle**;
- No two electrons in the same atom can have the same set of quantum numbers or occupy the same orbital.
- To occupy the same orbital, two electrons must spin in opposite directions.
- The Pauli Exclusion Principle can therefore be stated as ‘an orbital can hold at most two electrons only if the electrons have opposite spins’.

General Rules

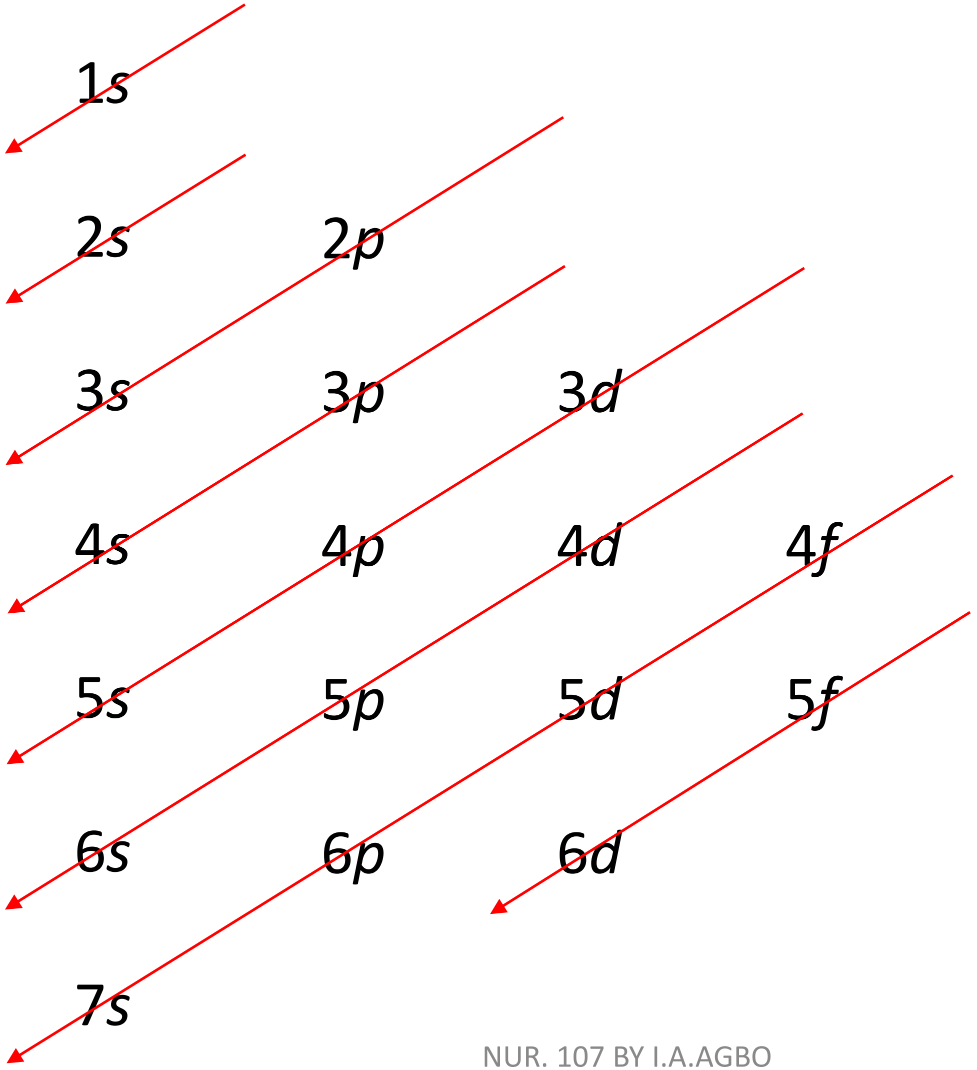
- Pauli Exclusion Principle
  - Each orbital can hold TWO electrons with opposite spins.



Aufbau Principle

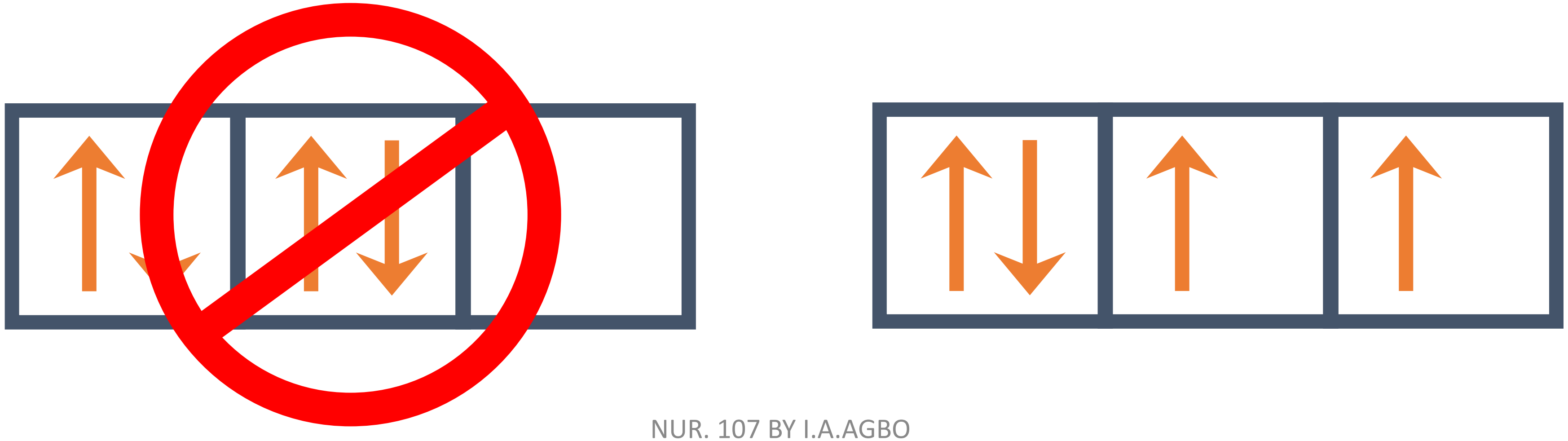
- According to the **Aufbau principle**, the electrons occupy quantum levels or orbitals starting from the lowest energy level, and proceeding to the highest, with each orbital holding a maximum of two paired electrons (opposite spins).
- In other words Electrons are added one at a time to the lowest energy orbitals available until all the electrons of the atom have been accounted for.
- Aufbau principle is also called the **building-up principle** and is a scheme used to reproduce the electron configurations of the ground states of atoms by successively filling subshells with electrons in a specific order (the building-up order).
- Following this principle, you obtain the electron configuration of an atom by successively filling subshells in the following order:
- 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 6f, 7d, 7f. This order reproduces the experimentally determined electron configurations.

Order in which subshells are filled with electrons



Hund's Rule

- Within a sublevel, place one electron per orbital before pairing them.
- "Empty Bus Seat Rule"



H = $1s^1$

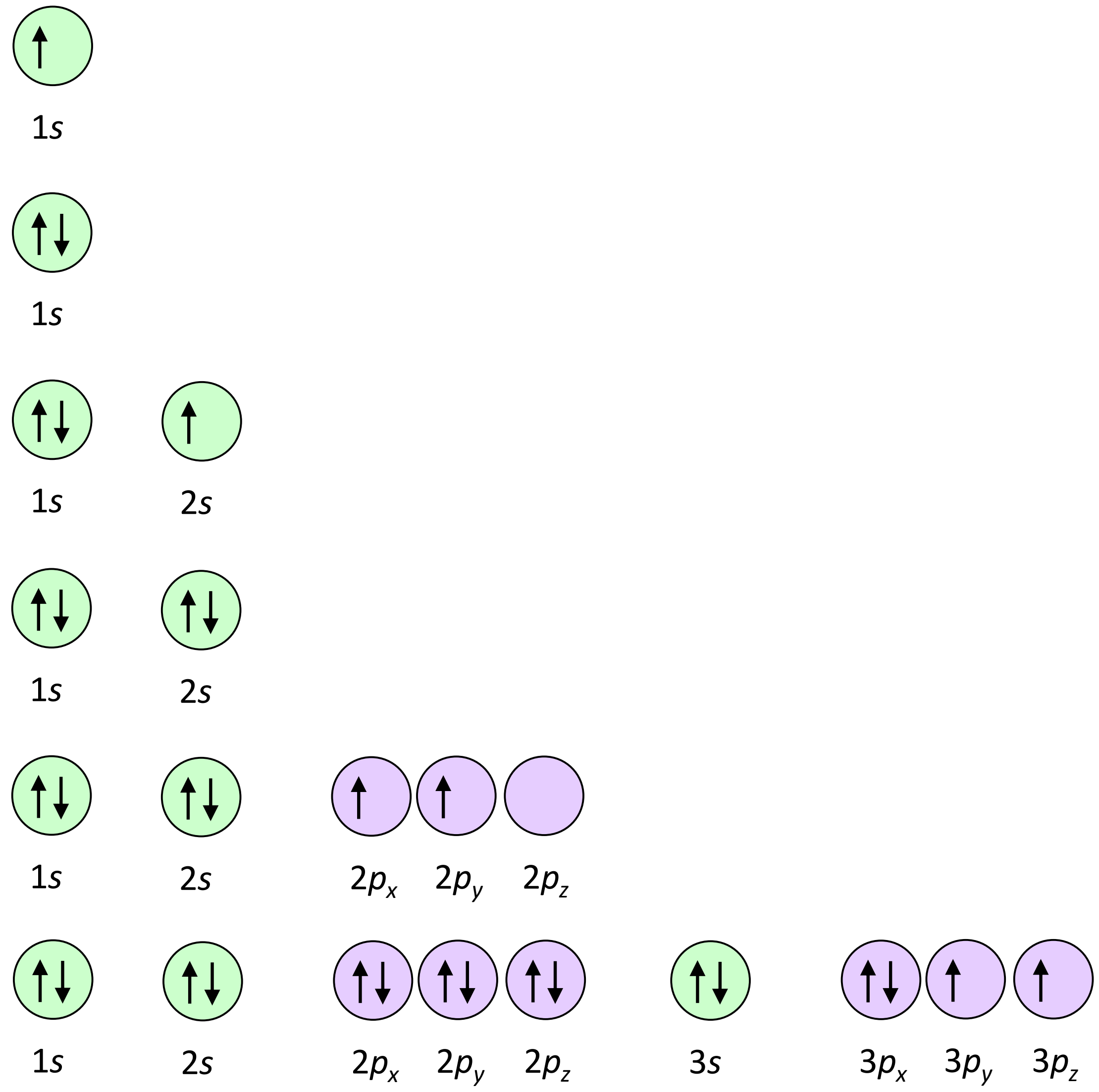
He = $1s^2$

Li = $1s^2\,2s^1$

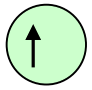
Be = $1s^2\,2s^2$

C = $1s^2\,2s^2\,2p^2$

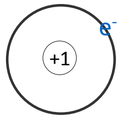
S = $1s^2\,2s^2\,2p^4$



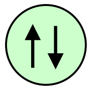
H = $1s^1$



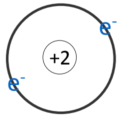
$1s$



He = $1s^2$

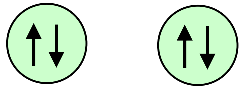


$1s$

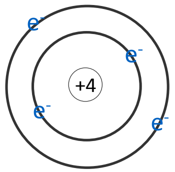


Coulombic attraction holds valence electrons to atom.

Be = $1s^2 2s^2$



$1s$ $2s$

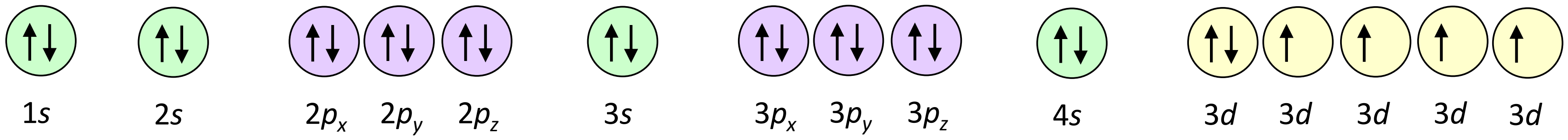


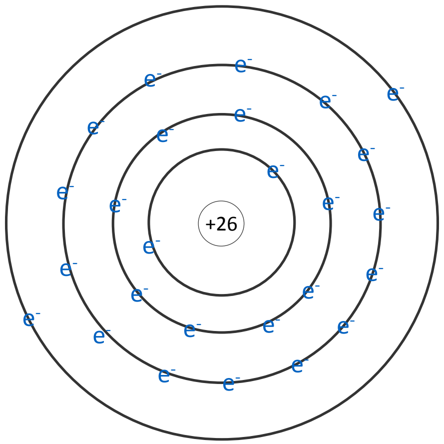
Coulombic attraction holds valence electrons to atom.

