ATOMIC THEORIES

FROM THE PAST TO THE MODERN ERA

First theories

- *440 B.C.* ***EMPEDOCLES*** – all matter is composed of *FOUR ELEMENTS: fire, earth, water, air*.
- *470-370 B.C.* ***DEMOCRITUS*** – matter is composed of *ATOMS* that move randomly in an empty space and collide to form the reality. (*atomos – indivisible*)
- *350 B.C.* ***ARISTOTLE*** – favored Empedocles' theory.

Later

DALTON'S ATOMIC THEORY (1800 ca)

THEORY → CAN BE MODIFIED

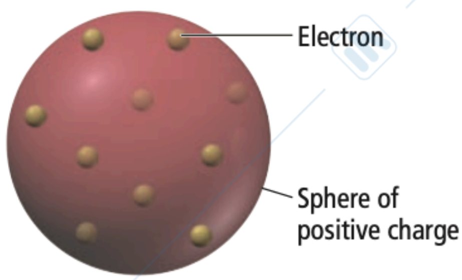
DALTON'S THEORY	LATER DISCOVERIES
1. Each element is composed of tiny, indestructible particles called atoms.	Atoms are composed of subatomic particles.
2. All atoms of a given element have the same mass and size.	Not all the atoms of a specific element have the same mass and size → ISOTOPES and IONS
3. Atoms of different elements have different mass and size.	ISOTOPES and IONS exist.
4. Atoms combine in simple, whole-number ratios to form compounds.	

THOMSON'S PLUM PUDDING MODEL (1904)

J.J. Thomson proposed that the negatively charged electrons were small particles held within a positively charged sphere.

CONCLUSIONS:

1) Atoms are made of SUBPARTICLES – they are not indivisible
2) Atoms are NEUTRAL – they can become ions by losing or gaining electrons.
3) Positive charges distributed evenly do not create a strong electric field as it would be if the charge was condensed in one point.



Plum-pudding model

RUTHERFORD – NUCLEAR MODEL (1911)

Experiment based on the assumption of the plum pudding model → the weak electric field exerted by the positive charge will not perturbate the direction of the alpha particles.

DISCOVERIES:

1) POSITIVE NUCLEUS: atoms have a heavy and dense nucleus that occupies only a tiny volume compared to the actual volume of the atom.
   This was the reason of the deflected alpha particles that according to Thomson's model should have passed all undisturbed
2) MOST OF THE NUCLEUS CONSISTS OF EMPTY SPACE: reason why most alpha particles passed undisturbed.
3) ELECTRONS ARE SET ON ORBITS IN THE EMPTY SPACE

DISCOVERY OF SUBATOMIC PARTICLES

ELECTRONS – J.J. THOMSON (1897)

Experiments with Crookes tube – a discharge tube: a gas-filled tube with an applied voltage between two electrodes with partial vacuum.
Cathode rays → traveled from the negatively charged electrode (*CATHODE*) to the positively charged one (*ANODE*).

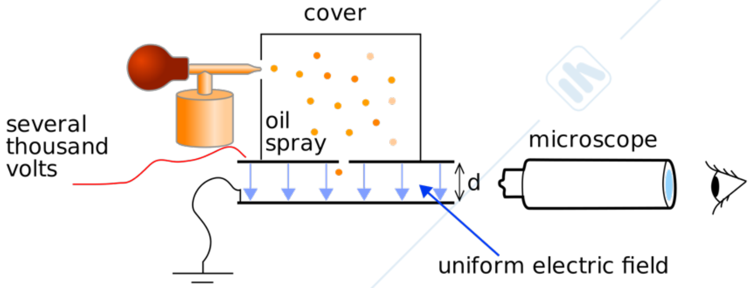
Thomson found that the particles that compose the cathode ray have the following properties:

1) They travel in *straight lines*
2) They are *independent of the composition of the material* from which they originate
3) They carry a *negative electrical charge*
4) They are *deflected* by electric and magnetic fields

Thomson measured the charge-to-mass ratio of the cathode ray particles by deflecting them using electric and magnetic fields.
The value he measured was about 2000 times lighter than hydrogen, the lightest known atom.

