

BOHR MODEL (approx 1913)

- The Bohr model of the atom was based on the line spectra of the **Hydrogen** atom. The model also incorporated the concept developed by Einstein regarding the particle behaviour of light during emission or absorption (photon or quanta of energy).



Main Points:

1. ENERGY LEVELS

- an electron can only have specific energy values in an atom
the path followed by the electrons is a circular orbit (spherical in 3-D)
these energies are called energy levels given the name **Principal Quantum Number, n**

- the orbit closest to the nucleus is given $n=1$, with the **lowest** energy as one moves outward the energies get larger and " n " increases ($n=1,2,3,4,\dots$)
- an electron can only circle in one of the allowed orbits **WITHOUT** a loss of energy

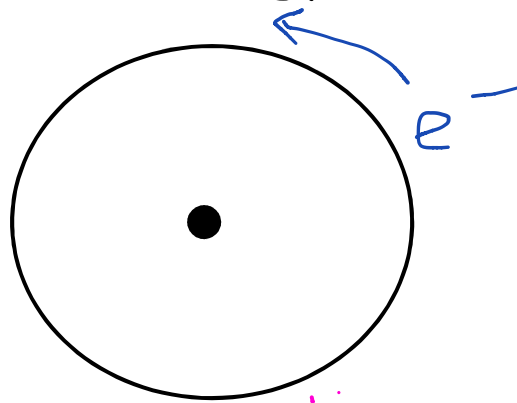
2. TRANSITION BETWEEN ENERGY LEVELS

- an electron in an atom can only change energy by going from one energy level to another level, i.e. NOT in-between
- **light is** emitted when an electron **falls** from a **higher** energy level to a **lower** energy level → **photon**
- an electron generally remains in its **ground state** - the lowest energy level possible ($n=1$ for hydrogen)
- when an **electron is given** energy it can be bumped to a higher energy level called the **excited state**
- as the electron **drops** from the excited state down to lower energy levels it **emits** light
- Bohr was able to show that his model was able to match the **Balmer** series (Visible light, drop to $n=2$) and predict the **Paschen** series (IR light, drop to $n=3$) and the **Lyman** series (UV light, drop to $n=1$)
- Although the Bohr model could explain the behaviour of the hydrogen atom, it could not fully explain the behaviour of other atoms