Valence electrons are shielded by the kernel electrons.
Therefore the valence electrons are not held as tightly in Be than in He.

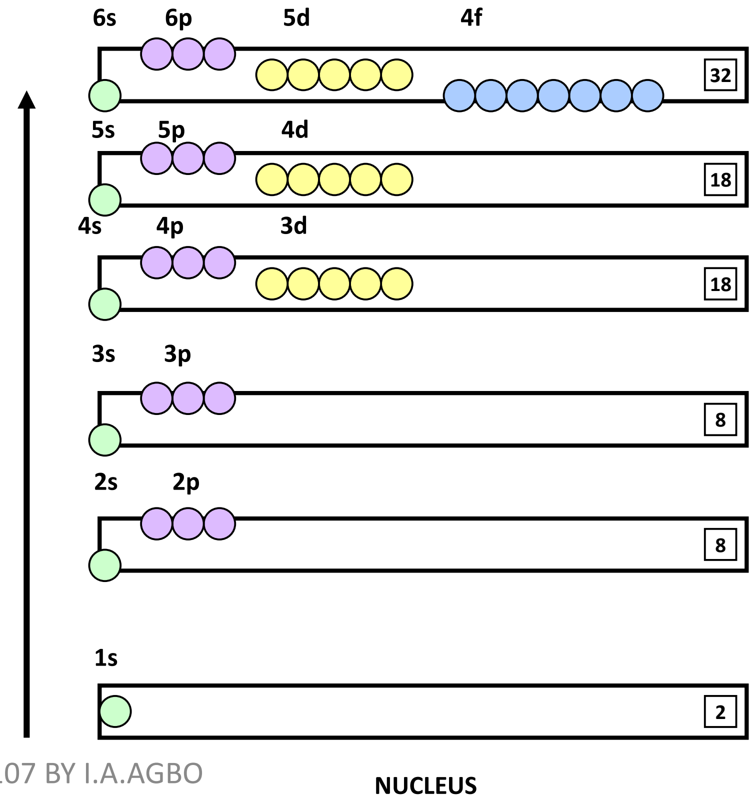
$Fe\ =\ 1s^1\, 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Iron has __26__ electrons.





Arbitrary Energy Scale



Electron Configurations

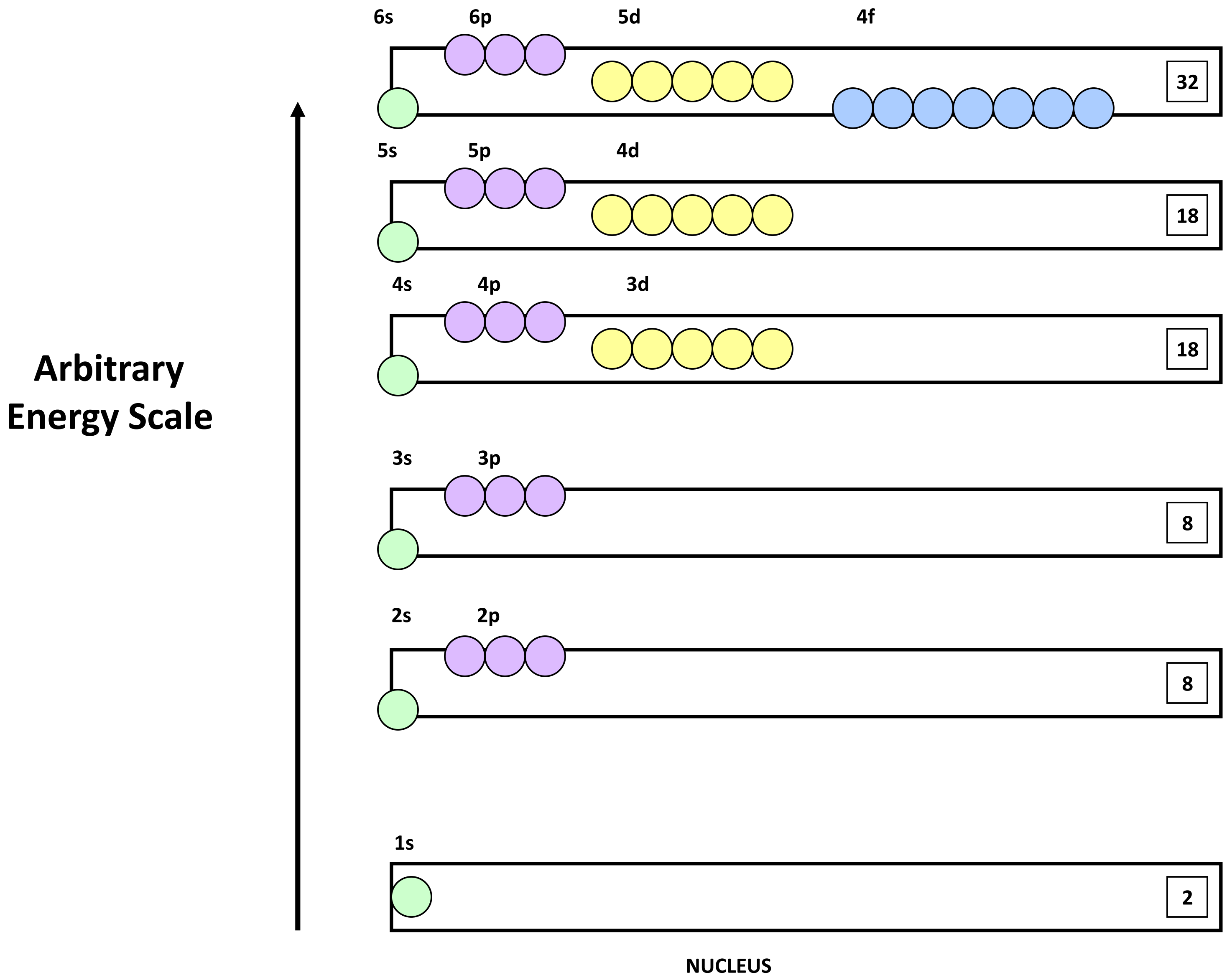
Element	1s	2s	$2p_x$	$2p_y$	$2p_z$	3s	Electron Configuration
H	↑						$1s^1$
He	↑↓						$1s^2$
Li	↑↓	↑					$1s^2 2s^1$
C	↑↓	↑↓	↑	↑			$1s^2 2s^2 2p^2$
N	↑↓	↑↓	↑	↑	↑		$1s^2 2s^2 2p^3$
O	↑↓	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p^4$
F	↑↓	↑↓	↑↓	↑↓	↑		$1s^2 2s^2 2p^5$
Ne	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^2 2s^2 2p^6$
Na	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

NOT CORRECT
…ates …nd's Rule

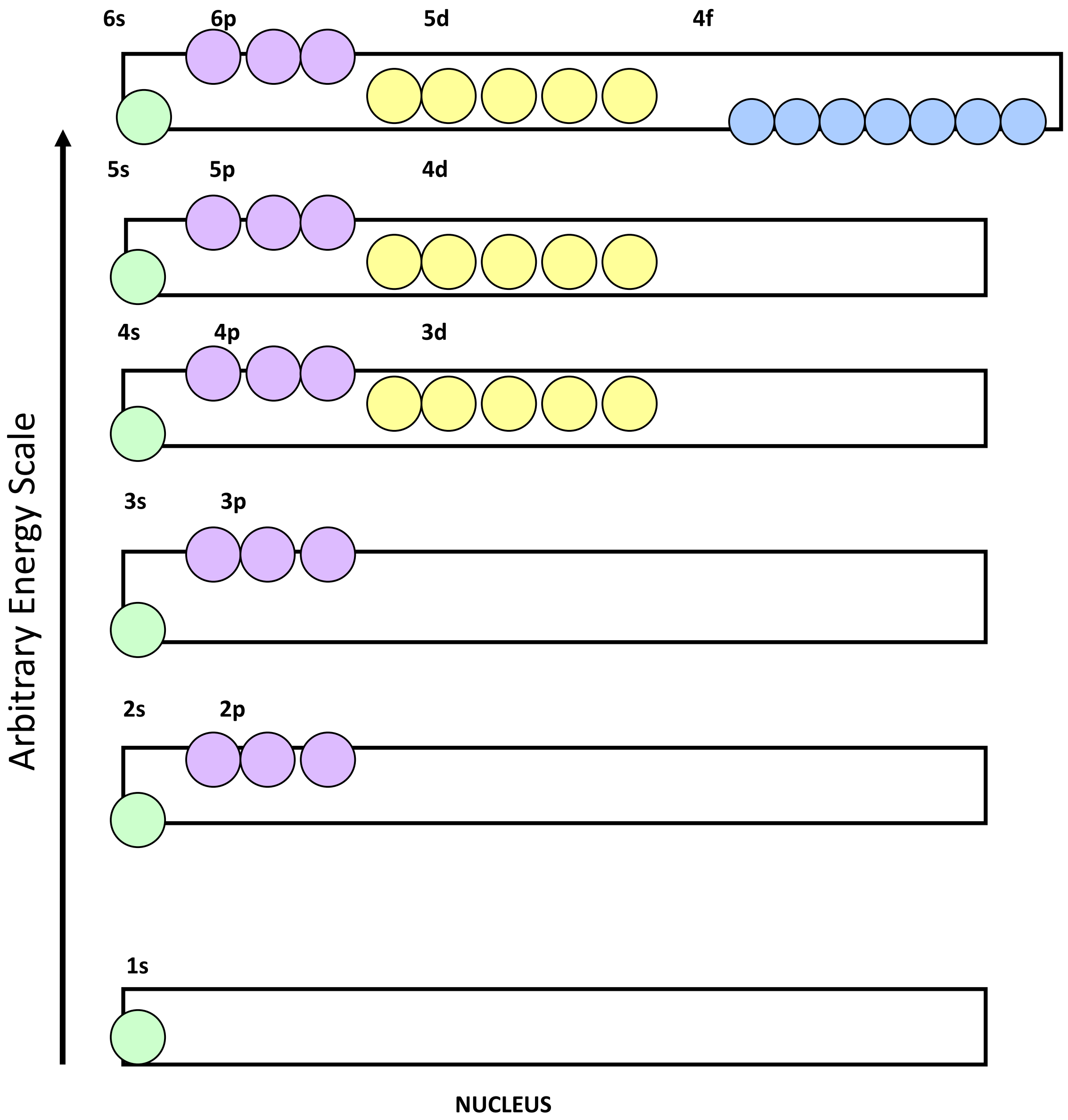
Electron Configurations

Element	1s	2s	$2p_x$	$2p_y$	$2p_z$	3s	Electron Configuration
H	↑						$1s^1$
He	↑↓						$1s^2$
Li	↑↓	↑					$1s^2 2s^1$
C	↑↓	↑↓	↑	↑			$1s^2 2s^2 2p^2$
N	↑↓	↑↓	↑	↑	↑		$1s^2 2s^2 2p^3$
O	↑↓	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p^4$
F	↑↓	↑↓	↑↓	↑↓	↑		$1s^2 2s^2 2p^5$
Ne	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^2 2s^2 2p^6$
Na	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

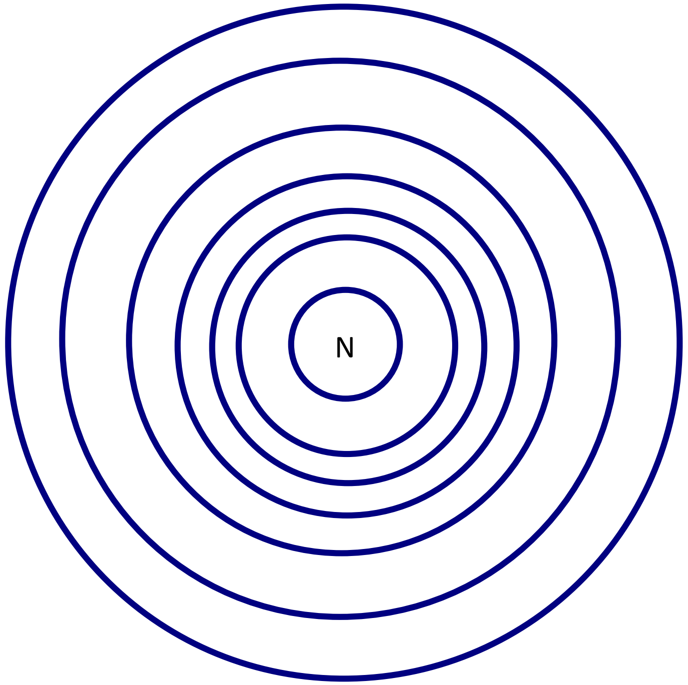
Energy Level Diagram of a Many-Electron Atom



