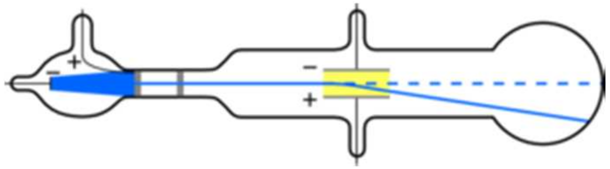
TOPIC 1:
Atoms

- Brief review: nuclear particles
- Elementary particles
- Nuclear stability
- Nuclear binding energy
- Energy units
- Nuclear transformations
- Decay chains
- Ionizing radiation units
- Uses of radioisotopes
- Radioactive decay rate

- Ancient ideas about atoms
- Experiments and concepts that led to Bohr's model
- Black body radiation
- Photoelectric effect
- Hydrogen emission spectrum
- Foundations of quantum mechanics
- Hydrogen atom
- Quantum numbers and electronic configuration
- Multielectronic atoms
- Periodic table
- Periodicity of atomic properties

Brief review: nuclear particles

e^- JJ. Thomson (1912) discovered electron (catodic rays) and the ratio q/m= -1.7588·10^8 C·g^{-1}. RA. Millikan (1909) measured electron electric charge q = -1.602·10^{-19} C



http://en.wikipedia.org/wiki/File:JJ_Thomson_exp2.png

p E. Goldstein (1886) and W. Wien discovered proton (anodic rays) and the ratio q/m = +9.576·10^4 C·g^{-1}.

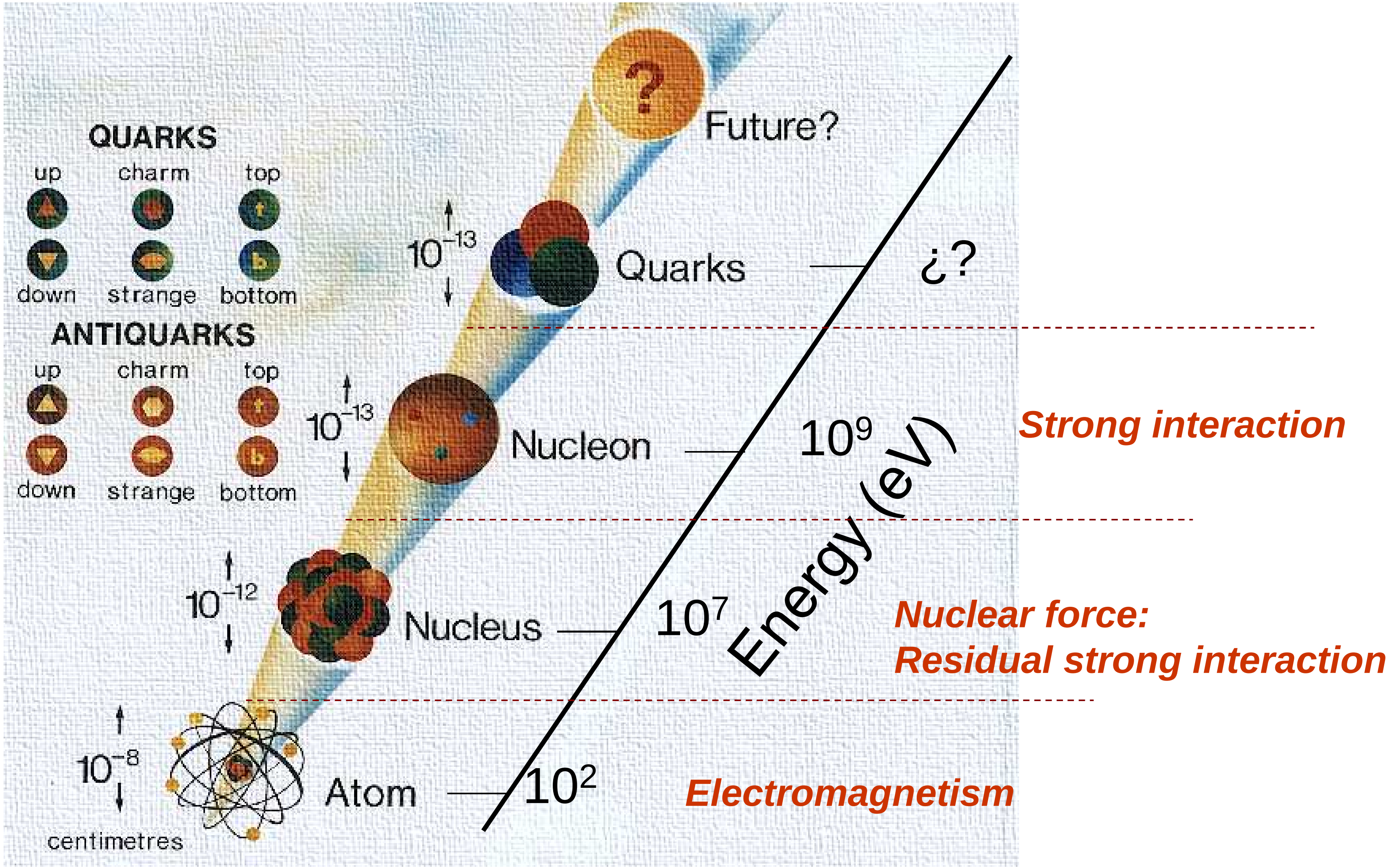
n J. Chadwick (1932) discovered neutrons pumping a thin film of Beryllium with He^{2+} ions (α particles)

e^+ Although predicted by P. Dirac (1931), positron was discovered by C. Anderson (1932); same mass as *e^-* but positive charge.

ν Postulated by W. Pauli (1930), named by E. Fermi (1934), neutrino was detected in 1956 by C. Cowan, F. Reines, FB. Harrison, HW. Kruse, and AD. McGuire.

By the 50's atomic theories were able to explain matter in terms of these 5 particles. Nowadays the picture is extremely complex (subatomic particles) and out of scope of this course.

Elementary particles



Strong interaction

Nuclear force:
Residual strong interaction

Electromagnetism

Energy units

- Electronvolt (eV): it is equal to the amount of kinetic energy gained by a single unbound electron when it accelerates through an electric potential difference of one volt.

$$E = q_e V = 1.6021 \cdot 10^{-19}(C) \times 1(V) = 1.6021 \cdot 10^{-19} J = 1.6021 \cdot\ 10^{-12}\, erg$$
$$1eV = 1.6021 \cdot 10^{-19} J = \ 1.6021 \cdot\ 10^{-12}\, erg$$
$$Derived\ units: MeV = 10^6 eV$$

- Useful unit in physics:
  - Equivalence with temperature through Boltzmann eq.

$$E = k_B T;\ \ T = \frac{E}{k_B} = \frac{1eV}{1.3807 \cdot 10^{-23} JK^{-1}} = \frac{1.6021 \cdot 10^{-19} J}{1.3807 \cdot 10^{-23} JK^{-1}} = 11604K$$

  - Equivalence with radiation wavelength

$$E = h\nu = \frac{hc}{\lambda} = \frac{(84.1357 \cdot 10^{-15} eV \cdot s) \times (2.998 \cdot 10^8 m \cdot s^{-1})}{\lambda} = \frac{1240 eV \cdot nm}{\lambda nm}$$

  - Equivalence with mass

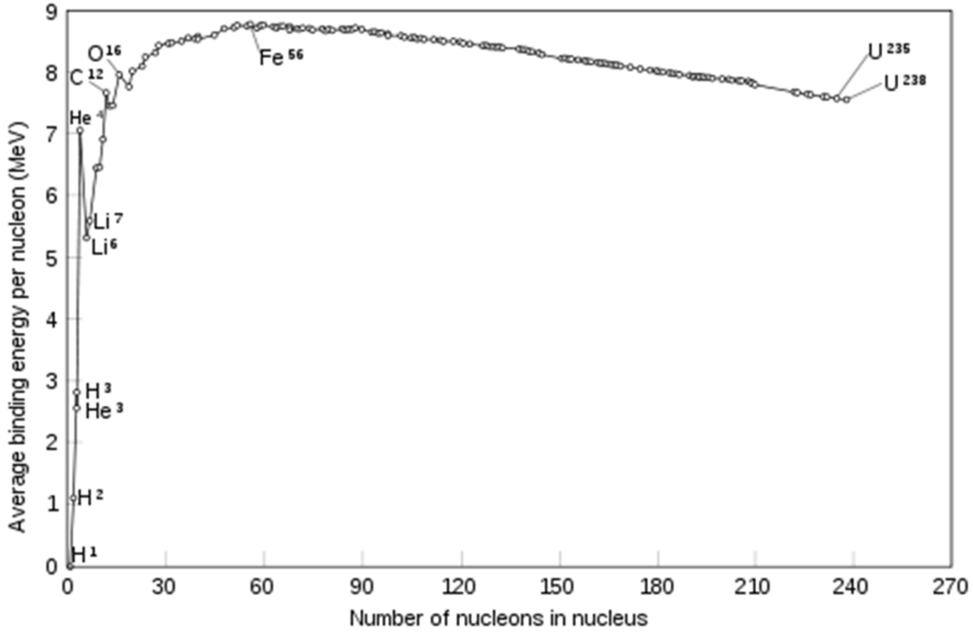
$$E = mc^2 = (1u) \times (299{,}792{,}458 m \cdot s^{-1})^2 = (1.6605 \cdot 10^{-27} kg) \times (299{,}792{,}458 m \cdot s^{-1})^2$$
$$= 4.97805 \cdot 10^{-19} J <> 931{,}516{,}743 eV = 931.5 MeV$$

Nuclear binding energy

Is the energy required to disassemble a nucleus into the same number of free unbound neutrons and protons it is composed of, in such a way that the particles are far/distant enough from each other so that the strong nuclear force can no longer cause the particles to interact

Calculation: difference between the mass of the atom and the sum of the masses of the particles the atom is composed of divided by the number of nucleons.

http://en.wikipedia.org/wiki/File:Binding_energy_curve_-_common_isotopes.svg



Example: binding energy of a deuteron (^2H, isotope of hydrogen with a neutron and a proton in the nucleus.

$$\Delta m = (m_p + m_n) - m_D = 1.007825 + 1.008665 - 2.014102 = 0.002388u$$

$$E = \Delta mc^2 = 2.224MeV; \quad E_B = \frac{E}{A} = 1.112MeV$$

For comparison, ionization potential of ^1H is only 13.6 eV

Nuclear stability

A **nuclide** is an atomic species characterized by the specific constitution of its nucleus, i.e., by its number of protons *Z*, its number of neutrons *N*, and its energy state.

About 256 stable and about 83 unstable (radioactive) nuclides exist naturally on Earth. About 2700 nuclides have been artificially synthesized in nuclear reactors.

Primordial nuclides or **primordial isotopes** are nuclides found on the earth that have existed in their current form since before Earth was formed, according to stellar evolution theory. Only about 288 such nuclides are known.