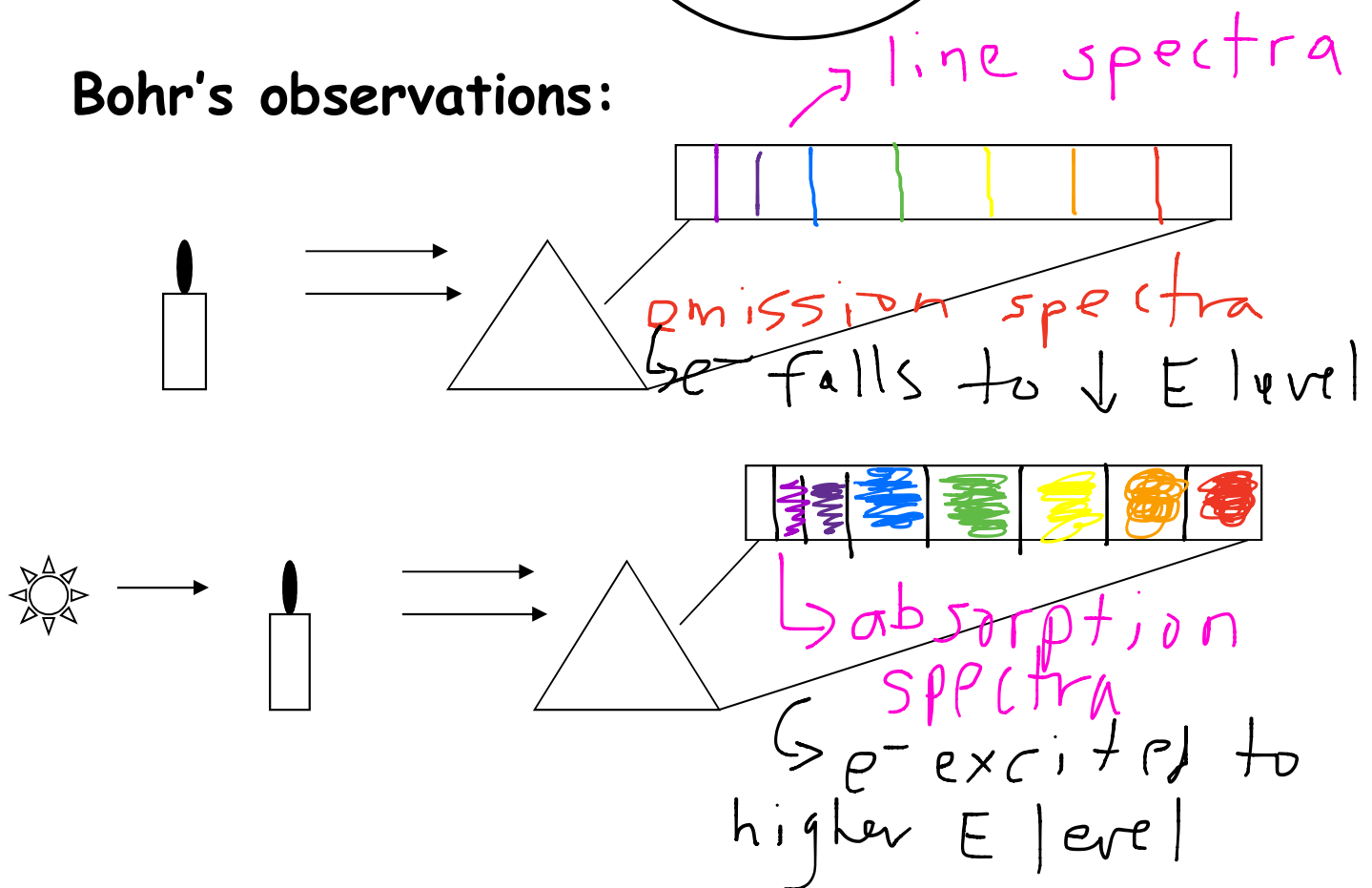
The Bohr Model of the Atom

One major question with respect to the atom's structure remained:

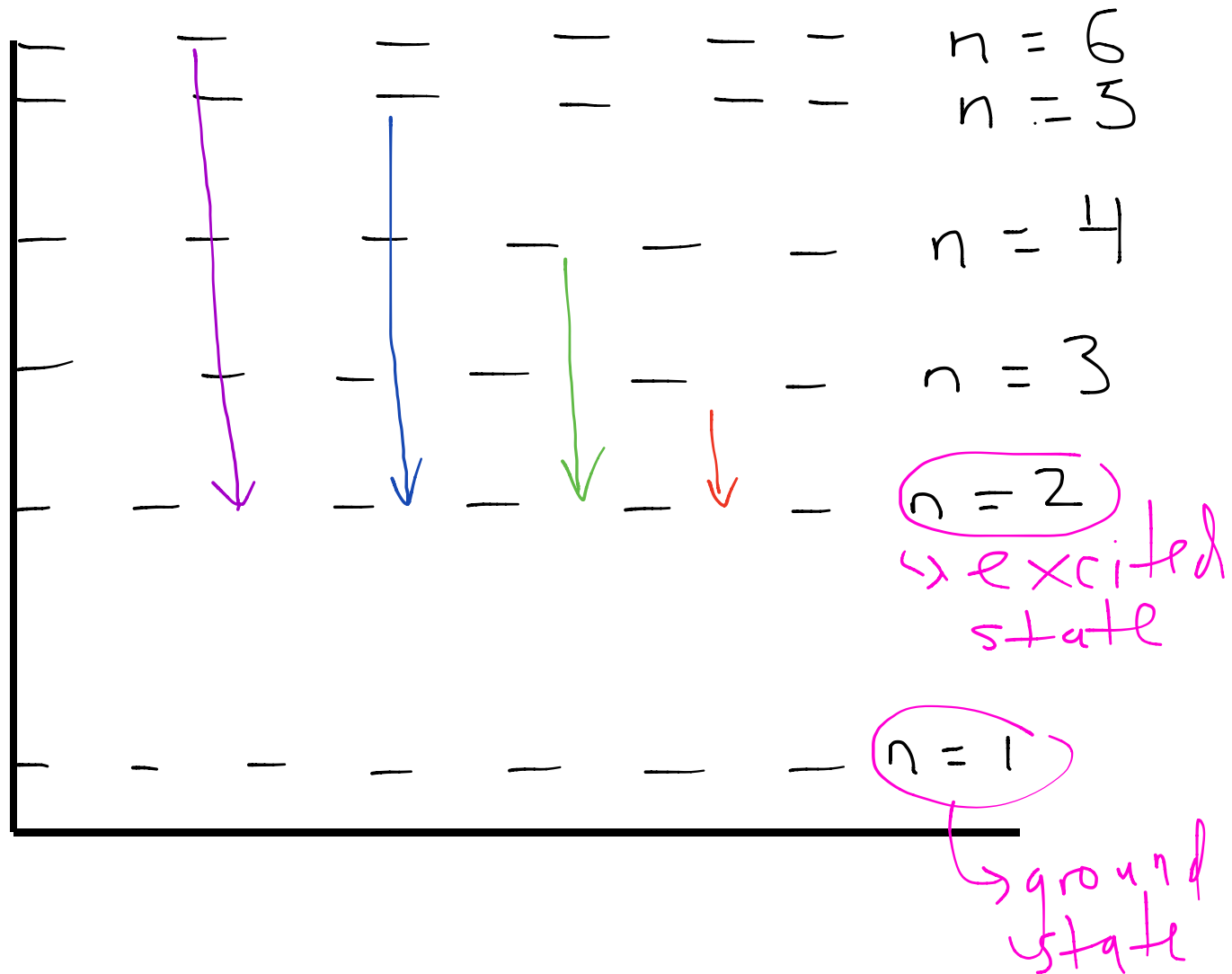
An orbiting electron emits radiation that should cause it to **lose** energy and collapse into the **nucleus**.