Energy Level Diagram



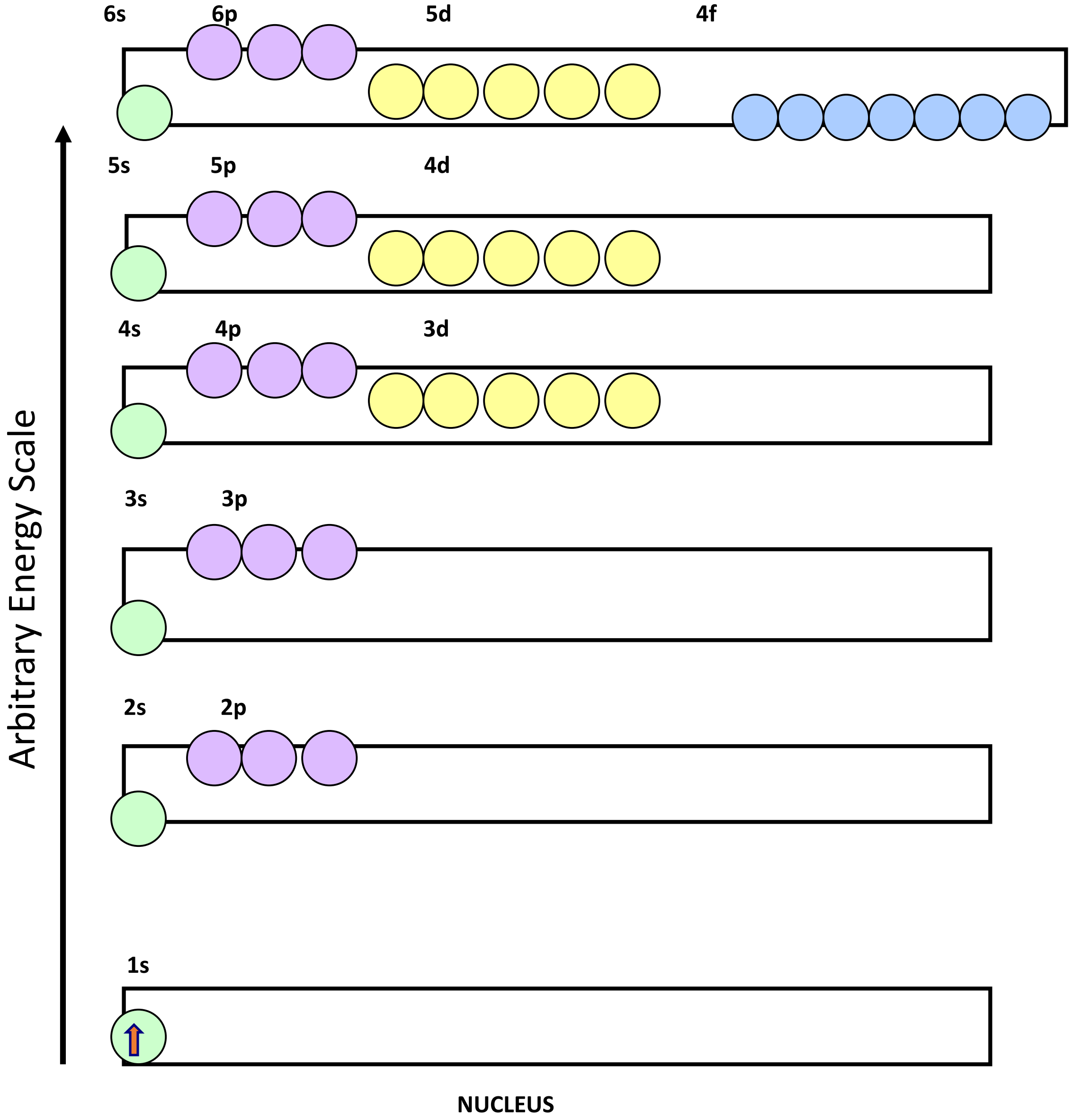
Bohr Model



Electron Configuration

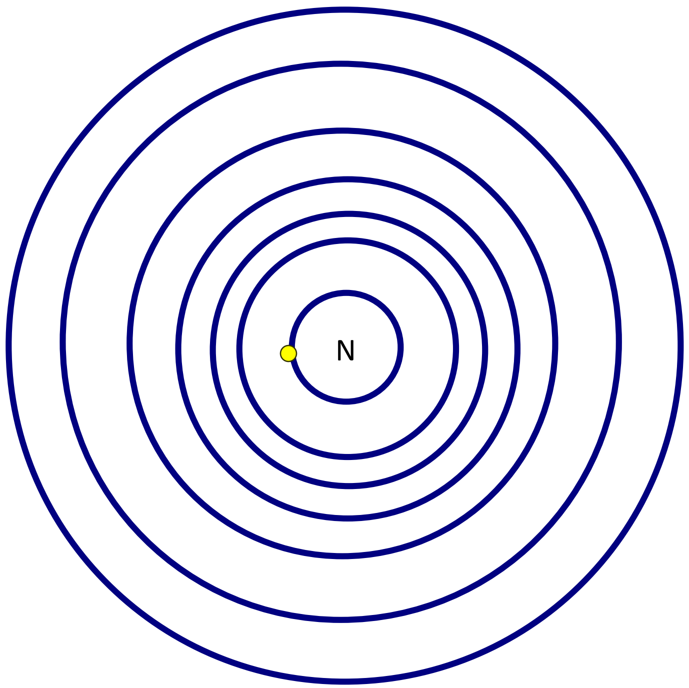
H He Li C N Al Ar F Fe La

Energy Level Diagram



Hydrogen

Bohr Model



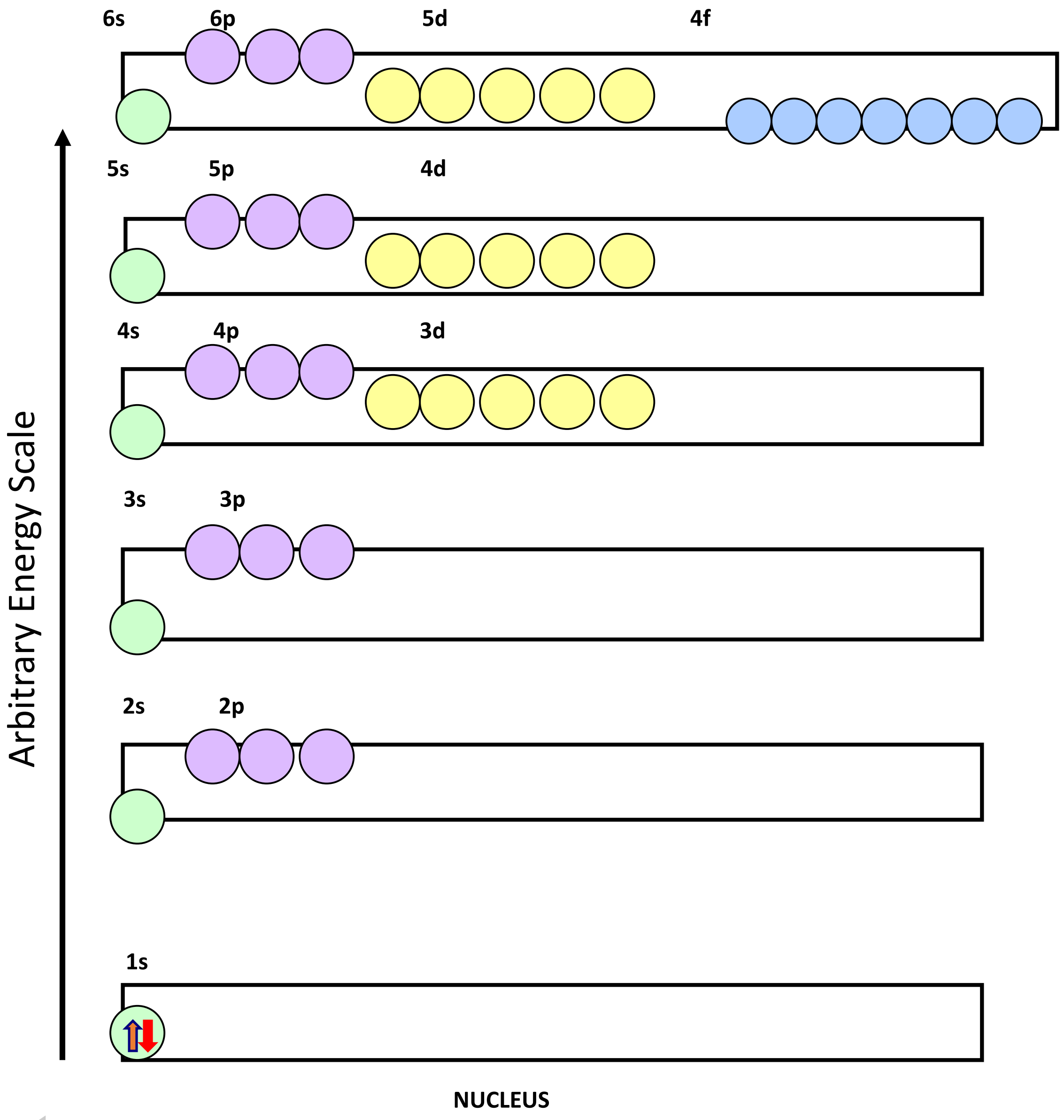
Electron Configuration

H = $1s^1$

H He Li C N Al Ar F Fe La

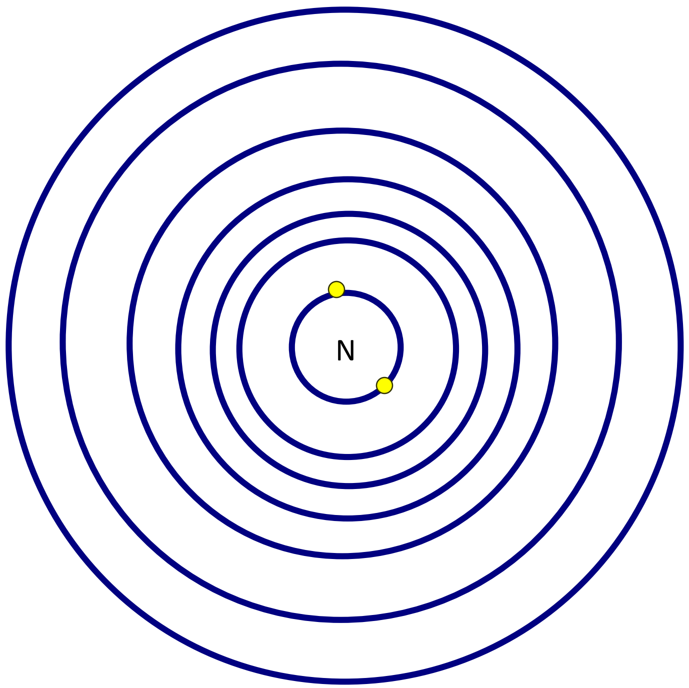
CLICK ON ELEMENT TO FILL IN CHARTS

Energy Level Diagram



Helium

Bohr Model



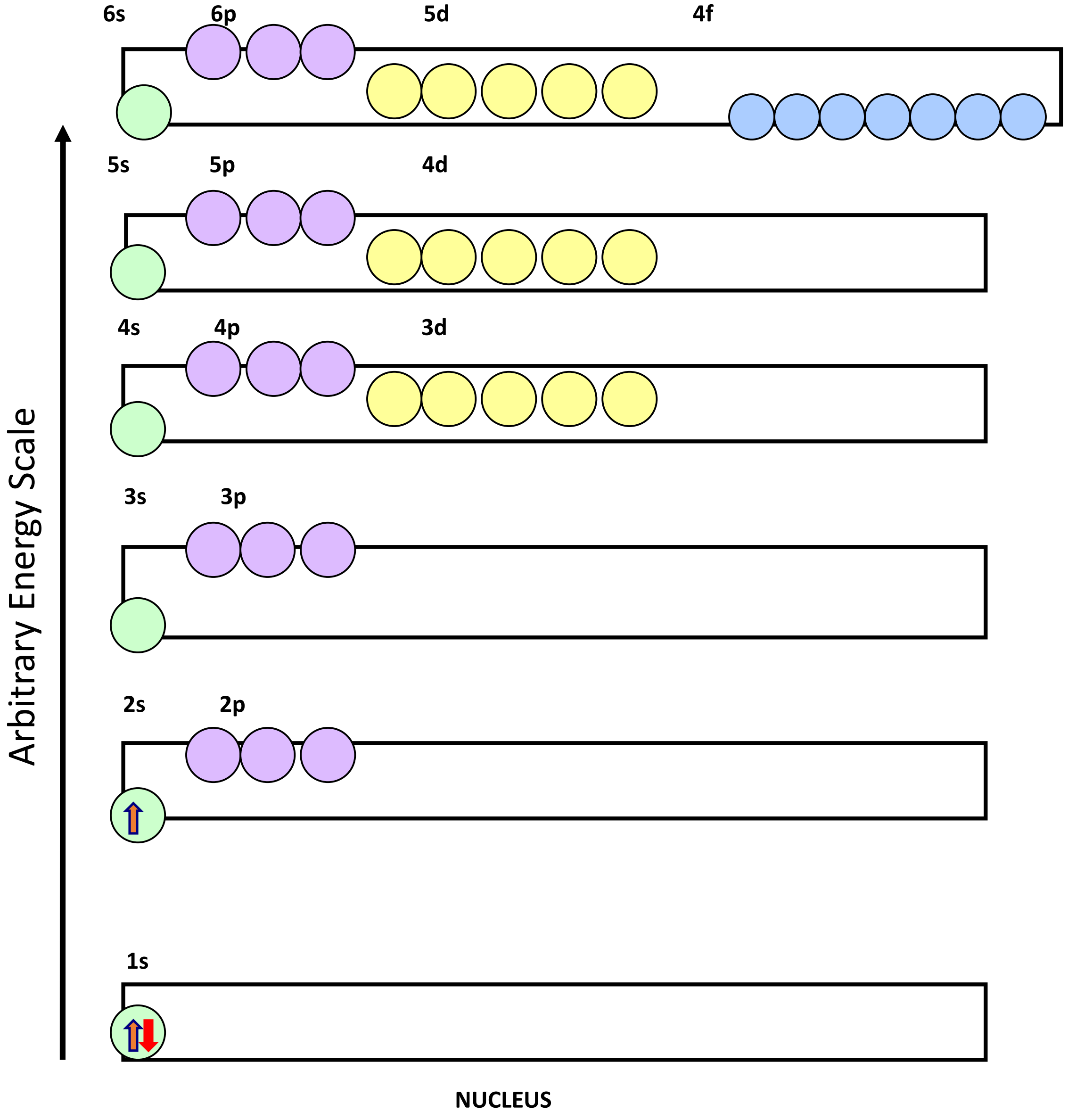
Electron Configuration

He = $1s^2$

H He Li C N Al Ar F Fe La

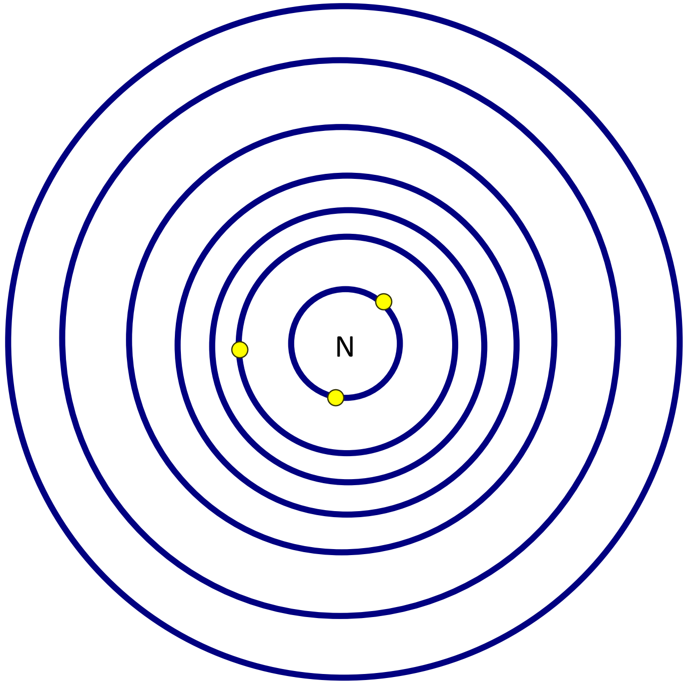
CLICK ON ELEMENT TO FILL IN CHARTS