Designation	**Characteristics**	**Example**
Isotopes	equal proton number	${}^{12}_{6}C$, ${}^{13}_{6}C$
Isotones	equal neutron number	${}^{13}_{6}C$, ${}^{14}_{7}N$
Isobars	equal mass number	${}^{17}_{7}N$, ${}^{17}_{8}O$, ${}^{17}_{9}F$
Mirror nuclei	neutron and proton number exchanged	${}^{3}_{1}H$, ${}^{3}_{2}He$
Nuclear isomers	different energy states	${}^{99}_{43}Tc$, ${}^{99m}_{43}Tc$

- Light nuclides Z ≈ N
- As Z increases, N > Z to be stable

- Nuclides with N>>Z or N<<Z are unstable
  - For N/Z >>1, excess of neutrons or defect of protons (blue region). Z→Z+1

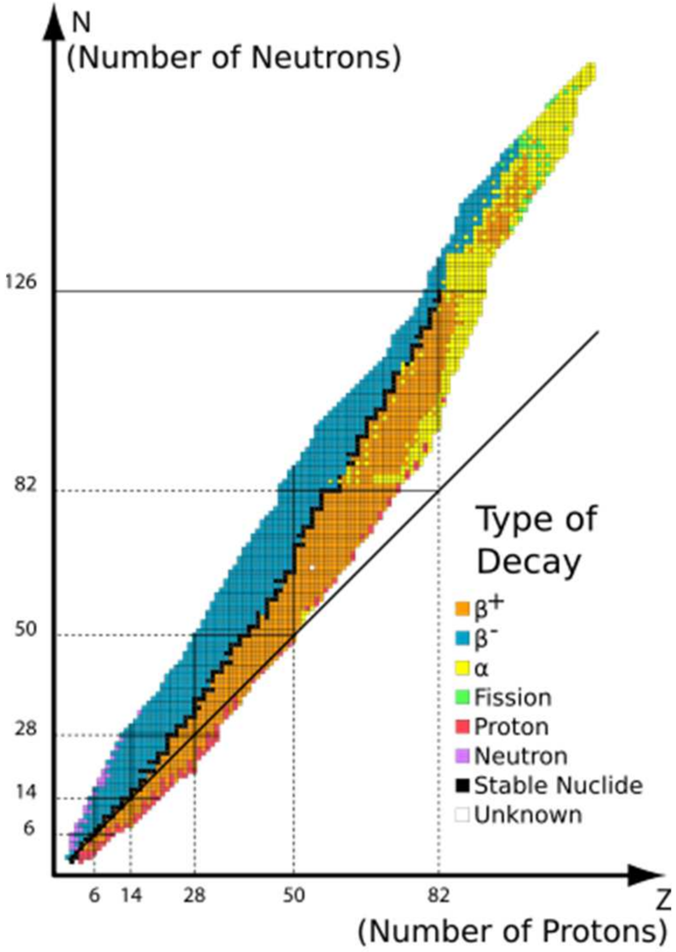
$$n \rightarrow p + e^- \qquad electron\ emission$$
$${}^{20}_{9}F \rightarrow {}^{20}_{10}Ne^+ + e^-$$

  - For N/Z <<1 excess of protons or defect of neutrons (orange region). Z→Z-1

$$p \rightarrow n + e^+ \qquad positron\ emission$$
$${}^{13}_{7}N \rightarrow {}^{13}_{6}C^- + e^+$$

  - Heavy nuclides emit heavy particles (α)

$${}^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn + {}^{4}_{2}\alpha$$



http://en.wikipedia.org/wiki/File:Table_isotopes_en.svg

Nuclear transformations: Natural

- Alfa emitters (α)
  - Soddy's law
  - Typical for nuclides with A>150
  - Penetration in air: depends on energy
    - ^{210}Po (5.3 MeV) : 3.8 cm
    - ^{214}Po (7.7 MeV) : 7.0 cm

$$^{A}_{Z}E \rightarrow {}^{A-4}_{Z-2}E + {}^{4}_{2}\alpha$$

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}\alpha$$

Under STP they are absorbed by a thin aluminimum foil

  - Biological effects:
    - Generally not dangerous to life unless the source is ingested or inhaled.
    - If α emitting radionuclides are inhaled, ingested or injected: most destructive form of ionizing radiation: radiation poisoning - ***acute radiation syndrome*** (**ARS**).
    - 1 mg of ^{210}Po emits as many α particles per second as 4.215 grams of ^{226}Ra. Suspected to play a role in lung and bladder cancer related to tobacco smoking (was used to kill Russian dissident and ex-FSB officer Alexander V. Litvinenko in 2006)
    - Approximately equal ionization is caused by the recoiling nucleus damaging genetic material, since the positive cations of many soluble transuranic elements which emit alphas, are chemically attracted to the net negative charge of DNA, causing the recoiling atomic nucleus to be close to the DNA.

- Beta (β^-) emitters
  - Fajans law: typical for N/Z>>
  - Maximum energy liberated:

$${}^{A}_{Z}E \rightarrow {}_{Z+1}^{A}E + {}^{0}_{-1}\beta$$

$${}^{14}_{6}C \rightarrow {}^{14}_{7}N^{+} + {}^{0}_{-1}\beta$$

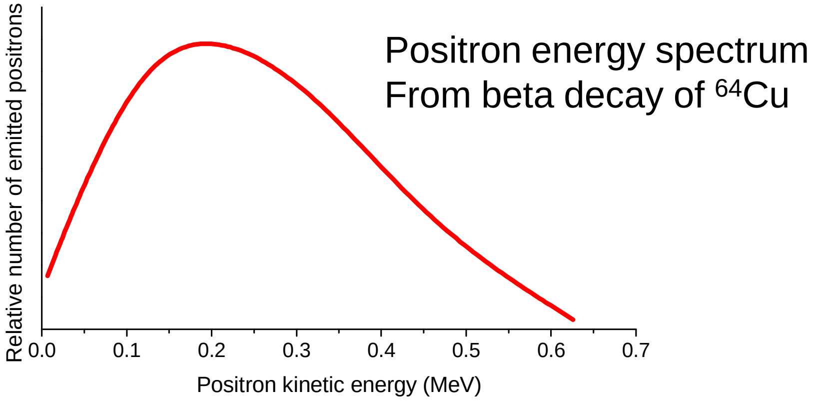
$$\Delta m = m_{N^+} + m_e - m_C \approx m_N - m_C = 14.003074 - 14.003242 = 0.000168u$$
$$E = \Delta m \times 931.5(MeV \cdot u^{-1}) = 0.156MeV$$

  - Medium penetrating power and medium ionising power: can be stopped by a few mm of Al.
  - Beta particles can be used to treat health conditions such as eye and bone cancer, and are also used as tracers. Strontium-90 is the element most commonly used to produce beta particles.
  - Beta particles are also used in quality control to test the thickness of an item, measuring the amount of absorbed particles

$$^{A}_{Z}E \rightarrow {}_{Z-1}^{A}E + {}_{+1}^{0}\beta$$

$$^{11}_{6}C \rightarrow {}^{11}_{5}B^{-} + e^{+}$$

- Positron (β+) emitters
  - Typical for N/Z<<
- In the process of beta decay, either an electron or a positron is emitted. But they present a spectrum of energies. To preserve energy and momentum conservation laws it is necessary the existence of another particle: neutrino and antineutrino that should be emitted as well.
- Origin of the energy spectrum: depending upon what fraction of the reaction energy Q is carried by the massive particle (electron or positron) in each emitting event the energy may be different



$$^{A}_{Z}E \rightarrow {}_{Z-1}^{A}E + {}_{+1}^{0}\beta + \nu \quad neutrino$$

$$^{A}_{Z}E \rightarrow {}_{Z+1}^{A}E + {}_{-1}^{0}\beta + \bar{\nu} \quad antineutrino$$

- Uses of positron emitters: PET-positron emission tomography
  - A radioisotope is injected in the body. The most common is fluorine-18.
  - As it emits a positron, the emitted positron travels in tissue for a short distance (~1 mm), during which time it loses kinetic energy, until it can interact with an electron.
  - The encounter annihilates both electron and positron, producing a pair of annihilation (gamma) photons moving in approximately opposite directions.

$$e^- + e^+ \rightarrow \gamma + \gamma$$

  - These are detected when they reach the detector. The technique depends on simultaneous or coincident detection of the pair of photons moving in approximately opposite direction

- Gamma emitters
  - As atoms, nucleus also have energy states. The state with minimum energy is the ground state. A state with higher energy is called isomer state.
  - After α or β emission the produced nuclei generally start its existence in an excited state. They can lower their energy relaxing to lower energy states or even to the ground state. These transitions are accompanied by the emission of radiation of energy equal to the difference in energy between both states: gamma radiation.
  - The most stable known isomers are:

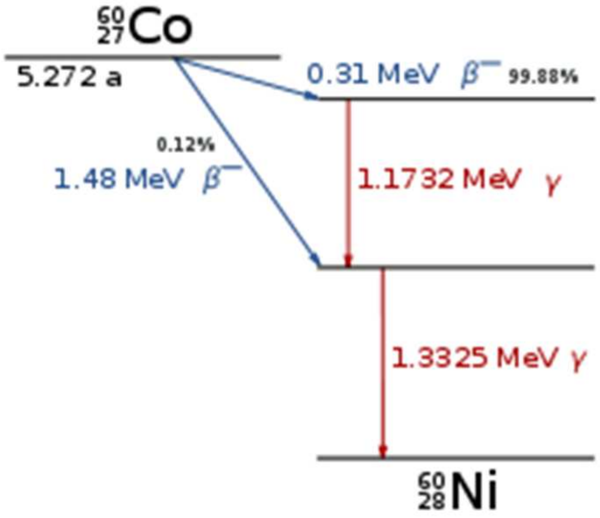
$$ {}^{180m}_{73}Ta \qquad t_{1/2} = 10^{15}\ years $$

$$ {}^{180m2}_{72}Ta \qquad t_{1/2} = 31\ years $$

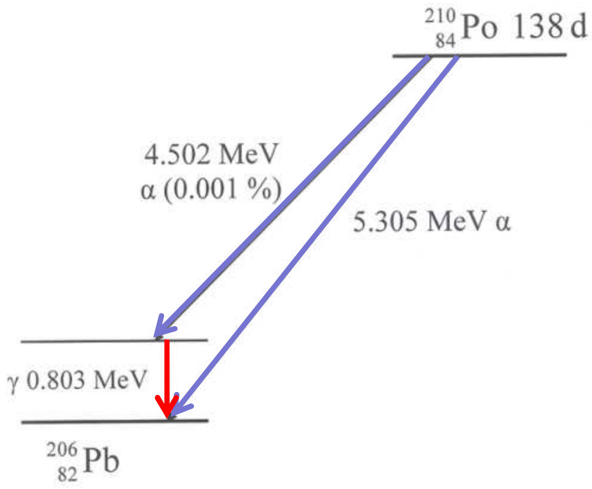
  - γ rays and neutrons are more penetrating that α or β, causing diffuse damage throughout the body (e.g. radiation sickness, increased incidence of cancer) rather than burns.
  - The most biological damaging forms of gamma radiation occur in the gamma ray window, between 3 and 10 MeV, with higher energy gamma rays being less harmful because the body is relatively transparent to them.

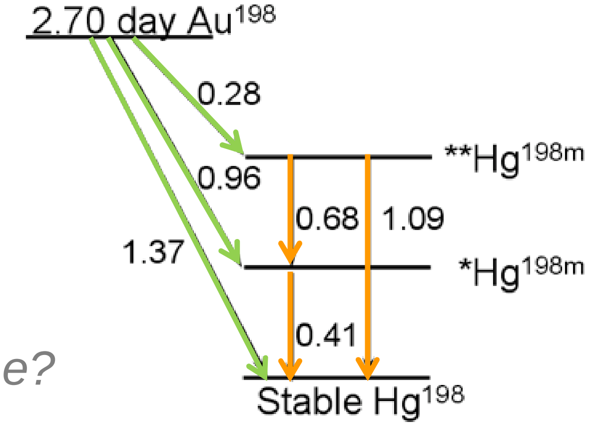
Nuclear transformations

- Decay schemes



http://en.wikipedia.org/wiki/File:Cobalt-60_Decay_Scheme.svg





Are you able to understand this one?