Bohr's observations:



How Bohr explained the emission spectra and absorption spectrum of hydrogen gas:



Quantum Mechanics: Describing the Electron

An e^- 's address

The Quantum Numbers

These numbers are used to describe the, probable location of an electron.

i) The Principal Quantum Number (n)

The value for the energy level or **orbital** of an e^- ($n = 1, 2, 3$ to ∞).

ii) The Secondary Quantum Number (l)

Divides the energy levels into **sub-levels** or **orbital types** (smaller spaces or shapes) called s (0), p (1), d (2) and f (3). To determine the shape: $l = 0$ to $n-1$.

iii) The Magnetic Quantum Number (m_l)

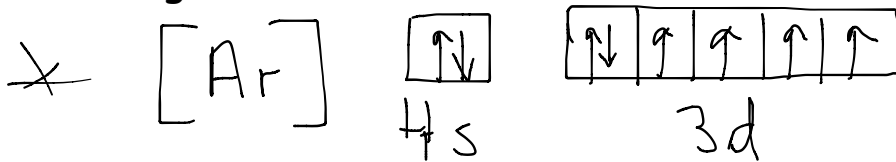
Describes the **direction** of orientation (pointing) for p, d and f orbital types (ie. p_x, p_y, p_z) To determine the direction: $m_l = -l$ to $+l$.

iv) The Spin Quantum Number (m_s)

An e^- can spin in only 2 directions ($m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$)

Spin Quantum Number, m_s

- needed to explain additional spectral line-splitting & different kinds of magnetism
- **ferromagnetism**-associated with substances containing Fe, Co & Ni
- **paramagnetism**-weak attraction to strong magnets (individual atoms vs. collection of atoms)
- To explain magnetism we can draw the electron configuration of a ferromagnetic element, e.g. Fe [Ar] 4s² 3d⁶ = 1 pair + 4 unpaired. It is the **unpaired** electrons cause the magnetism



- paramagnetism couldn't be explained until Wolfgang Pauli suggested that electrons spin on their axis (1925)
- could spin only 2 ways (clockwise vs. counterclockwise) and he used only 2 numbers to describe this:
 - $m_s = +1/2$ (clockwise) or $-1/2$ (counterclockwise)
- **opposite** pairs of electron spins represent a **stable** arrangement
- when electrons are **paired** - spin in opposite directions - the magnetic field is **neutralized**, while an individual electron spin can be affected by a **magnet**

diamagnetic

Quantum Numbers Questions

1) An electron has the following set of quantum numbers:

$$n = 3, l = 1, m_l = 1, m_s = -\frac{1}{2}.$$

In which orbital is this electron found?

- a. ~~3s~~ b. 3p c. 3d d. ~~3f~~ e. ~~4p~~

2) Which set of quantum numbers is not possible?

~~a.~~ $n = 3, l = 0, m_l = 0, m_s = -\frac{1}{2}$

~~b.~~ $n = 5, l = 3, m_l = 2, m_s = \frac{1}{2}$

~~c.~~ $n = 4, l = 3, m_l = -1, m_s = -\frac{1}{2}$

~~d.~~ $n = 5, l = 3, m_l = -3, m_s = \frac{1}{2}$

e. $n = 4, l = 4, m_l = 2, m_s = -\frac{1}{2}$

3) Which set of quantum numbers is not possible?

a. $n = 5, l = 3, m_l = 0, m_s = -\frac{1}{2}$

b. $n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$

c. $n = 3, l = 2, m_l = 1, m_s = \frac{1}{2}$

d. $n = 4, l = 3, m_l = -3, m_s = 0$

e. $n = 5, l = 2, m_l = 0, m_s = \frac{1}{2}$

4) What are the allowed values of m_l for an electron with each orbital-shape quantum number.

a) $l = 3$

$-3, -2, -1, 0, +1, +2, +3$

b) $l = 1$

$-1, 0, +1$

5a) What are the possible values of m_l if $n = 4$ and $l = 2$?

$-2, -1, 0, +1, +2$

b) What kind of orbital is described by these quantum numbers?

$4d$

c) How many orbitals can be described by these quantum numbers?

5 orbitals

PROBABILITY MODEL

(WAVE MECHANICAL MODEL or QUANTUM MECHANICAL MODEL)

DeBroglie (1924)

➤ Proposed that moving electrons could be considered to behave like **waves**

➤ experimentation showed that electrons can exhibit **diffraction** patterns like light - a key part of the wave model of light derived expression relating wave properties to particle properties

$\lambda = h/mv$ where: λ = wavelength of a particle wave

h = Planck's Constant

m = mass of particle

v = speed of particle

for a baseball of $m = 0.145$ g with $v = 27$ m/s

$$10 = \lambda \times 10^{-34} \text{ m}$$

for an electron of $m =$ with $v = 3.00 \times 10^8$ m/s

$$100 = \lambda \times 10^{-12} \text{ m (100 pm)}$$

visible light has a wavelength range of 400 to 750 nm

Schrodinger's Theory (1926)

➤ extended wave properties of electrons to their behaviour in atoms and molecules

➤ consider Bohr's Model - electron orbits nucleus like the earth around the sun in a continuous path

➤ in quantum mechanics - electron does **NOT** have a precise orbit in an atom

➤ using principle of standing waves (wave theory) and the quantum numbers, Schrodinger was able to devise an expression, called the wave equation, that could identify the **space** an electron will occupy

$$e^{-}^{\max} = 2n^2$$

Energy Level Diagrams and Electron Configurations

Both methods are used to show the distribution of electrons among the various orbitals in an atom according to quantum mechanics. Rules to follow when drawing diagrams and writing electron configurations:

Aufbau (building up) Principle

Electrons are added to the **lowest** energy orbital available.