Energy Level Diagram



Lithium

Bohr Model



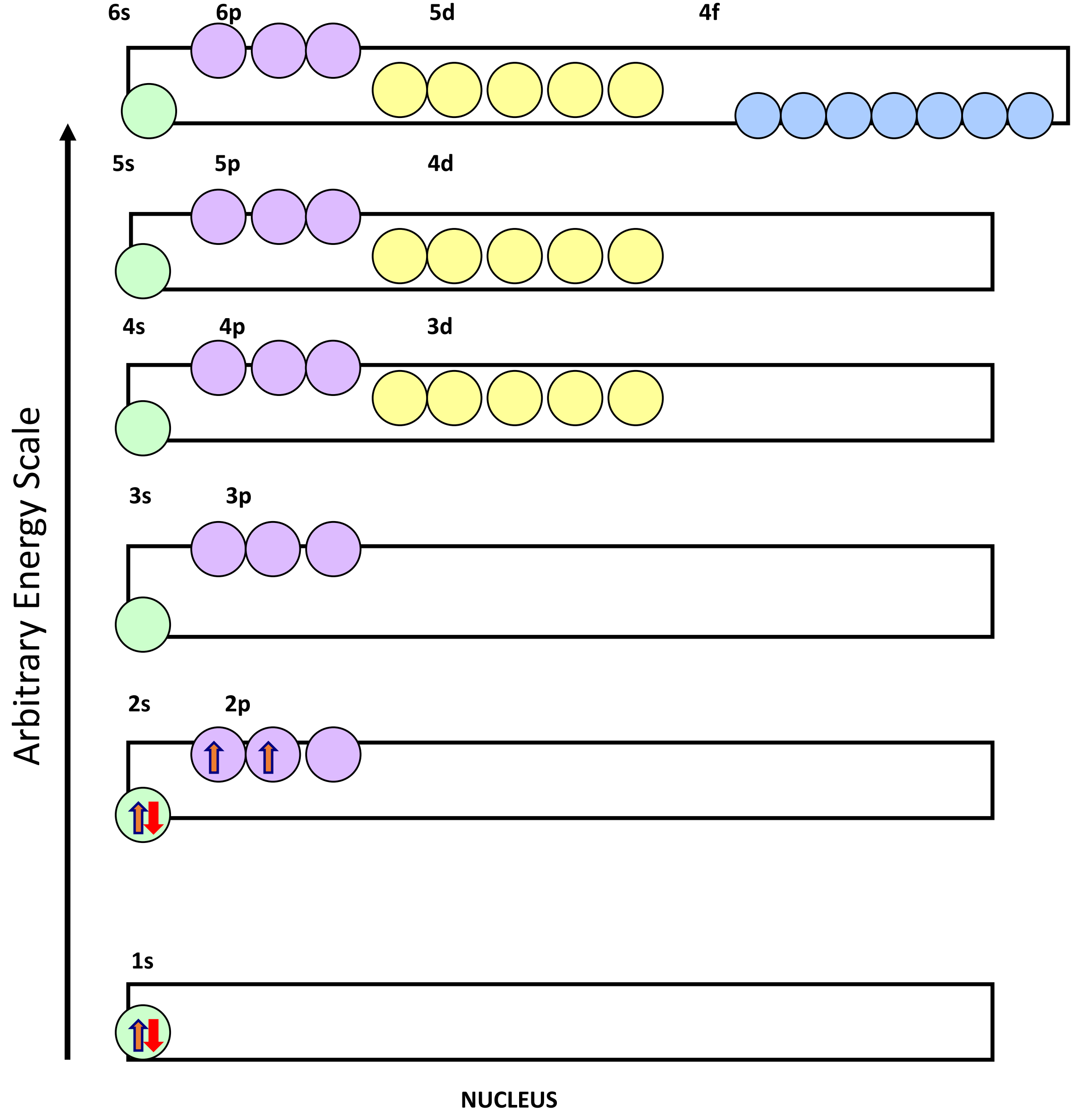
Electron Configuration

Li = $1s^2 2s^1$

H He Li C N Al Ar F Fe La

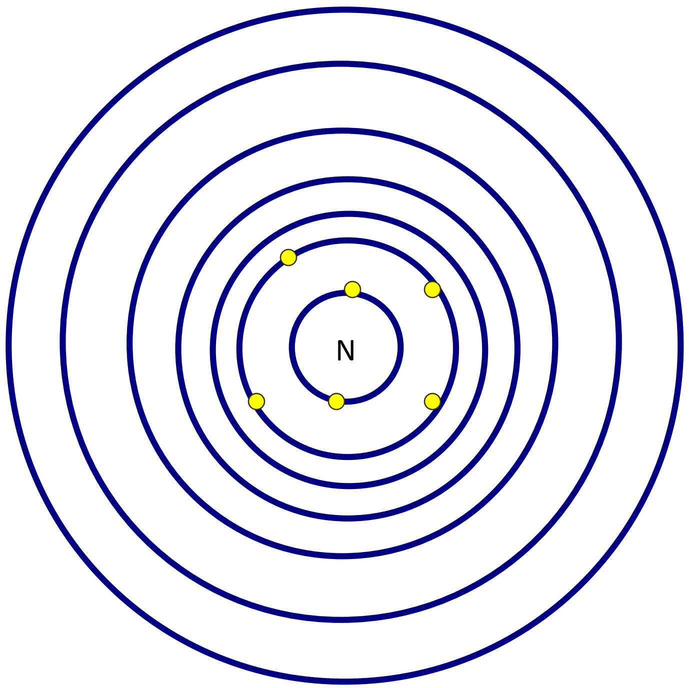
CLICK ON ELEMENT TO FILL IN CHARTS

Energy Level Diagram



Carbon

Bohr Model



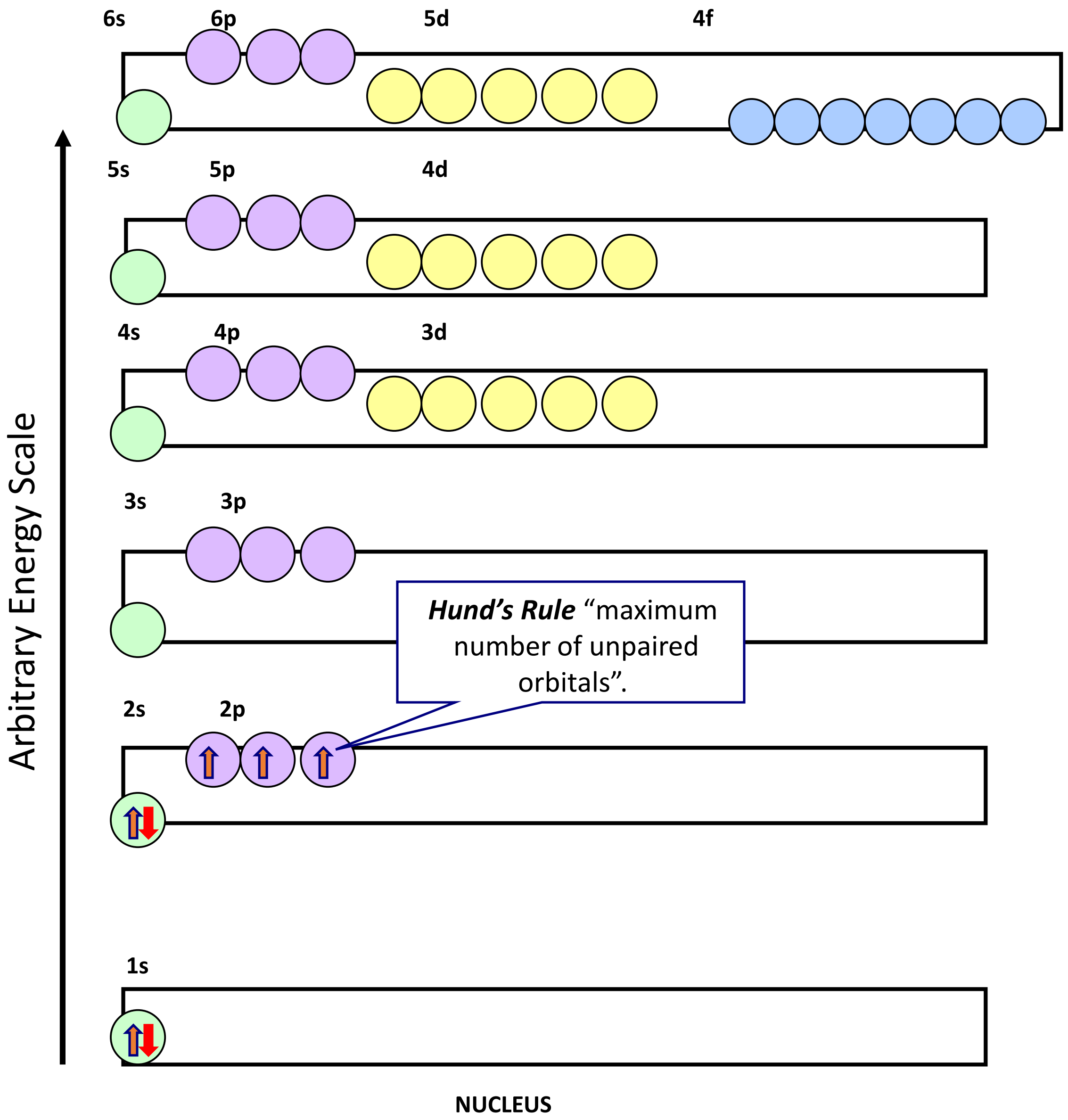
Electron Configuration

$C = 1s^2 2s^2 2p^2$

H He Li C N Al Ar F Fe La

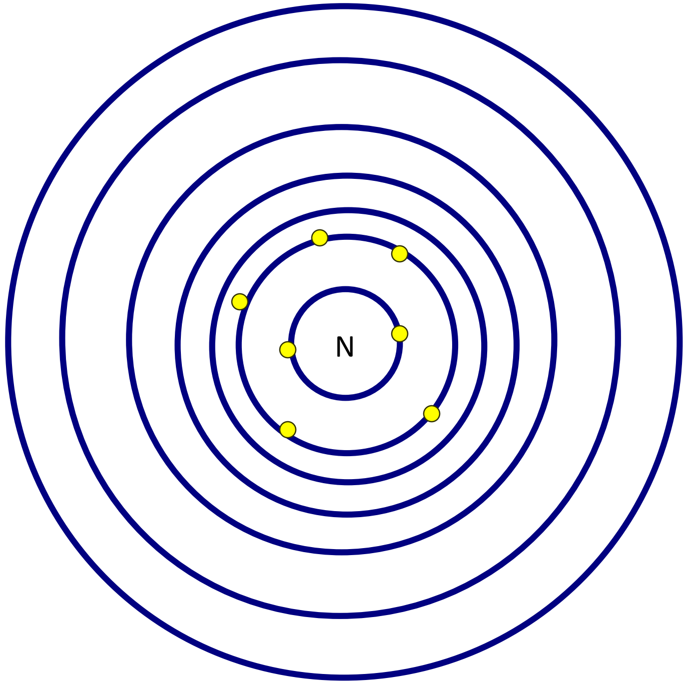
CLICK ON ELEMENT TO FILL IN CHARTS

Energy Level Diagram



Nitrogen

Bohr Model



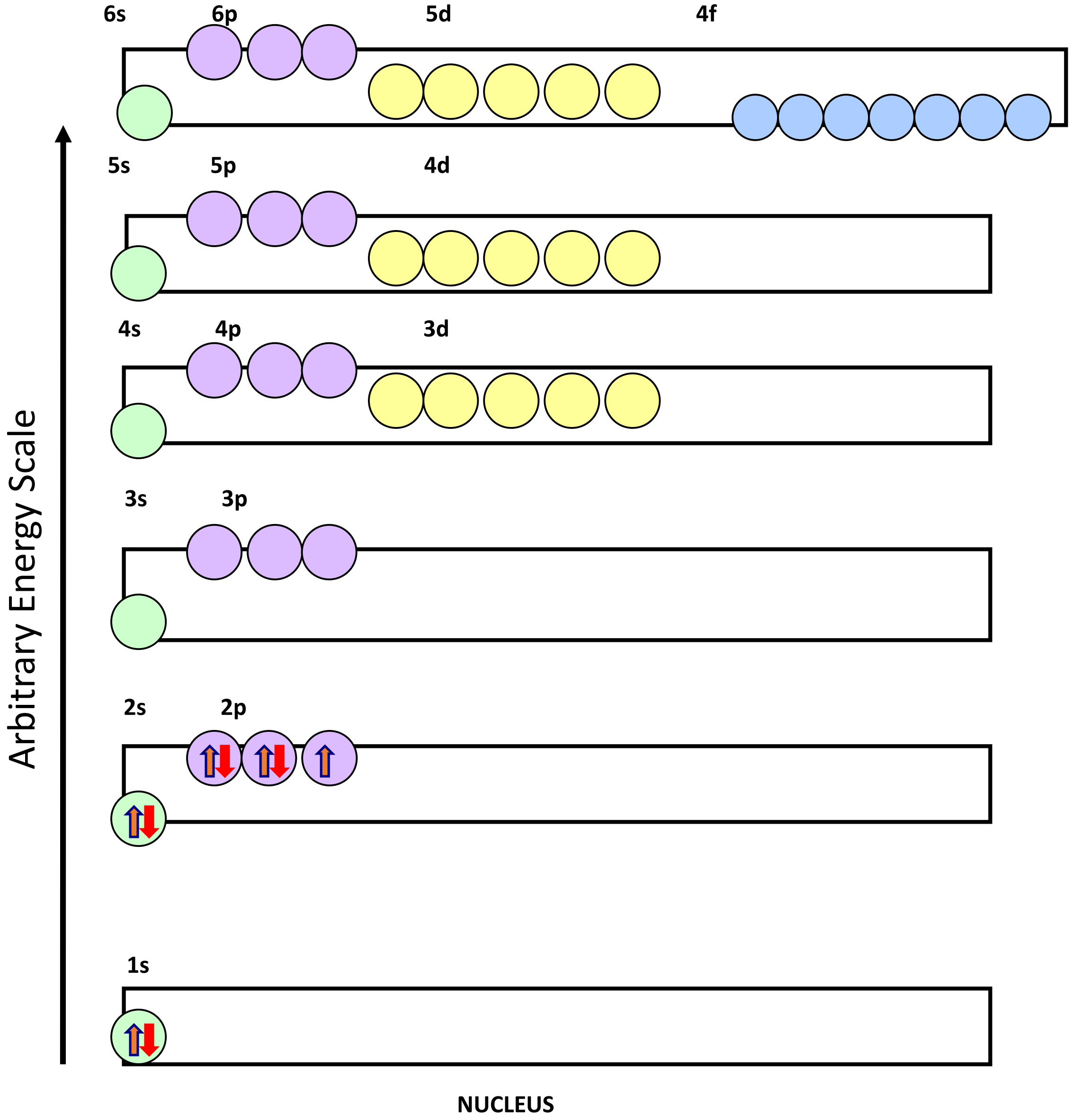
Electron Configuration

$N = 1s^2 2s^2 2p^3$

H He Li C N Al Ar F Fe La