Decay chains

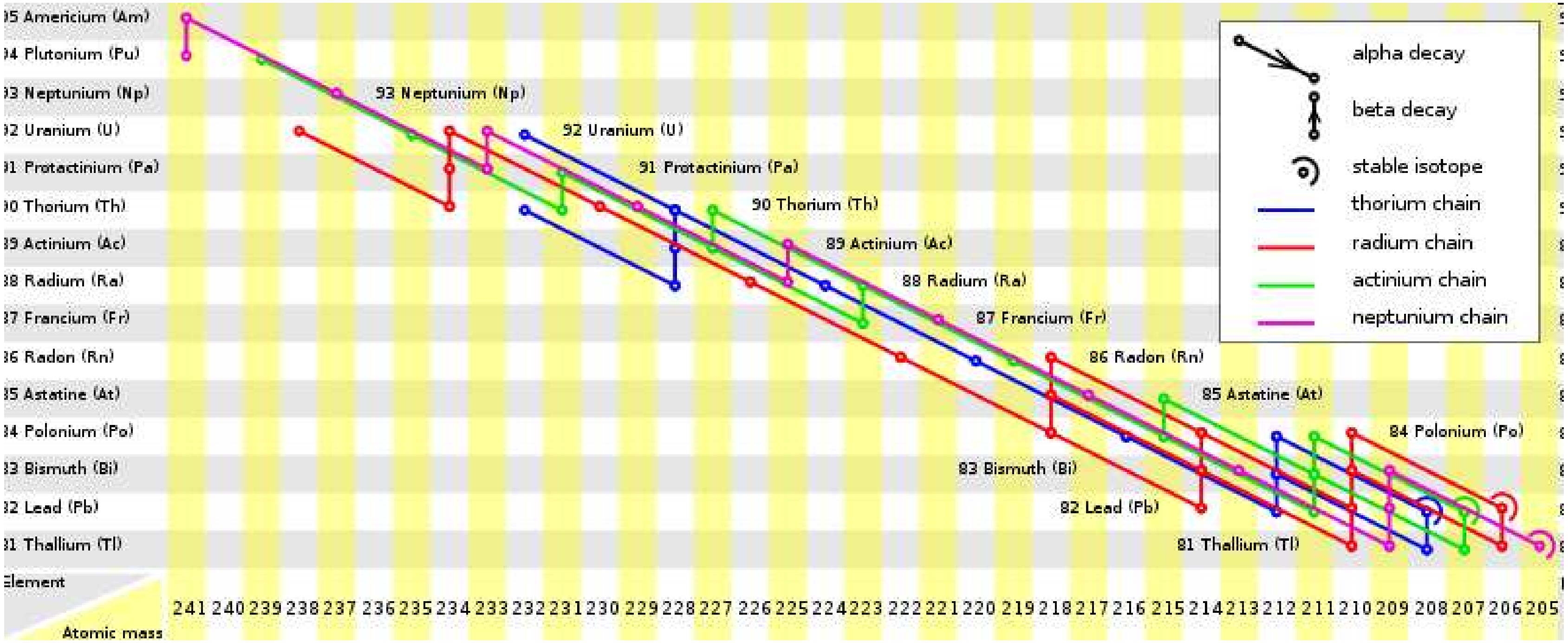
- Becquerel discovered that after a period of time, a piece of ^{238}U contained more than 15 different elements, all of them linked by the mass law 4n+2.
- Decay chains: 3 natural, 1 artificial

		Initial	Final	Mass law
Thorium	Nat	$^{232}_{90}Th$	$^{208}_{82}Pb$	4n
Neptunium	Art	$^{237}_{93}Np$	$^{209}_{83}Bi$	4n+1
Uranium (Radium)	Nat	$^{238}_{92}U$	$^{206}_{82}Pb$	4n+2
Actinium	Nat	$^{235}_{92}U$	$^{207}_{82}Pb$	4n+3

↑

STABLE

Decay chains



http://en.wikipedia.org/wiki/File:Radioactive_decay_chains_diagram.svg

Are you able to understand this graph?

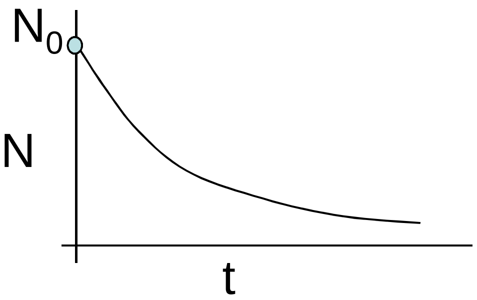
Radioactive decay rate

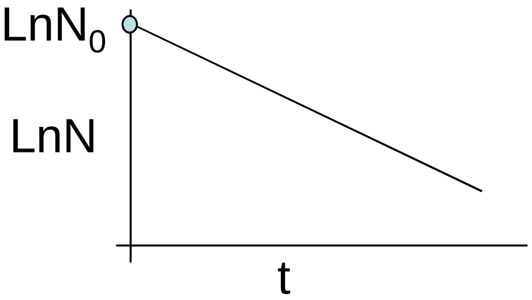
- In a radioactive decay process parent atoms disappear and convert in other atoms
- It a spontaneous process
- It is a random process
- It is impossible to predict when a given atom is going to decay
- Suppose a sample with N atoms and let -ΔN to be the number of decay events within a given period of time Δt.
- Suppose now that you have a sample with N/2 atoms and you wait the same time Δt. How many decay events will you observe?
  - If the sample is large enough, you will probably observe -ΔN/2 events
  - CONCLUSION: the number of decay events in a given period of time is proportional to the number of atoms initially present in a sample
- In mathematical terms

$$-\frac{dN}{dt} = \lambda N; -\frac{dN}{N} = \lambda dt; \qquad -\int_{N_0}^{N} \frac{dN}{N} = \int_{t=0}^{t=t} \lambda dt; \qquad N = N_0 e^{-\lambda t}$$

- λ is called decay constant and has units of s^{-1}
- 1/ λ = τ (s) is the characteristic time of the process: Mean Lifetime, the amount of time an atom "lives" before decaying.

- In graphical terms: exponential decay





- Half-life: time taken for half the radionuclide's atoms to decay. Can be calculated putting as $N_0/2$ the upper integration limit. The half life is related to the decay constant as follows:

$$t_{1/2} = \frac{0.693}{\lambda}$$

Nuclide	Decay type, E	λ (s^{-1})	$t_{1/2}$	τ
${}^{232}_{90}Th$	α, 4.1MeV	$1.6\cdot10^{-18}$	$1.4\cdot10^{10}$ a	$2.0\cdot10^{10}$ a
${}^{237}_{93}Np$	α, .9 MeV	$1.0\cdot10^{-14}$	$2.1\cdot10^{6}$ a	$3.1\cdot10^{6}$ a
${}^{238}_{92}U$	α, 4.3 MeV	$4.9\cdot10^{-18}$	$4.5\cdot10^{9}$ a	$6.5\cdot10^{9}$ a
${}^{235}_{92}U$	α,4.7 MeV	$3.1\cdot10^{-17}$	$7.1\cdot10^{8}$ a	$1.0\cdot10^{8}$ a
${}^{214}_{84}Po$	α. 7.8 MeV	$4.2\cdot10^{3}$	$1.6\cdot10^{-4}$ s	$2.4\cdot10^{-4}$ s

Ionizing radiation units

- Ionizing radiation consists of subatomic particles or electromagnetic waves that are energetic enough to detach electrons from atoms or molecules, thus ionizing them (includes x-rays).

- Activity: number of disintegrations per unit time = decay rate
  - SI unit Becquerel (Bq); number of decays per second (dps)
  - Older unit (still used) Curie (Ci): equivalent to $3.7 \cdot 10^{10}$ Bq.
  - 1Ci is very high activity. Acceptable radiation levels are in the range of milli Ci or less (mCi).

- Absorbed radiation dose: absorption of one joule of ionizing radiation by one kilogram of matter (usually human tissue).
  - SI unit Gray (Gy):
  - Exposure of an adult (75 kg) to 5 or more Gy at one time usually leads to death within 14 days. This dosage represents 375 joules absorbed energy. Medical use of radiation is typically measured in milligray (mGy).
  - Abdominal x-ray is 1.4 mGy; pelvic CT scan is 25 mGy.
  - Old unit rad: equivalent to 10 mGy

Uses of radioisotopes

- Radiation treatment of foodstuffs. 1000Gy can eradicate any insects in perishable goods (potatoes). 10 000 Gy reduces salmonella in meat and fish. Public concern when marking “radiochemically protected”.

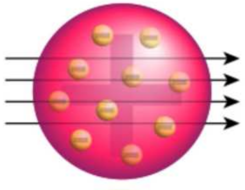
- Analytical tool. ^{32}P is used to analyse sequences of RNA and DNA via the use of phosphoryl transfer catalyzing enzymes. ^{14}C is used to trace metabolic pathways and to age “ancient” materials.

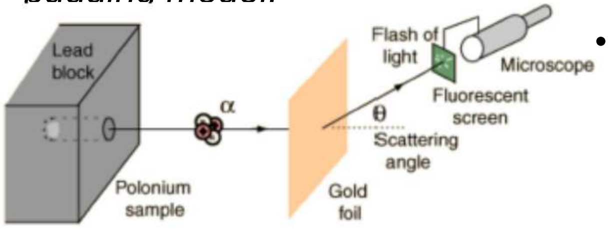
- Nuclear medicine.
  - Radiopharmaceuticals are taken internally (intravenously or orally). External detectors (gamma cameras) capture and form images from the radiation emitted.
  - Diagnostic tests primarily show the physiological function of the system being investigated as opposed to traditional anatomical imaging such as CT or MRI:
    - ^{18}F (fluorodeoxyglucose-FDG) for PET scan; ^{67}Ga to image inflammation and chronic infections; ^{111}In….
  - Therapy:
    - ^{131}I for hyperthyroidism and thyroid cancer; ^{90}Y and ^{131}I for refractory Lymphoma, and palliative bone pain treatment with ^{153}Sa or ^{89}Sr

Ancient ideas about atoms

The concept that matter is composed of discrete units and cannot be divided into arbitrarily tiny quantities has been around for millennia.

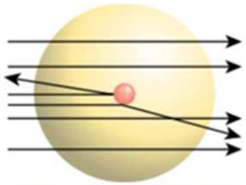
- *Jainism*. 6th century BCE, India, earliest references to the concept of atoms
- *Atomism*. 450 BCE, Democritus coined the term átomos (Greek: ἄτομος), which means "uncuttable“.
- *Corpuscularianism*. 13th-century, Paul of Taranto postulates that all physical bodies possess an inner and outer layer of corpuscles that can be divided.
- In 1661, Robert Boyle (*The Sceptical Chymist or Chymico-Physical Doubts & Paradoxes*) argued that matter was composed of various combinations of different "corpuscules" rather than the *classical elements of air, earth, fire and water*.
- In 1803, John Dalton used the concept of atoms to explain the law of multiple proportions. It is considered the father of modern atomic theory.
- In 1897 J. J. Thomson discovered the electron, and concluded that it was a component of every atom. He postulated that *the low mass, negatively charged* electrons were distributed throughout the atom, possibly rotating in rings, with their charge balanced by the presence of a uniform sea of positive charge. This became known as the *plum pudding model.*





http://ocw.uv.es/ciencias/2/1-2/112733mats70.pdf

- In 1909 E. Rutherford made an experiment to probe the structure of atoms. A very thin Au film foil was bombarded with a highly collimated beam of α particles. The majority passed through the foil but from time to time some were dispersed an angle θ and even backscattered. He postulated the planetary model where all positive charge was in the center



http://en.wikipedia.org/wiki/File:Rutherford_gold_foil_experiment_results.svg

Problem: If e^- are
stationary they will be attracted by nucleus.
moving around, they will emit radiation until stop

Bohr’s Model of Atom

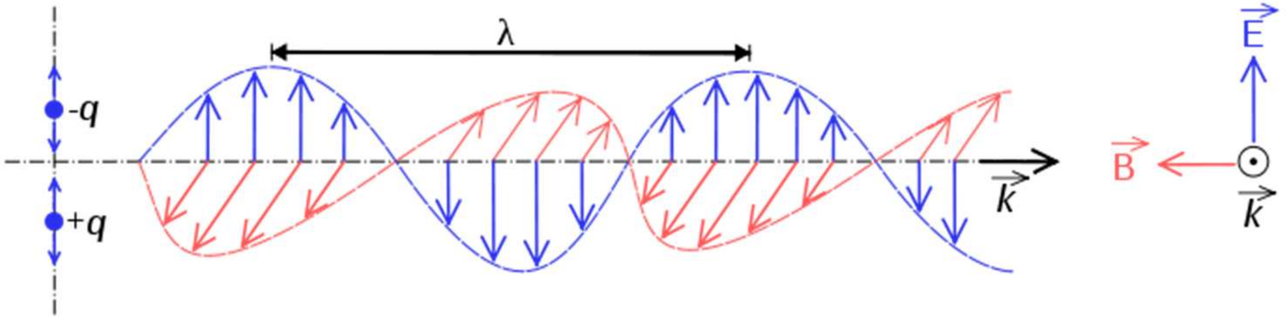
Experiments and concepts that led to Bohr's model

Electromagnetic radiation

Wave = vibrational disturbance through which energy is transmitted

An **electromagnetic wave** is the way electromagnetic radiation propagates through space