Pauli Exclusion Principle

An orbital can be **empty**, have **one** electron or have **two** electrons (at most).

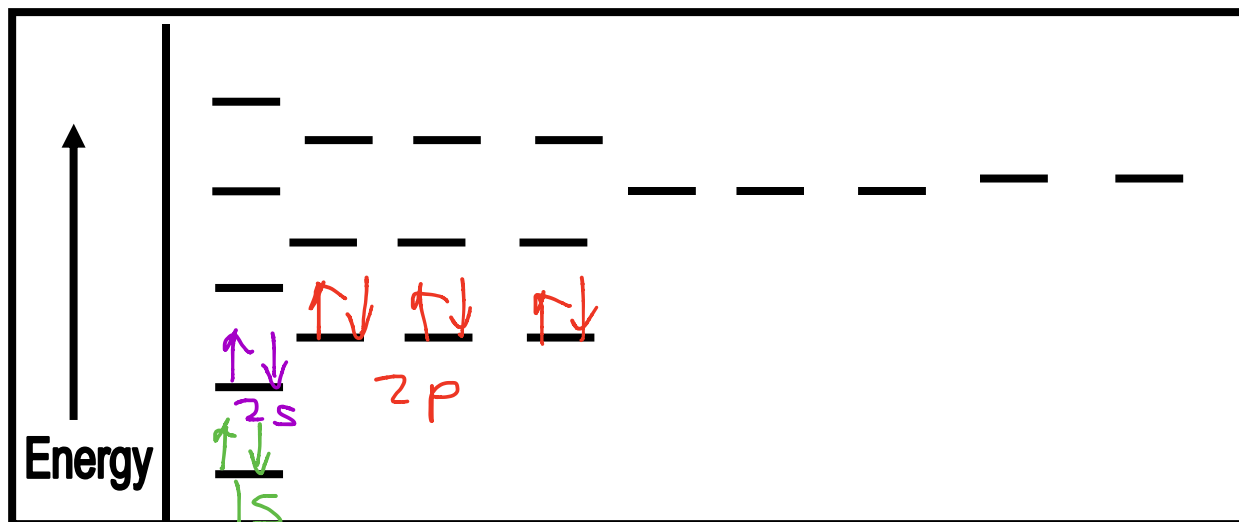
Hund's Rule

Electrons in the same sub-level will **not** pair up (occupy the same orbital) until **all** orbitals in the sub-level are **half-filled** (have 1 electron).

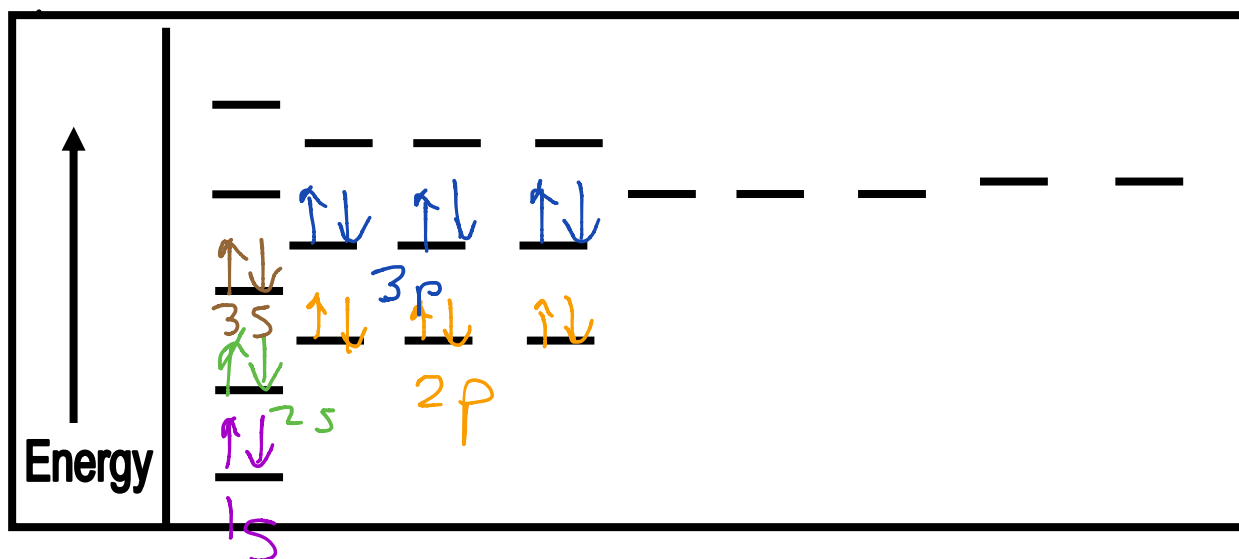
Energy Level Diagrams

Graphs the distribution of electrons according to energy and indicates direction of spin. e.g.