CHARGE OF THE ELECTRON – MILLIKAN (1909)

Oil-drop experiment



NEUTRONS – J. CHADWICK (1932)

James Chadwick demonstrated that the unaccounted mass was due to NEUTRONS: neutral particles within the nucleus with a mass similar to that of a proton.

DISCOVERY OF IONS

MICHAEL FARADAY

Observations:

1) Certain substances, when dissolved in water, conduct an electric current
2) Certain compounds decompose into their elements when they're passed through a current and atoms of some elements are attracted to the positive electrode while atoms of the others are attracted to the negative one.

ION = WANDERER

SVANTE ARRHENIUS

ION = ATOM CARRYING A CHARGE.

Ionic compound can conduct electricity if melted, even without water.

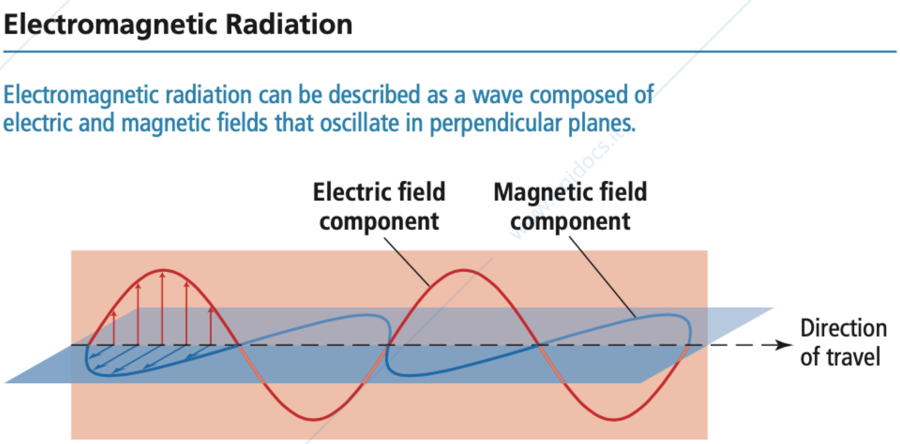
THE QUANTUM-MECHANICAL MODEL OF THE ATOM

WAVE–PARTICLE DUALITY OF LIGHT

Certain properties of light are best described by thinking of it as a ***wave***, while other properties are best described by thinking of it as a ***particle***.

LIGHT AS A WAVE

LIGHT: ELECTROMAGNETIC RADIATION → a type of energy composed of an electric and a magnetic field that oscillate perpendicularly through space.

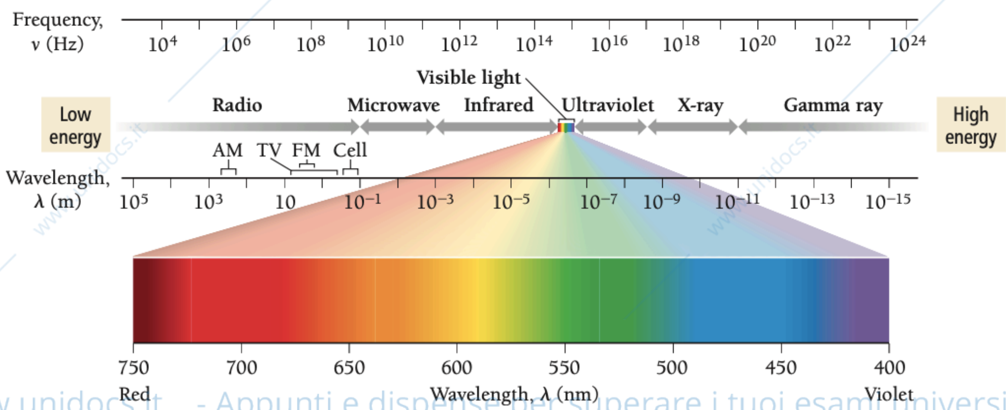


PROPERTIES OF WAVES

- *AMPLITUDE*
- *FREQUENCY* – $\nu = {}^{c}/_{\lambda}$
- *WAVELENGHT*
- *VELOCITY* – in a vacuum, waves move at a constant speed of 3.00×10^8 m/s