According to Electromagnetism, a spatially-varying electric field generates a time-varying magnetic field and vice versa. Therefore, as an oscillating electric field generates an oscillating magnetic field, the magnetic field in turn generates an oscillating electric field, and so on. These oscillating fields together form an **electromagnetic wave**



wikimedia.org/wikipedia/commons/3/35/Onde_electromagnetique.svg

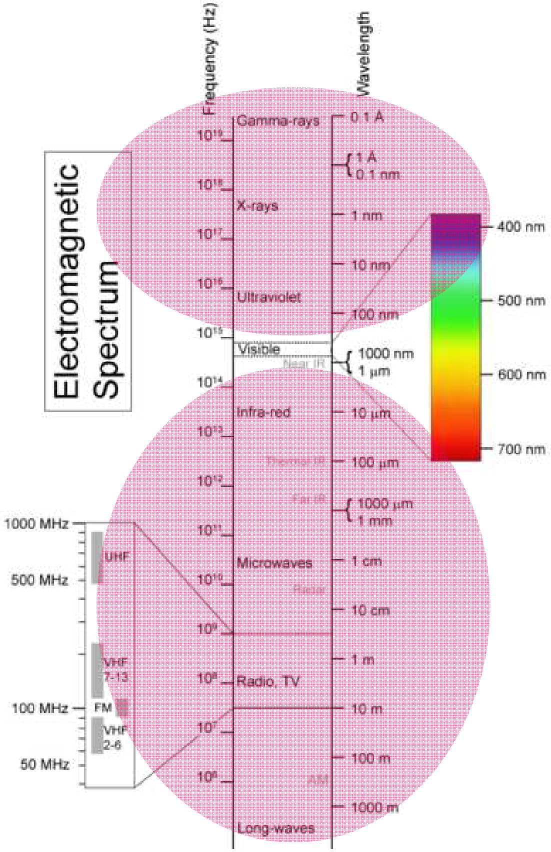
Electromagnetic waves can be imagined as a self-propagating transverse oscillating wave of electric and magnetic fields that are mutually perpendicular

Oscillations of the waves are perpendicular to the direction of energy transfer and travel

Waves are characterized by:

Amplitude, A: the maximum distance from the highest point of the disturbance in the medium (crest) to the equilibrium point during one wave cycle.
Wavelength, λ: distance between two sequential crests (m).
Period, T: time for one complete cycle of an oscillation of a wave
Frequency, ν: reciprocal of a period (Hz, s^{-1})

λ and ν are related by $\lambda\nu$ **= c**, where c is the propagation speed: **c** $\approx 3\times10^8\ m\cdot s^{-1}$



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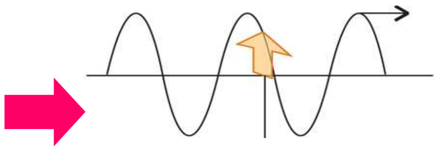
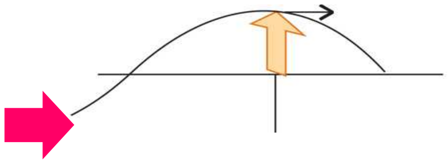
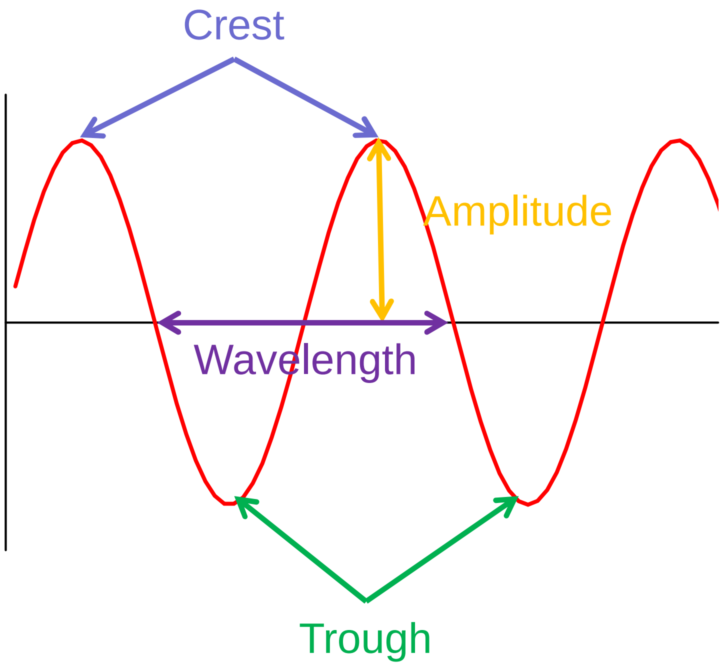


λ short ; ν high



λ long ; ν small

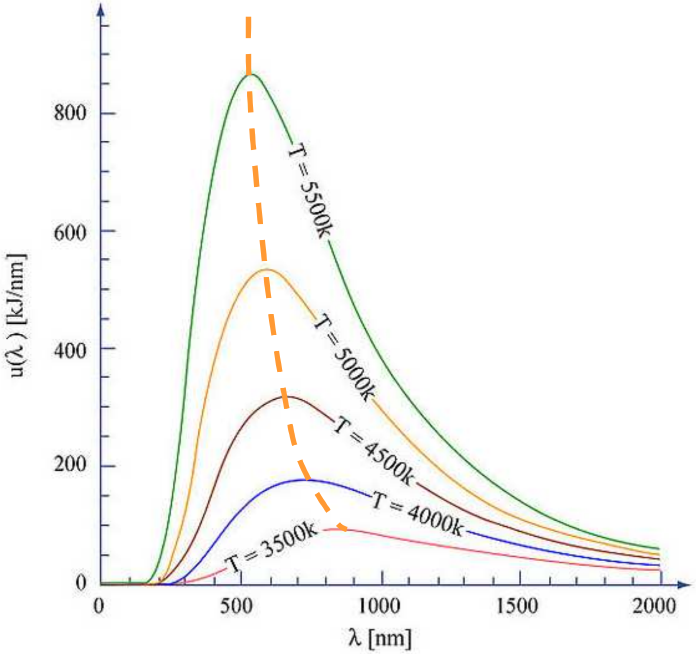


Black body radiation (advanced)

Classical electromagnetism assumed that the energy of a wave was a function of squared Amplitude (A^2).

BBR experiments showed that as T increases, maximum intensity shifts to shorter wavelengths (higher frequencies).

M. Planck (1900) solved this discrepancy assuming that:



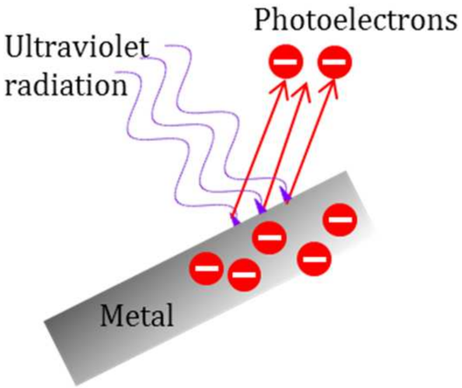
- Radiation came from atoms oscillating inside the cavity
- The energy of these oscillators was limited to a set of discrete, integer multiples of a fundamental unit of energy, E, proportional to the oscillation frequency v:

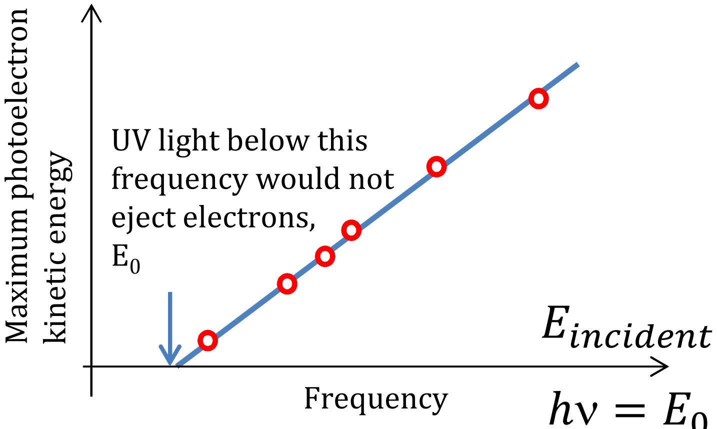
$$E = nh\nu \qquad h = 6.62606896(33) \times 10^{-34}\ \mathrm{J{\cdot}s}$$

- This was the Planck's Quantum Hypothesis

MIT OCW. Biological Engineering II: Instrumentation and Measurement. Fall 2006

Photoelectric effect



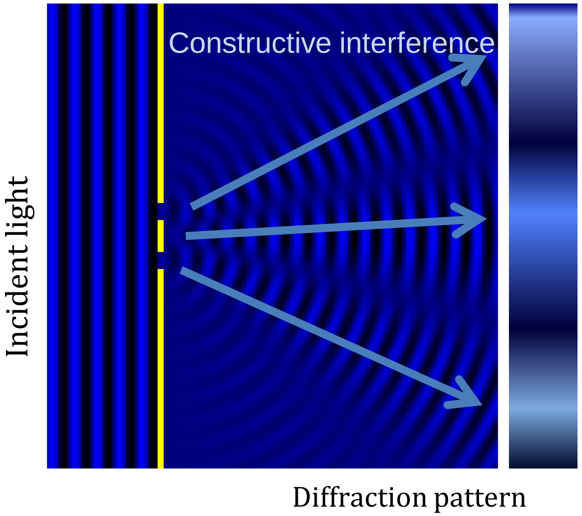


Einstein (1905) explained the photoelectric effect assuming that light was formed by discrete particles or *photons* with energy $h\nu$

$$E_{incident} = E_{threshold} + E_{kinetic\ electron}$$

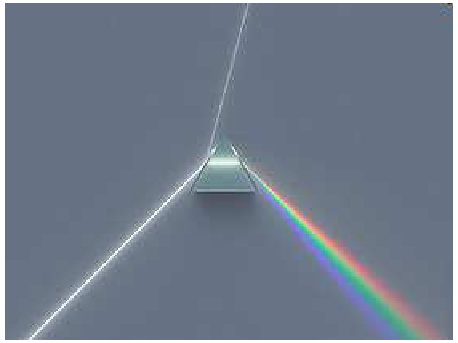
$$h\nu = E_0 + \frac{1}{2}mu^2; \quad \frac{1}{2}mu^2 = h\nu - h\nu_0$$

But electromagnetic radiations behave also as waves experiencing:



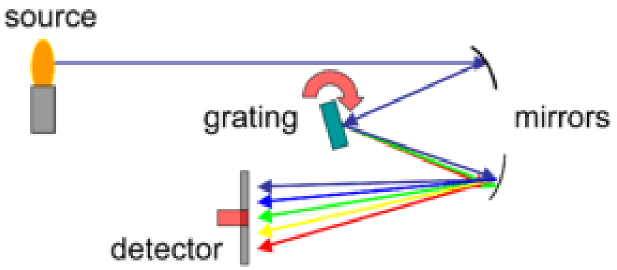
Interference

Reflection
Refraction
Transmission
Dispersion



http://en.wikipedia.org/wiki/File:Dispersive_Prism_Illustration_by_Spigget.jpg

Hydrogen emission spectrum



When hydrogen gas (H_2) is subjected to an electrical discharge molecules split into two atoms. Some atoms acquire an excess of energy that is released in the form photons. These are collimated through a slit and dispersed by a grating (prism). The intensity of the photons of different wavelengths is registered by a detector.

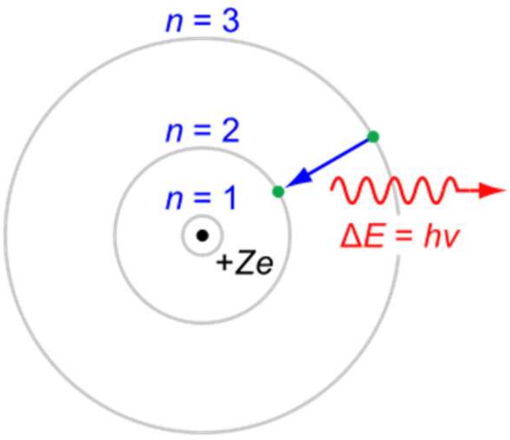
Hydrogen does not emit all the wavelengths but only some of them, called emission lines. The lines that appear in the *visible part* of the spectrum Balmer lines

http://en.wikipedia.org/wiki/Emission_spectrum

$$\frac{1}{\lambda} = R_H \left(\frac{1}{(n')^2} - \frac{1}{(n)^2} \right) = 1.097373 \cdot 10^7 (m^{-1}) \left(\frac{1}{(2)^2} - \frac{1}{(n)^2} \right)$$

For n’=1: Lymann; n’=3: Paschen; n’=4: Brackett; n’=5: Pfund; n’=6: Humphreys

Bohr's theory of hydrogen atom



http://en.wikipedia.org/wiki/File:Bohr-atom-PAR.svg

- Obsolete: electrons only have certain classical motions.
- Postulates:Electrons can only travel in circular orbits, each at a fixed distance from the nucleus, with fixed energies ($F_{centripetal}$=$F_{Coulomb}$).