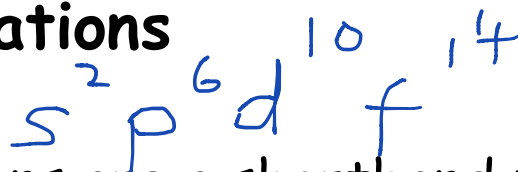
i) Neon: $10p^+$ $10e^-$



ii) Calcium $+2$ $18e^-$



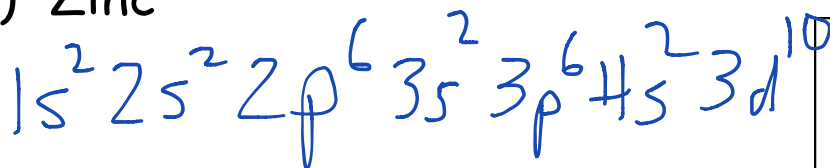
Electron Configurations



Electron configurations are a shorthand notation of energy level diagrams and provide information about the first two quantum numbers, n and l

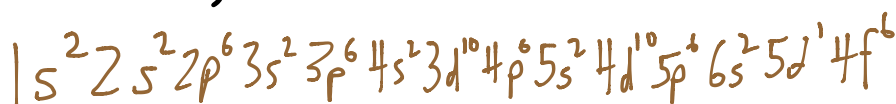
Write electron configurations for the following:

i) Zinc



ii) Stable Calcium Cation

iii) ^{Eu} Neon



iv) Mn

Memory Trick

7s 7p

6s 6p 6d

5s 5p 5d 5f

4s 4p 4d 4f

3s 3p 3d

2s 2p

1s

Principal Level Distribution

Indicates the number of electrons with the same principal quantum number (n). e.g.

i) Zinc:


ii) Calcium⁺²

iii) Neon:

iv) Mn: $[\text{Ar}] 4s^2 3d^5$

Orbital Diagrams

Represents the electron configuration and electron spin direction using boxes to represent orbitals e.g.

i) Zinc: 
1s 2s 2p 3s 3p 4s

ii) Calcium⁺²

iii) Neon:

iv) Mn: 

Periodic Trends

Atomic Radius

The distance from the center of the nucleus to the outermost electrons occupying an energy level is the atomic radius. Factors affecting atomic radii include:

i) Principal Quantum Number (n)

Probability of finding electrons increases farther away from the nucleus.

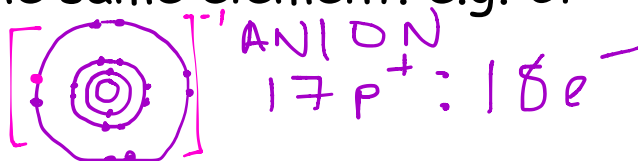
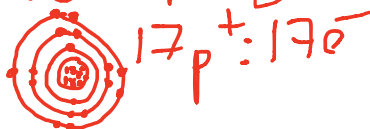
\therefore as $n \uparrow$ atomic radius \uparrow .

ii) Effective Nuclear Charge (Z_{eff})

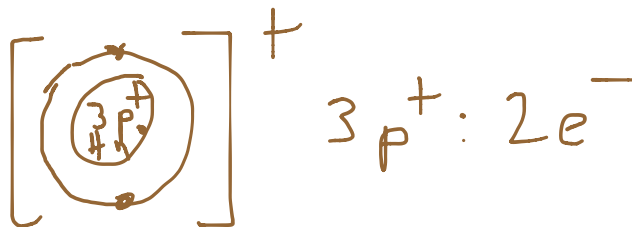
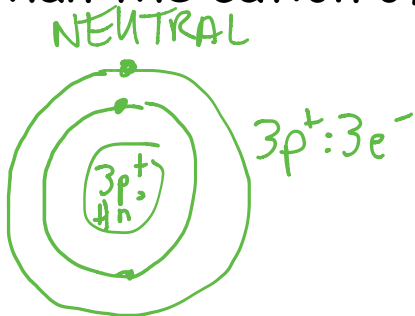
The net force of attraction between electrons and the nucleus they surround.

\therefore as $Z_{\text{eff}} \uparrow$ atomic radius \downarrow .

A neutral atom will have a **smaller** atomic radius than the anion of the same element. e.g. Cl



A neutral atom will have a **larger** atomic radius than the cation of the same element. e.g. Li



Ionization Energy (kJ)

The energy required to remove an electron from an atom is called the ionization energy.

The **1st I.E.** is the energy required to remove the weakest held electron from the neutral atom.

