Teaching Tools

- http://archi745.wixsite.com/chimicadiarchi - sito docente
- https://moodle2.unime.it/enrol/index.php?id= 49496 – UNIVERSITY PLATFORM MOODLE
- https://moodle2.unime.it/course/view.php?id=49496
- ESSE3 – UNIME PLATFORM (Programs, exams, in-itinere …….)
- FACEBOOK «Corsi di chimica generale BIOMORF»
- Chimica: Ed. 2019 a colori (Archimede e Enrico Rotondo) available in Italian

Textbooks and Material

- General Chemistry – Raymond Chang
- Inorganic Chemistry – Atkins and Shriver
- Chemistry – Bruce Mahan
- Chemistry, a molecular approach – N. Tro
- Chimica – A. Rotondo in italian– not yet available in english
- Many tests and excercises are available in the teams repositories as well as these slides

Definitions

- **Chemistry concerns matter and its transformations**
- **Matter is whatever occupies room the three states of aggregation**
- **Substances are matter of the same type (simple substances and complex substances)**
- **Several substances constitute mixtures that can be homogeneous or heterogeneous systems**
- **Matter properties are physical (without breakage or transformation of substances) or chemical (evidenced only after bond cleavages and arrangements caused by other substances)**

Beginning of the MODERN CHEMISTRY

- **Law of Definite Proportions (Prust) -same atomic proportion or weight ratio**

- **Law of Multiple Proportions, Dalton Atomic Theory (1806)**

- **Conservation of mass (Lavoisier 1789)**

The Laws

Mass conservation: if substances react, they give rise to products where weight is identical to that of the reacting matter

Constant composition: H_2O substance, comes from oxygen and hydrogen always in the weight ratio of 16 to 2, i.e. 89% O and 11% H

Multiple proportions: the combination of hydrogen and oxygen lead to H_2O or H_2O_2 with H:O weights of 2:16 and 2:32, i.e. multiples of each other

Dalton's Atomic Hypothesis (1804)

1. Matter is made by atoms: small and indivisible (Greek word) particles.
2. Atoms of a certain element are the identical, whereas atoms of different elements are distinguished by their mass (later understood as internal charge).
3. A compound is a combination of atoms of one or more elements that occurs in integer numbers.
4. In a chemical reaction, atoms are neither created nor destroyed, but change their relative arrangement to form new substances.

It's like playing with legos

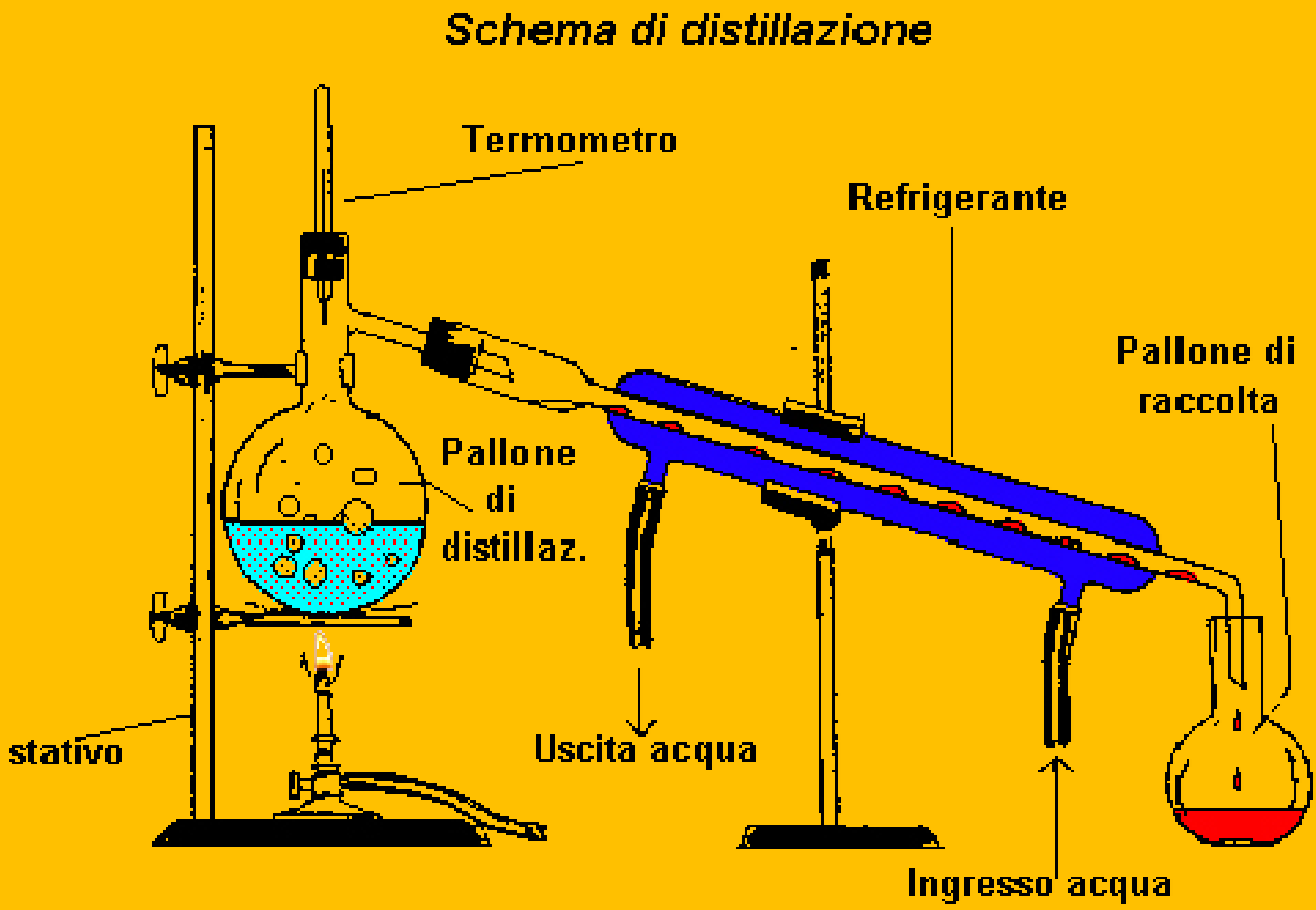
Formulas and Molecules

- **The general formula**: Defines the number and type of atoms present in the molecule. It can be empirical or molecular.
- **The empirical formula**: Defines the minimum ratio between/among the elements within a molecule (HO).
- **The molecular formula**: Reports the exact number of atoms present in the molecule through a subscript placed to the right of the element (H_2O_2).
- **The structural formula**: Tell us about topology and connectivity, how atoms are bound together, and sometimes space arrangement (3D). It can be implicit (implying some links) or explicit (all links are made explicit)

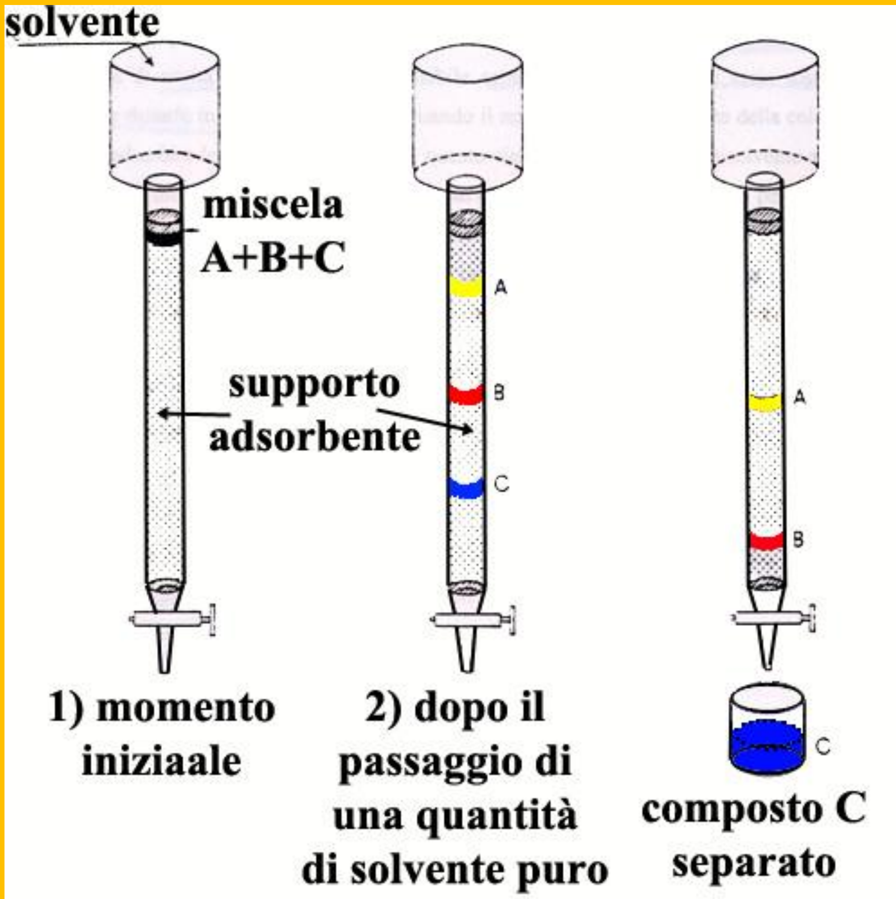
Chemical analysis

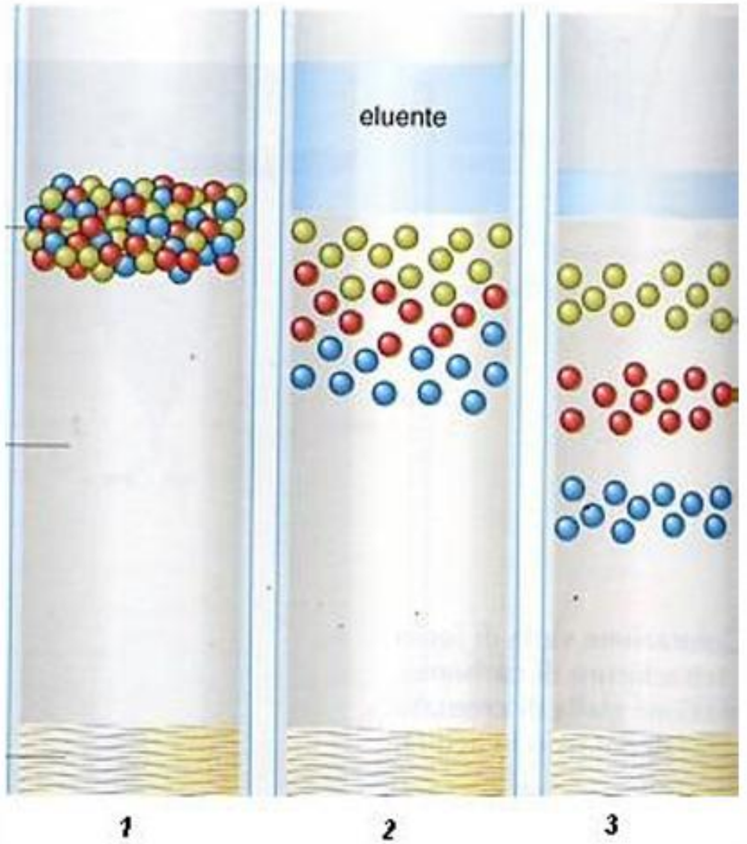
- A sample is a representative part of matter
- Mixtures can be homogeneous or heterogeneous if portions of space with different characteristics (physical, chemical, to what extent?) are distinguishable or not.
- There are methods of separation of phases and substances, used for the analysis and dosage of different substances.

Distillation



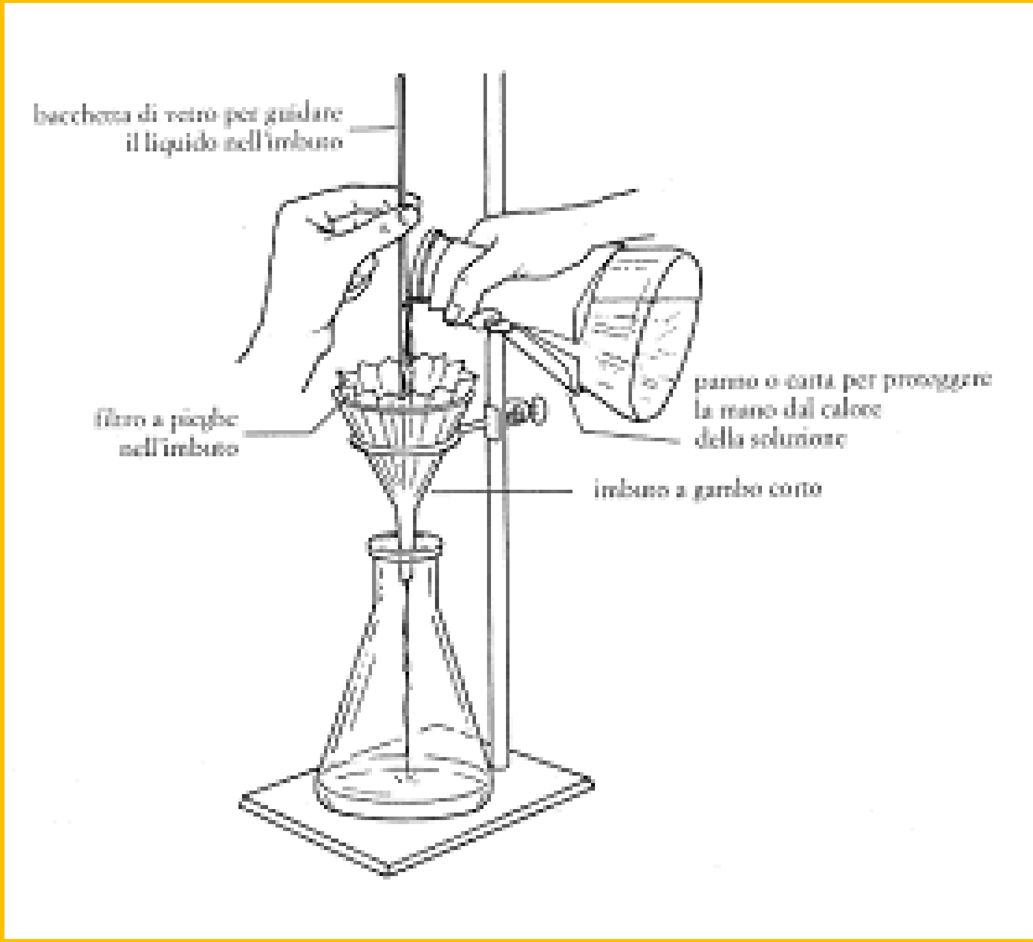
Chromatography



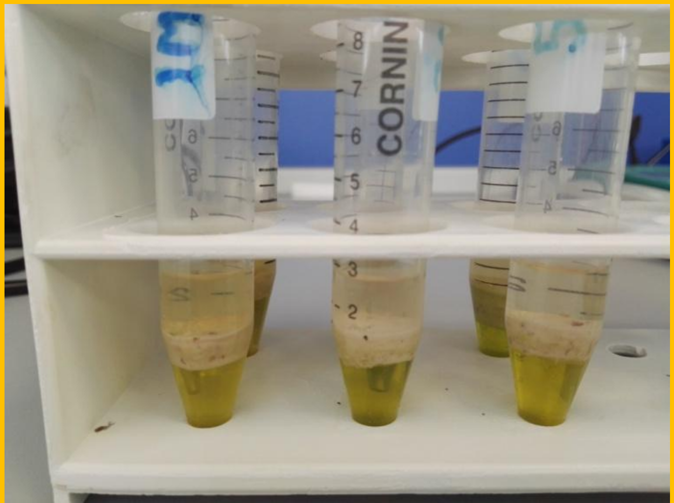


Filtration

test modification 17-08-25



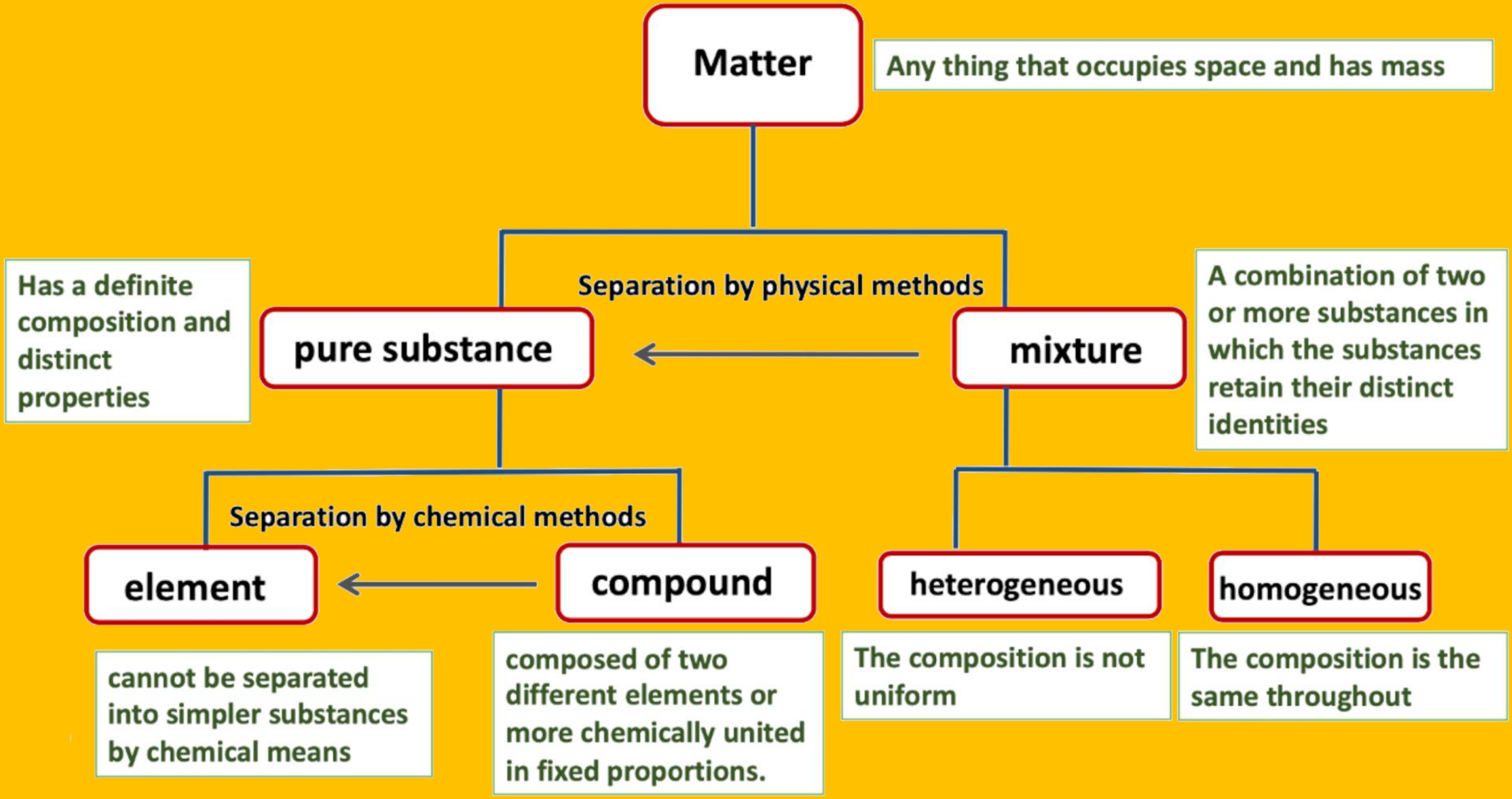
Sample Treatment



Summary (definitions)

- **Chemistry** studies matter and how is it transformed
- **Matter** is anything that occupies a space and is in one of the three states of aggregation, it enjoys physical (without breaking bonds) and chemical properties (with breaking bonds that transform matter itself). Usually the matter is made up of several substances in a mixture that can be homogeneous or heterogeneous depending on whether different phases are distinguished or not
- A (pure) **substance** is all matter of the same type, therefore it contains the same type of molecules, which are the smallest part of matter, which retains the same chemical properties.
- From atomic theory it can be inferred that substances can consist of only one type of atom and are called elementary substances or elements (O_2, N_2, S_8, Cl_2, Cu, Fe, Zn, Ti, C, Si), or of different types of atoms and will be called compound substances or compounds (H_2O, CO_2, C_2H_6O, CH_4, NH_3)

General Scheme



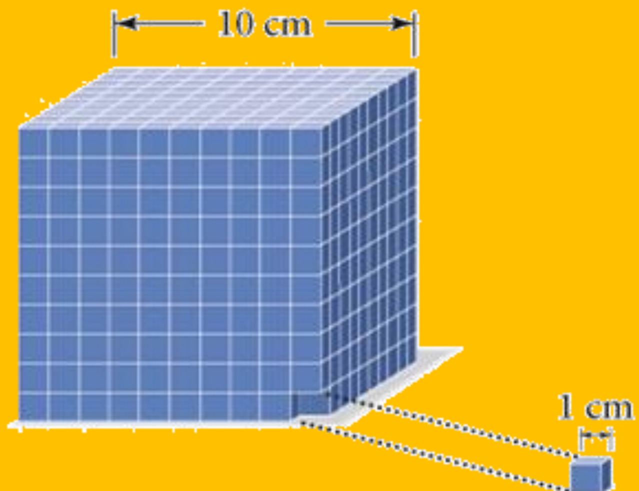
7 FUNDAMENTAL QUANTITIES and units

Quantity	Unit (SI)	Symbol
Mass	Kilograms	Kg
Length	Meters	m
Time	Seconds	s
Temperature	Kelvin degrees	K
Number of Particles	Mole	mol
Current intensity	Ampere	A
Lunminous Intensity	Candela	cd

Derived quantities

$v = s/t$ (m·sec-1); $a = s/t^2$ ($m \cdot sec^{-2}$); $E = m \cdot a \cdot l$ ($kg \cdot m^2 \cdot sec^{-2}$)

$V = l^3$(m^3) SI but beware of conversion $1\ m^3 = 10^6\ cm^3$ SI conversion



Un cubo di 10 cm contiene
1000 cubi da 1 cm

Multiple and submultiples

Prefisso	Simbolo	Moltiplicatore	
exa	E	1 000 000 000 000 000 000	(10^{18})
peta	P	1 000 000 000 000 000	(10^{15})
tera	T	1 000 000 000 000	(10^{12})
giga	G	1 000 000 000	(10^{9})
mega	M	1 000 000	(10^{6})
kilo	k	1000	(10^{3})
deci	d	0.1	(10^{-1})
centi	c	0.01	(10^{-2})
milli	m	0.001	(10^{-3})
micro	µ	0.000001	(10^{-6})
nano	n	0.000000001	(10^{-9})
pico	p	0.000000000001	(10^{-12})
femto	f	0.000000000000001	(10^{-15})
atto	a	0.000000000000000001	(10^{-18})

Properties of matter

- Physical (reversibly measurable)
- Chemical (observable only after a transformation)
-
- <u>Extensive</u> (depending on the amount of matter and following the additivity: V, m, E)
- <u>Intensive</u> (intrinsic of a sample: T, dens.)