1. Electrons do not lose energy while traveling, but they can gain or lose energy jumping to other orbits. The energy gained or lost is the energy difference between the two states. $\Delta E = E_2 - E_1 = h\nu$
2. The angular momentum L is restricted to be an integer multiple of a fixed unit.

$$L = mur = n\frac{h}{2\pi} = n\hbar$$

- Success in explaining minimum e^- - n^+ distance and emission spectra

$$F_{Coulomb} = \frac{Ze^2}{4\pi\varepsilon_0 r^2} = F_{Centripetal} = \frac{mu^2}{r}$$

$$r = \frac{n^2h^2\varepsilon_0}{\pi mZe^2} \qquad n = 1,2,3...;\ r_{n=1} = a_0 = 0.05291\,nm$$

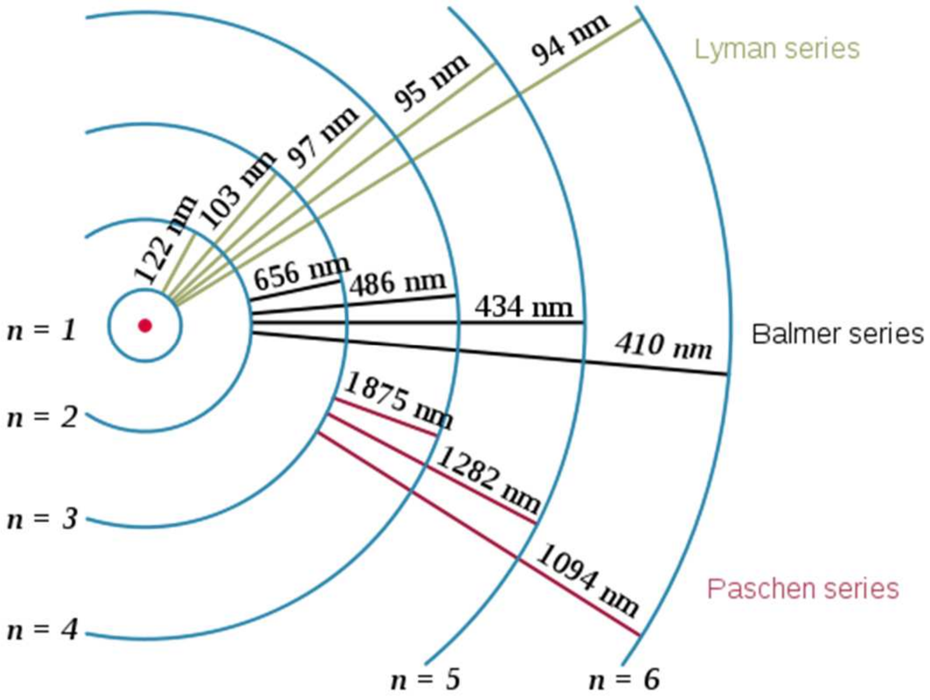
$$E = E_{kinetic} + E_{potential} = \tfrac{1}{2}mu^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$E = -\frac{Z^2}{2n^2}\frac{e^2}{4\pi\varepsilon_0 a_0}$$

$$E_i - E_f = h\nu = \frac{Z^2}{2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)\frac{e^2}{4\pi\varepsilon_0 a_0}$$

An e-n system to be stable should have less energy than e and n separately ⇒ energy must be negative

- Hydrogen emission spectrum: jumps between several n_i levels to a fixed n_f level (f < i): origin of spectroscopic series.
- Alternatively, electron jumps from a scarcely negative level to a more negative one.
- Bohr's formula can be applied to other one-electron atoms: He^+, Li^{2+}, Be^{3+}. Z must be changed accordingly



http://en.wikipedia.org/wiki/File:Hydrogen_transitions.svg

Foundations of quantum mechanics

- Quantization of physical properties (energy)
- Wave- particle duality
- Uncertainty principle
- …

Wave- particle duality

If a photon is a particle (photoelectric effect) it should bear momentum ($p = E/c$) but if a photon is a wave it should have a wavelength $\lambda = c/\nu$.... Louis de Broglie (1924) claimed that *all matter* has a wave-like nature. He coupled these equations giving

$$\lambda = \frac{h}{p}$$

Particle	**Mass (kg)**	**Velocity (ms^{-1})**	**Wavelength (pm)**
Electron gas phase (300 K)	$9 \cdot 10^{-31}$	10^{5}	7 000
Electron in H atom (n=1)	$9 \cdot 10^{-31}$	$2.2 \cdot 10^{6}$	33
He atom in gas phase (300 K)	$7 \cdot 10^{-27}$	1 000	90
Baseball	0.1	20	$3 \cdot 10^{-22}$

Uncertainty principle

Classical mechanics: particles describe defined and precise trajectories and their position and momentum can be known at any instant of time

But:

If a particle behaves as a wave the concept of position becomes meaningless or nonsensical

Heisenberg's Uncertaintly principle:

It is impossible to determine simultaneously both the position and velocity of an electron or any other particle with any great degree of accuracy or certainty

$$\boxed{\Delta p \Delta x \geq \frac{1}{2}\hbar} \qquad (\hbar = h/2\pi)$$

Hydrogen atom

E. Schrödinger considered the system formed by the electron and the nucleus in an hydrogen atom. He fixed in space the position of the nucleus and tried to calculate the "quantum state" of the system. The equation he set out is:

$$H\psi_i = E_i\, \psi_i$$

ψ is a function called "wave function", a mathematical tool that depends on the position (x,y,z) and momentum (p_x,p_y,p_z) of the electron.

ψ has no physical meaning (probability amplitude) but $|\psi|^2$ is equal to the chance of finding the electron at a certain position.

H is the Hamiltonian operator or energy operator. When H is applied over a wave function, ψ_i is recovered but multiplied by the energy of that state E_i.

Electron wave function ψ of electrons in atoms is called atomic orbital

Quantum numbers and electronic configuration

Unlike Borh's model, quantum numbers appear naturally solving Scrödinger's equation.

In quantum mechanics three quantum numbers are necessary to describe the position and energy of an electron and a fourth one to describe the spin (relativistic effects, Dirac).

Principal quantum number (n)	n=1, 2, 3, ...	Describes the average distance with respect nucleus and determines de energy
Angular momentum quantum number (l)	l=0, 1, 2, ..., n - 1	Specifies the shape of an atomic orbital
Magnetic quantum number (m_l)	m_l =-l,-(l 1),···,0,···,(l-1),l	Describes the orientation in space of an atomic orbital. It is the projection of l over an axis
Spin quantum number (m_s)	m_s= +1/2, -1/2	It is the projection over an axis of the magnetic field described by an electron rotating around its own axis

Orbital names

l	0	1	2	3	4	5
Orbital	s	p	d	f	g	h

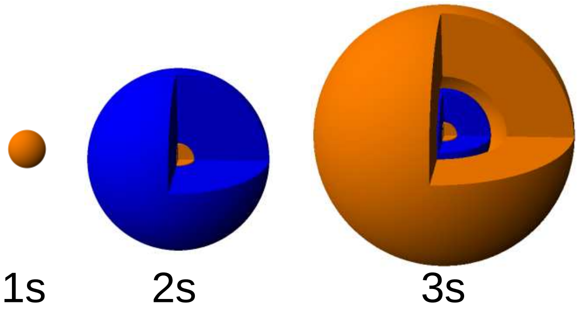
Naming

nº e
n **Orbital**

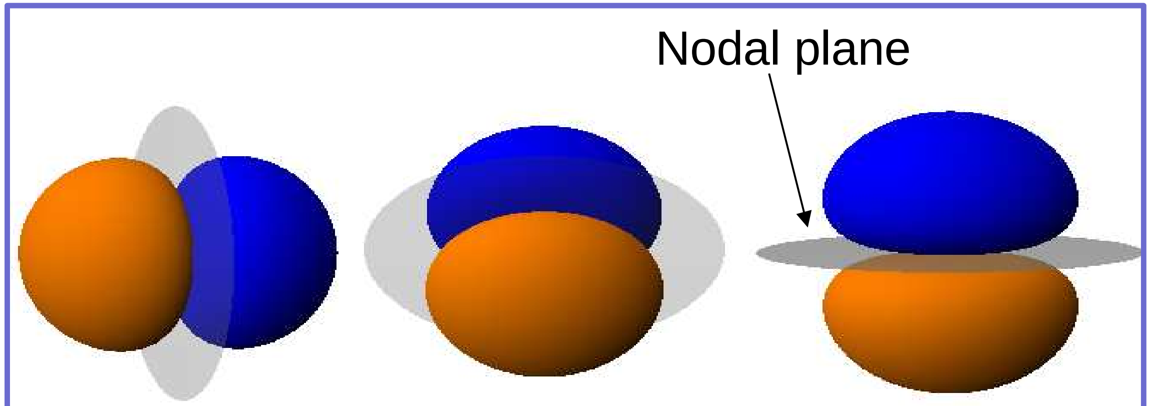
$2s^2$
$3p^3$
$4d^5$

Atomic orbital: physical region defined by a function where the electron is likely to be.