Trends in Ionization energy are linked to atomic radius and therefore are under control of:

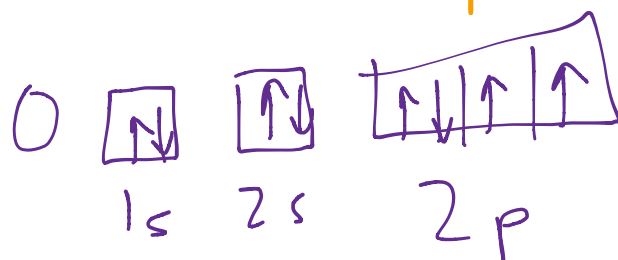
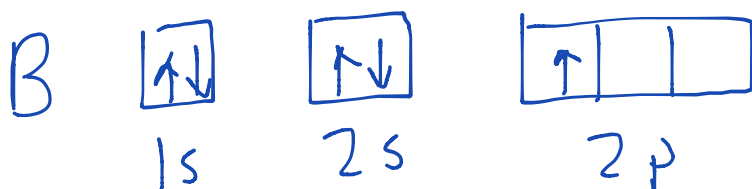
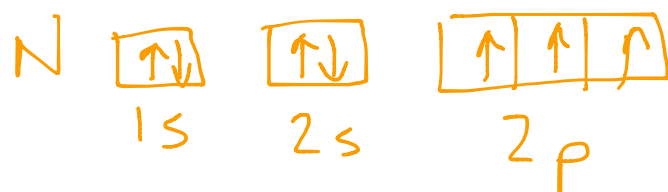
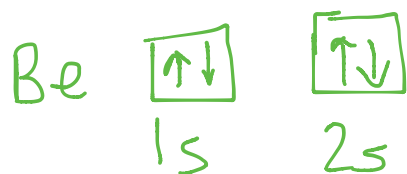
i) Principal Quantum Number (n)

\therefore as $n \uparrow$ I.E. \downarrow .

ii) Effective Nuclear Charge (Z_{eff})

\therefore as $Z_{\text{eff}} \uparrow$ I.E. \uparrow .

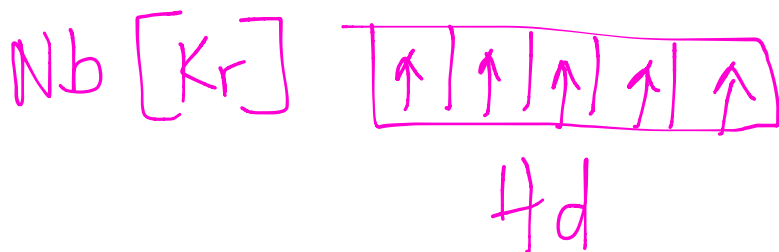
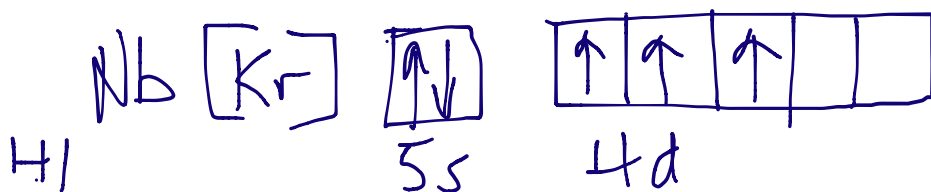
Also, some variations in I.E. trends can be explained by the presence of half filled p orbitals or full s orbitals. (e.g. Be, B and N, O).



➤ evidence suggests that half-filled and filled subshells are more **stable** (lower energy) than unfilled subshells

${}_{24}\text{Cr} [\text{Ar}] \uparrow \downarrow$ $4s$ $\uparrow \uparrow \uparrow \uparrow$ $3d$
 $\text{Cr} [\text{Ar}] \uparrow$ $4s$ $\uparrow \uparrow \uparrow \uparrow \uparrow$ $3d$
 the justification is that the overall ex

➤ Other examples include:



Electron Affinity (kJ/mol)

Electron affinity is the ~~energy given off~~ ^{CHANGE in} when an electron is added to an atom.

The 1st E.A results in the formation of an anion with a charge of 1-

Trends in electron affinity are more irregular than those for atomic radius and ionization energy.

Intermolecular Forces

Intermolecular forces act between molecules or ions. These forces must be overcome during a physical change.

i) Dipole-Dipole e.g. CHCl_3

Hydrogen bonding is a special case of dipole-dipole bonding that involves a molecule containing H and a very electronegative element. e.g. H_2O , NH_3 etc.

ii) Ion-Dipole e.g. Na^+ and H_2O

iii) Ion-Induced Dipole e.g. Na^+ and O_2

iv) Dipole-Induced Dipole e.g. HCl and O_2

v) Dispersion Forces e.g. F_2 and F_2

Drawing Lewis Structures for Complex Molecules

The following steps can help when determining the Lewis Structure for more complex molecules.
e.g. NO_3^-

1. Identify the central atom (usually lowest EN).

$$N_{\text{EN}} = 3.04 \quad O_{\text{EN}} = 3.44$$

2. Determine the total number of Noble Gas e^-

$$\begin{aligned} \text{NGe}^- & \quad 1N \times 8e^- = 8e^- \\ & \quad 3O \times 8e^- = 24e^- \end{aligned}$$

3. Determine the total number of valence e^-

$$\begin{aligned} \text{Ve}^- & \quad 1N \times 5e^- = 5e^- \\ & \quad 3O \times 6e^- = 18e^- \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} 24e^-$$