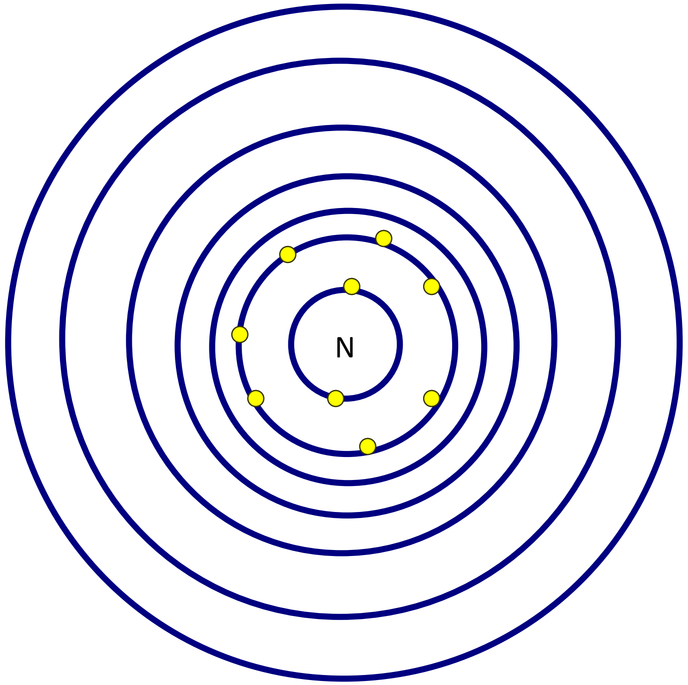
CLICK ON ELEMENT TO FILL IN CHARTS

Energy Level Diagram



Fluorine

Bohr Model



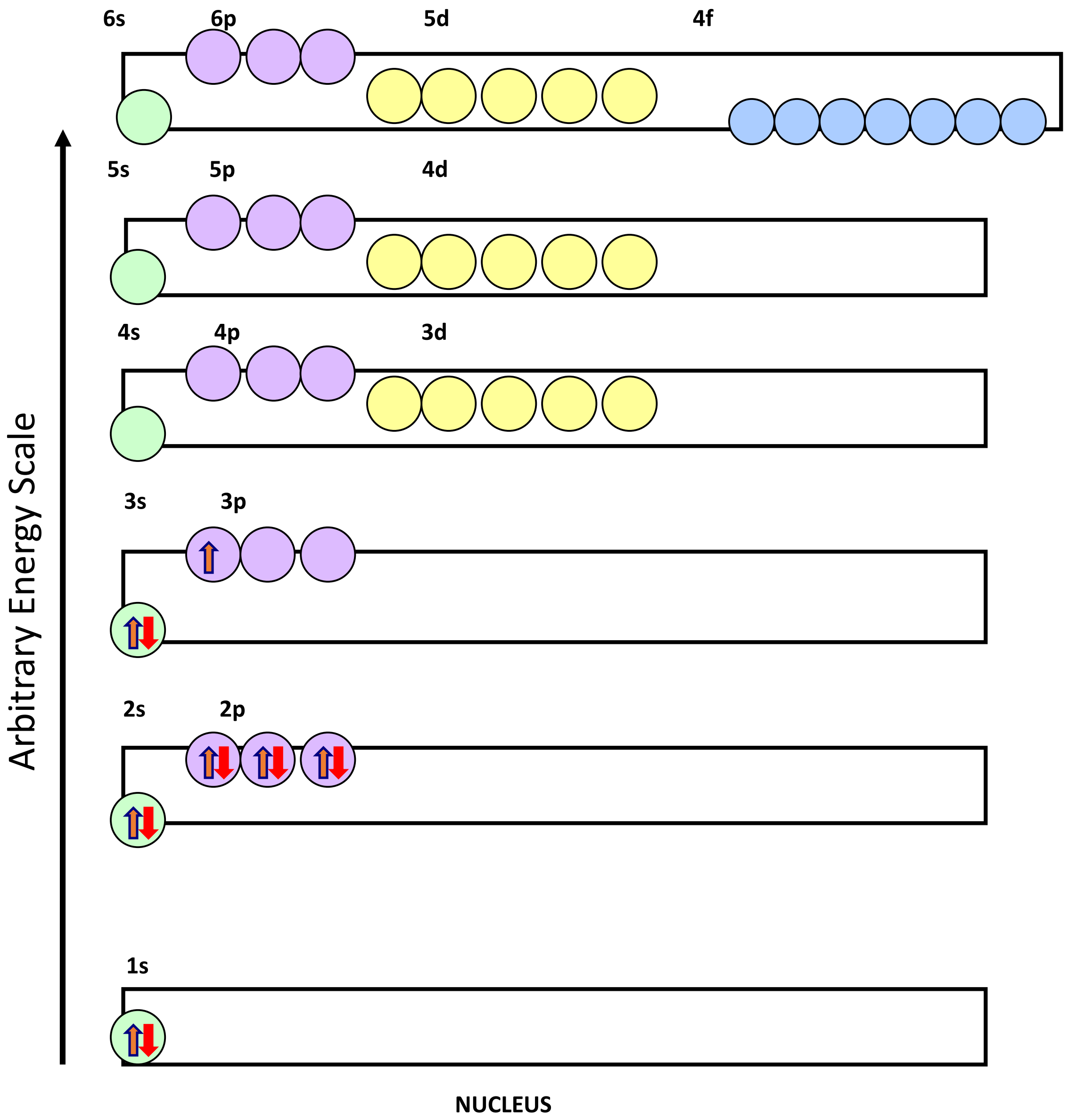
Electron Configuration

$F = 1s^2 2s^2 2p^5$

H He Li C N Al Ar F Fe La

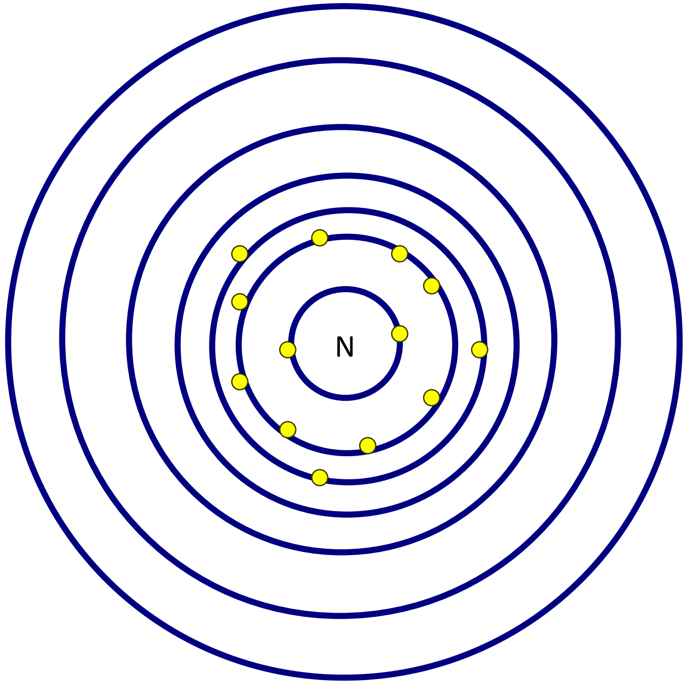
CLICK ON ELEMENT TO FILL IN CHARTS

Energy Level Diagram



Aluminum

Bohr Model

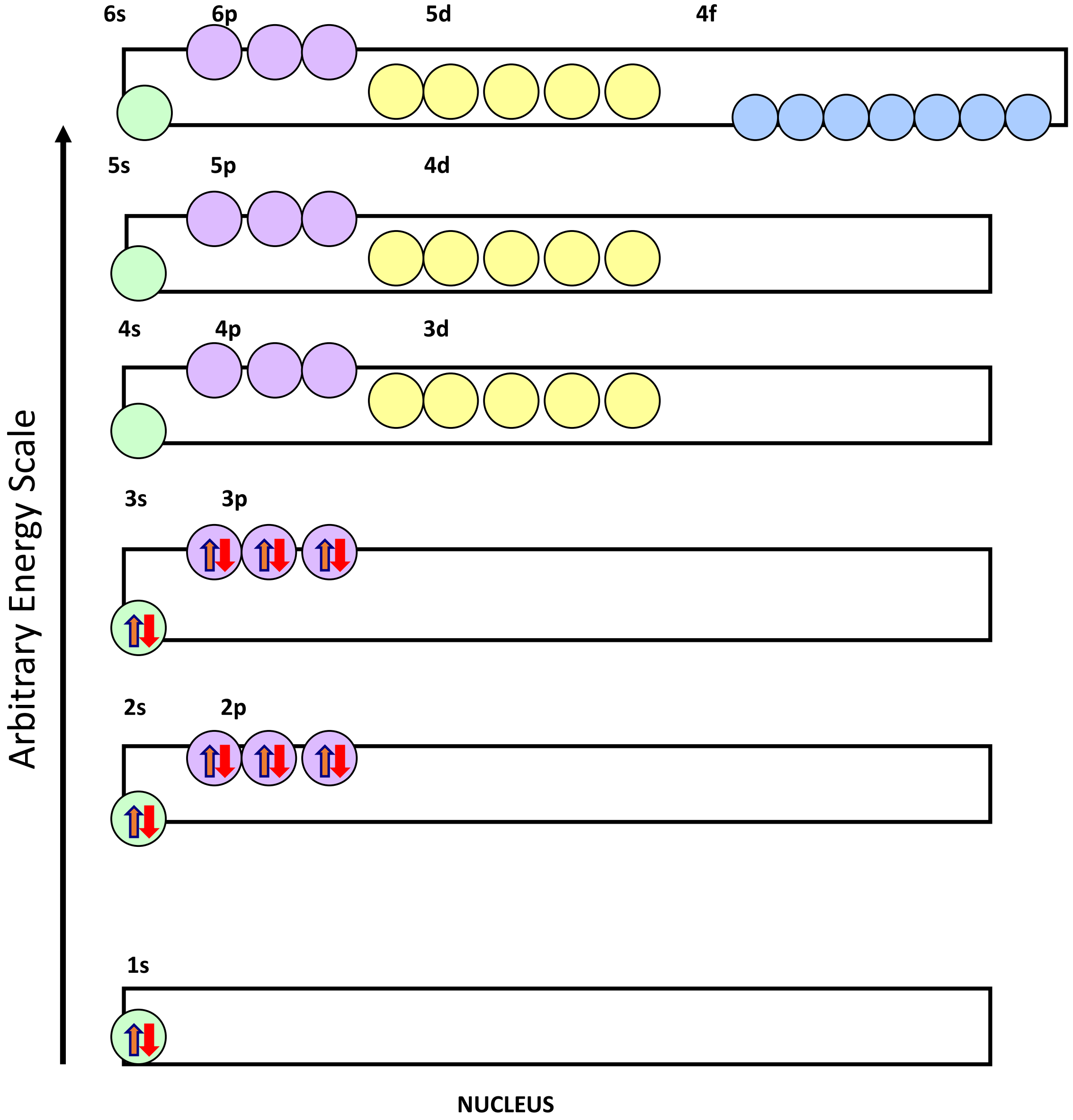


Electron Configuration

Al = $1s^2 2s^2 2p^6 3s^2 3p^1$

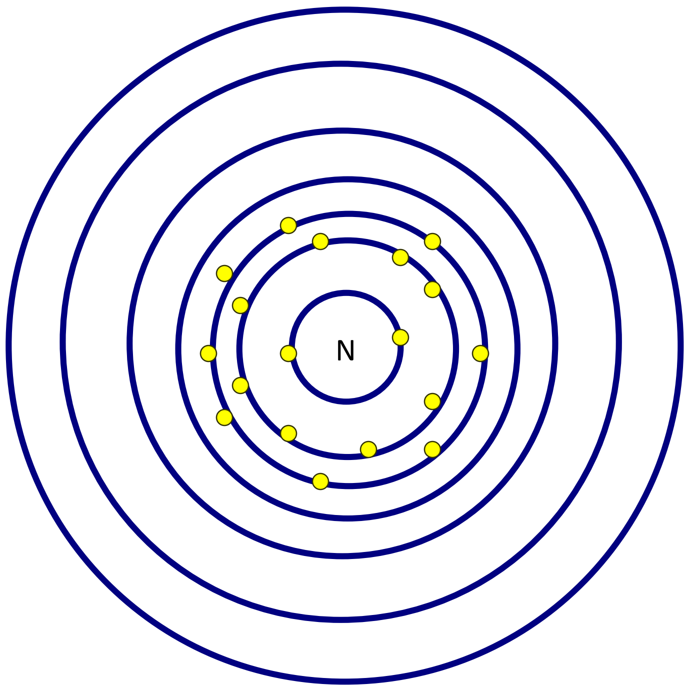
H He Li C N Al Ar F Fe La

Energy Level Diagram



Argon

Bohr Model

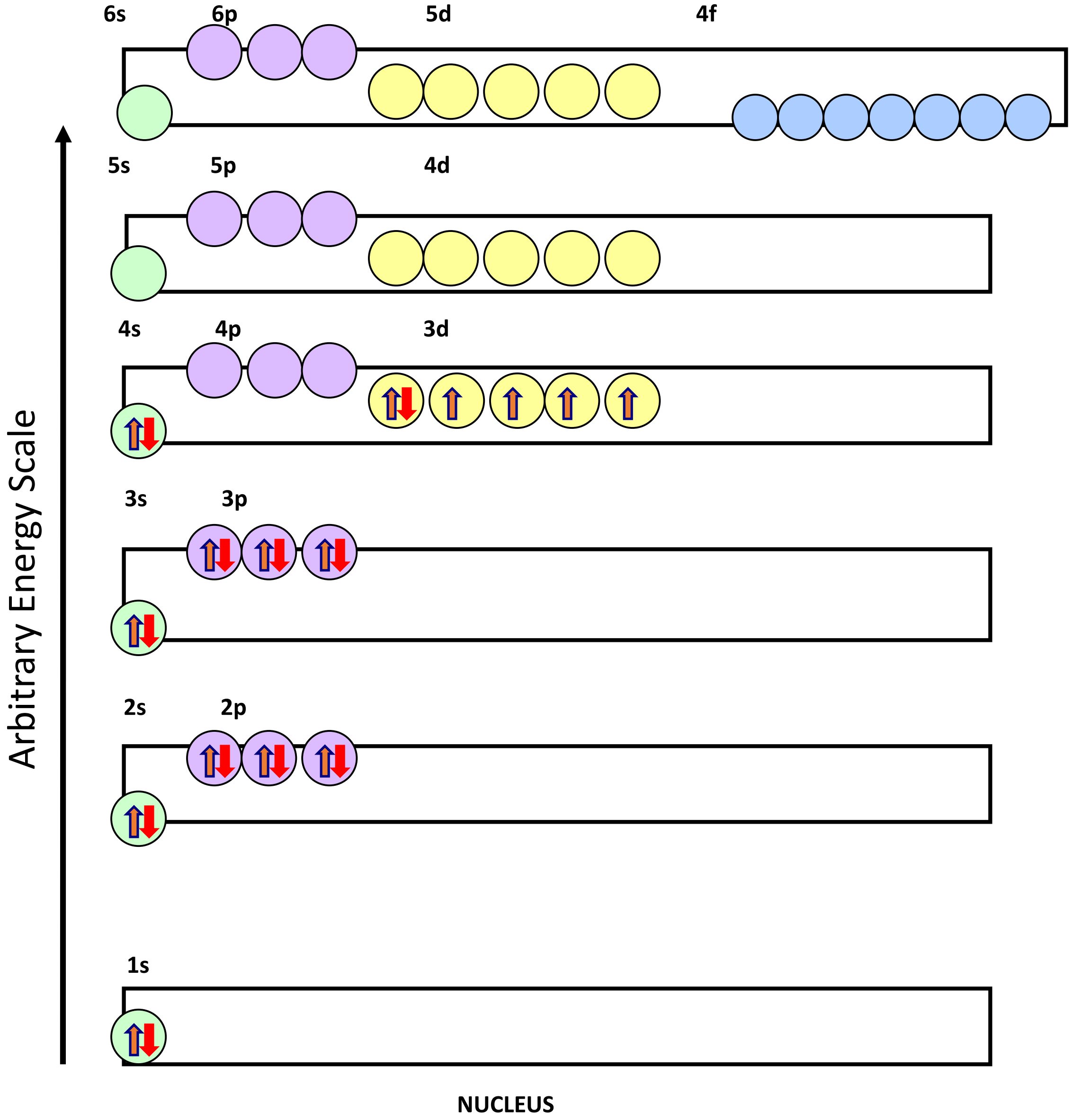


Electron Configuration