Blocco s (alcalini e alcalini terrosi)

Blocco p

Blocco d (metalli di transizione)

Blocco f (Lantanidi - Attinidi)

gas nobili

gruppi o colonne di elementi

simbolo — numero atomico (§2.1) — numero di massa (§2.1) — elettronegatività (§5.7) — numeri di ossidazione (§ 10.15) — nome

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	H 1 1.00794 2.20 1 -1 Idrogeno																	He 2 4.002602 - 0 Elio
2	Li 3 6.941 0.98 1 Litio	Be 4 9.012182 1.5 2 Berilio											B 5 10.811 2.04 3 Boro	C 6 12.0107 2.55 4 -4 Carbonio	N 7 14.0067 3.04 5,3 -3 Azoto	O 8 15.9994 3.44 -2 Ossigeno	F 9 18.998403 3.98 -1 Fluoro	Ne 10 20.1797 - 0 Neon
3	Na 11 22.989769 0.93 1 Sodio	Mg 12 24.3050 1.31 2 Magnesio											Al 13 26.981539 1.61 3 Alluminio	Si 14 28.0855 1.90 4 -4 Silicio	P 15 30.973762 2.19 5,3 -3 Fosforo	S 16 32.065 2.58 6,4,2 -2 Zolfo	Cl 17 35.453 3.16 -1 7,5,3,1 Cloro	Ar 18 39.948 - 0 Argon
4	K 19 39.0983 0.82 1+ Potassio	Ca 20 40.078 1.00 2 Calcio	Sc 21 44.95592 1.36 3 Scandio	Ti 22 47.867 1.54 4 Titanio	V 23 50.9415 1.63 5 Vanadio	Cr 24 51.9961 1.66 6,3 Cromo	Mn 25 54.938045 1.55 7,4,2 Manganese	Fe 26 55.845 1.83 3,2 Ferro	Co 27 58.933195 1.88 3,2 Cobalto	Ni 28 58.6934 1.91 2 Nichel	Cu 29 63.546 1.88 2,1 Rame	Zn 30 65.38 1.65 2 Zinco	Ga 31 69.723 1.81 3 Gallio	Ge 32 72.64 2.01 4,2 -4 Germanio	As 33 74.92160 2.18 5,3 -3 Arsenico	Se 34 78.96 2.55 6,4,2 -2 Selenio	Br 35 79.904 2.96 -1 5,3,1 Bromo	Kr 36 83.798 3.00 0,2 Krypton
5	Rb 37 85.4678 0.82 1+ Rubidio	Sr 38 87.62 0.95 2 Stronzio	Y 39 88.90585 1.22 3 Ittrio	Zr 40 91.224 1.33 4 Zirconio	Nb 41 92.90638 1.6 5 Niobio	Mo 42 95.96 2.16 6,4 Molibdeno	Tc 43 98.9062 1.9 7,4 Technezio	Ru 44 101.07 2.2 4,3 Rutenio	Rh 45 102.90550 2.28 3 Rodio	Pd 46 106.42 2.20 4,2 Palladio	Ag 47 107.8682 1.93 1 Argento	Cd 48 112.411 1.69 2 Cadmio	In 49 114.818 1.78 3 Indio	Sn 50 118.710 1.96 4,2 -4 Stagno	Sb 51 121.760 2.05 5,3 -3 Antimonio	Te 52 127.60 2.1 6,4,2 -2 Tellurio	I 53 126.90447 2.66 -1 7,5,3,1 Iodio	Xe 54 131.293 2.60 0,6 4,2 Xenon
6	Cs 55 132.90545 0.79 1+ Cesio	Ba 56 137.327 0.89 2 Bario	La 57 138.90547 1.1 3 Lantanio	Hf 72 178.49 1.3 4 Afnio	Ta 73 180.94788 1.5 5 Tantalio	W 74 183.84 2.36 6,4 Tungsteno	Re 75 186.207 1.9 4 Renio	Os 76 190.23 2.2 4 Osmio	Ir 77 192.217 2.20 4,3 Iridio	Pt 78 195.084 2.28 4,2 Platino	Au 79 196.96657 2.54 3 Oro	Hg 80 200.59 2.00 2,1 Mercurio	Tl 81 204.3833 1.62 3,1 Thallio	Pb 82 207.2 2.33 4,2 Piombo	Bi 83 208.98040 2.02 3 Bismuto	Po 84 208.9824 2.0 4,2 Polonio	At 85 209.9871 2.2 -1 Astato	Rn 86 222.0176 2.2 0 Radon
7	Fr 87 223.0197 0.7 1+ Francio	Ra 88 226.0254 0.9 2 Radio	Ac 89 227.0278 1.1 3 Attinio	Rf 104 261.11 - - Ruterfordio	Db 105 262.11 - - Dubnio	Sg 106 263.12 - - Seaborgio	Bh 107 262.12 - - Bohrio	Hs 108 264 - - Hassio	Mt 109 266.1378 - - Meitnerio	Ds 110 269 - - Darmstadtio	Rg 111 272 - - Roentgenio	Cn 112 277 - - Copernicio	Uut 113 284 - - Ununtrio	Uuq 114 289 - - Ununquadio	Uup 115 288 - - Ununpentio	Uuh 116 292 - - Ununhexio	Uus 117 293 - - Ununseptio	Uuo 118 294 - - Ununoctio

numeri che indicano il periodo o la riga

Lantanidi 6	Ce 58 140.116 1.12 4,3 Cerio	Pr 59 140.90765 1.13 3 Praseodimio	Nd 60 144.242 1.14 3 Neodimio	Pm 61 144.9127 1.13 3 Prometio	Sm 62 150.36 1.17 3 Samario	Eu 63 151.964 1.2 3+ Europio	Gd 64 157.25 1.2 3,2 Gadolinio	Tb 65 158.92535 1.1 3 Terbio	Dy 66 162.500 1.22 3 Disprosio	Ho 67 164.93032 1.23 3 Holmio	Er 68 167.259 1.24 3 Erbio	Tm 69 168.93421 1.25 3 Tulio	Yb 70 173.054 1.1 3 Itterbio	Lu 71 174.9668 1.27 3 Lutezio
Attinidi 7	Th 90 232.03806 1.3 4 Torio	Pa 91 231.03588 1.5 5 Protattinio	U 92 238.02891 1.38 6 Uranio	Np 93 237.0482 1.36 5 Nettunio	Pu 94 244.0642 1.28 4 Plutonio	Am 95 243.0614 1.13 3 Americio	Cm 96 247 1.28 3 Curio	Bk 97 247.0703 1.3 3 Berkelio	Cf 98 251.0796 1.3 3 Californio	Es 99 252.03 1.3 3 Einstenio	Fm 100 257.0951 1.3 3 Fermio	Md 101 258.01 1.3 3 Mendelevio	No 102 259.1009 1.3 3 Nobelio	Lr 103 260.1053 1.3 3 Laurenzio

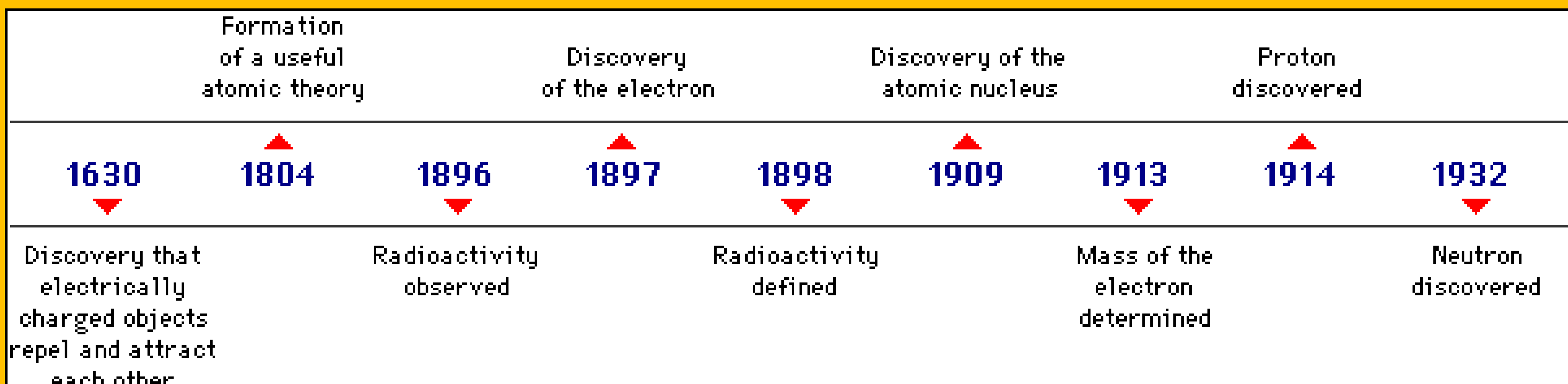
L'unità di massa atomica (uma) vale 1/12 della massa dell'isotopo 12 dell carbonio (IUPAC - 2007).

The mole

- It is not possible to measure a particle weight, or an atom weight; It is therefore necessary to relate objects on a molecular scale to the macroscopic world. The conversion factor is N.
- The mole is: 1)Number of particles equal to N = $6.022 \cdot 10^{23}$; 2) Quantity in grams equal to the mass number or molecular weight of an atom, molecule, or particle, ion
- How big mole is? Just think that 10 moles of oranges make the entire mass of earth

Structure of matter and atoms

The main findings

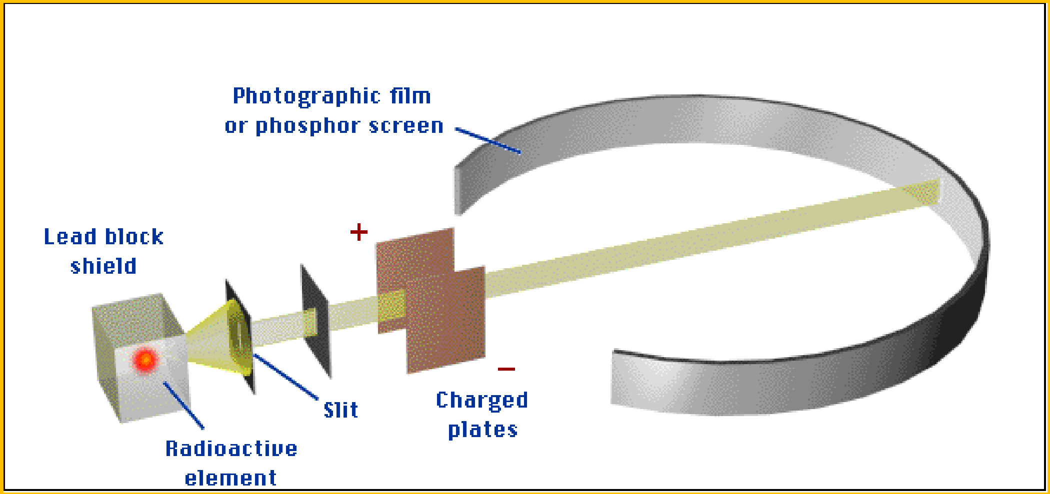


Atomic Structure

- How an atom is made
- How electrons are arranged
- Atomic Models
- Rutherford
- Bohr (quantum mechanics)
- Schrodinger (De Broglie, Eisenberg) (wave mechanics)
- Atomic orbitals

Subatomic particles

The studies on radioactivity by Bequerel and M. Curie (1896) showed the existence of three types of radiation:



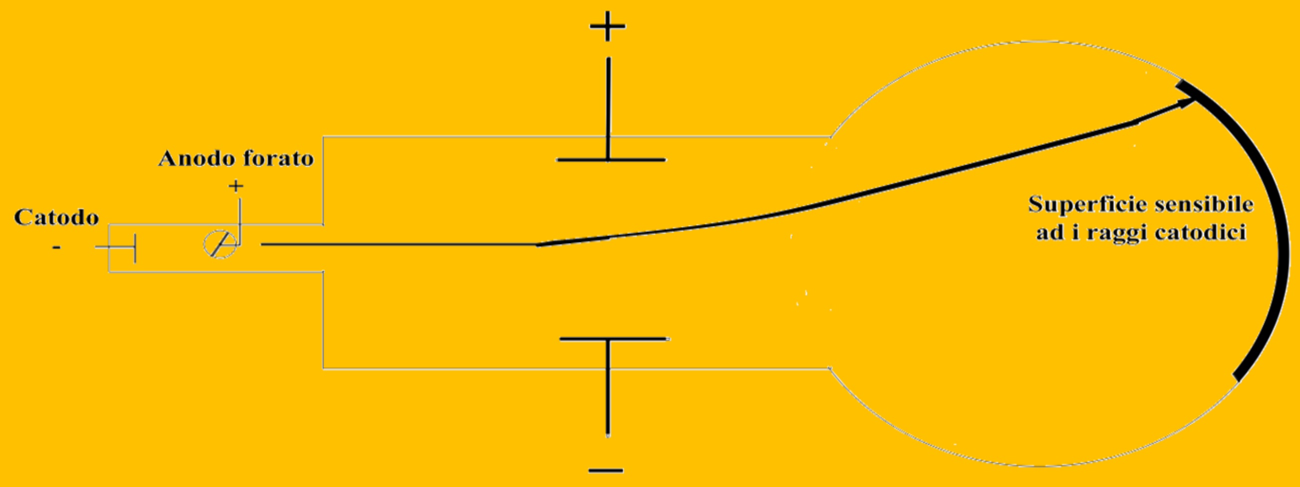
Alpha: Positively Charged

Beta: Negatively Charged

Gamma: No charge.

(alpha and beta are patially contained in atoms)

Cathode rays (electrons)

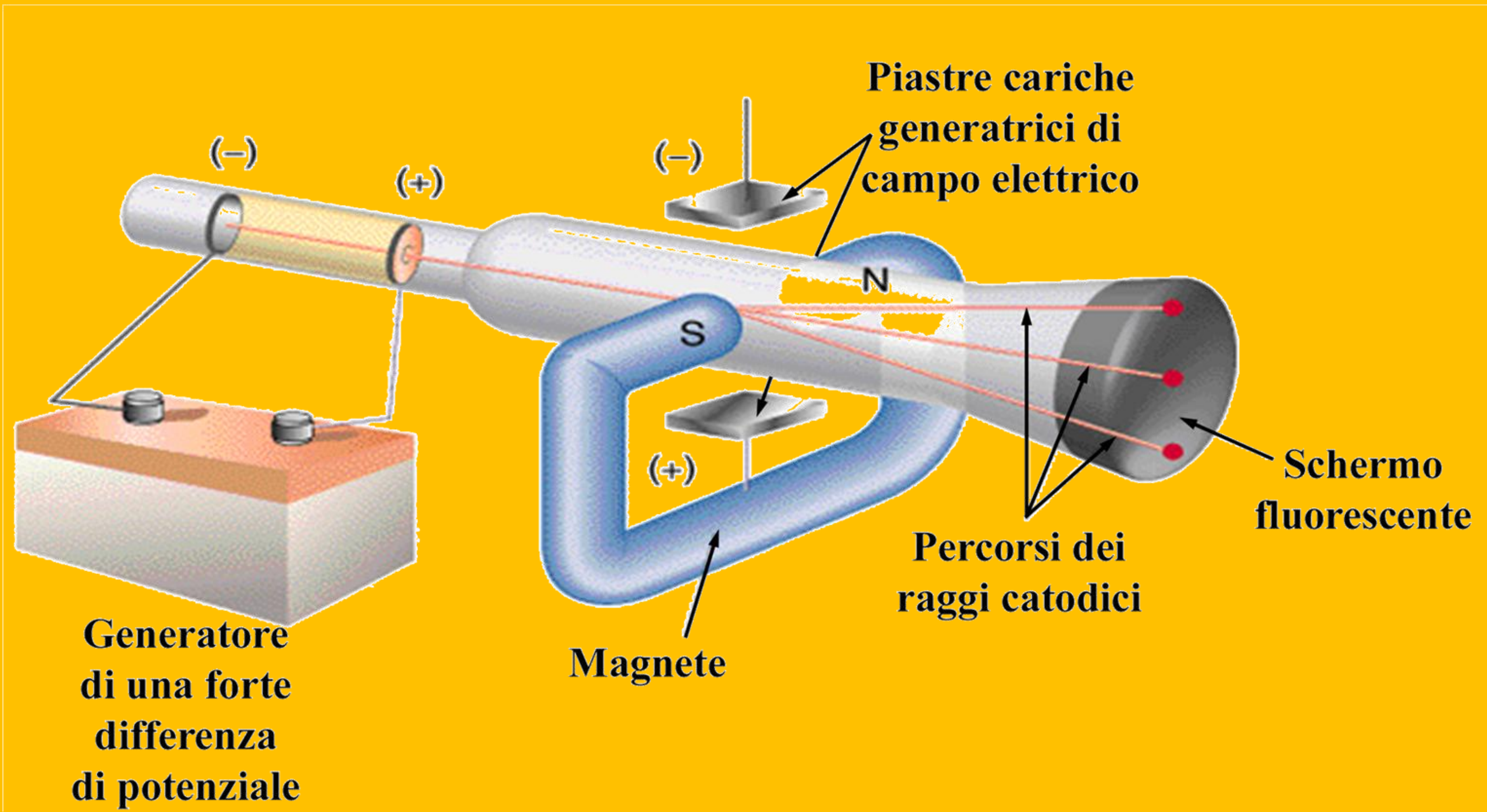


The electron: Thompson in 1897, studying negatively charged cathode rays, was able to measure the charge/mass ratio of particles called electrons. Millikan, studying oil droplets, measured the charge of the electron.

Its mass is $9.109389 \cdot 10^{-28}$ grams

His charge is $1.60217733 \cdot 10^{-19}$ Coulomb

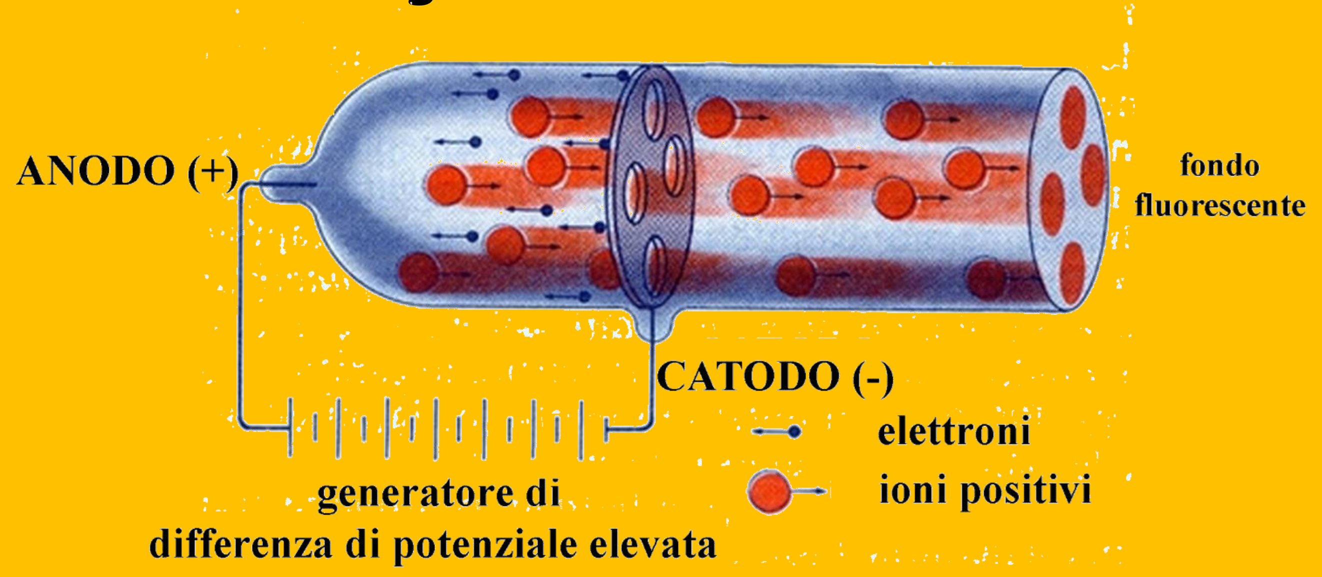
Modified Thomson device



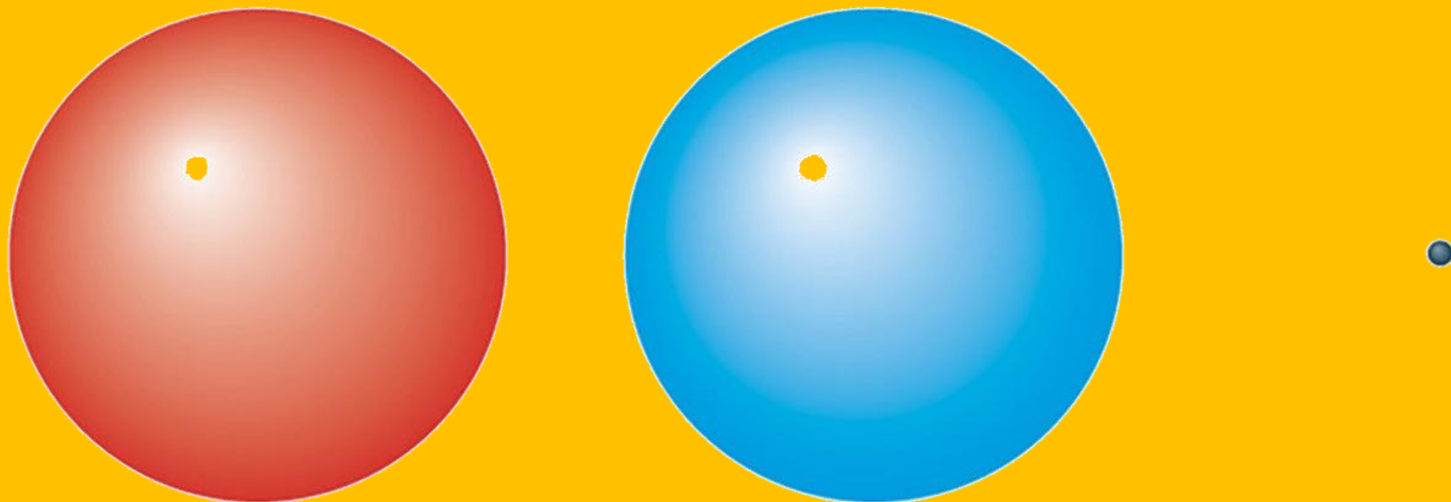
The proton

- Rutheford, analyzing the channel rays (positive), showed that the mass/charge ratio differed with the type of gas used (as opposed to the constant cathode rays). The highest ratio (lower mass) was obtained with hydrogen. The particle, called proton, has a charge equal to, but opposite to, that of the electron and a mass of:

$1{,}672623 \times 10^{-24}$ g

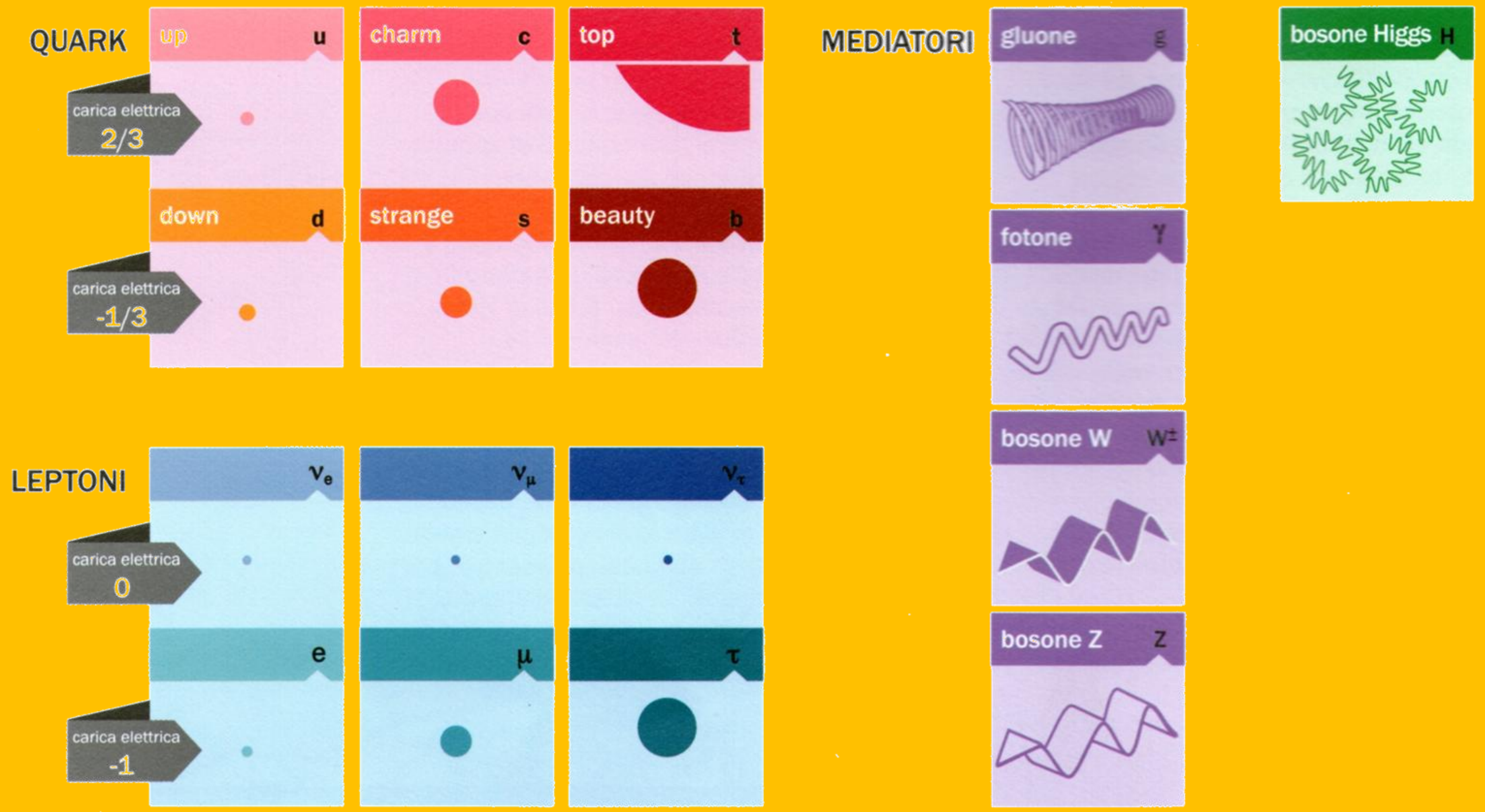


Atomic Particles

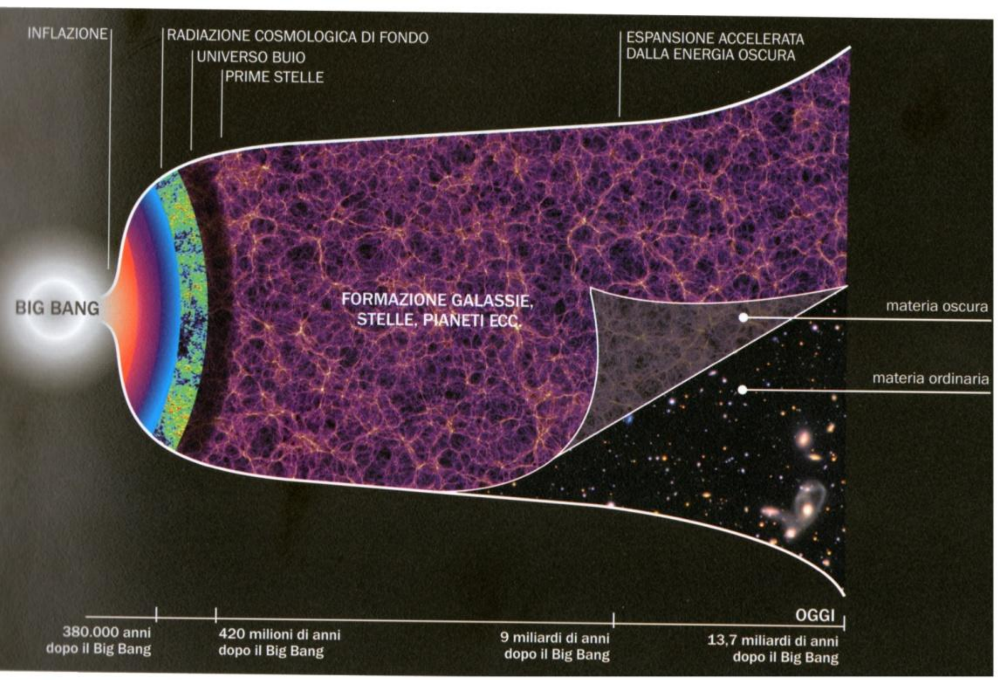


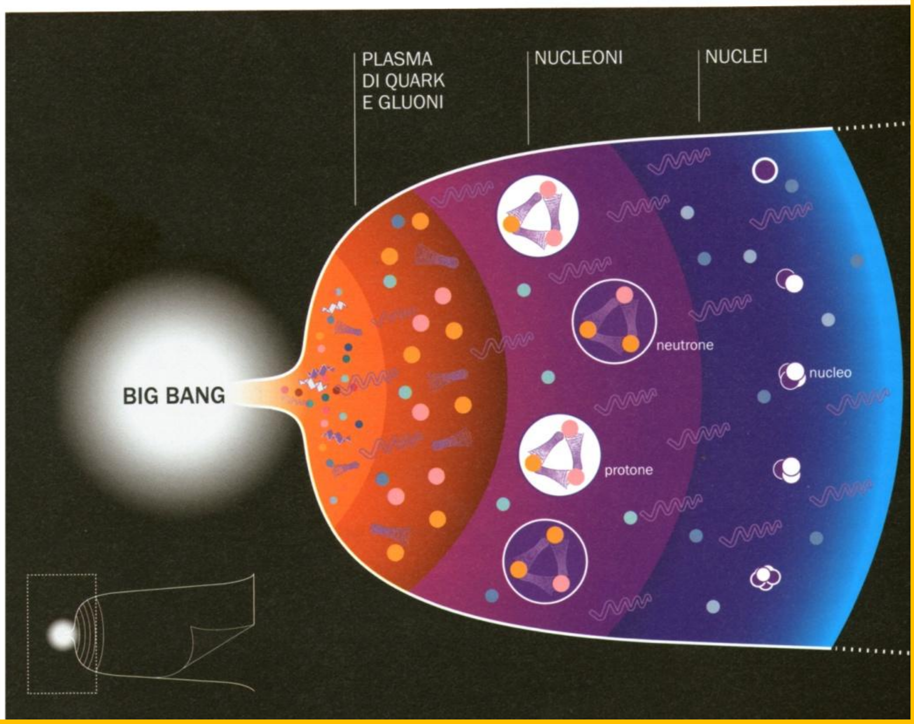
particella	protone	neutrone	elettrone
massa (kg)	$1{,}673 \cdot 10^{-27}$	$1{,}675 \cdot 10^{-27}$	$9{,}1094 \cdot 10^{-31}$
carica (C)	$1{,}6022 \cdot 10^{-19}$	0	$-1{,}6022 \cdot 10^{-19}$

Subatomic particles and Genesis of the Universe



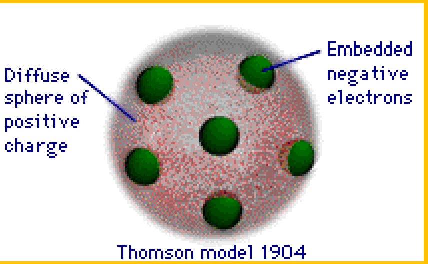
Universe Evolution





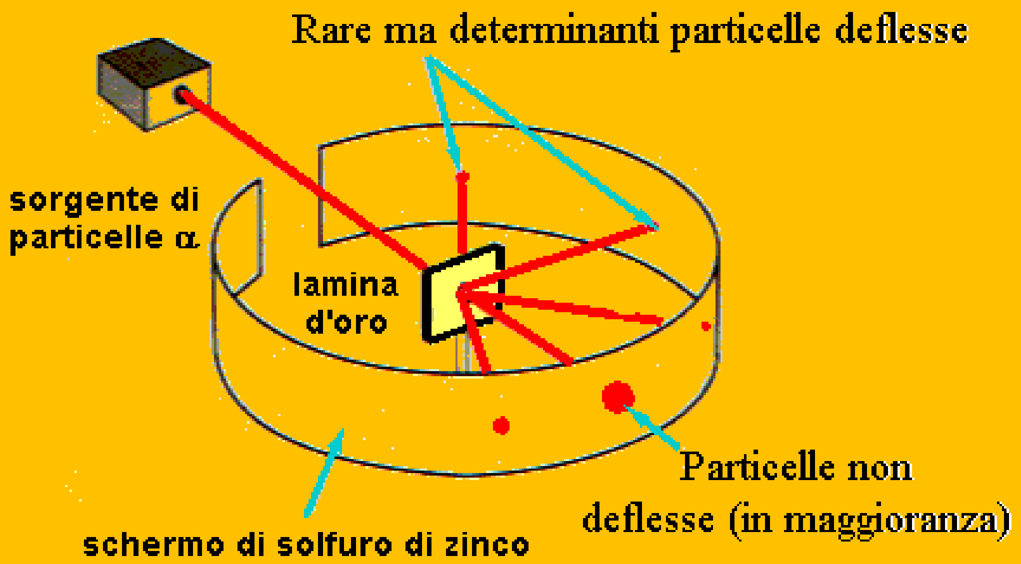
Nuclei

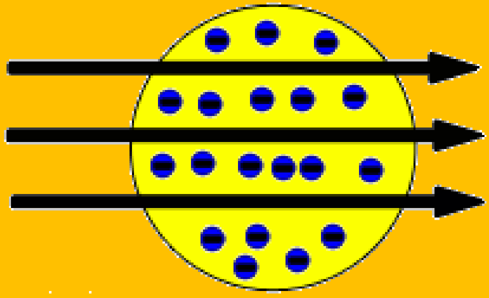
- Thompson proposed that the electrons were diffused into a positively charged gel-like substance. (figure)
- Rutherford bombarded a thin sheet of gold with alpha particles (helium atoms without electrons) and observed that a small fraction of these was deflected by more than 90°. They hit something very small and hard: the NUCLEUS. (video)
- He proposed the atomic model in which all the positive charge and mass of an atom are concentrated in the atomic nucleus, and electrons orbit around it.
- The nucleus radius is about 1/10,000 of the atomic radius.



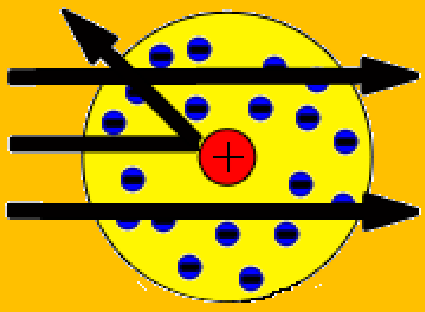
Modello di Thompson

Rutherford image



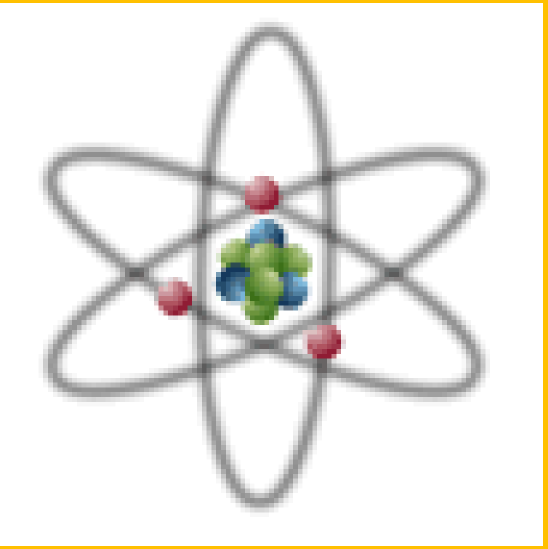


Modello
non più accettabile



Modello
proposto

Atomic structure



- Atoms consist of a positive nucleus and negative electrons.
-
- The core has a radius of about 10-5 Å.
-
- The radius of an atom is about 1 Å (1Å=10-10m)

Proportion: 100 m vs 1 mm

Core-mantle size analogy

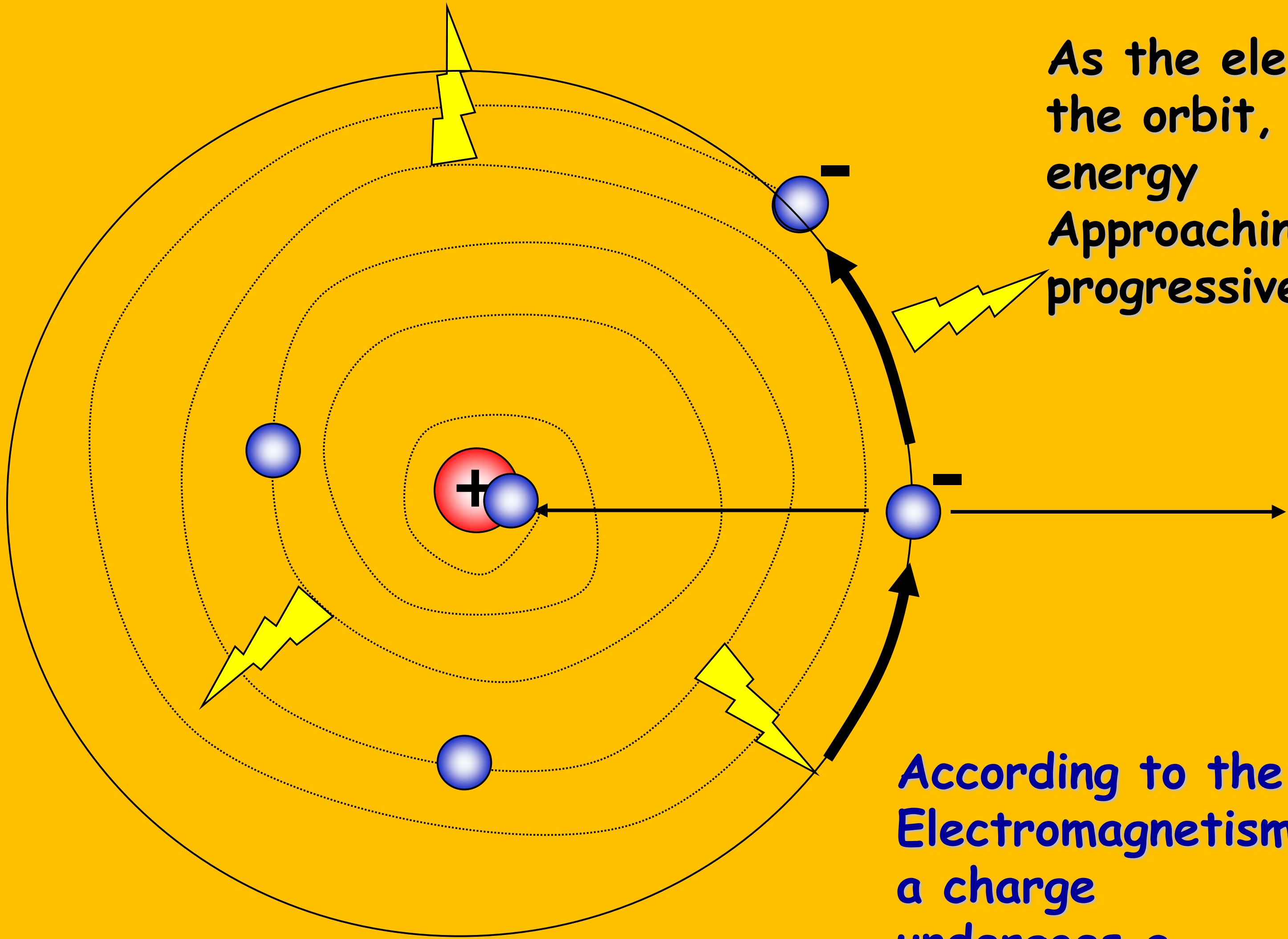
The atom

- The nucleus is made up of Protons and Neutrons (Nucleons)
- Electrons orbit the nucleus
- In an electrically neutral atom, the number of protons must be equal to the number of electrons.
- All atoms of an element have the same number of protons: atomic number, Z.
- The mass of an atom is measured in Atomic Mass Units (amu or uma). The ^{12}C has a mass of 12 uma
- The mass number (A) is the number of nucleons (Protons + Neutrons). It gives a fairly accurate estimate of the mass in um.
- Each element has a name and a symbol (e.g. Sodium = Na, Z=11, A=23 for the most common isotope).

Atomic Masses

- Atomic masses (A) or moleculal masses (MM-FW) are measured with the mass spectrometer. Atoms or molecules are injected into the ionization chamber where they are then exposed to a high-speed electron beam. These extract electrons from atoms thus forming positive "ions".
- Ions are accelerated by a high electrostatic potential: lighter ions reach higher speeds than heavier ones, and their mass is calculated by the speed reached.
- One isotope is described: neon-20, neon-21 and neon-22: ^{20}Ne, ^{21}Ne and ^{22}Ne.
- The atomic masses are all very small, between 10^{-24} and 10^{-22} g. They are expressed in "atomic mass units" (6×10^{23}amu = 1 g). (Dalton=amu)
- amu is 1/12 part of the mass of the atom of 12C
- An ion is an atom or group of atoms with an electric charge.