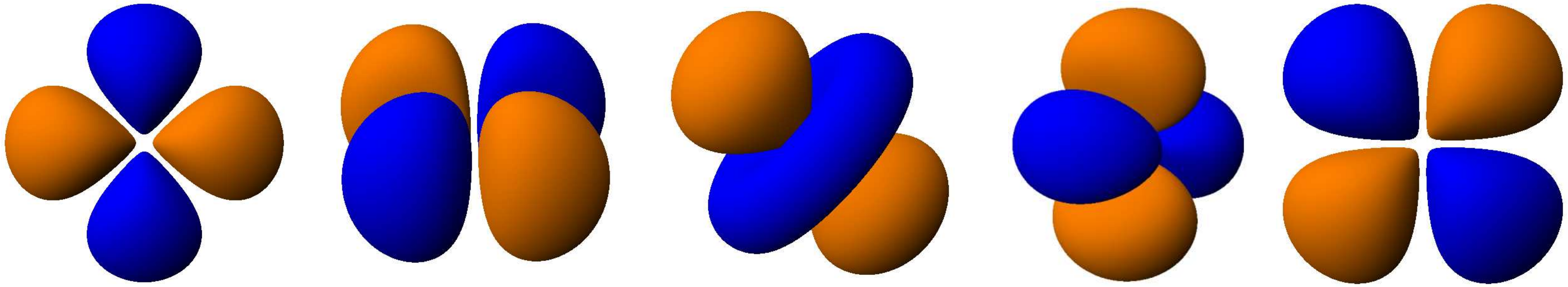
Shapes of atomic orbitals: isosurfaces



s orbital: spherical symmetry



p orbitals

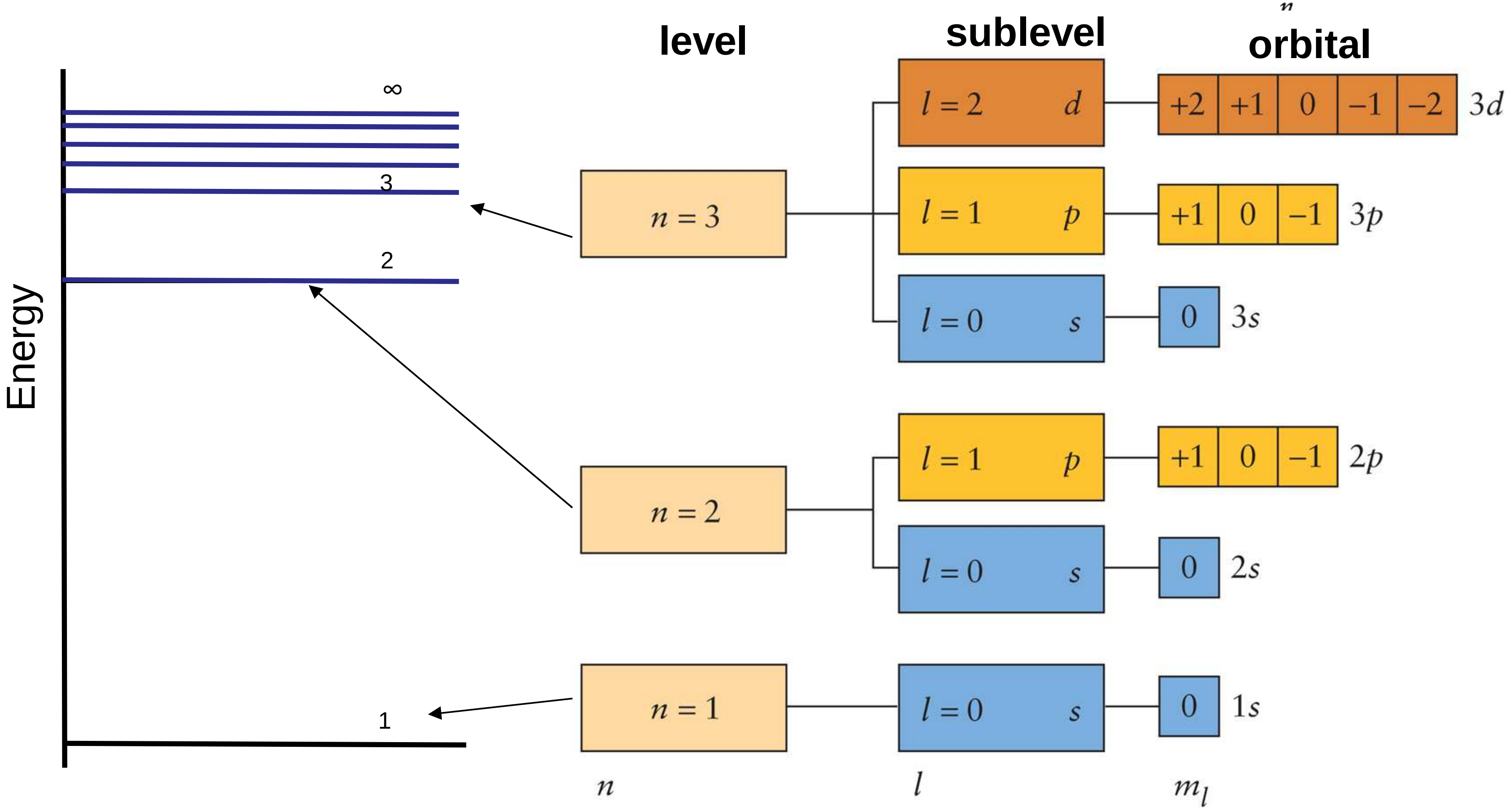


d orbitals

*Orbitals plotted using **"Orbital-viewer"** software. http://www.orbitals.com/orb/ov.htm*

Quantum numbers and energy

n: principal quantum number determines the orbital energy …



Compare with transp 26. There n were orbits. Here, there are orbitals.
The electron in Hydrogen atom is normally in level 1(n=1) (ground state), where energy is minimum

Quantum numbers and orbitals in hydrogen atom

n=1	**l=0**	**m_l=0**	**Orbital 1s**

n=2	**l=0**	**m_l=0**	**Orbital 2s**
	l=1	**m_l=-1**	**Orbital $2p_x$**
		m_l=0	**Orbital $2p_y$**
		m_l=1	**Orbital $2p_z$**

n=3	**l=0**	**m_l=0**	**Orbital 3s**
	l=1	**m_l=-1**	**Orbital $3p_x$**
		m_l=0	**Orbital $3p_y$**
		m_l=1	**Orbital $3p_z$**
	l=2	**m_l=-2**	**Orbital $3d_{xy}$**
		m_l=-1	**Orbital $3d_{xz}$**
		m_l=0	**Orbital $3d_{yz}$**
		m_l=1	**Orbital $3d_{x^2-y^2}$**
		m_l=2	**Orbital $3d_{z^2}$**

Degenerate orbitals: the have the same energy

Summarizing:

The energy and position of an electron in hydrogen atoms is described by a mathematical function named wave function whose square gives the probability density. For each set of quantum numbers (n, l, m_l) there is a single wave function or atomic orbital.

Spin is a property of electrons. It is described by spin quantum number m_s which can have two possible values +1/2 and -1/2

Multielectronic atoms

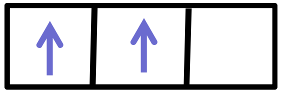
In multielectronic atoms, degeneracy no longer holds because of electron-electron repulsion.

- Atoms are filled with electrons in order of increasing energy (Aufbau Principle).
- Energy increases as n+l (Madelung's Rule).
- No two electrons can have the same four quantum numbers (Pauli Exclusion Principle). If *n*, *l*, and m_l are the same, m_s must be different such that the electrons have opposite spins.
- For a given electron configuration, the term with maximum multiplicity has the lowest energy (Hund's rule).

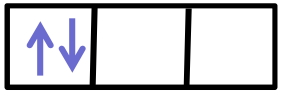
Multiplicity is defined as:

P = 2S+1 where: $S = \sum m_s$

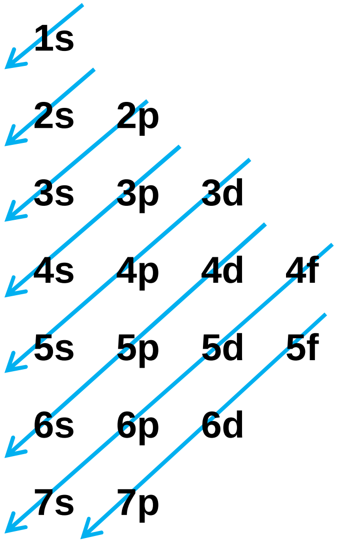
Assume two electrons in p orbitals. Two possibilites: a) or b)

a) 

$$S = +\frac{1}{2} + \frac{1}{2} = 1 \quad P = 2 \times 1 + 1 = 3$$

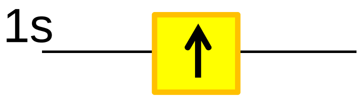
b) 

$$S = +\frac{1}{2} - \frac{1}{2} = 0 \quad P = 2 \times 0 + 1 = 1$$

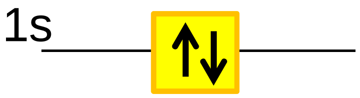


a) Has maximum multiplicity, so minimum energy, so is more stable than b). Electrons are unpaired

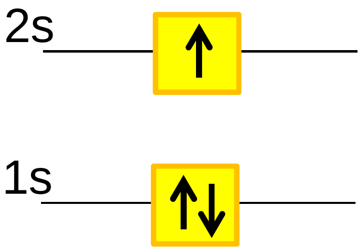
b) Has less multiplicty, so more energy (less negative), so less stable than a). Electrons are paired



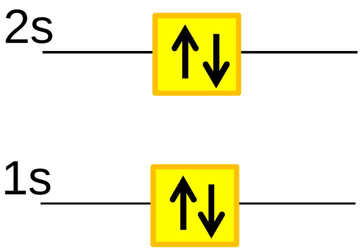
H $1s^1$



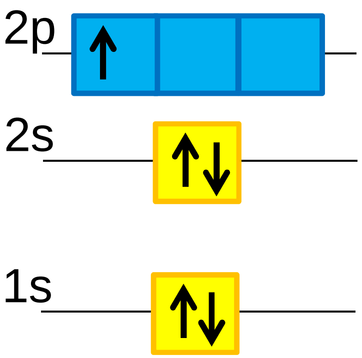
He $1s^2$



Li $1s^2\ 2s^1$, [He] $2s^1$



Be $1s^2\ 2s^2$, [He] $2s^2$



B $1s^2\ 2s^2\ 2p^1$, [He] $2s^2\ 2p^1$

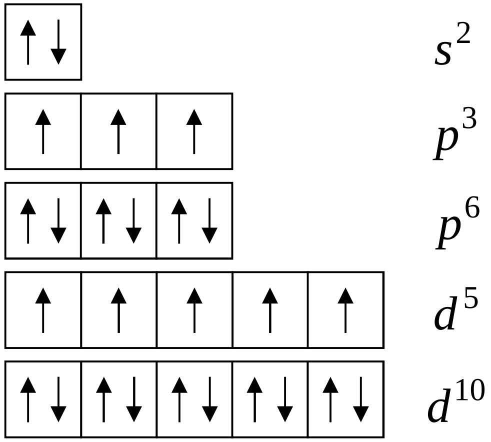
Unpaired electrons: total magnetic moment = sum of magnetic moments → PARAMAGNETISM

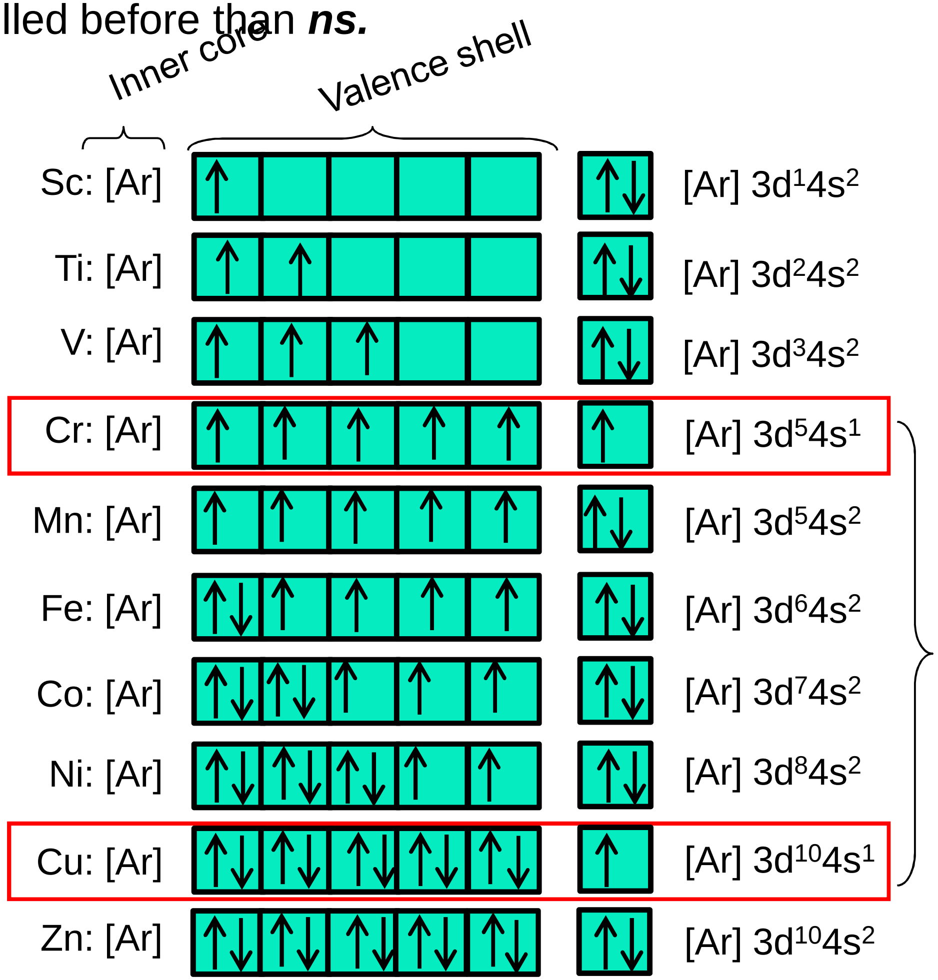
Paired electrons: sum of magnetic moments cancels → DIAMAGNETISM

Shortcomings of the Aufbau Principle.

When orbitals are completely filled or half-filled acquire an additional stability.