Ar = $1s^2 2s^2 2p^6 3s^2 3p^6$

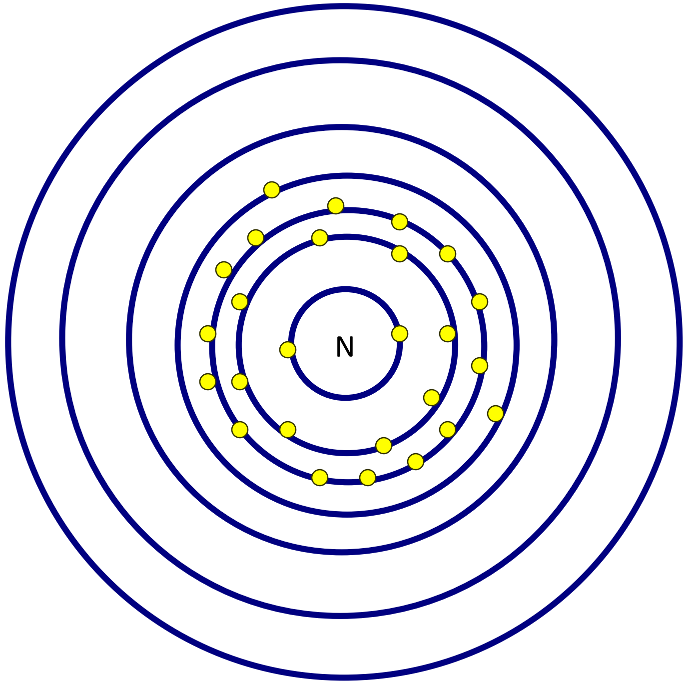
H He Li C N Al Ar F Fe La

Energy Level Diagram



Iron

Bohr Model



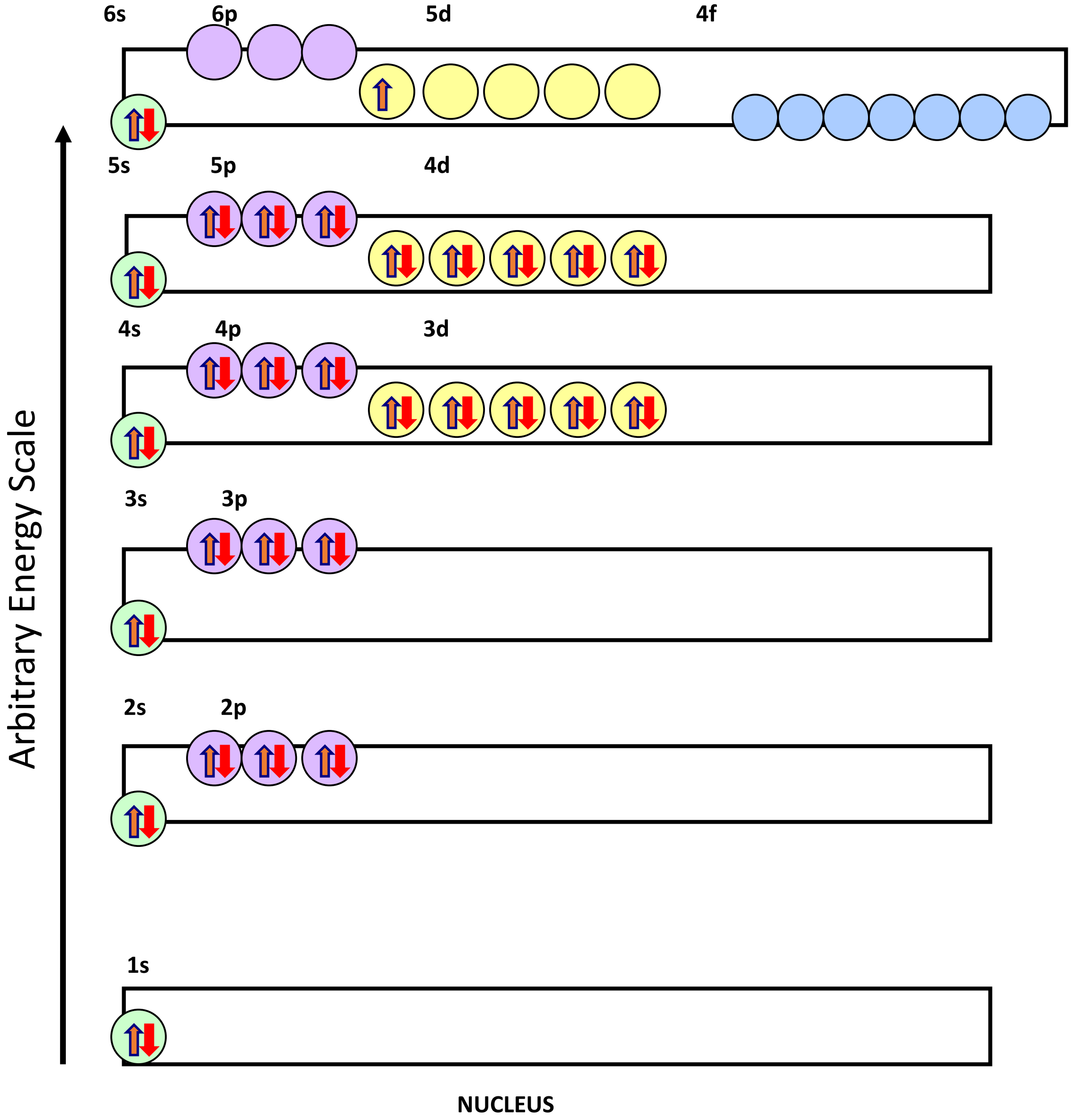
Electron Configuration

Fe = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

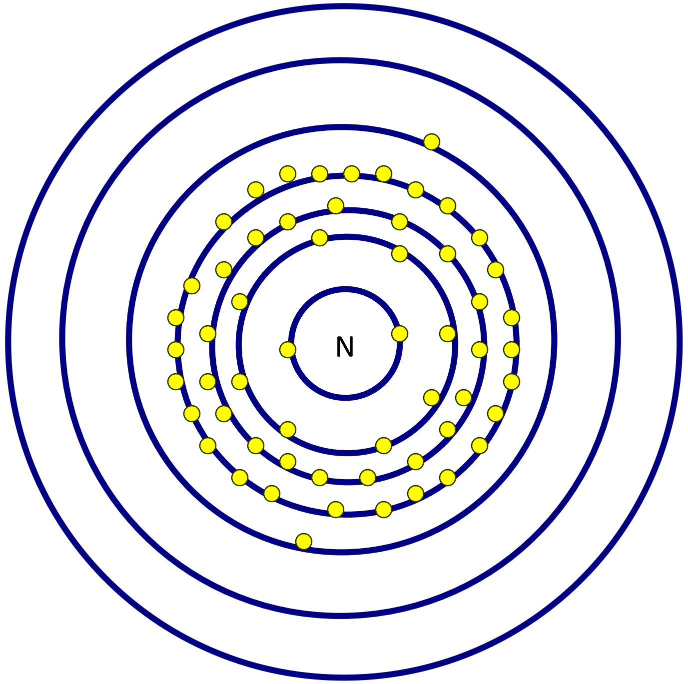
H He Li C N Al Ar F Fe La

Lanthanum

Energy Level Diagram



Bohr Model

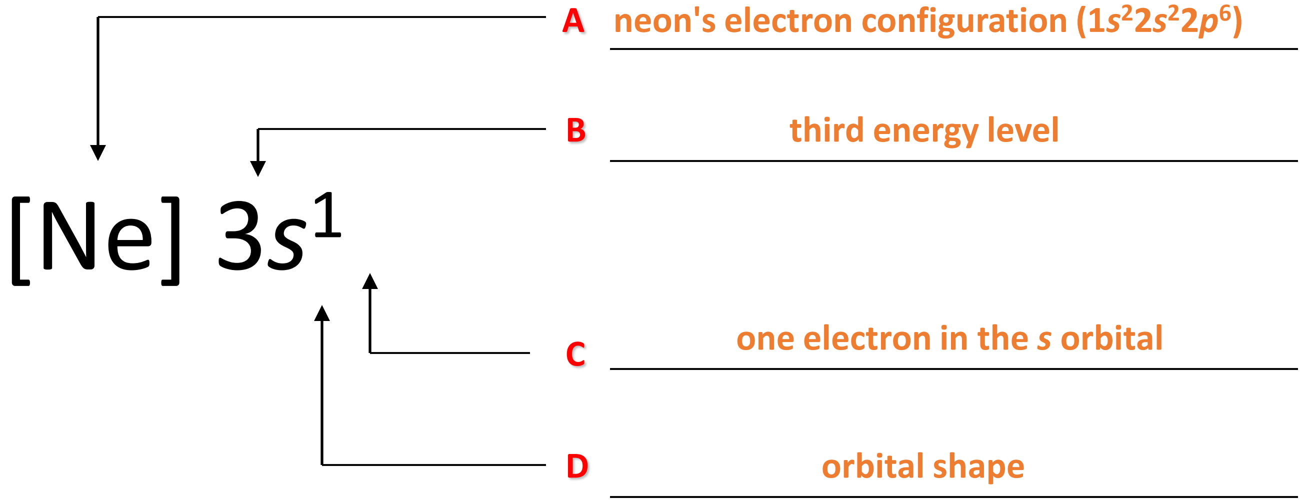


Electron Configuration

La = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 5d^1$

H He Li C N Al Ar F Fe La

Shorthand Configuration



$Na = [1s^2 2s^2 2p^6]\ 3s^1$ electron configuration