Rutherford's planetary model
And Bohr's problem



As the electron moves in the orbit, it would lose energy
Approaching Kinetics progressively to the nucleu

According to the Electromagnetism laws, when a charge undergoes a Acceleration loses energy

Plank's equation. n = 1, 2, 3

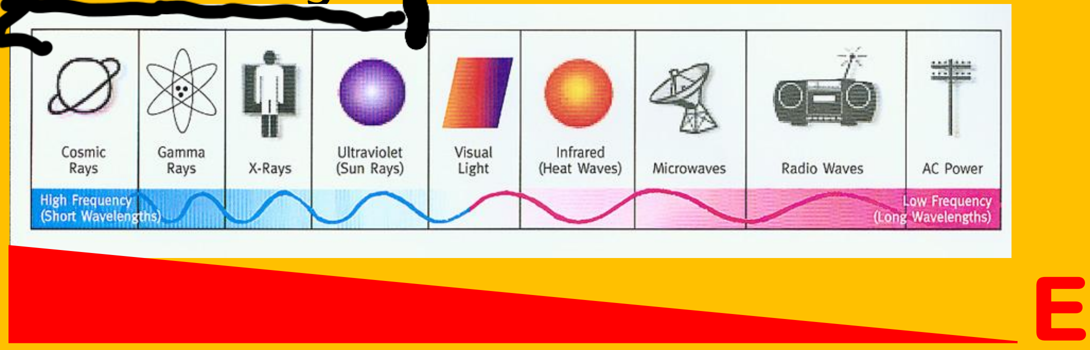
- Heated objects emit light (radiation) whose wavelength depends on the temperature
- Plank (1900): Energy exists in small aliquots (quanta).
- The radiation energy is proportional to the frequency

$$E = h \cdot \nu = h \cdot c/\lambda$$

n

- λ: wavelength
- ν: frequency
- c: Light-speed in vacum = 3×10^8 m/s
- h: Plank's constant 6.6×10^{-34} J·s

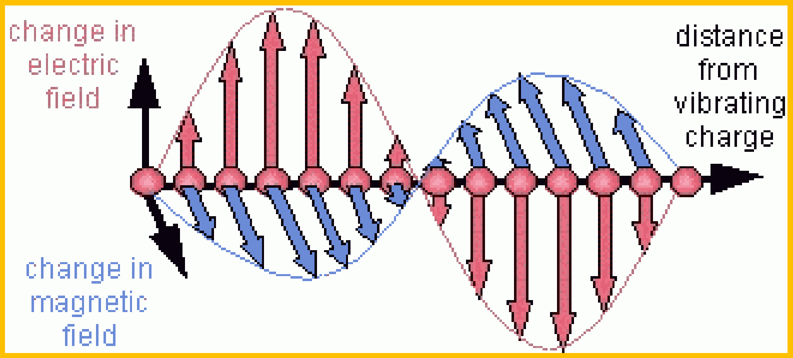
The energy of the radiation increases with frequency but decreases with wavelength

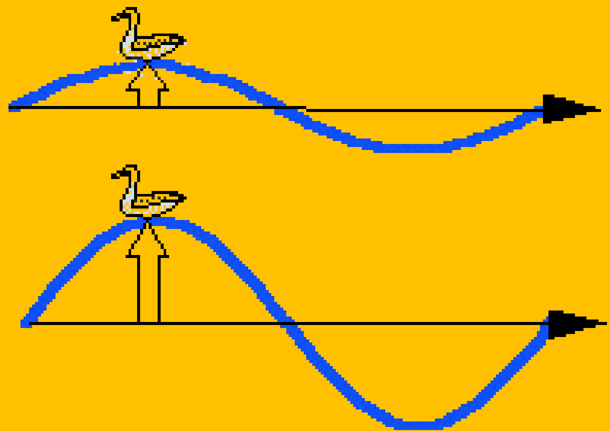


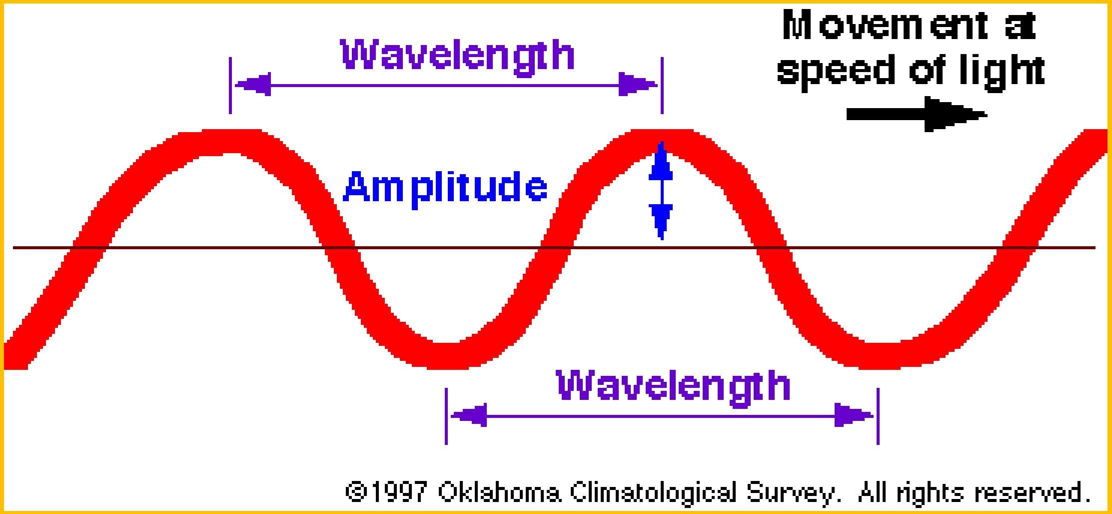
Electromagnetic radiation

- In 1864 James Maxwell developed a theory to describe radiation: oscillating waves of the electric and magnetic fields, perpendicular to each other.
- Wavelength λ (la lettera greca lambda)
  - Amplitude
  - Speed of Light c ($3 \cdot 10^8$ m/s)
  - Frequency ν (nu, misurata in Hz = cicli/Sec)

$$\lambda \cdot \nu = c$$





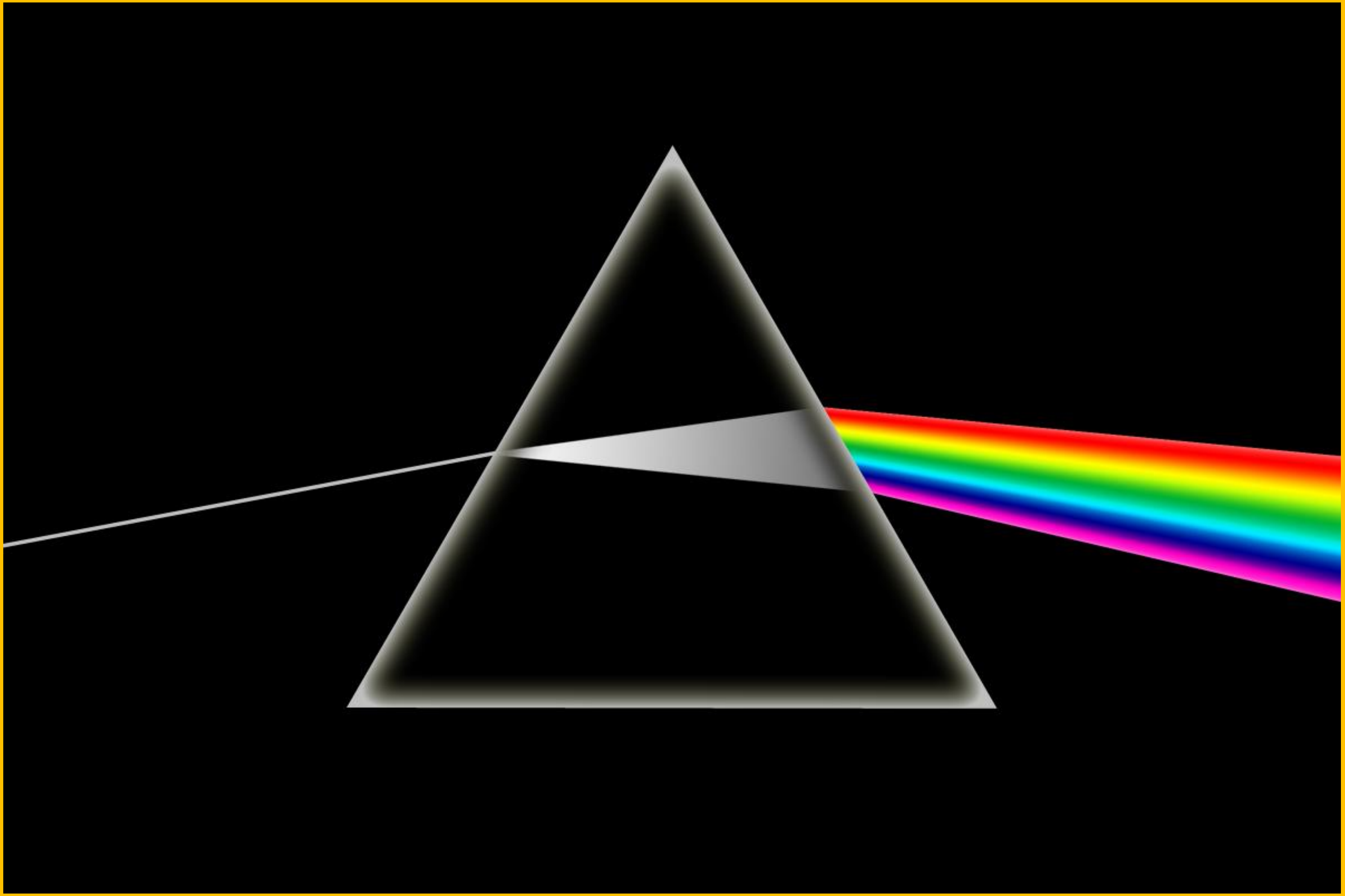


Wavelength λ = space-span corresponding to the entire cycle of values

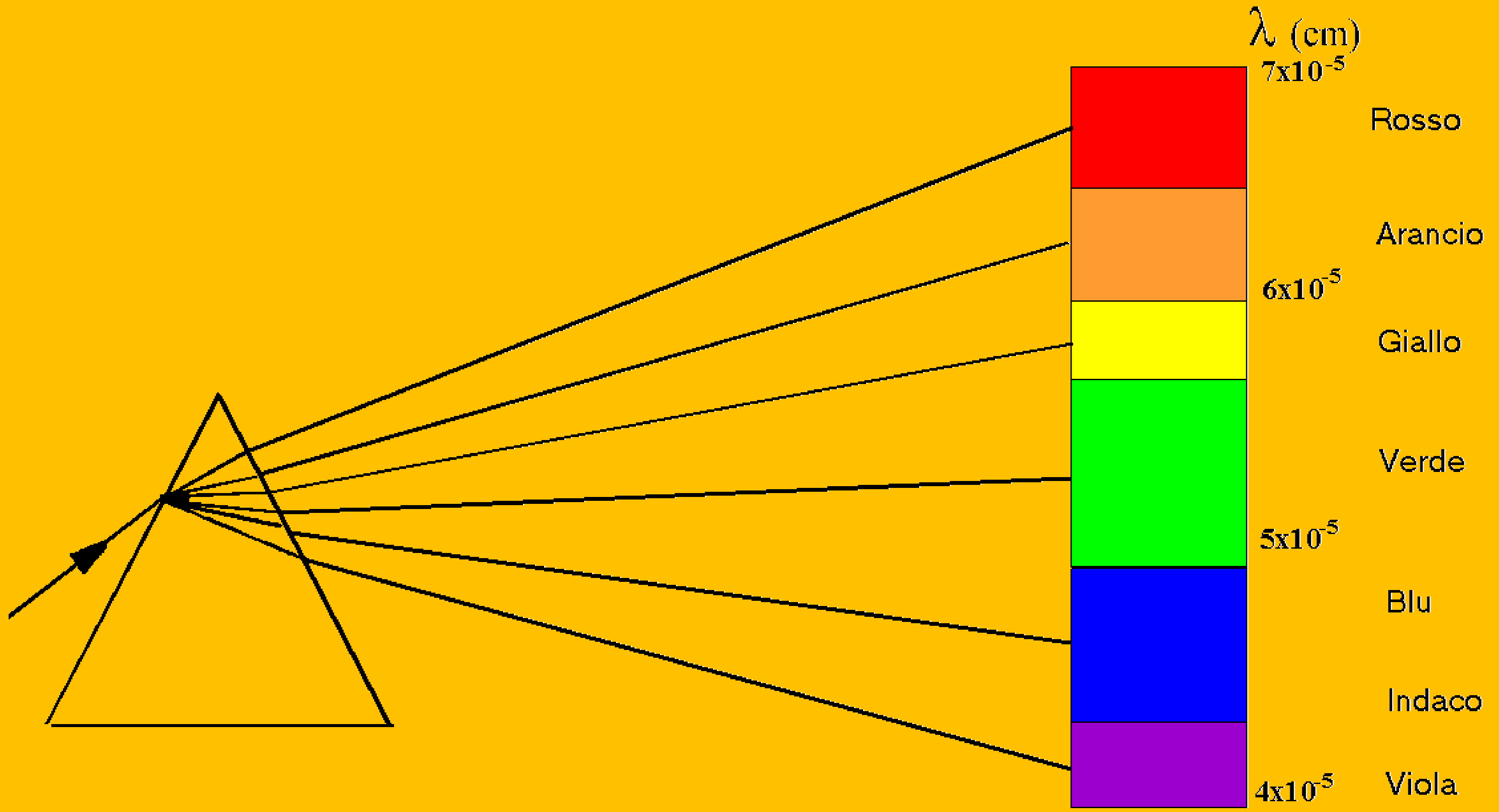
Frequency ν = number of times per second that the vector takes on the entire cycle of values

$$\nu\ (\mathrm{Hz}) = \mathbf{c}(\mathrm{m\ s^{-1}})/\lambda(\mathrm{m})$$

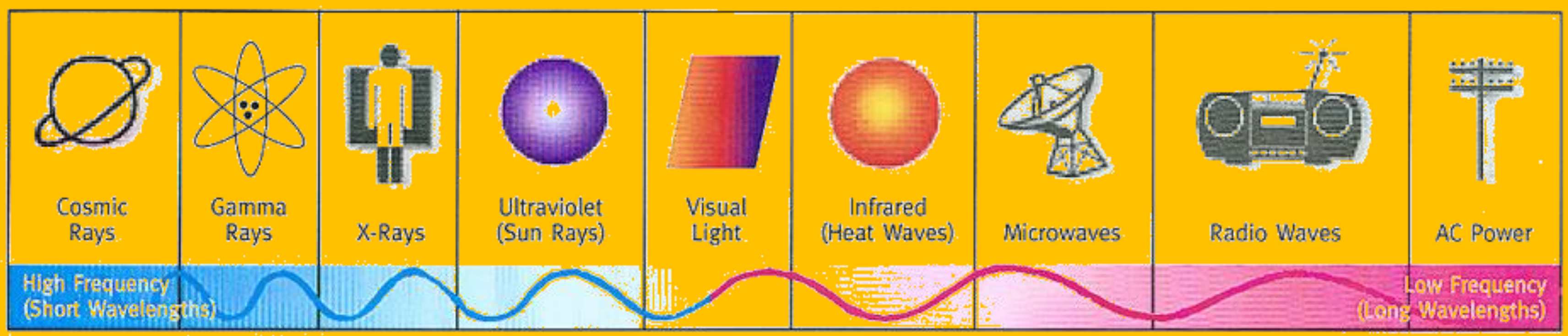
The Dark Side of the Moon

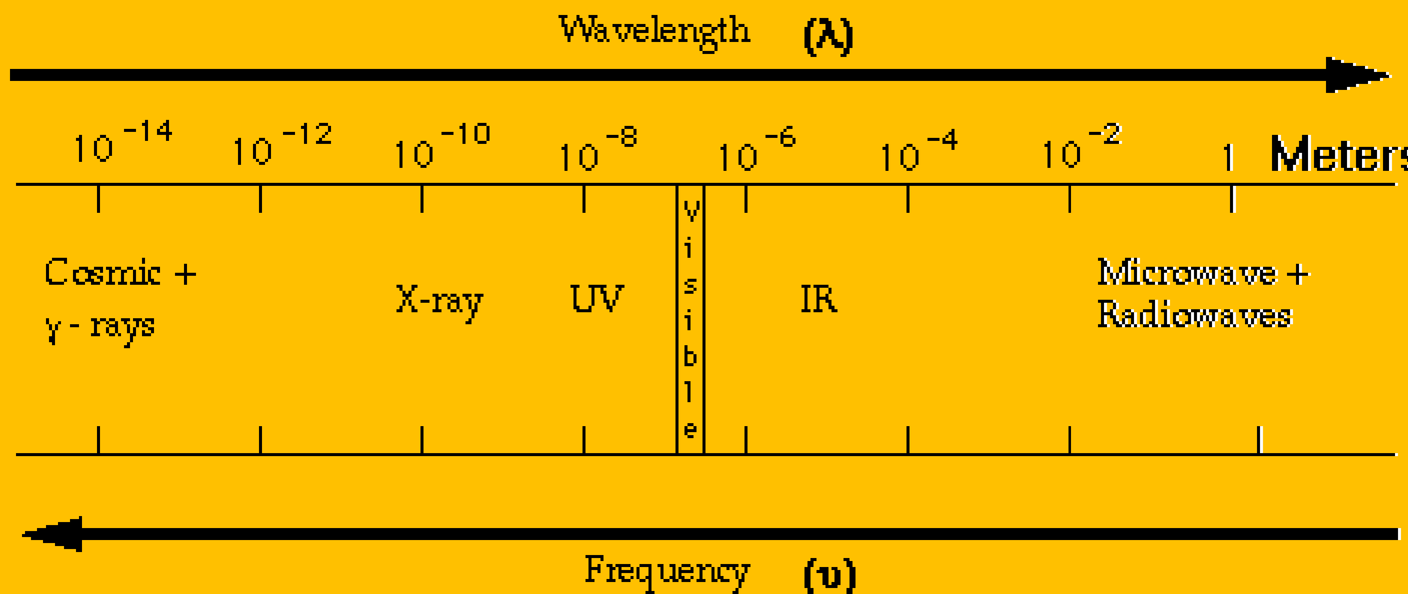


Diffraction of visible light by a prism and light-spectrum.



Electromagnetic radiation spectrum





Postulates of Bohr's atomic model

There are stationary orbits that allow the electron to spin around the nucleus without emitting energy

-The angular momentum of orbiting electrons (mvr) is quantized

$$mvr = n \cdot (h/2\pi)$$

But the quantization of angular momentum also quantizes the radius

$R = n^2 \cdot 53pm$

$E = 2.18\ 10^{-18}\ 1/n^2\ J$

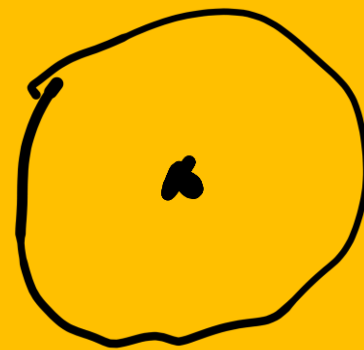
orbit

orbital

stationary

$$mvr = n\left(\frac{h}{2\pi}\right)$$

$$R = n^2 (R_0)$$



$L = n h$

$$= -\frac{1}{n^2}(R_H)$$

$n = 2$

1, 2, 3

$n = 1$

CONTINUUM . . . . .

DISCRETE VALUES

Energy and radius of the first stationary orbits hypothesized by Bohr

Quantum N°(n) Level	Radius (pm)	Total Energy (J)
1	53	$E_1 = -R_H/1 = -2.18 \cdot 10^{-18}$
2	212	$E_2 = -R_H/4 = -0.545 \cdot 10^{-18}$
3	477	$E_3 = -R_H/9 = -0.24 \cdot 10^{-18}$
4	848	$E_4 = -R_H/16 = -0.14 \cdot 10^{-18}$

Centripetal force = $\dfrac{ke^2}{r^2}$

Centrifugal force = $\dfrac{mv^2}{r}$

Under equilibrium conditions, the centripetal force is equal to the centrifuge:

$$\frac{ke^2}{r^2} = \frac{mv^2}{r}$$

from which : r = ROOTSQUARE $\dfrac{ke^2}{mv^2}$

I continue on the blackboard.........

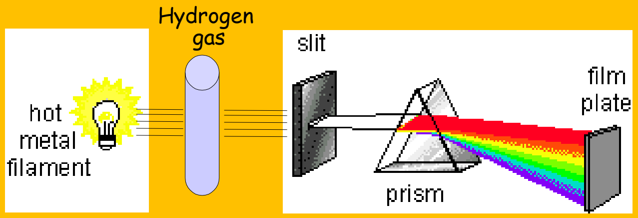
LIMITATIONS

It is not "orthodox"; it starts from traditional mechanics (Newtonian) and arrives at a discontinuous physical model by introducing unproven assumptions.

SUCCESS

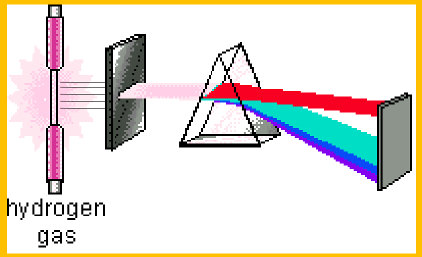
The model provides an explanation of the spectroscopic properties of the hydrogen atom but is not sufficiently robust to interpret the energy spectra of other polyelectronic elements.