VISIBLE LIGHT

- Tiny part of the electromagnetic spectrum, which includes all wavelengths of electromagnetic radiation.
- *WAVELENGTH DETERMINES COLOR*
- *WAVELENGTH DETERMINES THE ENERGY LEVEL* → high energy, short wavelengths: GAMMA RAY – excessive exposure to gamma rays is dangerous to humans because the high energy of gamma rays can damage biological molecules.



Early 1900s: **DISCOVERY OF THE DIFFRACTION OF LIGHT**
→ Light was thought to be purely a wave phenomenon.
→ A wave deviates its path when it encounters an obstacle.

However, later discoveries brought the classical view into question: **PHOTOELECTRIC EFFECT**

PHOTOELECTRIC EFFECT: MANY METALS EMIT ELECTRONS WHEN LIGHT SHINES UPON THEM

Classical electromagnetic theory:
Effect due only to the **amplitude** (intensity) of the light.
The rate at which electrons leave the metal due to the photoelectric effect increases with increasing intensity of the light.

Experimental results:
A **high-frequency, low-intensity light** produces electrons without the predicted lag time.
Low-frequency light **does not** eject electrons from a metal, regardless of its intensity.
High-frequency light does eject electrons, even if its intensity is low.

1905, Albert Einstein: bold explanation for the photoelectric effect → *LIGHT ENERGY MUST COME IN PACKETS*

LIGHT AS A PARTICLE

Since the electrons on the surface of the metal were able to escape, their kinetic energy varied. This variation, caused by light, implies that the same *light must have its own kinetic energy*, and, in order to do so, it must have mass and velocity.

According to Einstein, the amount of energy (E) in a light packet depends on its frequency (v)

$$E = hv$$

$$h = 6.626\,x\ 10^{-34}\,m^2\,kg/s$$

Planck's constant

A packet of light is called a **PHOTON** or a **QUANTUM** of light.

MATTER HAS A DOUBLE NATURE

Just as the photoelectric effect suggested the particle nature of light, so certain observations about atoms began to suggest a wave nature for particles.

OBSERVATIONS FROM ATOMIC SPECTROSCOPY – the study of the electromagnetic radiation absorbed and emitted by atoms.

Basic assumptions:
- WHEN AN ATOM ABSORBS ENERGY, IT OFTEN REEMITS THAT ENERGY AS LIGHT
- ATOMS CAN RADIATE ENERGY

When a gas-filled tube is passed through an electric current, the gas atoms absorb some of the electrical energy and reemit light of a different color.

The light emitted can be separated into its constituent wavelengths by passing it through a prism.

The result is a series of bright lines called an **EMISSION SPECTRUM**.

The light emitted by a certain element has a characteristic color.
E.g. Mercury atoms, for example, emit light that appears blue, helium atoms emit light that appears violet, and hydrogen atoms emit light that appears reddish.

The emission spectrum of a particular element is always the same, so we can use the emission spectrum to identify the element.

ABSORPTION SPECTRUM – white light through a gas of an element → atoms absorbs radiations at the same frequencies of those emitted.

DIFFERENCES BETWEEN A WHITE LIGHT SPECTRUM AND THE EMISSION SPECTRA OF ATOMS.

WHITE LIGHT SPECTRUM: continuous – spectrum consists of light of all wavelengths.

EMISSION SPECTRA OF ATOMS: not continuous – bright lines at specific, discrete wavelengths, with darkness in between.
These colored lines indicate that the light is being emitted only at certain wavelengths, or frequencies, that correspond to specific colors

In the emission spectrum of an element, we can distinguish three regions that correspond to three different sets of lines.

1) **LYMAN SERIES**
2) **BALMER SERIES**
3) **PASCHEN SERIES**

Classical physics could not explain why these spectra consisted of discrete lines.
→ According to classical physics, an atom composed of an electron orbiting a nucleus should emit a continuous white light spectrum.