Shorthand Configuration

Element symbol	Electron configuration
Ca	[Ar] $4s^2$
V	[Ar] $4s^2\ 3d^3$
F	[He] $2s^2\ 2p^5$
Ag	[Kr] $5s^2\ 4d^9$
I	[Kr] $5s^2\ 4d^{10}\ 5p^5$
Xe	[Kr] $5s^2\ 4d^{10}\ 5p^6$
Fe	[He] $2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Sg	[Rn] $7s^2\ 5f^{14}\ 6d^4$

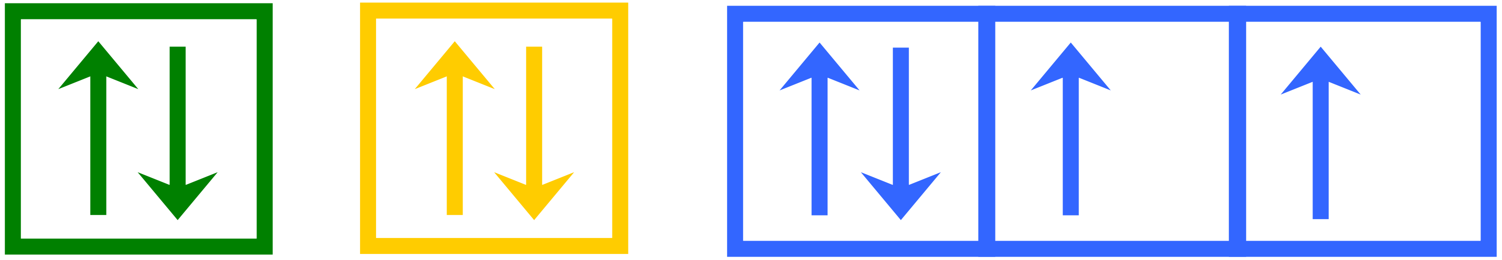
[Ar] $4s^2 3d^6$

8
O
15.9994

Notation

- **Orbital Diagram**

O



$8e^-$ 1s 2s 2p

- **Electron Configuration**

$1s^2\ 2s^2\ 2p^4$

16
S
32.066

Notation

- **Longhand Configuration**

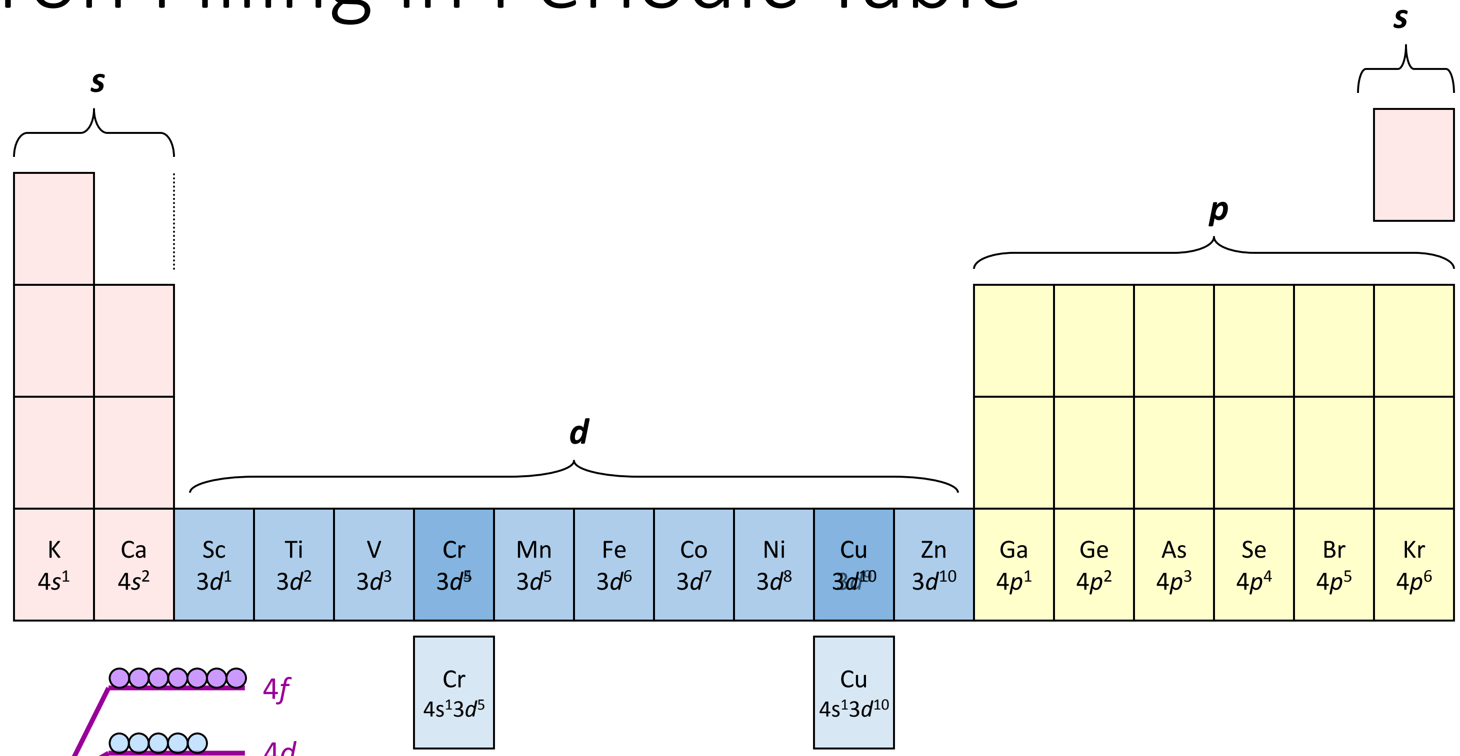
S 16e$^-$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