Atomic spectral lines



Spettro di assorbimento

atomic absorption spectrum



Spettro di emissione

Atomic Emission Spectrum

The light emitted by a substance can be analysed (emission spectrum)

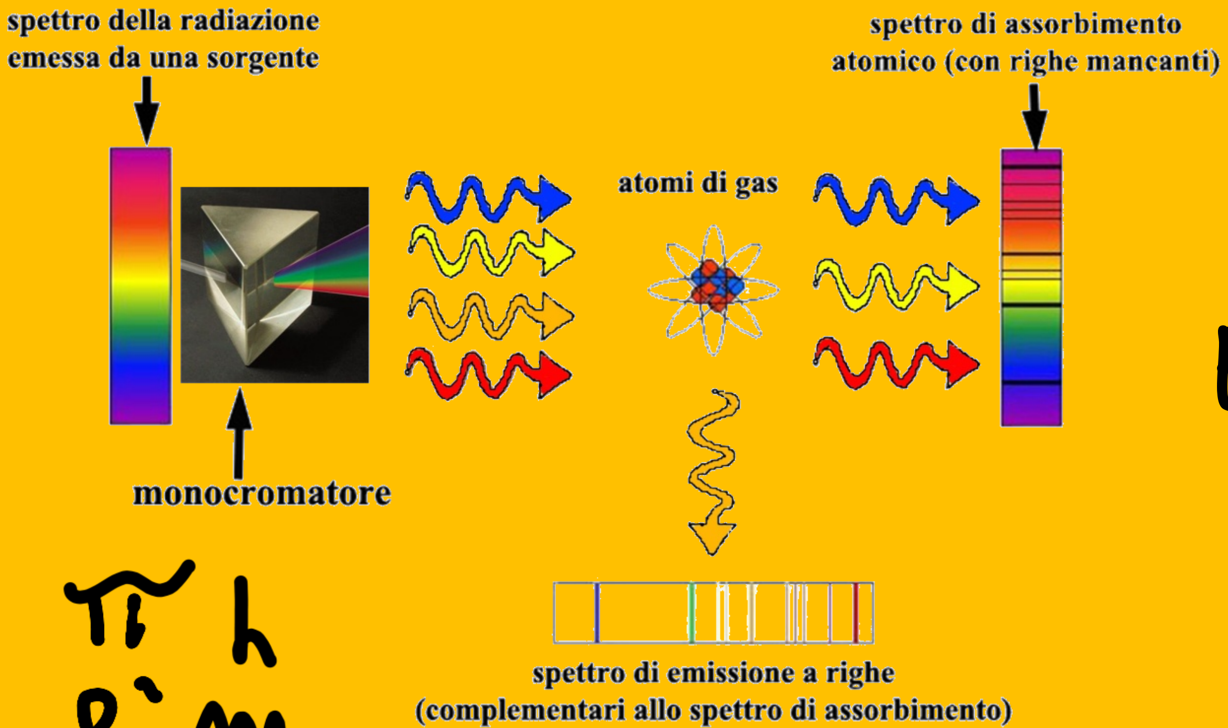
Each element (substance) produces lines of different wavelengths

Balmer (1885) and Rydberg found equations describing the wavelengths emitted by hydrogen

$$\nu = R\,(1/n_f^2 - 1/n_i^2)$$

$$(n_f = (1),\ 2,\ 3,\ 4\ldots \qquad n_i = n_f + 1,\ n_f + 2\ \ldots)$$

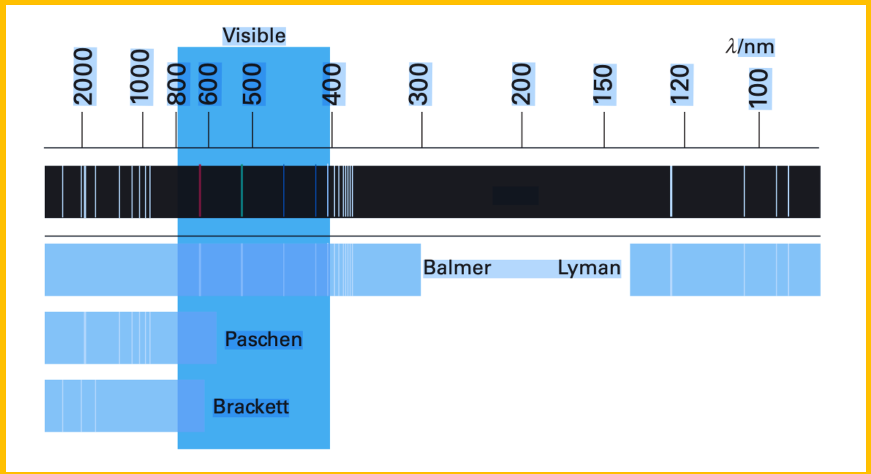
Emission and Absorption



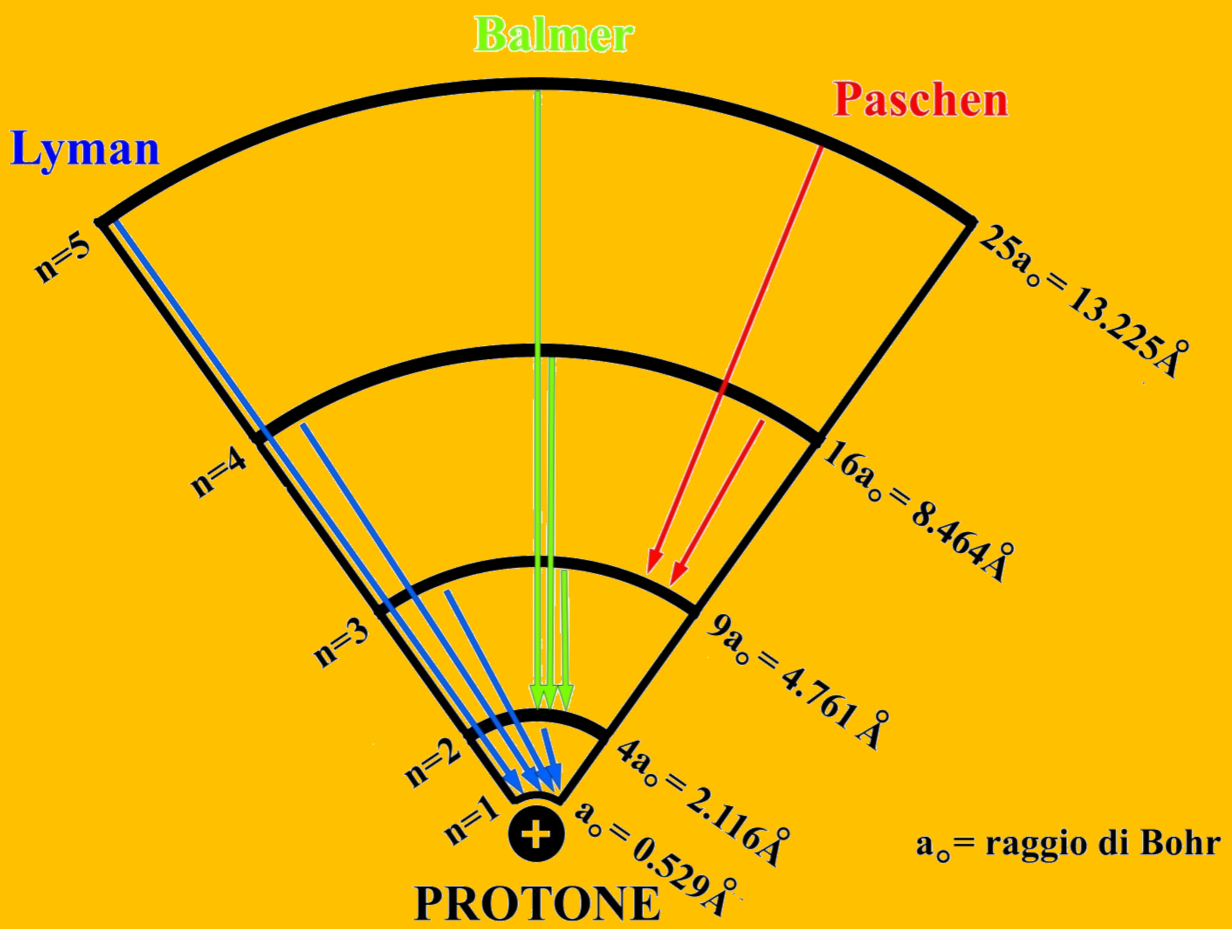
atomic line emission spectra

$\hbar$ h

e m_e → R_H



Emission

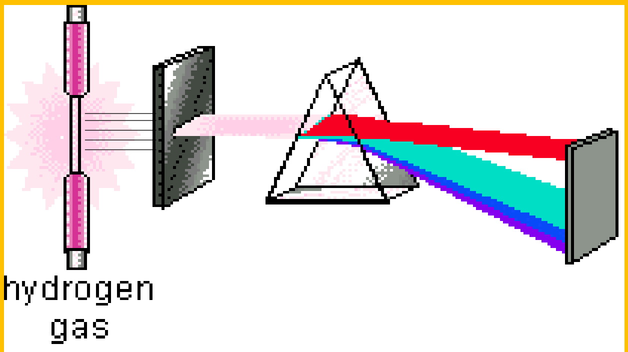


$$\nu = R\,(1/n_f^2 - 1/n_i^2)$$

(L, $n_f = 1$; B, $n_f = 2$; P, $n_f = 3$)

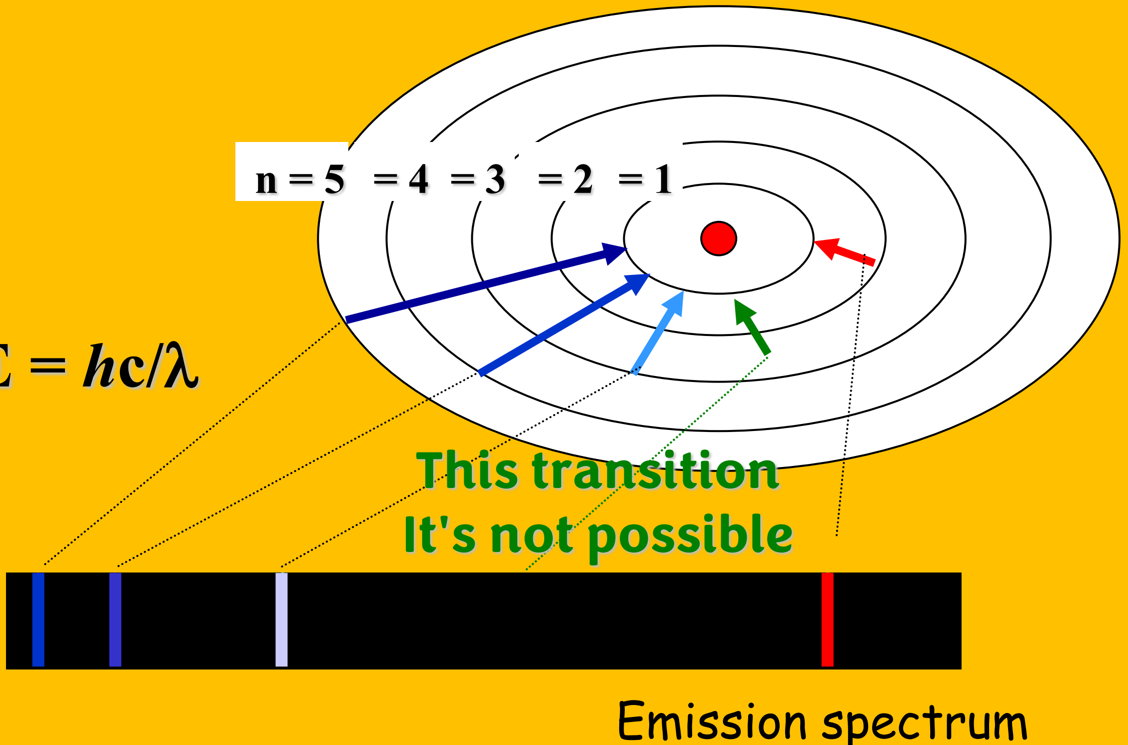
$R_H = 2.18 \cdot 10^{-18}$ J; experimental value exactly fitting Bohr's calculations

Bohr's atomic model



- Excited elements emit specific "quanta" of energy (light) so electrons can only occupy specific orbits around the nucleus, and each orbit has quantized energy.

$$E = hc/\lambda$$



It refers to the spectra that display the specific wavelengths of light emitted by atoms of an element when electrons transition from an excited energy state to a lower one, releasing energy in the form of photons. Each chemical element has a unique set of spectral lines, characteristic of its **electronic structure** undergoing the specific electric field excerted by **Z**


LiCl
NaCl
KCl
RbCl
CsCl
$CaCl_2$
$SrCl_2$
$BaCl_2$
$CuCl_2$
TlCl

Why doesn't the atom collapse?

- Electrons in the atom have to move
- **The nucleus attracts the electrons, which should accelerate toward it**
- If the electrons are moving
- Movement emits electromagnetic radiation
- This causes loss of energy, the atom collapses.
- Why doesn't it collapse?
- Classical physics doesn't explain it
- **Electrons behave as waves/particles**

De Broglie's Wave-Particle Duality Hypothesis (1924)

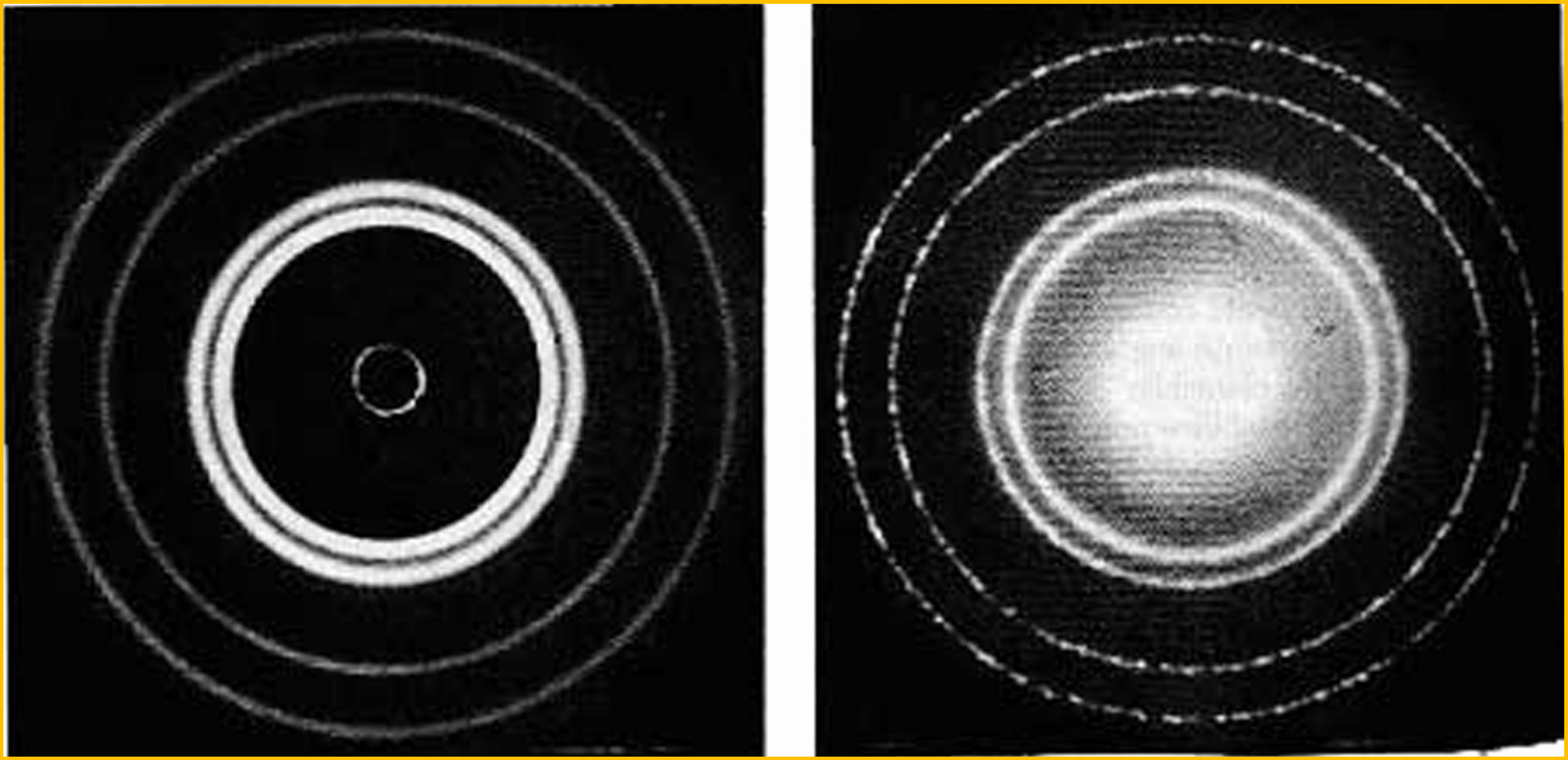
- All moving objects can be assigned a wavelength

- The smaller the object, the greater the associated wavelength (and therefore its wave-like behaviour will be more noticeable)

$$\lambda = \frac{h}{m v}$$

p

Devisson and Germer diffraction



Heisenberg's uncertainty principle

Δ is the variation of error in the determination

$$\Delta x \, \Delta p > \frac{h}{4\pi}$$

$$\Delta t \, \Delta E > \frac{h}{4\pi}$$

p= mv

Coupled properties of an electron such as position and momentum, or energy and residence time in a given volume they cannot be determined simultaneously with infinite precision.

Insurmountable limit to the simultaneous knowledge of the momentum and position of an object

Non-commuting observables correspond to physical quantities whose simultaneous values are subject to the limitations imposed by Heisenberg's uncertainty principle

Operatori che commutano

$$[\hat{A}\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \equiv 0$$

Operatori che non commutano

$$[\hat{A}\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$$

Heisenberg's Uncertainty Principle

Macroscopic phenomena:

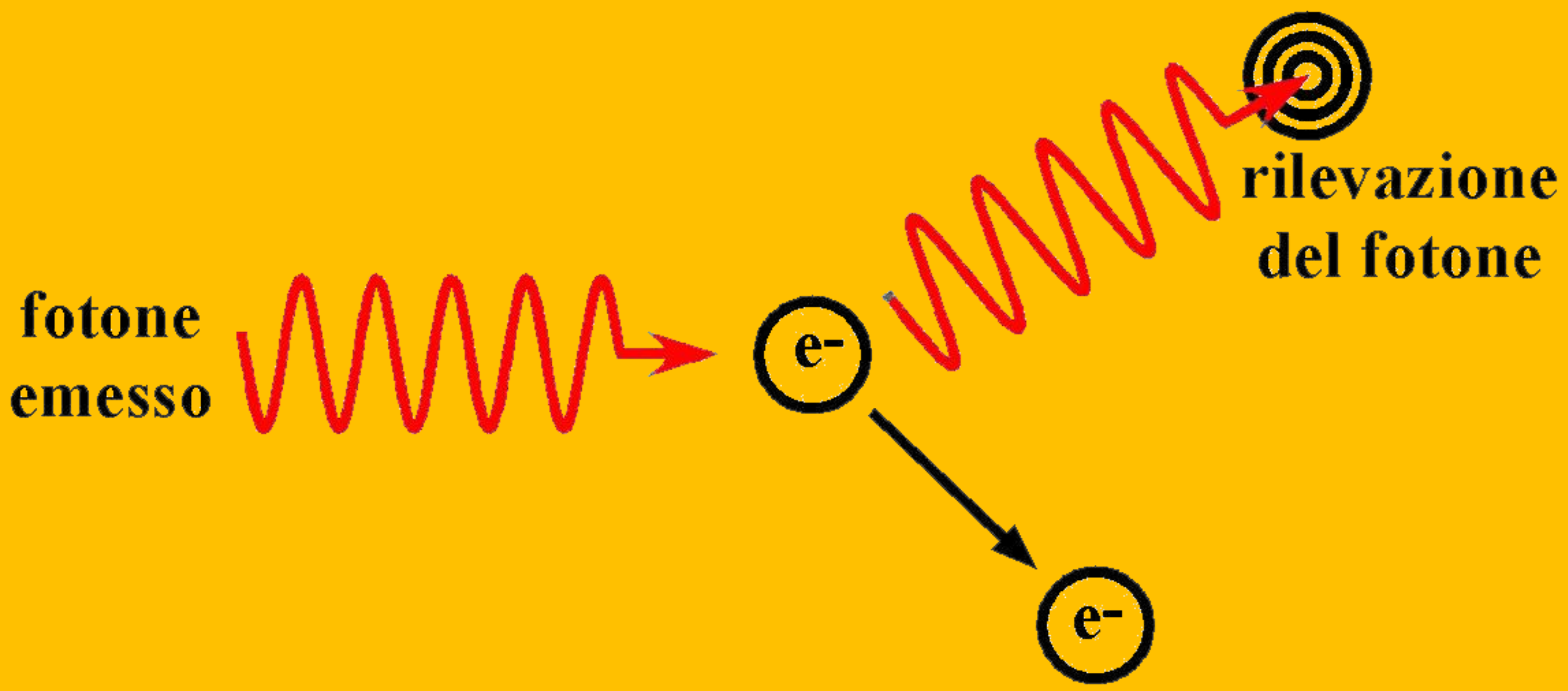
No practical consequences

Atomic Size:

It is not possible to define the trajectory of an electron around the nucleus

We can only talk about the position of the electron in probabilistic terms: it will be in a region of space with a certain probability.