BOHR'S ATOM (1913)

Niels Bohr attempted to develop a model for the hydrogen atom that explained its atomic spectrum.

Starting point: PLANCK'S CONCEPT OF ENERGY QUANTA

Planck stated that energy is never emitted in a continuous stream but only in small, discrete packets called quanta.

ENERGY → QUANTIZED

Considerations:

1) Electrons exist in specific regions (***circular orbits***) at fixed distances from the nucleus.
2) Each orbit has a specific energy level.
3) Electron cannot exist between energy levels.
4) When an atom absorbed one or more quanta of energy, its electrons would "jump" to a higher energy level – ***stationary states***
5) A number of energy levels are available, the lowest of which is called the ***ground state***.
6) When an electron falls from a high energy level to a lower one ***a quantum of energy is emitted*** as light at a specific wavelength and this light corresponds to one of the lines visible in the spectrum.

Bohr proposed also that, in contradiction to classical electromagnetic theory, an electron orbiting the nucleus in a stationary state emits no radiation.

Radiation is emitted or absorbed only when an electron jumps from one stationary state to another.

WAVE NATURE OF MATTER

WAVE NATURE OF THE ELECTRON

The wave nature of the electron is seen most clearly in its **diffraction** → an electron beam created an *interference pattern* after passed through a slit.
It was thought that two smaller beams of particles were produced.

DE BROGLIE (1924)

All objects have wave properties.
For small particles, such as electrons, the wave properties are more visible.

$$\lambda = \frac{h}{mv} \quad \text{de Broglie relation}$$

Equation that puts in relation the double nature of the electron: **KE** and **WAVELENGTH**.
The faster the electron is moving, the higher its kinetic energy and the shorter its wavelength.

SCHRÖDINGER (1926)

Created a mathematical model that described electrons as waves.
His wave function can determine the **probability of finding an electron** in a certain region around the nucleus of the atom.
We cannot locate an electron precisely within an atom → electrons are not revolving around the nucleus in orbits as Bohr postulated, but they are found in orbitals.

ORBITAL: region around the nucleus where there is a high probability of finding a given electron.

HEISENBERG (1927) – UNCERTAINTY PRINCIPLE

WAVE NATURE AND PARTICLE NATURE – COMPLEMENTARY PROPERTIES
Complementary properties exclude one another—the more we know about one, the less we know about the other.
We re unable to observe the electron simultaneously as both a particle and a wave.

WE CANNOT SIMULTANEOUSLY MEASURE ITS POSITION AND ITS VELOCITY.
The more accurately we know the position of an electron, the less accurately we can know its velocity and vice versa.

QUANTUM NUMBERS

Each orbital is specified by three interrelated quantum numbers:

- ***n***, principal quantum number
    - Integer
    - Determines the overall size and energy of an orbital.
    - ***The higher n, the higher the energy***
- ***l***, angular momentum/ azimuthal quantum number
    - values: $0 < l < n-1$
- ***m***, magnetic quantum number
    - values: $-l < m < +l$
- ***m_s***, spin quantum number – way of spinning
    - half integer
    - if there is only one electron, it has *+spin*)

Orbitals with the same value of ***n*** are said to be in the same principal level (or principal shell). Orbitals with the same value of ***n*** and ***l*** are in the same sublevel (or subshell).

AUFBAU PRINCIPLE – PRINCIPLE OF MINIMUM ENERGY

Electrons tend to fill first the lowest available energy levels.

1s orbital has less energy than 2s.

PAULI EXCLUSION PRINCIPLE

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

Each orbital can have a maximum of only two electrons, with opposing spins.

HUND'S RULE

Electrons tend to first occupy singly all degenerate (same energy) orbitals with parallel spin before pairing with others with opposite spin.

This way, the electron-electron repulsion is reduced.