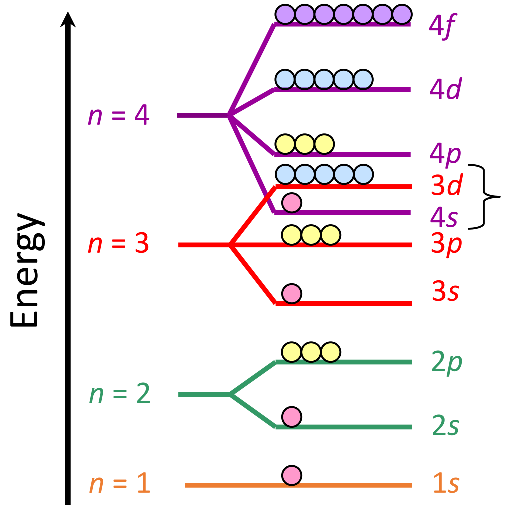
Core Electrons — Valence Electrons

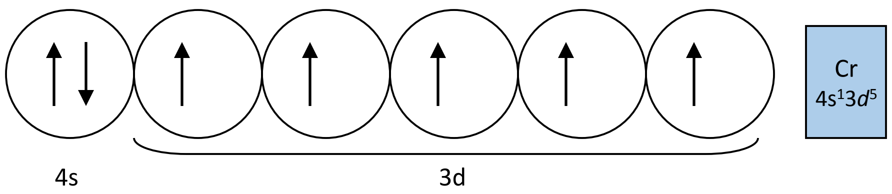
- **Shorthand Configuration**

S 16e$^-$ $[Ne]\ 3s^2\ 3p^4$

Electron Filling in Periodic Table

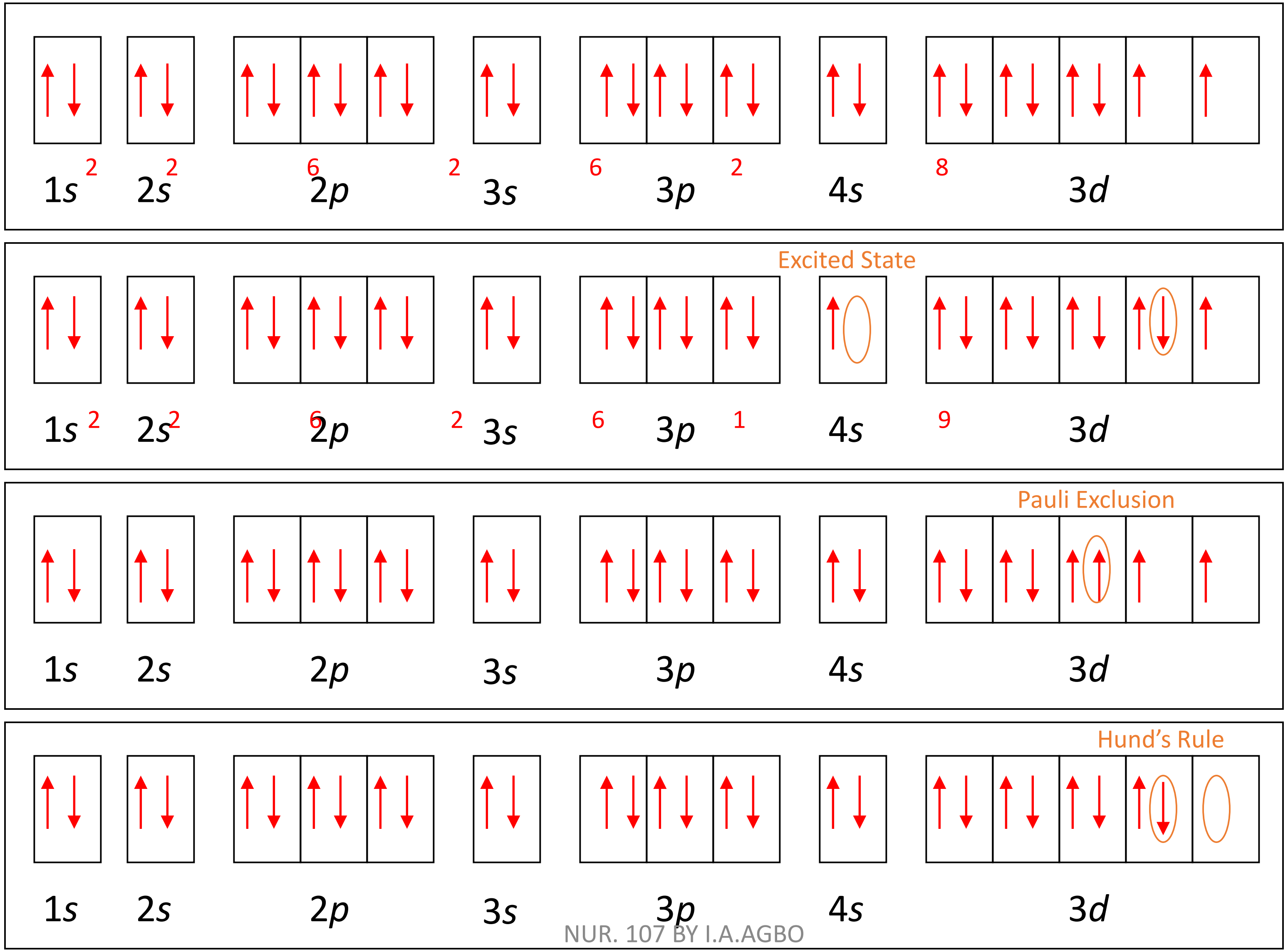






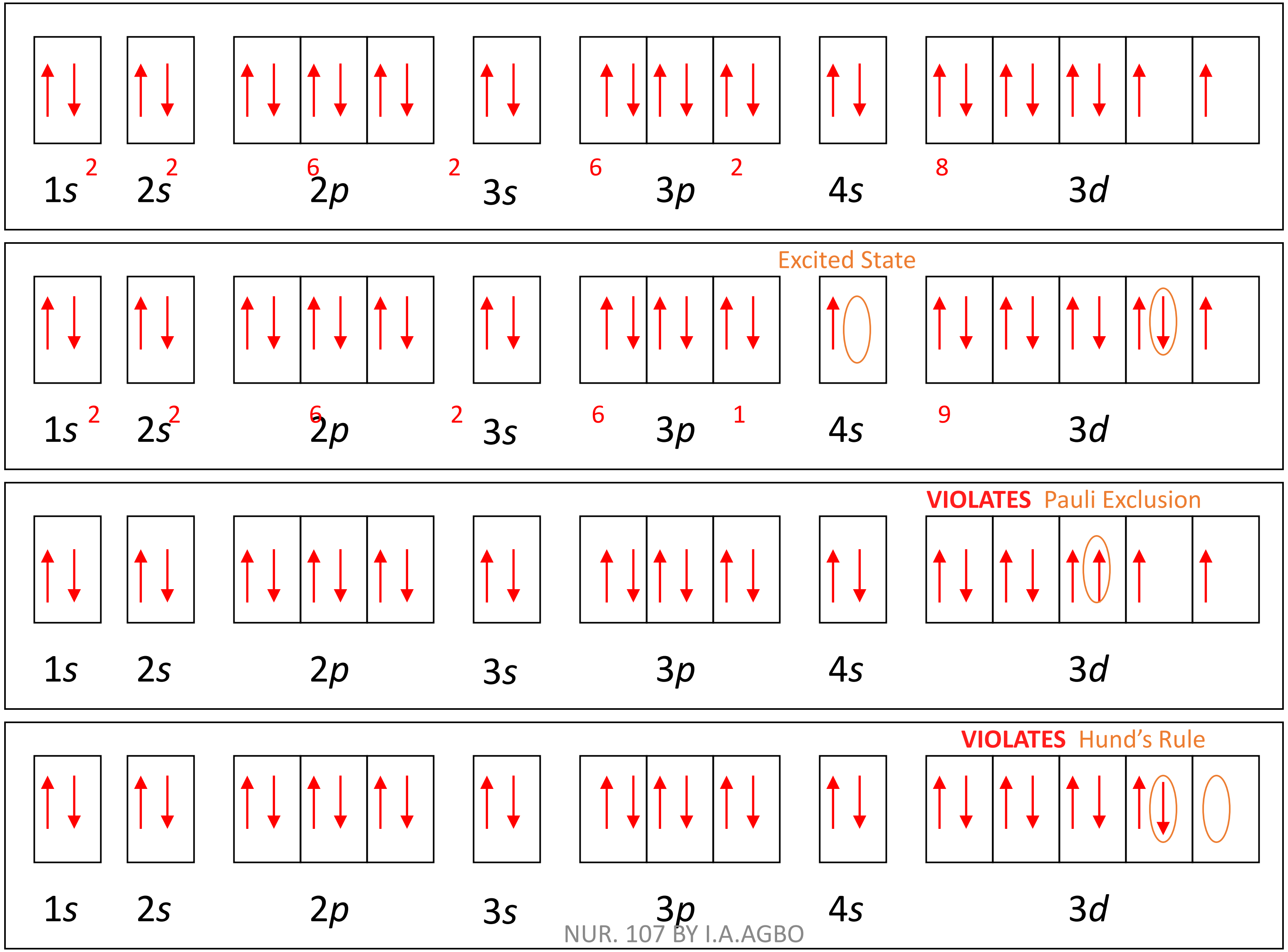
Orbital Diagrams for Nickel

28
Ni
58.6934



Orbital Diagrams for Nickel

28
Ni
58.6934



Assignment 2

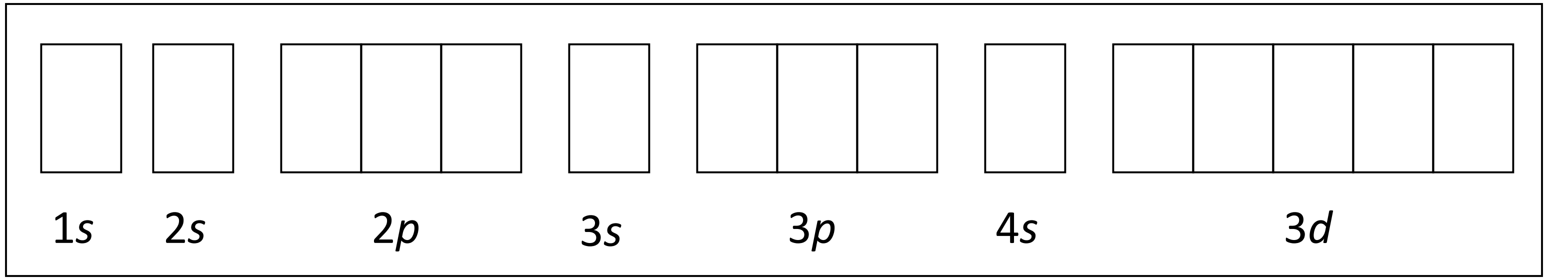
Write out the complete electron configuration for the following:

1) An atom of nitrogen

2) An atom of silver

3) An atom of uranium (shorthand)

Fill in the orbital boxes for an atom of nickel (Ni)



Which rule states no two electrons can spin the same direction in a single orbital?