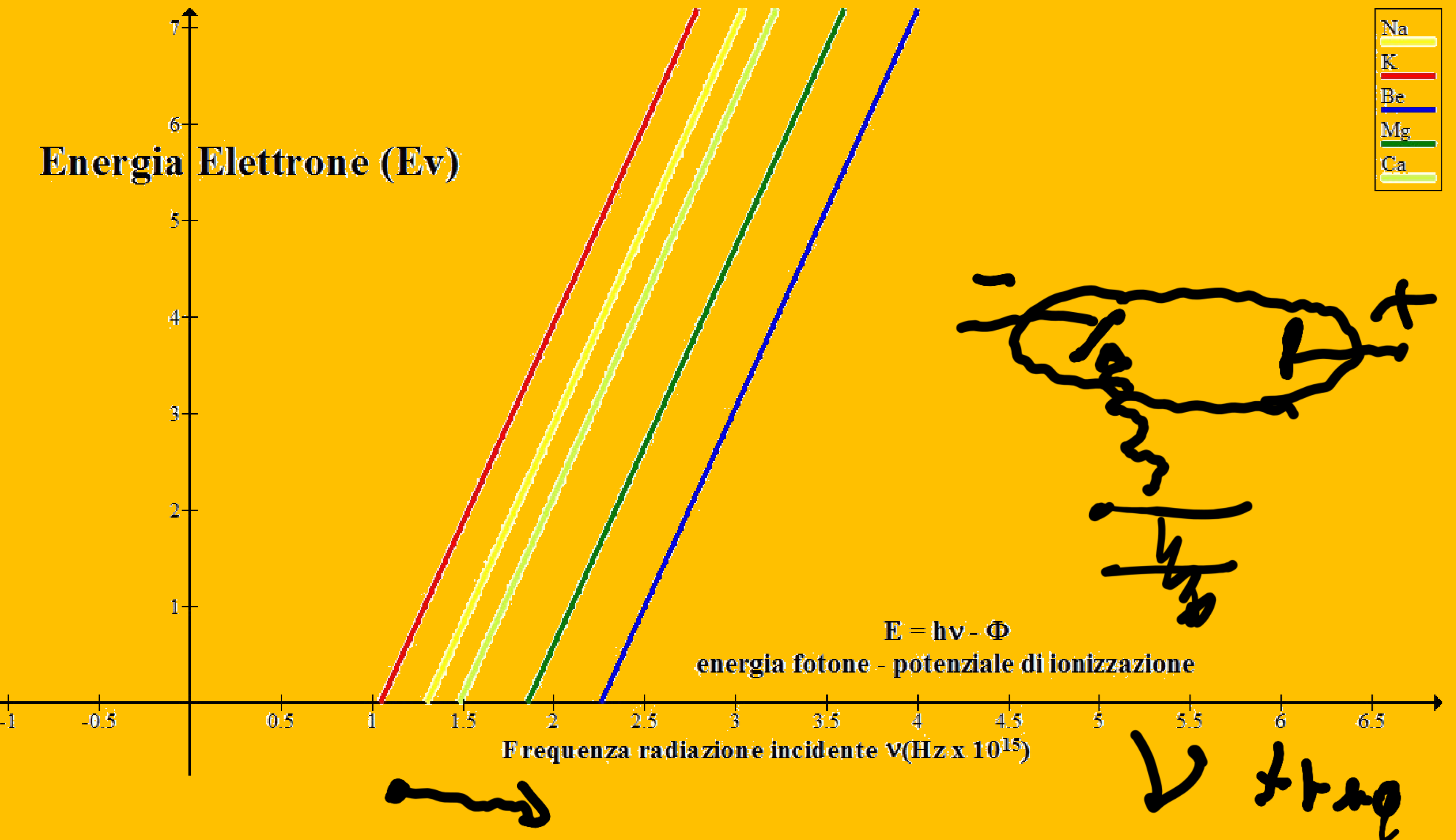
Compton effect



Electromagnetic Radiation Energy

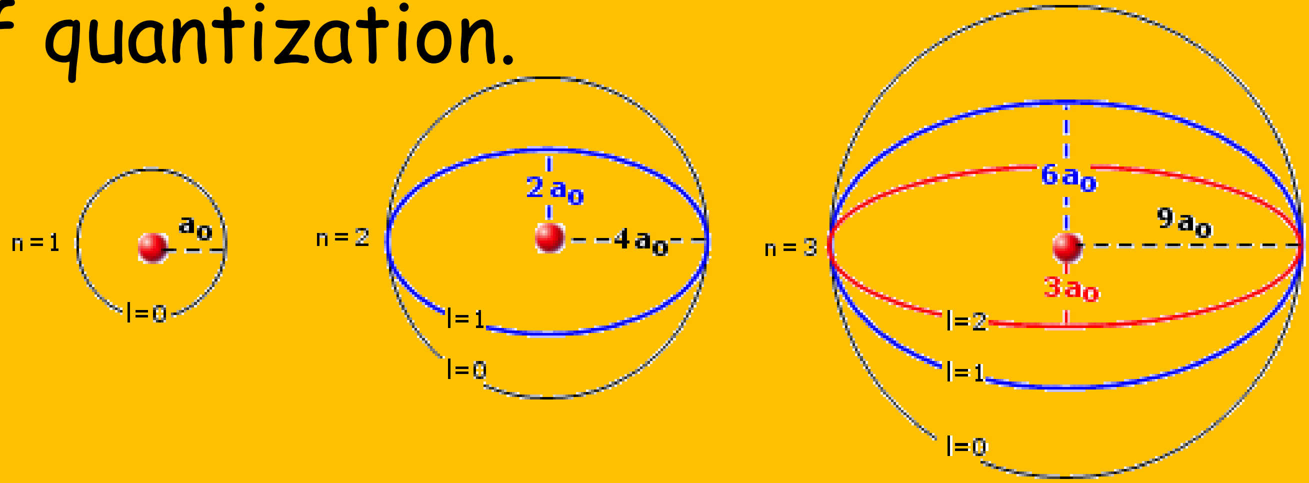
- Radiation carries energy
- Work to change the electromagnetic field
- The transmitter loses energy, the receiver gains it
- In classic waves
- The energy is related to the amplitude of the wave
- The brighter light should bear more energy...
- Photoelectric Effect:
- The intensity has no effect on the kinetic energy of the emitted electron (more photons, more electrons)
- Red light doesn't emit electrons, blue light does
- So: light is made from photons, more light = more photons.
- $E = h \cdot \nu$

Photoelectric effect
A. Einstein, 1905 (Nobel Prize 1921)

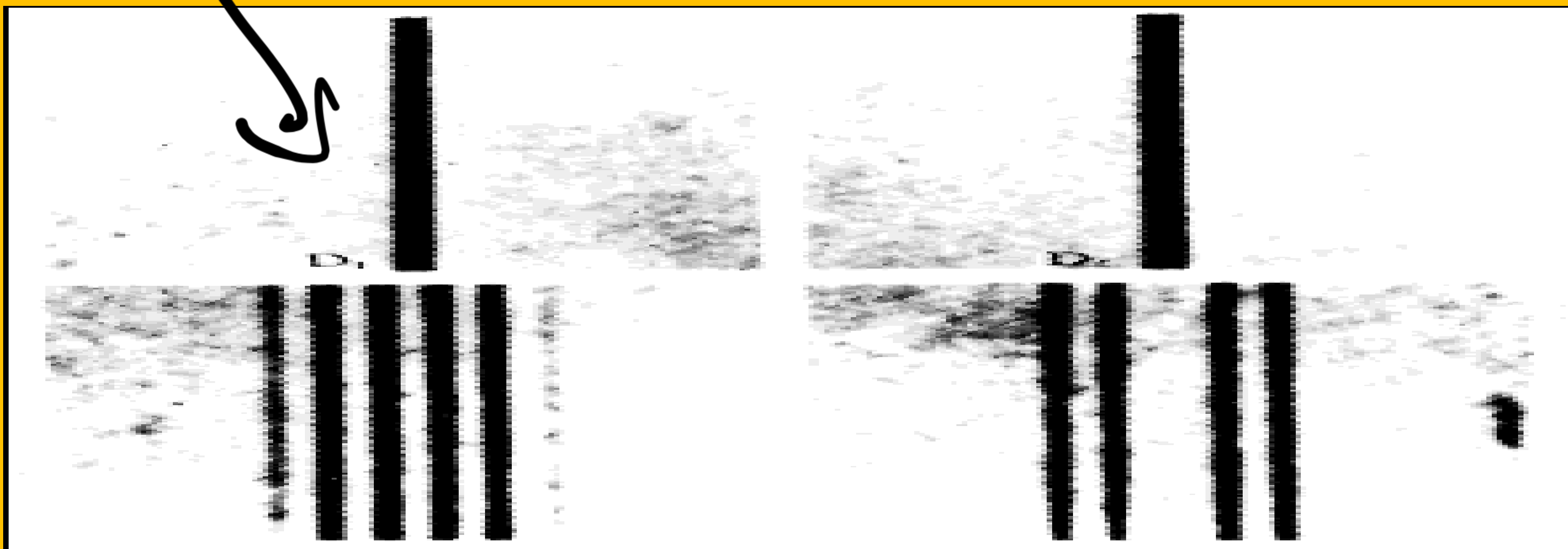


Sommerfeld

The improvement of spectrometric precision highlighted the limits of Bohr's theory. The German physicist proposed elliptical orbits, i.e. flattening of orbits that were not always circular, and this increased the number of hypothetical orbits and electron jumps, maintaining the concept of quantization.



Zeeman



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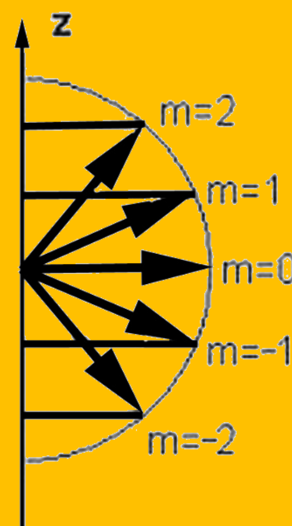
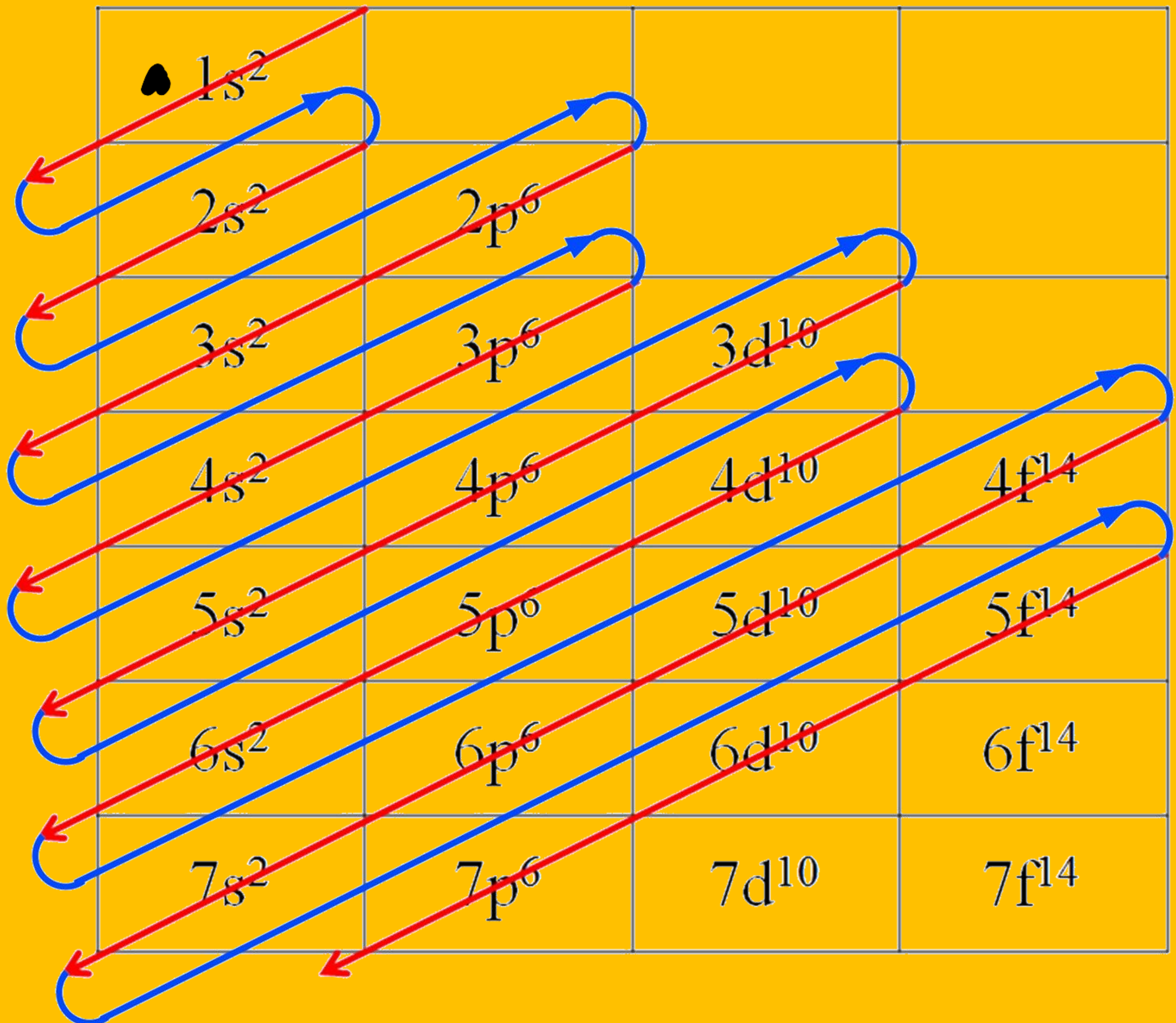


megnet.ic momenth

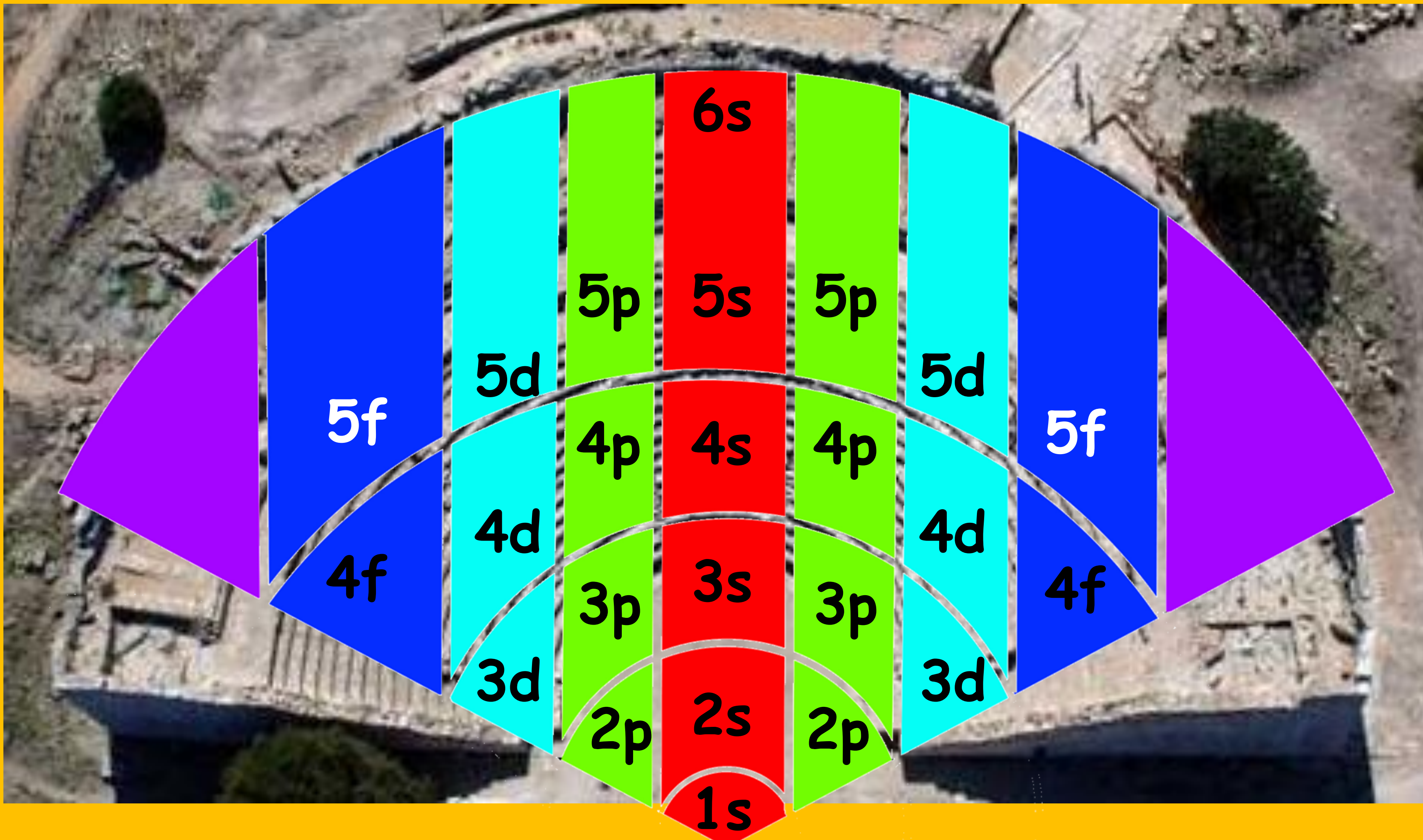
Quantum numbers

- Principal quantum number n (1, 2, 3, 4, …)
- Secondary or azimuthal quantum number (l = 0, …, n-1) **[orbital angular momentum quantum number]**
- Magnetic quantum number (ml = -l, …,0, …,+l)
- Spin quantum number (ms =±1/2)

Aufbau – Electronic build-up



Aufbau and Segesta Theater



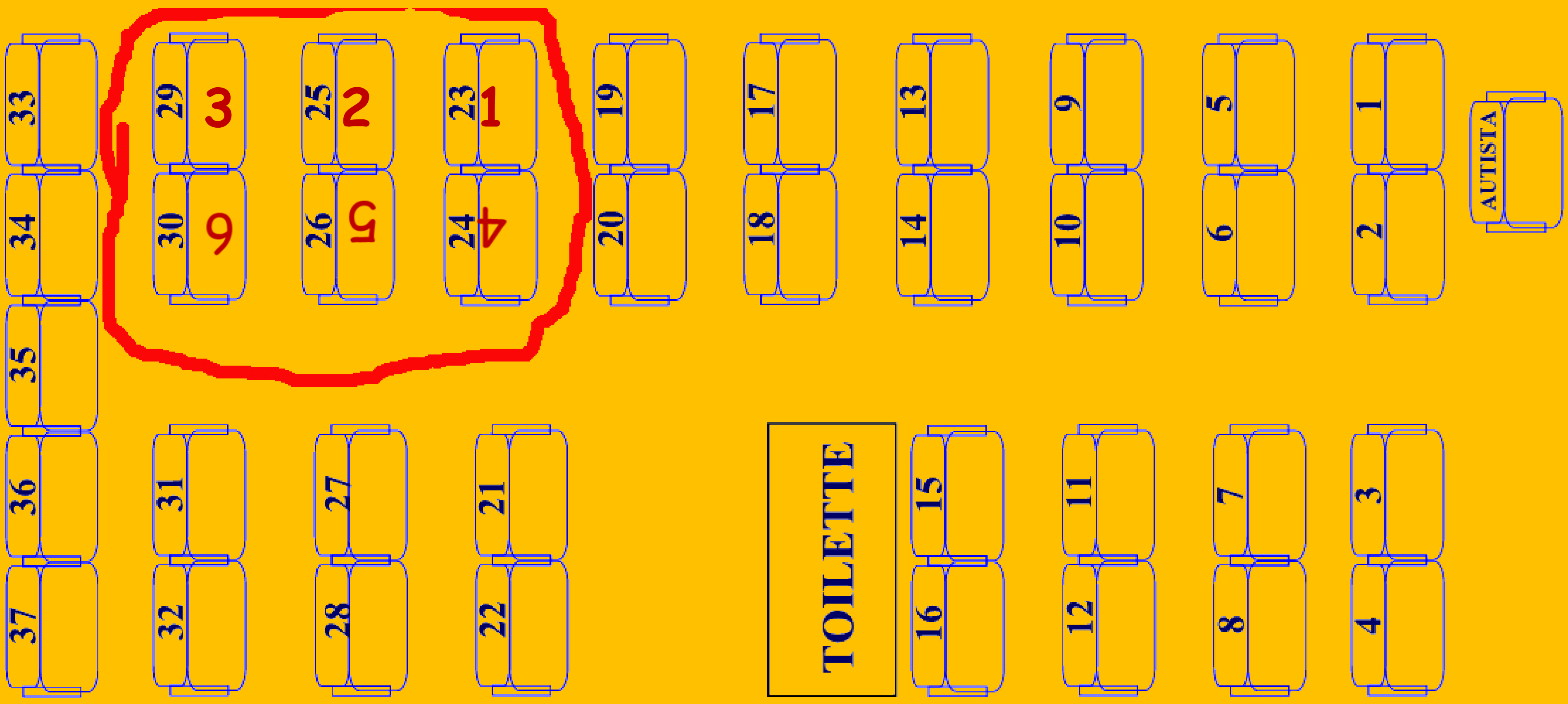
Build-up rules

- the level with the lowest n is occupied first;
- within the same level, the sublevel defined by the lowest azimuthal quantum number l is first occupied (Hund's rule I);
- degenerate orbitals (with the same energy) fill up according to the principle of maximum multiplicity (Hund's rule);

$p_x^1 \; p_y^1 \; p_z^1$

- the filling takes place in compliance with the Pauli exclusion principle.

Rules of Nature...



The "quantum-mechanical" atom

- The electrons in the atom have quantized energies
- Electron wavefunctions are three-dimensional, so defined by three spatial coordinates
- The wave function that describes an electron in an atom is the atomic orbital
- The energies and mathematical shapes of the orbitals are calculated using the Shrodinger equation
- Each electron adds 3 variables (x, y, and z) to the equation.
- The energy level differences calculated with the equation are in agreement with those calculated from the atomic spectra
- Each orbital is defined by three quantum numbers, plus a fourth that differentiates it from the other particle with which it shares the orbital

Orbital

- A wave function which is eigenfunction of the Schrö equation dependent on three quantum numbers and associated with specific energy, orientation and mean distance
- Portion of space (volume) within which there is a 90% chance of finding the electron or particle to which it is associated

Shells, sublevels, and orbitals

Orbitals are also classified:

Level (Shell) (n): 1 to 7. The greater the number, the greater the distance from the nucleus

Sublayer (subshell) (l): A group of orbitals within a layer. Identified by the letters s, p, d, f. The number of sublevels is equal to n (principal quantum number)

Single orbitals: These are identified by their spatial direction using Cartesian coordinates (m). The number of orbitals depends on the sublevel, it is odd: 1 in s, 3 in p, 5 in d, 7 in f.

Shells and subshells

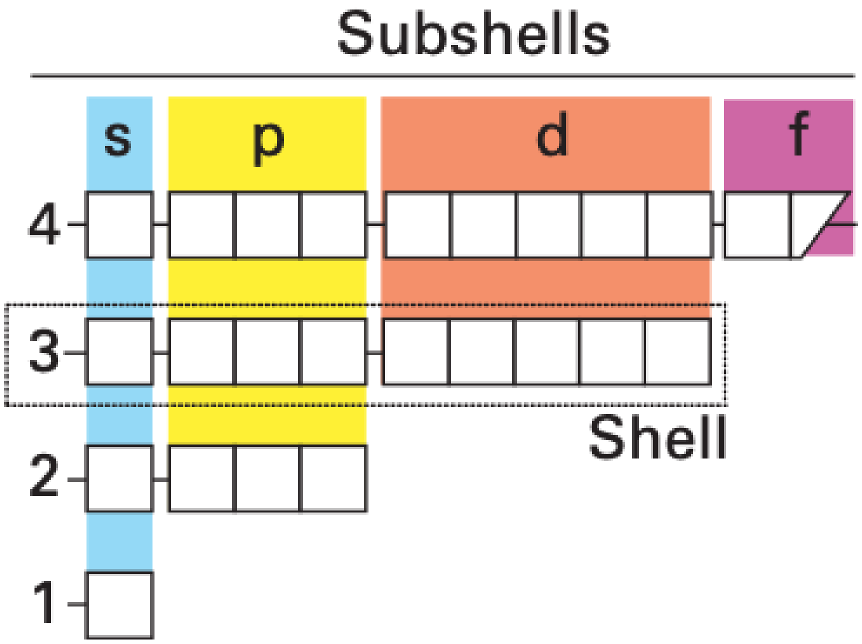
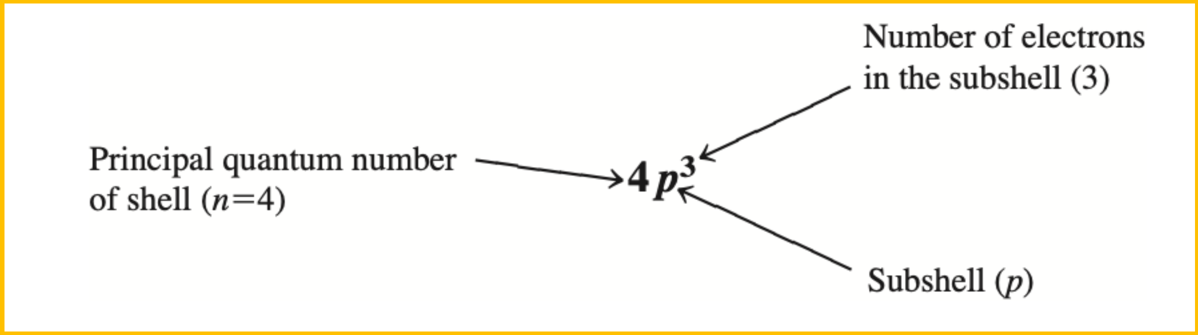


Figure 1.7 The classification of orbitals into subshells (same value of *l*) and shells (same value of *n*).