PERIODIC TABLE AND PERIODIC PROPERTIES

PERIODIC LAW: ELEMENTS IN THE PERIODIC TABLE ARE ARRANGED IN ORDER OF INCREASING ATOMIC NUMBER (Z).

GROUP – elements with the same outermost electron configuration.
Same number of valence electrons → similar chemical properties
Moving down a group, electrons are added on a new energy level-

PERIOD – elements with the same ***n*** – principal quantum number
Electrons are added on the same energy level.

PERIODIC PROPERTIES

ATOMIC RADIUS

Defined as one-half the distance between two nuclei of two atoms of the same element bonded together.

DECREASE MOVING ALONG A PERIOD – electrons are added on the same energy level so there are strong attractions between the protons in the nucleus and the electrons.
According to Coulomb's law, the attraction between a nucleus and an electron increases with increasing magnitude of nuclear charge.

INCREASE MOVING DOWN A GROUP – electrons are added on outer shells so the distance from the nucleus increases and the attraction force decreases.

IONIC RADIUS

CATION – SMALLER RADIUS
The loss of an electron causes a disparity between negative and positive charges.
The higher number of protons causes a greater nuclear charge that attract the electrons left.

ANION – BIGGER RADIUS
The adding of an electron causes the negative charges to prevail on the positive charges in order to increase the distance from the nucleus.

FIRST IONIZATION ENERGY

*ENERGY **REQUIRED** TO REMOVE AN ELECTRON FROM THE ATOM IN THE GASEOUS STATE.*
Ionization energy is always positive because removing an electron always takes energy.

INCREASE MOVING ALONG A PERIOD – more electrons on the same outermost level generally experience a greater effective nuclear charge and are therefore held more tightly, so it's harder to ionize the atom.

DECREASE MOVING DOWN A GROUP – electrons in the outermost principal level are increasingly farther away from the positively charged nucleus and are therefore held less tightly.

EXCEPTIONS

B and Be

Be (Z=4) → $1s^2 2s^2$

B (Z=5) → $1s^2 2s^2 2p^1$

B has a **smaller** ionization energy than Be, when it should've been higher.

This exception is caused by the difference between the *s block* and the *p block*.

It's easier to remove the lone electron in 2p (of B) than the electron in 2s (of Be), because 2p orbitals are higher in energy, and therefore the electron is easier to remove.

N and O

N (Z=7) → $1s^2 2s^2 2p^3$ → three 2p orbitals singly occupied.

O (Z=8) → $1s^2 2s^2 2p^4$ → three 2p orbitals, one double occupied → higher repulsion

O has a **smaller** ionization energy because it's easier to remove one electron from a double-occupied orbital where the electron-electron repulsions are higher.

ELECTRON AFFINITY

*ENERGY **RELEASED** WHEN AN ATOM IN THE GASEOUS STATE GAINS AN ELECTRON.*

Usually negative because an atom or ion usually releases energy when it gains an electron.

INCREASE MOVING ALONG A PERIOD – MORE NEGATIVE = MORE ENERGY RELEASED

→ elements release more energy to obtain a more stable configuration.

DECREASE MOVING DOWN A GROUP – MORE POSITIVE = LESS ENERGY RELEASED

→ electrons are placed in a higher energy level far from the nucleus, thus the **SHIELDING EFFECT** increases.

SHIELDING EFFECT: decrease in attraction between an electron and the nucleus in any atom with more than one electron shell.

As one goes down the period, the shielding effect increases, thus repulsion occurs between the electrons.

The atom is less stable and the adding of another electron doesn't change much its stability

EXCEPTIONS

B and Al

B should have a more negative value than Al, that is on the 3rd period.

B should be more eager to gain an electron but there is strong repulsion between the electrons in the n=2 energy level (2n orbitals are smaller than 3n) that makes B less stable and the adding of another electron doesn't change the situation.

ELECTRONEGATIVITY

*TENDENCY OF AN ATOM TO ATTRACT THE ELECTRONS **SHARED** IN A COVALENT BOND.*

Pauling scale – empirical scale of electronegativity values

F – most electronegative (then O, N)

Fr – most electropositive