This explains why half-filled ***nd*** orbitals are filled before than ***ns.***





Sc: [Ar] [Ar] $3d^14s^2$
Ti: [Ar] [Ar] $3d^24s^2$
V: [Ar] [Ar] $3d^34s^2$
Cr: [Ar] [Ar] $3d^54s^1$
Mn: [Ar] [Ar] $3d^54s^2$
Fe: [Ar] [Ar] $3d^64s^2$
Co: [Ar] [Ar] $3d^74s^2$
Ni: [Ar] [Ar] $3d^84s^2$
Cu: [Ar] [Ar] $3d^{10}4s^1$
Zn: [Ar] [Ar] $3d^{10}4s^2$

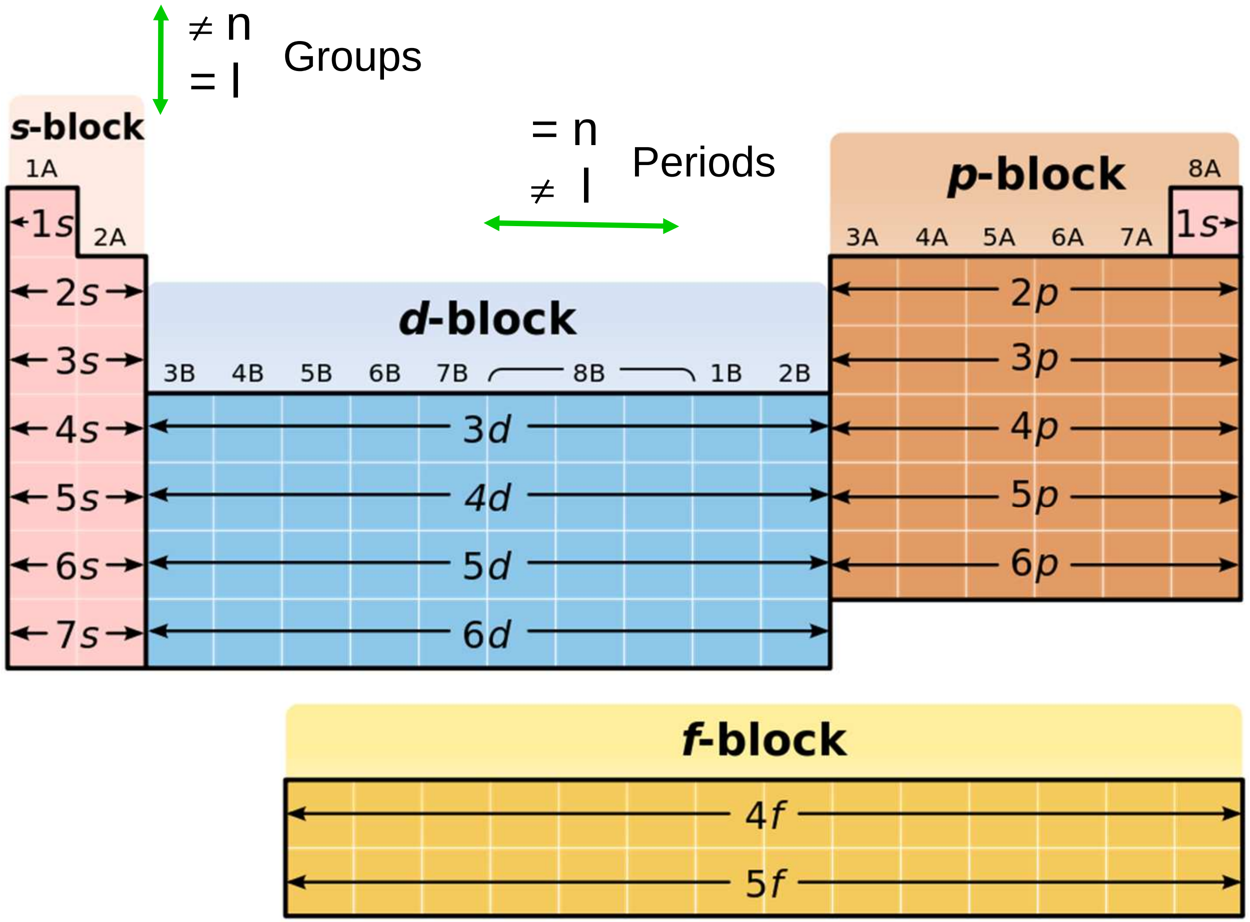
Electronic configuration of transition metals

Some exceptions to Aufbau Principle.
There are more but these suffice

Periodic table

Elements are ordered according to their electronic configuration (valence shell)

n	l		Nº m_l	Nº m_s	Nº electrons
1	**0**	**s**	**1**	**2**	**2×1= 2**
2	0	s	1	2	2×1= 2
	1	**p**	**3**	**2**	**2×3= 6**
3	0	s	1	2	2×1= 2
	1	p	3	2	2×3= 6
	2	**d**	**5**	**2**	**2×5=10**
4	0	s	1	2	2×1= 2
	1	p	3	2	2×3= 6
	2	d	5	2	2×5=10
	3	**f**	**7**	**2**	**2×7=14**

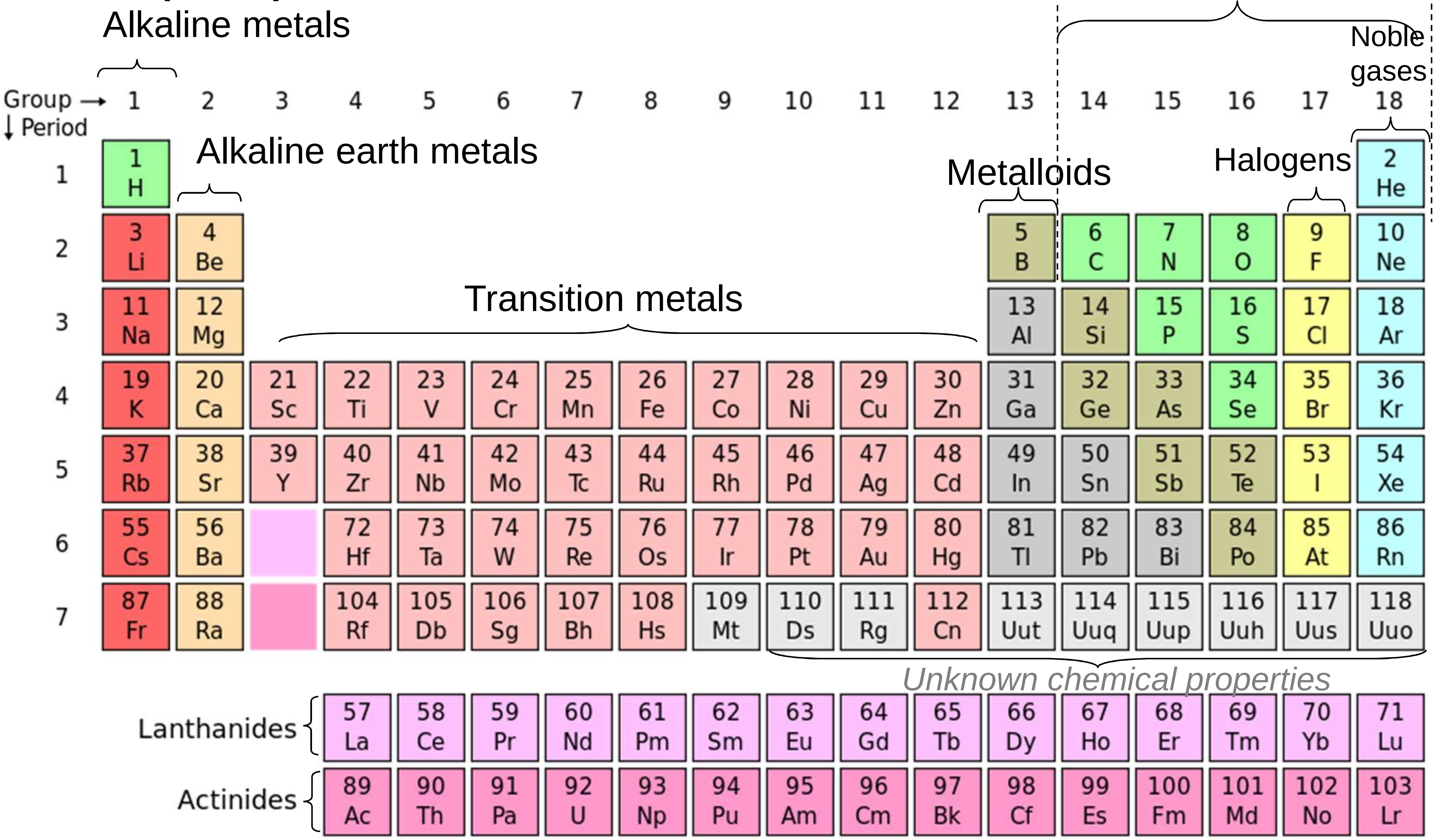


≠ n
= l
Groups

= n
≠ l
Periods

http://en.wikipedia.org/wiki/File:Periodic_Table_structure.svg

Group and period names



Non metals

Noble gases

Alkaline metals

Alkaline earth metals

Metalloids

Halogens

Transition metals

Unknown chemical properties

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

http://en.wikipedia.org/wiki/File:Periodic_table.svg

Periodicity of atomic properties

Atomic Radius
Ionic radius
Ionization potential
Electron affinity
Electronegativity

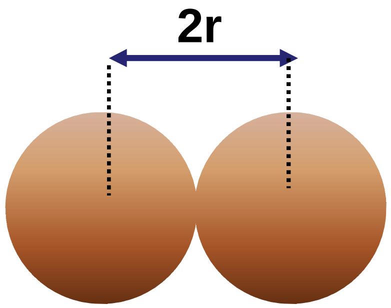
Effective nuclear charge

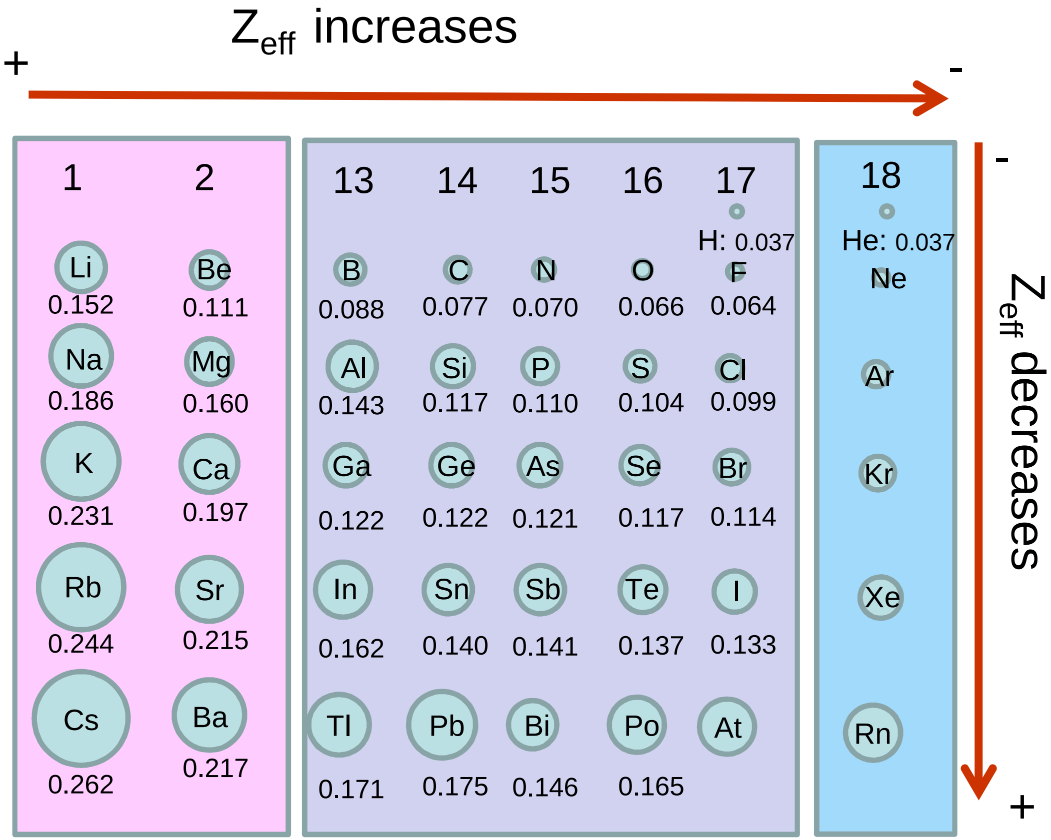
Is the net positive charge experienced by an electron in a multi-electron atom. The term "effective" is used because the shielding effect of negatively charged electrons prevents higher orbital electrons from experiencing the full nuclear charge by the repelling effect of inner-layer electrons

$Z_{eff} = Z - \sigma$, *where* σ *is the shielding constant.*

- The outer shell electrons do not experience the whole nuclear charge
- Shielding is more efficient by inner core electrons than electrons from the same subshell.

Atomic radius (r). The shortest distance between two contiguous atoms of an element.