Electron Filling roles

- **Hund's rule** *states that electrons occupy separate orbitals in the same subshell with parallel (i.e., identical) spins.*

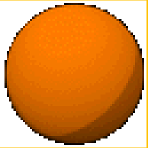


B:	$1s^2 2s^2 2p^1$	N:	$1s^2 2s^2 2p^3$	F:	$1s^2 2s^2 2p^5$
C:	$1s^2 2s^2 2p^2$	O:	$1s^2 2s^2 2p^4$	Ne:	$1s^2 2s^2 2p^6$

n	l	m_l	orbital name	Number of orbitals
1	0	0	1s	1
2	0	0	2s	1
2	1	-1, 0, 1	2p	3
3	0	0	3s	1
3	1	-1, 0, 1	3p	3
3	2	-2,-1,0,1,2	3d	5
4	0	0	4s	1
4	1	-1,0,1	4p	3
4	2	-2,-1,0,1,2	4d	5
4	3	-3, -2, -1, 0, 1, 2, 3	4f	7

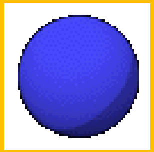
$n = x,\ l = 0 \ldots (x-1),\ m = -l \ldots +l$

$n = 1$
$l = 0,\ m = 0$



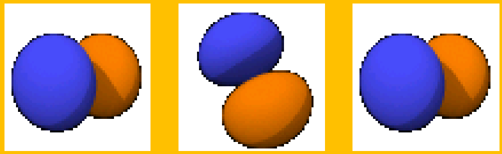
1s

$n = 2$
$l = 0,\ m = 0$



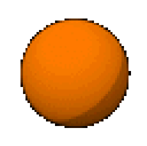
2s

$n = 2$
$l = 1,\ m = +1, 0, -1$



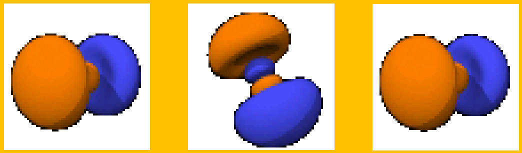
2p

$n = 3$
$l = 0,\ m = 0$



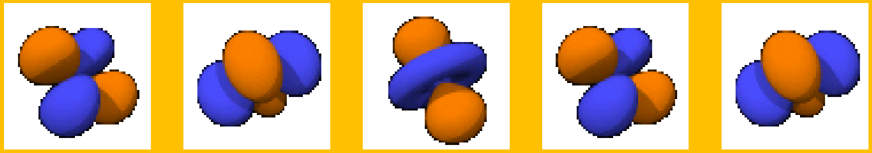
3s

$n = 3$
$l = 1,\ m = +1, 0, -1$



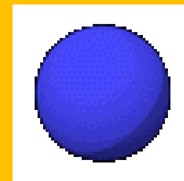
3p

$n = 3$
$l = 2,\ m = +2, +1, 0, -1, -2$



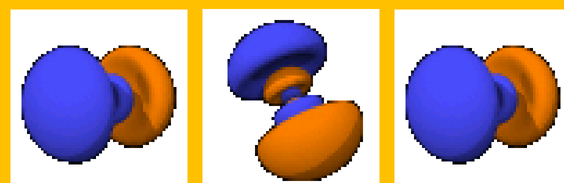
3d

n = 4
l = 0, m= 0



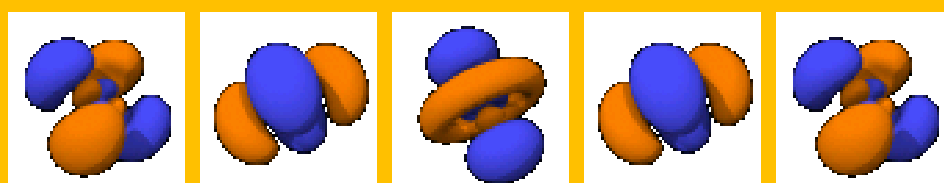
4s

n = 4
l = 1, m= +1, 0, -1



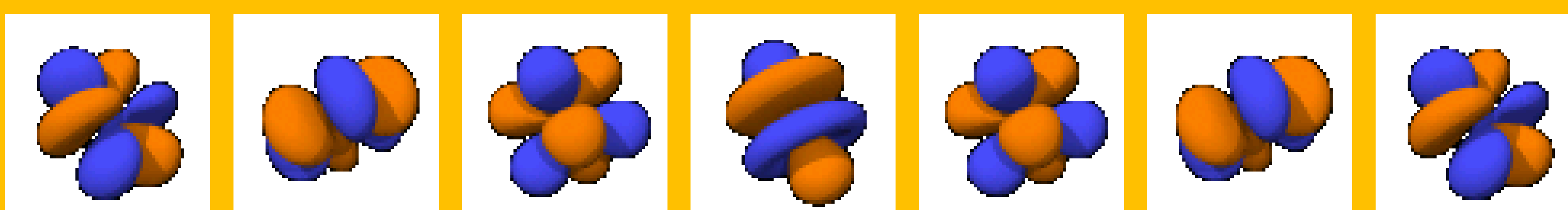
4p

n = 4
l = 2, m= +2, +1, 0, -1, -2



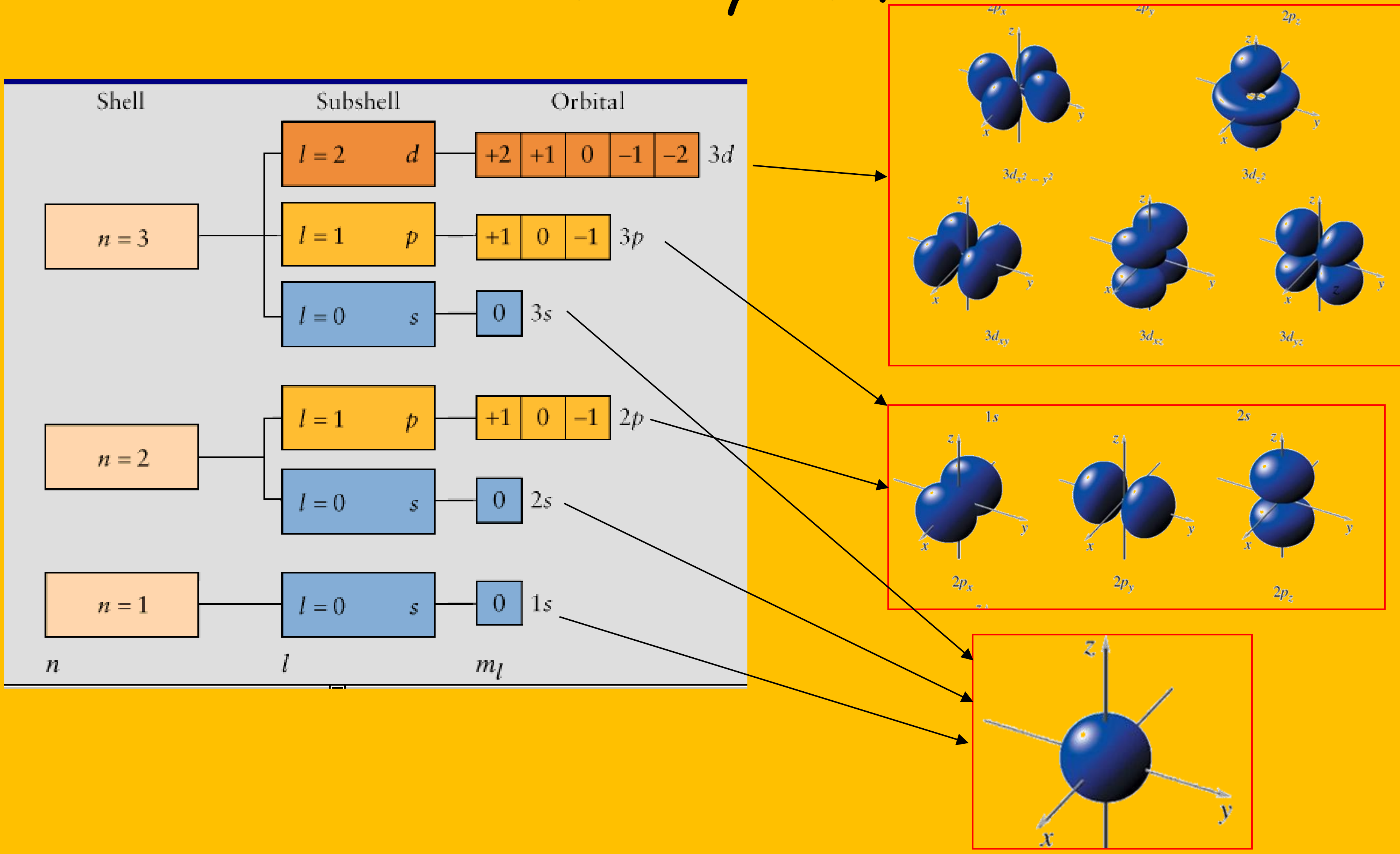
4d

n = 4
l = 3, m= +3, +2, +1, 0, -1, -2, -3



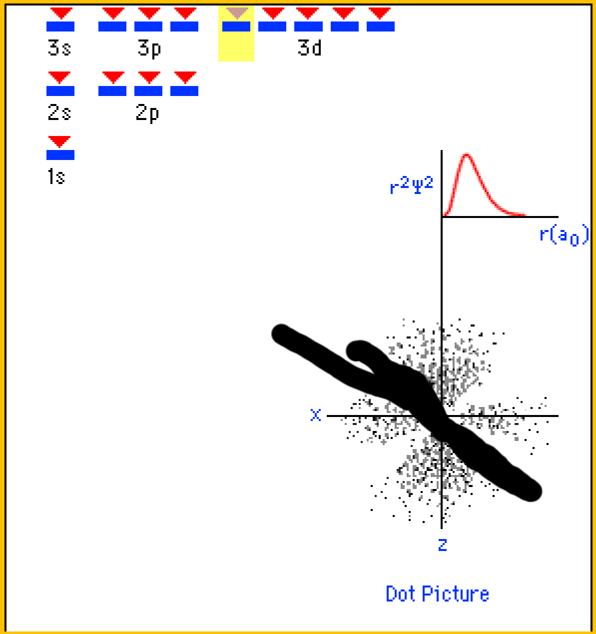
4f

Orbitals in the first three levels and boundary surfaces



Summary

- The nucleus is the mass of the atom
- Electrons define the size
- Electrons occupy areas around the nucleus, called orbitals
- These have definite shapes and energies
- Different atoms have different nuclear charges and therefore number of electrons



Wave Equation

- A differential equation describing the motion of an electron in a region of space surrounding an atomic nucleus
- The solution to a wave equation is called a **Wavefunction**, Ψ
- The probability of finding an electron in a given region of space is found to be proportional to Ψ^2

The Schrödinger Equation

$$\nabla^2 \Psi(x, y, z) + \frac{8\pi^2 m}{h^2} \{E - U(x, y, z)\} \Psi(x, y, z) = 0$$

Where: del, ∇ , is a triple derivative in x, y, and z; psi, Ψ , is the wave equation; h is Planck's constant; E is the energy of the system and U is the potential energy (often the Culombic field of the nucleus).

Schrödinger equation

$$\hat{H}\psi = E\psi$$ Equation of State

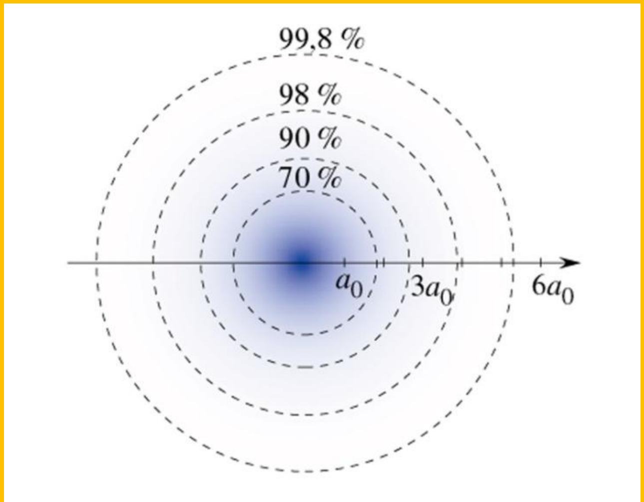
- Unknowns are both E and y (wave function).
- infinite ψ each of which is associated with an energy value E.
- It can be solved exactly for the hydrogen atom and approximately for polyelectron atoms.

$\Psi^2 \Delta V$: accounts for the probability that a particle described by the function is in the infinitesimal volume ΔV around a point of x, y, z coordinates.

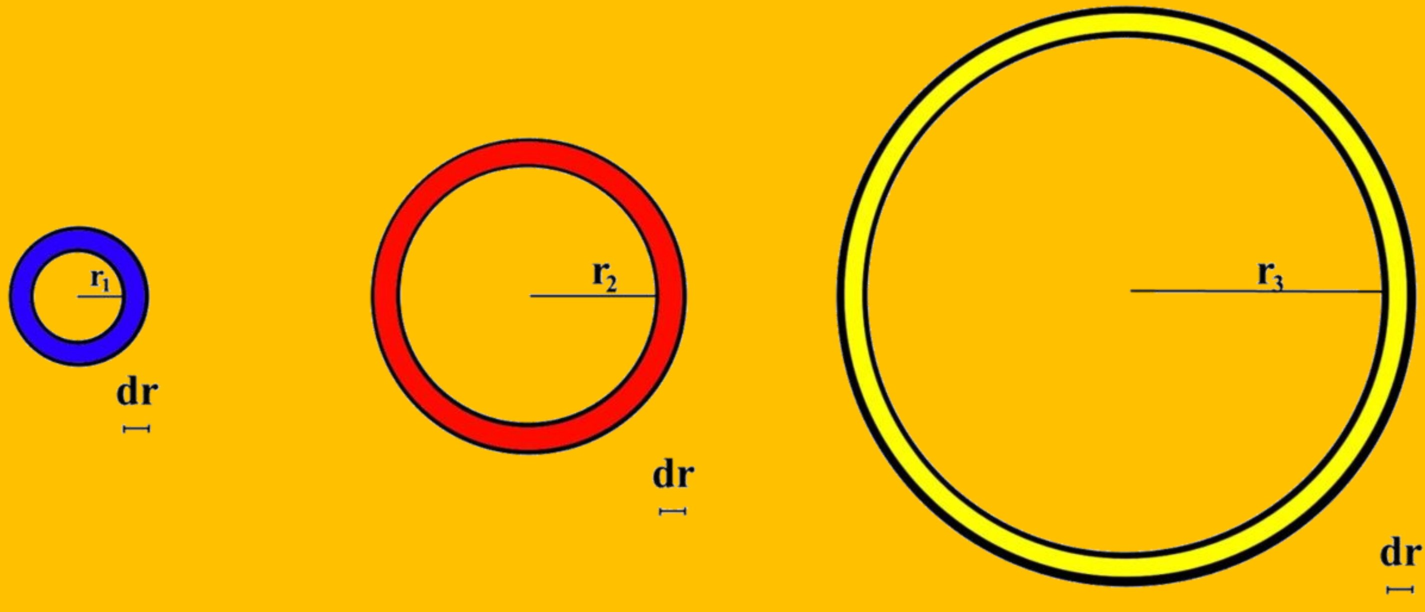
Atomic orbital

- A region of space around the nucleus bounded by a surface within which there is a 99% probability of finding the electron (boundary surface).
- Wavefunctions Ψ obtained from the solution of the Schroedinger equation

the probability of finding an electron within a certain area, $d\tau$, is given by the value of $\Psi^2 \, d\tau$.