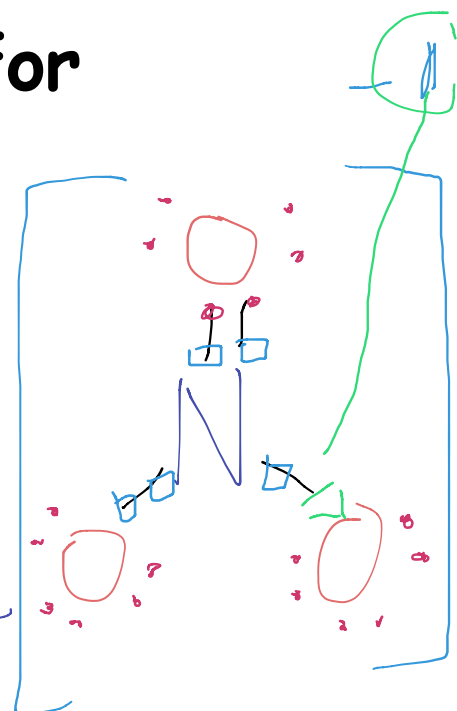
4. Determine the # of bonds by (taking total NG e^- subtract total valence e^-) and divide by 2.

$$\text{Bonds} = \frac{\text{NGe}^- - \text{Ve}^-}{2} \quad \text{Bonds} = \frac{(32 - 24)}{2} = 4 \text{ bonds}$$

5. Determine the number of lone pair e^- by subtracting the total valence e^- from the number of e^- involved in bonding.

$$\begin{aligned} \text{Le}^- &= \text{Ve}^- - \text{Be}^- = 16 \text{ Le}^- \\ &= 24 - 8 \end{aligned}$$

6. Place lone pairs of e^- around outside atoms first and then to the central atom if necessary.



Lewis Structures and Co-ordinate Covalent Bonds

A co-ordinate covalent bond is a covalent bond in which **one** atom donates **both** bonding electrons.

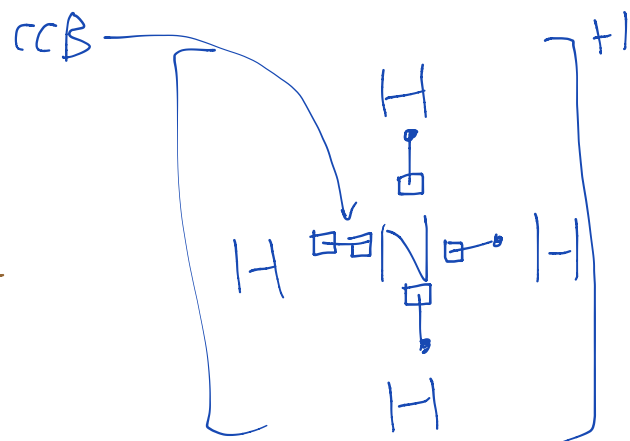
A filled atomic orbital overlaps with an empty atomic orbital. (This is an exception to regular covalent bonding where one electron is donated by each atom.) For example;

1. Ammonium (NH_4^{+1})

NGe^-	Ve^-	<u>BONDS</u>	Le^-
$1\text{N} \times 8e^- = 8e^-$	$1\text{N} \times 5e^- = 5e^-$	$\text{NGe}^- - \text{Ve}^-$	$\text{Ve}^- - \text{Be}^-$
$4\text{H} \times 2e^- = 8e^-$	$4\text{H} \times 1e^- = 4e^-$	$= 16 - 8$	$= 8e^- - 8e^-$
$\frac{16e^-}{}$	charge = $\frac{-1e^-}{8e^-}$	$= \frac{8}{2}$	$= 0$
		$= 4 \text{ bonds}$	

2. Hydronium (H_3O^{+1})

3. Nitrosyl trifluoride (NF_3O)



Lewis Structures and Resonance Structures

When a structure containing a double bond can be drawn with the double bond in two or more locations without changing the arrangement of atoms, a **resonance** structure is said to exist. These different structures for the same molecule are called "resonance **hybrids**". For example:

Sulfur trioxide (SO_3)



The bond lengths and strengths have been experimentally determined to fall between single and double bonds.

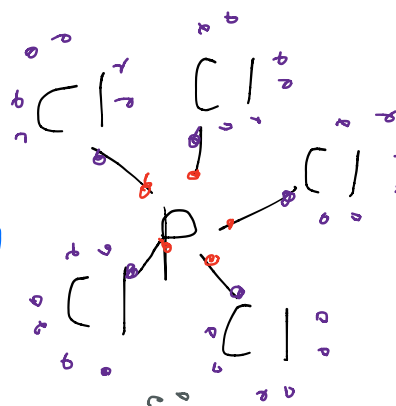
The electrons forming the double bond(s) are said to be "**delocalized**" (shared) over all the bonds.