1	2	13	14	15	16	17	18
						H: 0.037	He: 0.037
Li 0.152	Be 0.111	B 0.088	C 0.077	N 0.070	O 0.066	F 0.064	Ne
Na 0.186	Mg 0.160	Al 0.143	Si 0.117	P 0.110	S 0.104	Cl 0.099	Ar
K 0.231	Ca 0.197	Ga 0.122	Ge 0.122	As 0.121	Se 0.117	Br 0.114	Kr
Rb 0.244	Sr 0.215	In 0.162	Sn 0.140	Sb 0.141	Te 0.137	I 0.133	Xe
Cs 0.262	Ba 0.217	Tl 0.171	Pb 0.175	Bi 0.146	Po 0.165	At	Rn

As Z_{eff} increases, nucleus attract more the outer electrons and atom contracts.

r decreases in a period from the left to the right

r increases in a group from top to bottom

Ionic radius (r_{ion}). Is a measure of the size of an atom ion in a crystal lattice

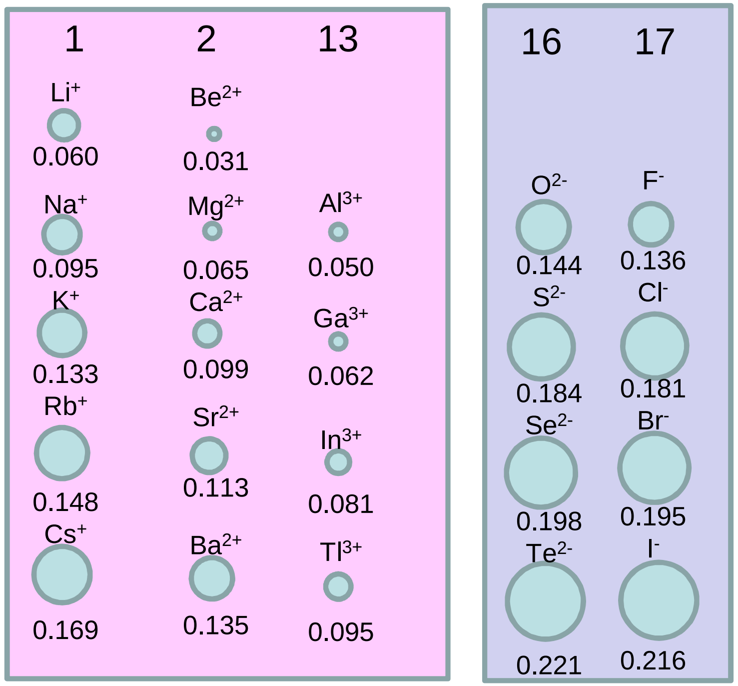
Its variation along the Periodic Table is equivalent to atomic radius.

As a cation looses electrons, Z_{eff} increases because electron-electron repulsion decreases. Therefore, atom contracts.

$r_{cation} < r_{atomic}$

As an anion gains electrons Z_{eff} decreases because electron-eletron repulsion increases. Therefore atom expands.

$r_{anion} > r_{atomic}$

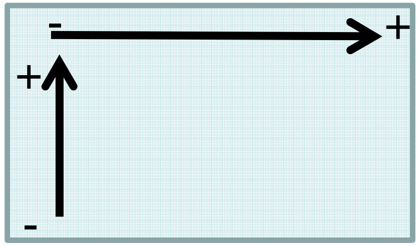


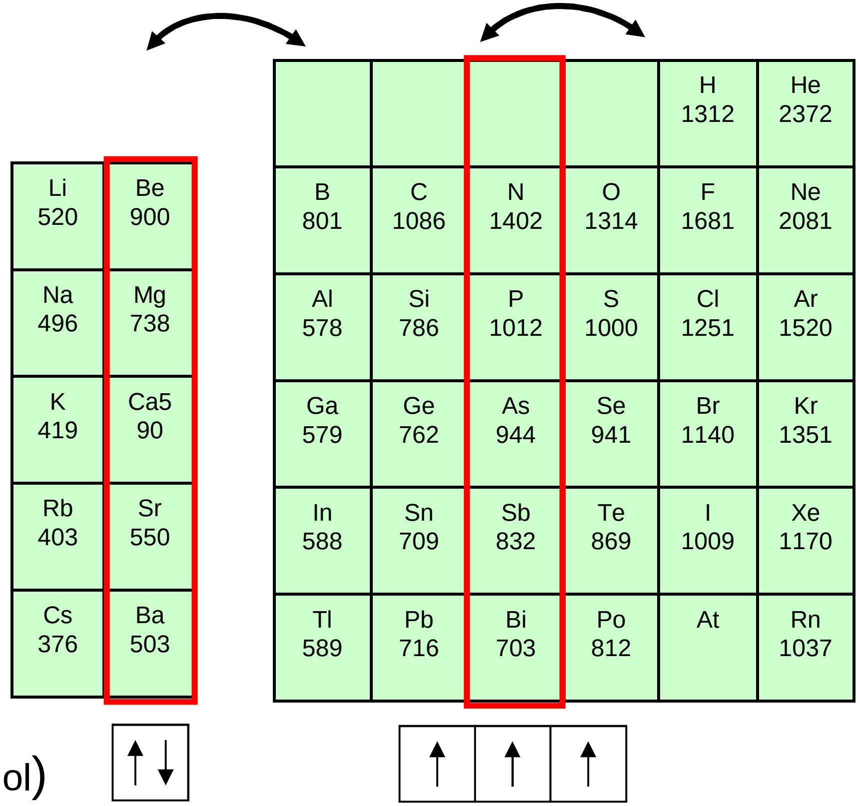
Ionization energy (I). Is the minimal energy required to remove (to infinity) one electron (1 mol) from a gaseous atom (1 mol) isolated in free space and in its ground electronic state.

The greater the energy, the more difficult to remove an electron. Low ionization energies, typical of alkaline metals, manifests as tendency to form cations.

$$\left.\begin{array}{ll} X_{(g)} \rightarrow X_{(g)}^{+} + e_{(g)}^{-} & I_1 \\ X_{(g)}^{+} \rightarrow X_{(g)}^{2+} + e_{(g)}^{-} & I_2 \ldots \end{array}\right\} \quad I_1 < I_2 < \ldots$$

Variation trend of Ionization Potential along Periodic Table:



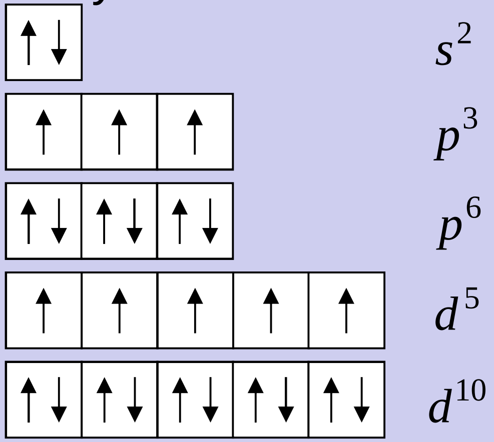


Li 520	Be 900
Na 496	Mg 738
K 419	Ca5 90
Rb 403	Sr 550
Cs 376	Ba 503

				H 1312	He 2372
B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
Al 578	Si 786	P 1012	S 1000	Cl 1251	Ar 1520
Ga 579	Ge 762	As 944	Se 941	Br 1140	Kr 1351
In 588	Sn 709	Sb 832	Te 869	I 1009	Xe 1170
Tl 589	Pb 716	Bi 703	Po 812	At	Rn 1037

(in kJ/mol)

Filled or half-filled orbitals are specially stable



s^2

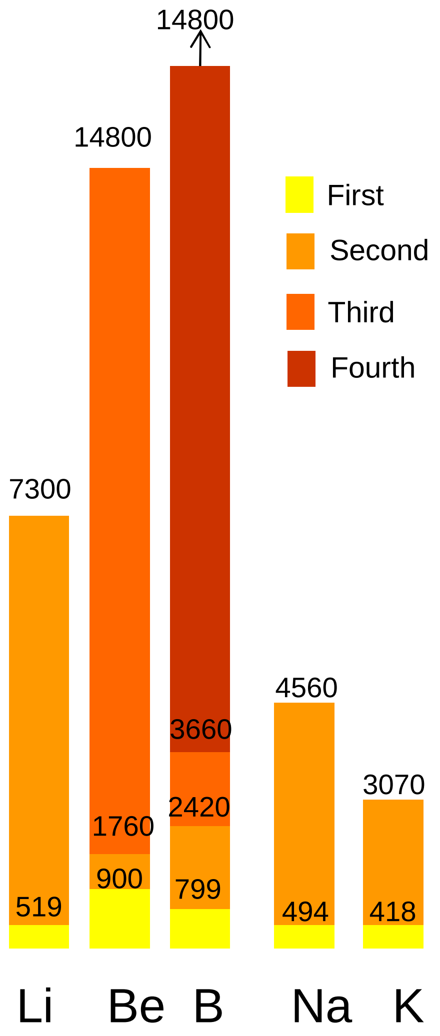
p^3

p^6

d^5

d^{10}

***n*th Ionization Energy** is the energy required to strip off the *n*th electron after the first *n* − 1 electrons have been removed



(Units: $kJ \cdot mol^{-1}$)

As an electron is removed, electron-electron repulsions decrease and, therefore, Z_{eff} increases raising the ionization energy

Electron affinity (A). Amount of energy required to detach an electron from a singly charged negative ion.

$$X^-_{(g)} \rightarrow X_{(g)} + e^-_{(g)} \qquad A = E_0(X_{(g)}) - E_0(X^-_{(g)})$$

Positive values mean that anions are more stable than neutral atoms. Negative values mean that anions are not stable

Trend less systematic than for IE

Li 60	Be <0
Na 53	Mg <0
K 48	Ca 2.4
Rb 47	Sr 4.7
Cs 45	Ba 14

↑↓

				H 73	He <0
B 27	C 122	N 0	O 141	F 328	Ne <0
Al 44	Si 134	P 72	S 200	Cl 349	Ar <0
Ga 29	Ge 118	As 77	Se 195	Br 325	Kr <0
In 29	Sn 121	Sb 101	Te 190	I 295	Xe <0
Tl 30	Pb 110	Bi 110	Po	At	Rn <0

↑ ↑ ↑

Electrons in *p* orbitals are very near nucleus and experience a high attraction ⇒A↑

(kJ/mol)

Filled and half-filled orbitals dominate trends

↑↓ s^2

↑ ↑ ↑ p^3

↑↓ ↑↓ ↑↓ p^6

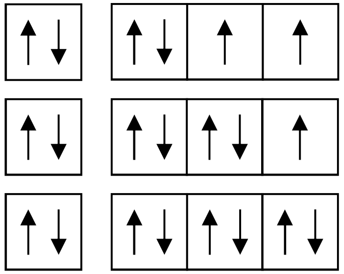
↑ ↑ ↑ ↑ ↑ d^5

↑↓ ↑↓ ↑↓ ↑↓ ↑↓ d^{10}

Example: *Consider the three last anions of the second period: N^-, O^- and F^-.*

Their electronic configurations will be

$$N^-\left(1s^2 2s^2 2p^4\right) \rightarrow N\left(1s^2 2s^2 2p^3\right) + e^-$$
$$O^-\left(1s^2 2s^2 2p^5\right) \rightarrow O\left(1s^2 2s^2 2p^4\right) + e^-$$
$$F^-\left(1s^2 2s^2 2p^6\right) \rightarrow F\left(1s^2 2s^2 2p^5\right) + e^-$$



It should be expected less energy to form O^{2-} from O^- than to obtain F^{2-} from F^-

A(N) (<0)< A(O)(141) < A(F)(328)

F^- has a filled last subshell so it is very stable. It is necessary a huge amount of energy to detach an electron to produce a neutral atom because the later has an incomplete subshell.

If O^- looses an electron neither a filled nor a half-filled orbital are produced; but it has a high nuclear charge so electron is strongly attracted.

If N^- looses an electron, the neutral atoms will have a half-filled orbital, which is very stable; this compensates the strong attraction due to a high nuclear charge.

Electronegativity:

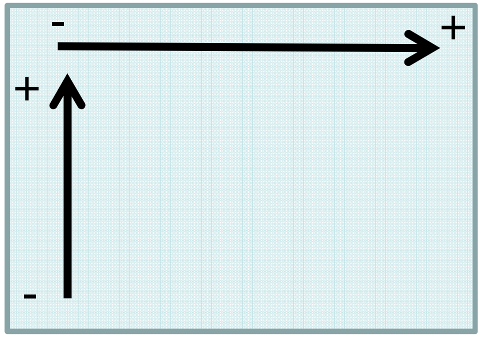
Describes the ability of an atom to attract the shared electrons (or electron density) in a compound towards itself. It is not strictly an atomic property, but rather a property of an atom in a molecule.

$$\chi_A - \chi_B = \sqrt{E_d(AB) - [E_d(AA) + E_d(BB)]}$$

where the terms containing E_d are dissociation energies of molecules AA, AB, and BB in eV

Pauli’s scale of electronegativity

Trend



Trends are similar to ionization energy.

Electropositive elements

Li 1.0	Be 1.6
Na 0.9	Mg 1.3
K 0.8	Ca 1.0
Rb 0.8	Sr 0.9
Cs 0.8	Ba 0.9

Electronegative elements

				H 2.2	He ---
B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ---
Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	Ar ---
Ga 1.4	Ge 2.0	As 2.2	Se 2.5	Br 3.0	Kr 3.3
	Sn 1.9	Sb 2.0	Te 2.1	I 2.7	Xe 3.0