Lewis Structures and Exceptions to the Octet Rule

$$\begin{array}{r} \text{Le}^- \\ 40 - 10 \\ \hline = 30 \text{Le}^- \end{array}$$

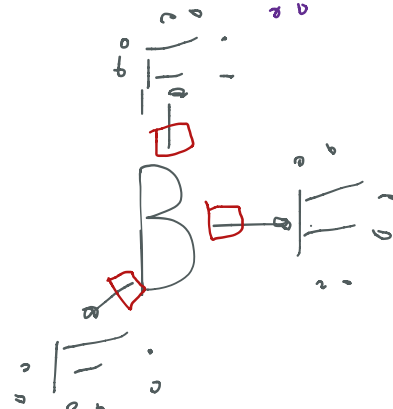
1. Molecules which have more than four atoms bonded to the central atom. e.g. PCl_5

$\begin{array}{r} \text{NGe}^- \\ 1 \text{P} \times 8e^- = 8e^- \\ 5 \text{Cl} \times 8e^- = 40e^- \\ \hline 48e^- \\ 50e^- \end{array}$	$\begin{array}{r} \text{Ve}^- \\ 1 \text{P} \times 5e^- = 5e^- \\ 5 \text{Cl} \times 7e^- = 35e^- \\ \hline 40 \end{array}$	$\begin{array}{r} \text{Bonds} \\ \text{NG-VP} \\ 2 \\ \hline 40 - 40 \\ \hline = 0 \end{array}$
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2. Molecules that contain no double bonds and whose central atom has fewer than four bonding electrons. e.g. BF_3

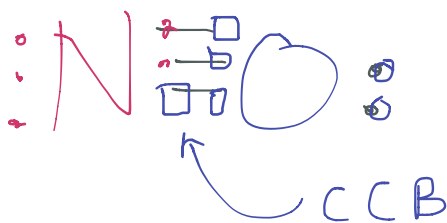
$\begin{array}{r} \text{NGe}^- \\ 1 \text{B} \times 6e^- = 6e^- \\ 3 \text{F} \times 8e^- = 24e^- \\ \hline 30 \end{array}$	$\begin{array}{r} \text{Ve}^- \\ 1 \text{B} \times 3e^- = 3e^- \\ 3 \text{F} \times 7e^- = 21e^- \\ \hline 24 \end{array}$	$\begin{array}{r} \text{Bonds} \\ \text{NG-Ve}^- \\ 3 - 24 \\ \hline = -21 \\ 24 \\ \hline = 3 \text{ bonds} \end{array}$	$\begin{array}{r} \text{Le}^- \\ \text{Ve}^- - \text{Be}^- \\ 24 - 6 \\ \hline = 18 \text{Le}^- \end{array}$
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3. Molecules containing an odd number of electrons. e.g. NO

$\begin{array}{r} \text{NGe}^- \\ 1 \text{N} \times 8e^- = 8e^- \\ 1 \text{O} \times 8e^- = 8e^- \\ \hline 16e^- \end{array}$	$\begin{array}{r} \text{Ve}^- \\ 1 \text{N} \times 5e^- = 5e^- \\ 1 \text{O} \times 6e^- = 6e^- \\ \hline 11e^- \end{array}$	$\begin{array}{r} \text{Bonds} \\ \text{NG-Ve} \\ 2 \\ \hline 16 - 11 = 5 \text{Le}^- \end{array}$	$\begin{array}{r} \text{Le}^- \\ \text{Ve}^- - \text{Be}^- \\ 11 - 6 \\ \hline = 5 \text{Le}^- \end{array}$
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Molecules of this type are called "paramagnetic" because they are attracted by a magnetic field.



Valence Shell Electron Pair Repulsion (VSEPR) Theory

Visualize bonding and/or lone (unbonded) pairs of electrons in the outer (valence) energy level as negatively charged "clouds" (orbitals).

Each negative cloud tends to **repel** other negative clouds in the vicinity (around the central atom).

To achieve the most stable condition (minimum potential energy), the negative clouds must be as **far apart** as possible (in 3-D space).

In this position, the electrostatic repulsion is reduced to a minimum. In terms of decreasing repulsion:

LP=lone pair



BP=bond pair

$$LP--LP > LP--BP > BP > BP$$

It is the position of the **electron clouds** around the **central atom** which determines the **shape** of the molecule. ~~Copy figure 4.11 on page 179.~~

The following diagrams represent the five basic electron-group arrangements and their bond angles:

General

1. Linear (180°)



2. Trigonal Planar (120°)

3 BP, 0 LP
2 BP, 1 LP

-trigonal planar



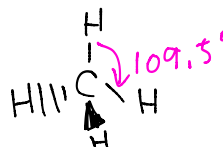
-angular/bent/v-shape



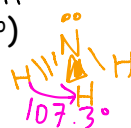
3. Tetrahedral (109.5° or less)

4 BP, 0 LP
3 BP, 1 LP
2 BP, 2 LP

-tetrahedral (109.5°)



-trigonal pyramidal (107.3°)



-angular/bent/v-shape
(104.5°)



4. Trigonal Bipyramidal (90° and 120°)

5 BP, 0 LP
4 BP, 1 LP
3 BP, 2 LP
2 BP, 3 LP

-trigonal bipyramidal



-seesaw

-T-shaped

-linear

5. Octahedral (90°)

6 BP, 0 LP
5 BP, 1 LP
4 BP, 2 LP

-octahedral

-square-based pyramid

-square planar