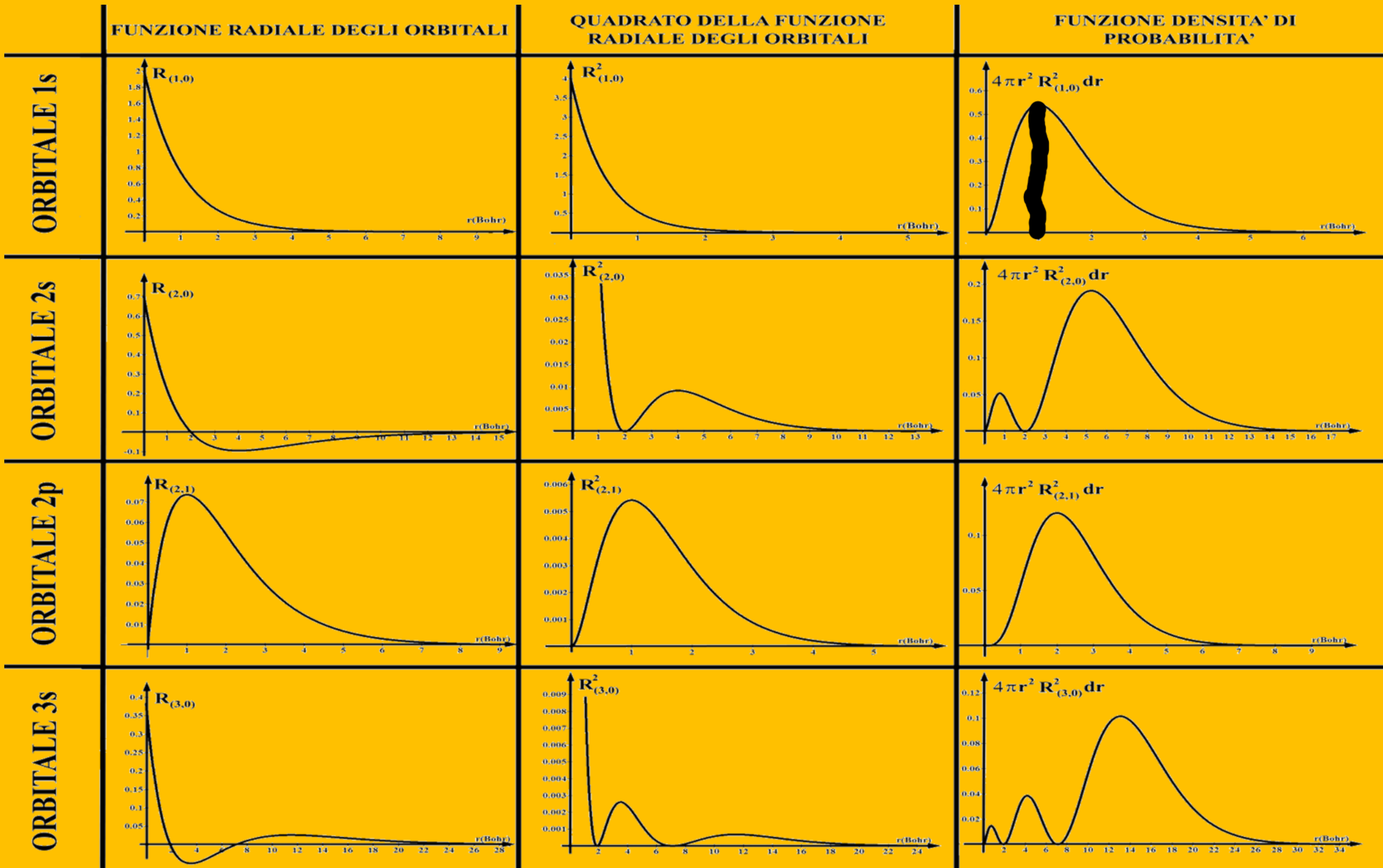


Spherical Volume Elements Function

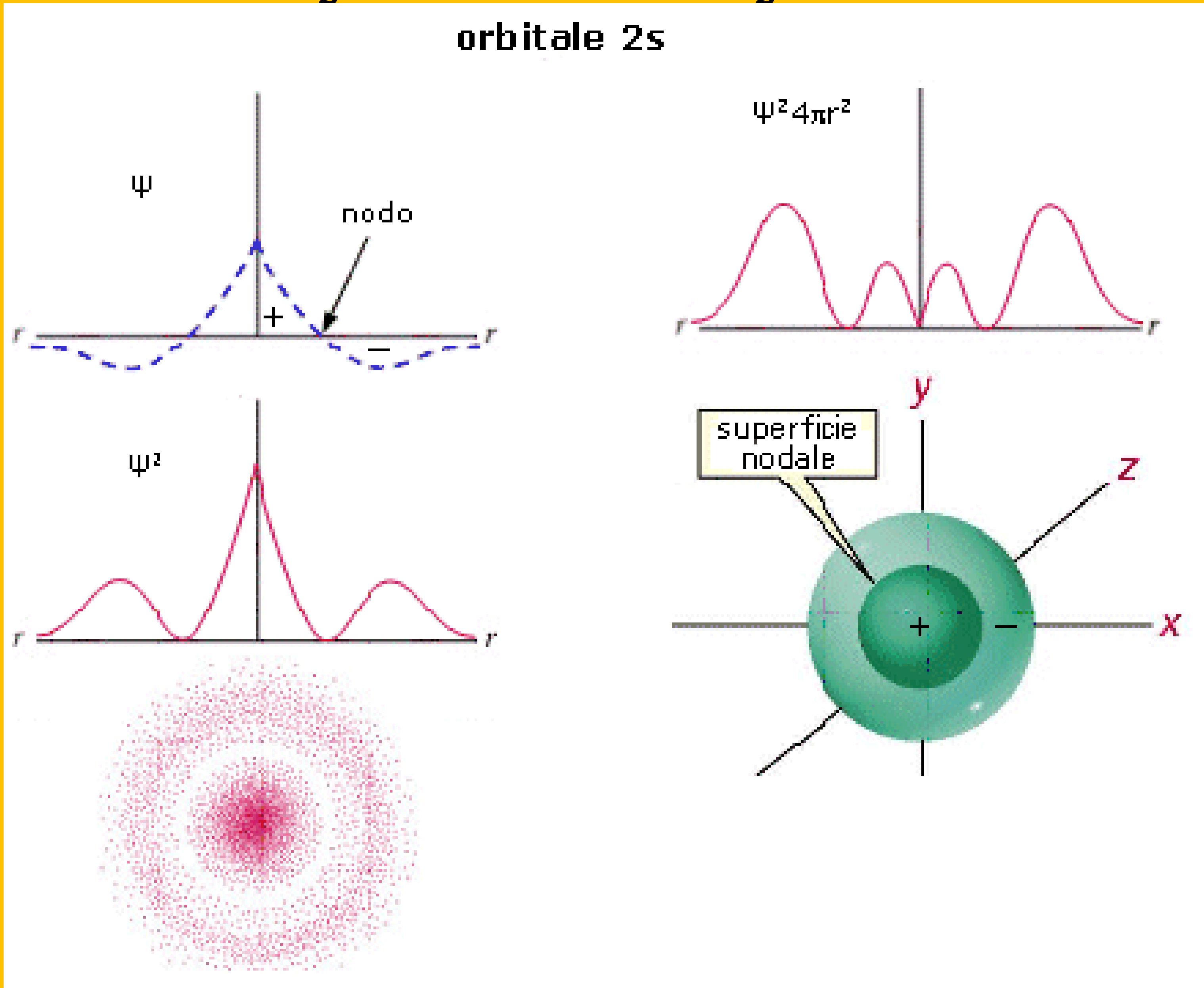


$V_1 = 4\pi r_1^2 dr$ $V_2 = 4\pi r_2^2 dr$ $V_3 = 4\pi r_3^2 dr$

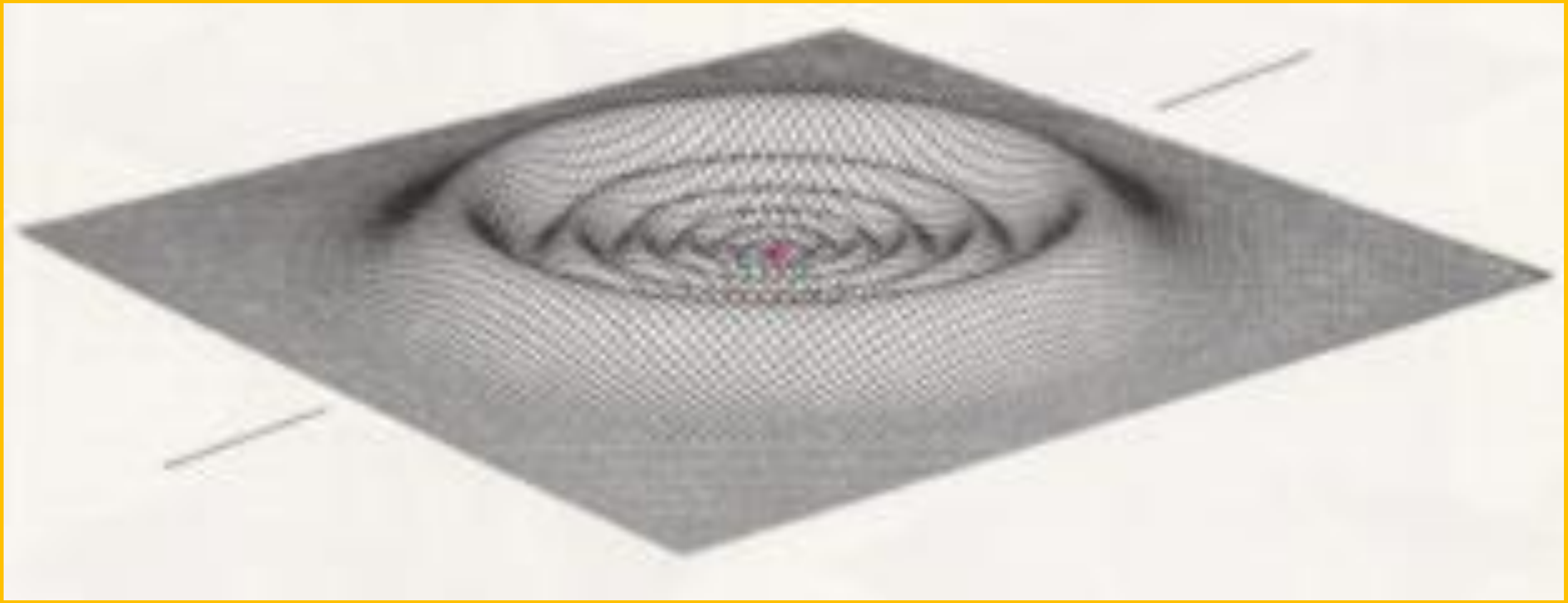
Wave Functions Ψ and derivatives



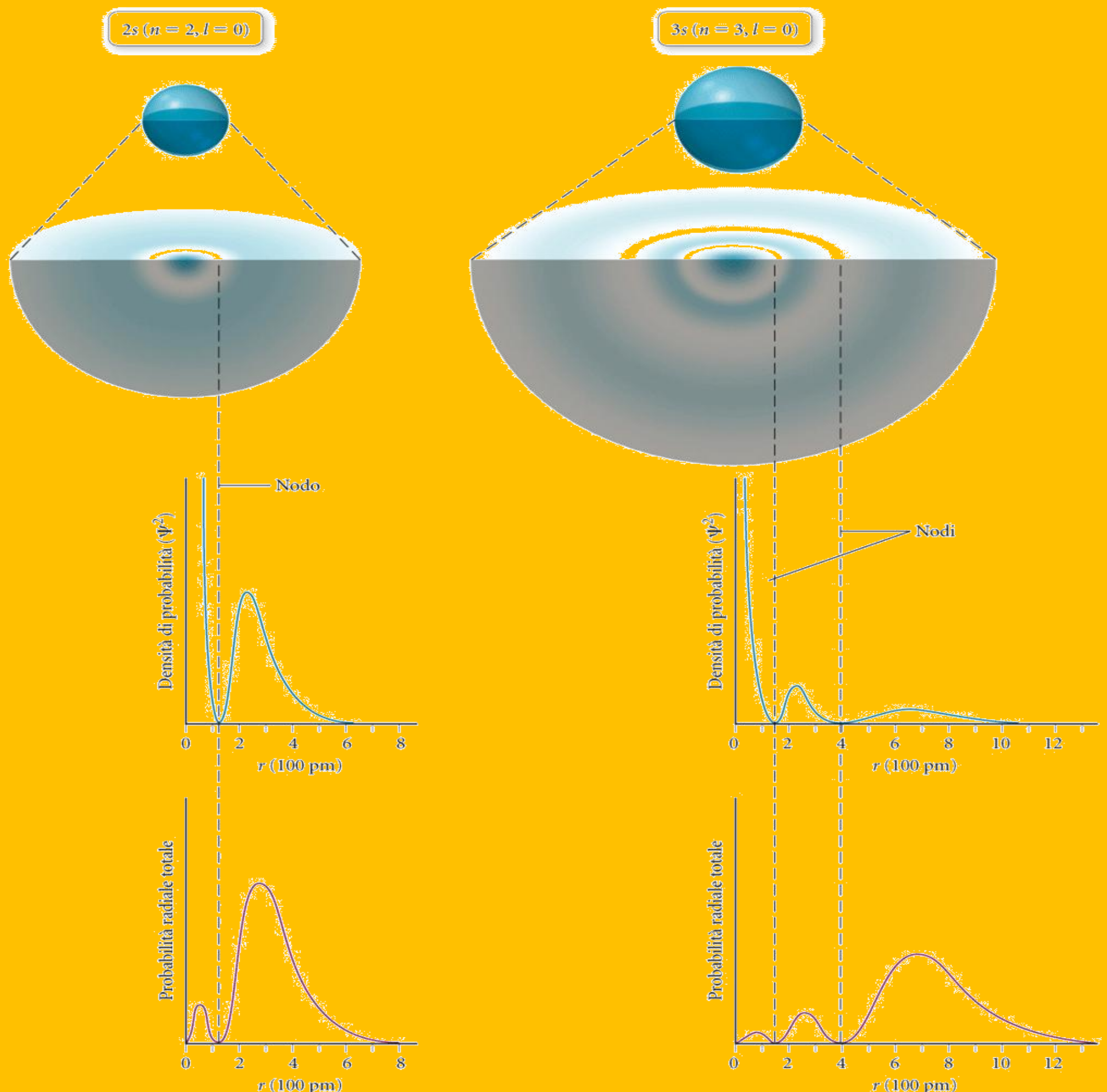
Density Probability function



5s-2D



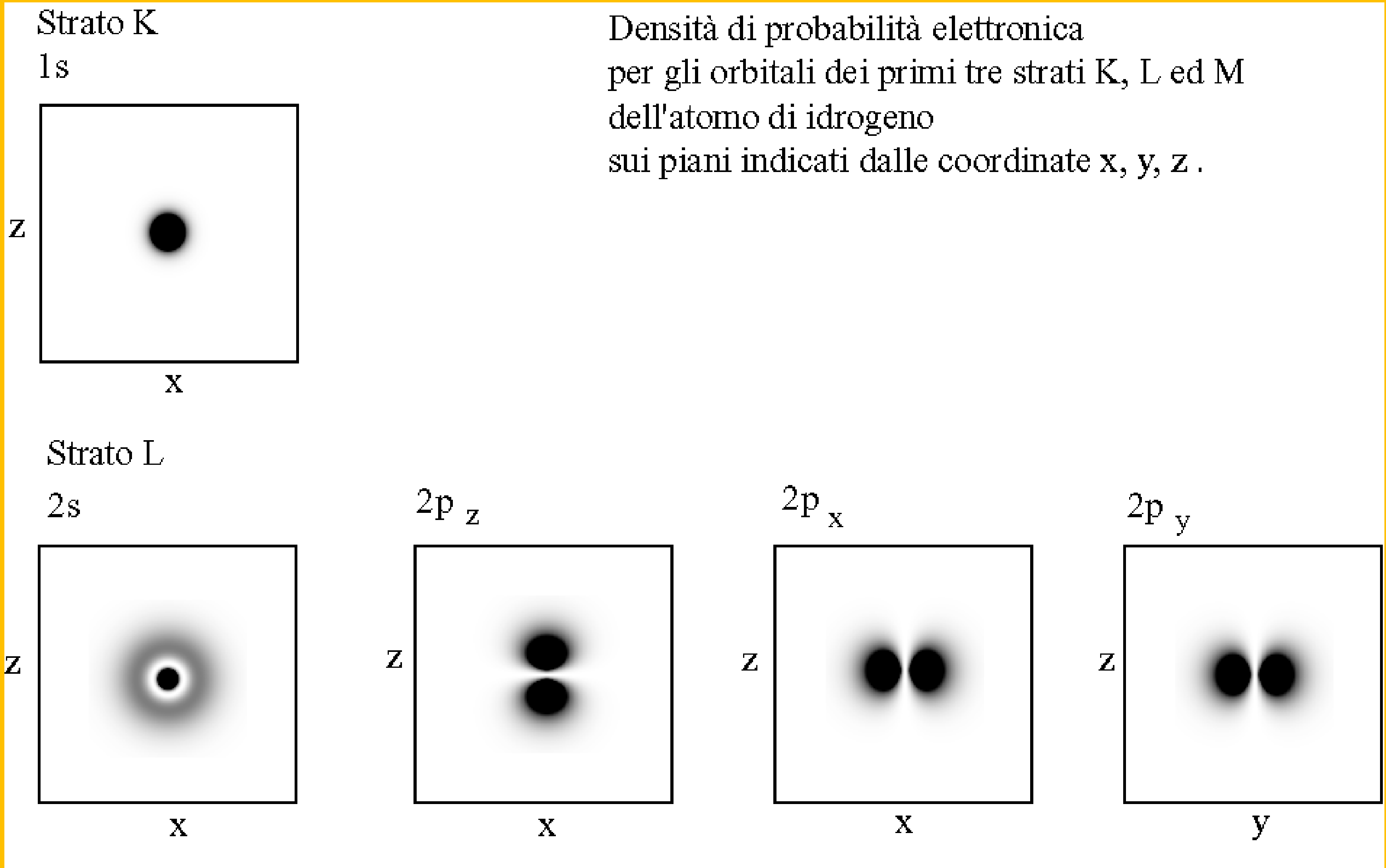
Orbitals 2s 3s



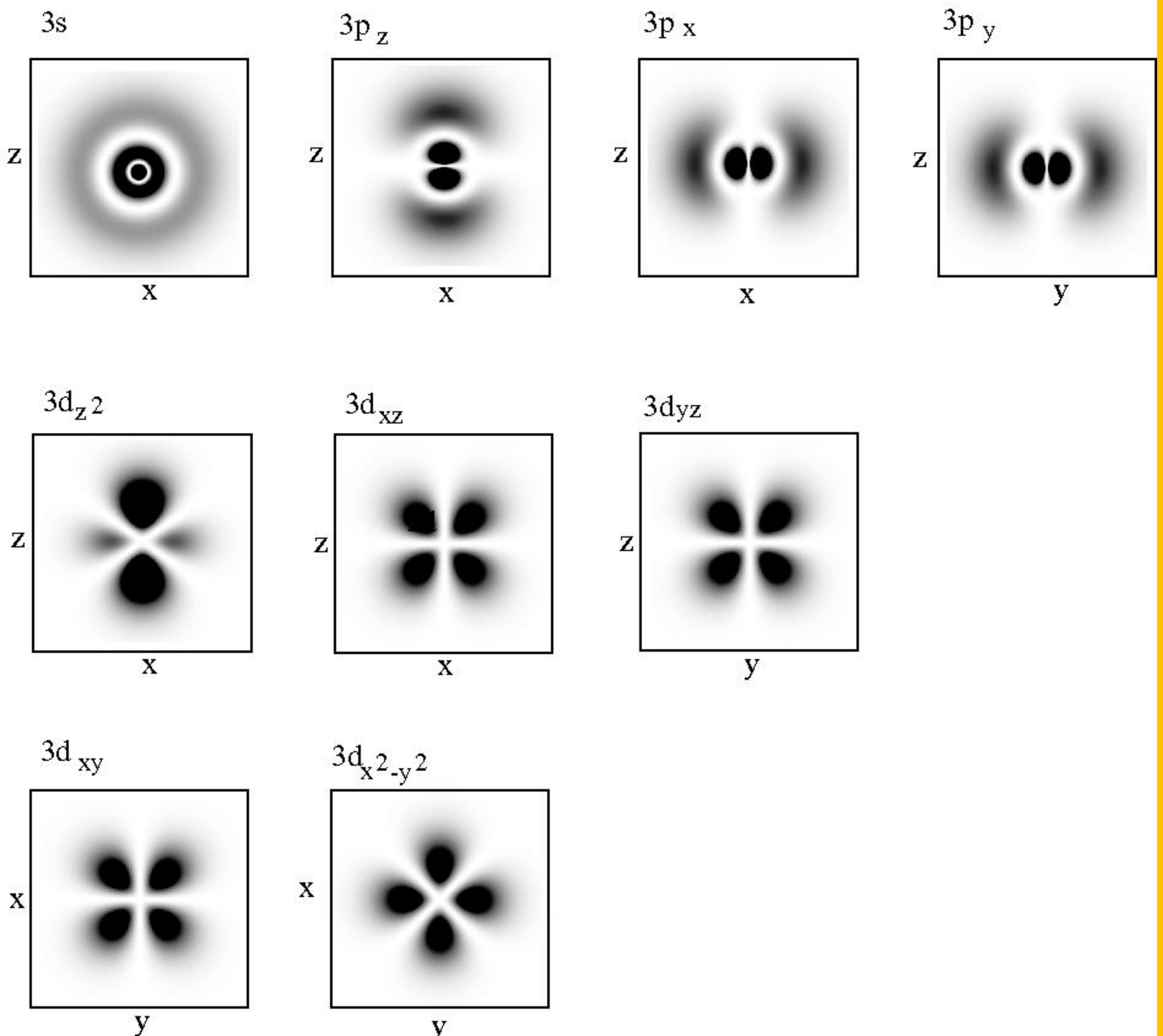
▲ FIGURA 7.25 Densità di probabilità e funzioni di distribuzione radiale per gli orbitali 2*s* e 3*s*

Probability Density

Densità di probabilità elettronica
per gli orbitali dei primi tre strati K, L ed M
dell'atomo di idrogeno
sui piani indicati dalle coordinate x, y, z .



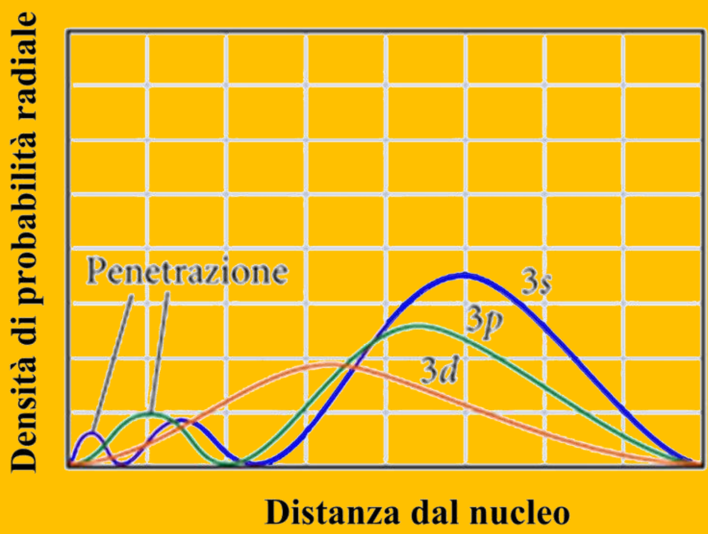
Strato M



Nodes

- Wherever $\Psi = 0$, $\Psi^2 = 0$ too, and guess… **density probability** = 0; these space elements are nodes (respect to a specific orbital).
- radial nodes ($R = 0$) are always n-l-1
- Any orbital bears the core node
- Gli orbitali possono avere superifici nodali o nodi angolari

Penetration



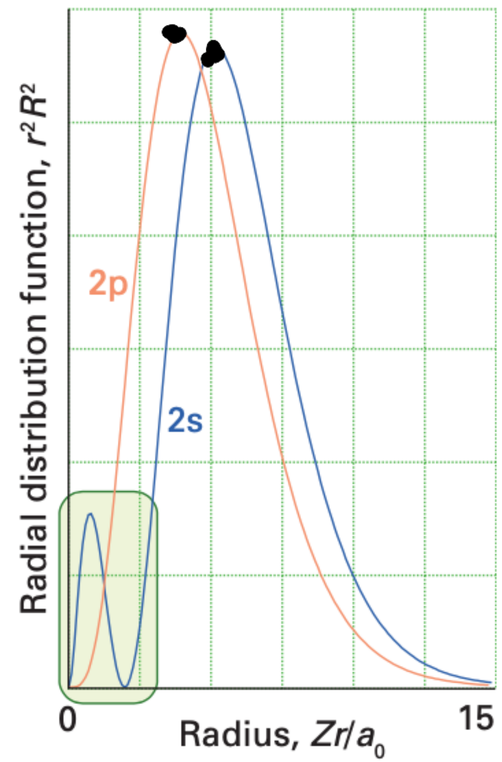


Figure 1.18 The penetration of a 2s electron through the inner core is greater than that of a 2p electron because the latter vanishes at the nucleus. Therefore, the 2s electrons are less shielded than the 2p electrons.

Z* e Z

The nuclear charge Z **is not** the effective nuclear charge Z* that is actually felt by the electron in the last layer.

In fact, the inner (core) electrons shield the charge felt by the

Slater set up an empirical parameterization of the electron shielding of the lower layers and of the same level occupied by the outermost electron

Calculations….. For the first atoms

Be : Z*= 4-(2x0,85) - (1x0,35) = +1.95;

B : Z*= 5-(2x0,85) - (2x0,35) = +2,60;

C : Z*= 6-(2x0,85) - (3x0,35) = +3,25;

N : Z*= 7-(2x0,85) - (4x0,35) = +3,90;

O : Z*= 8-(2x0,85) - (5x0,35) = +4,55;

F : Z*= 9-(2x0,85) - (6x0,35) = +5,20;

Atomic Properties

- They depend mainly on the effective nuclear charge Z* (or Z_{eff})
- Atomic radius (van der Waals)
- Ionization potential
- Electron Affinity
- Electronegativity

Atomic Radii

Li 257	Be 112	B 88	C 77	N 74	O 66	F 64	Ne
Na 191	Mg 160	Al 143	Si 118	P 110	S 104	Cl 99	Ar
K 235	Ca 197	Ga 153	Ge 122	As 121	Se 117	Br 114	Kr
Rb 250	Sr 215	In 167	Sn 158	Sb 141	Te 137	I 133	Xe
Cs 272	Ba 224	Tl 171	Pb 175	Bi 182	Po 167	At	Rn

Trends

Figura 8.21

Tendenze in tre proprietà atomiche

How to remind such things

- Little Naughty Kids Rub Cats Fur
- Bees Make Candy Sold By Raccoons
- Boys Always Grab Ice-T
- CaSe - GeStaPo
- Notorious Poets Assume Sonnets Biases
- Over Samples Search The Powder
- Frog Climbing Bridges Instantly Able
- He Never Argues; Krazy Xenophobic Rats

Electronic Affinity
EA = $-\Delta H$(electron addition)

$$A(g) + e^-(g) \rightarrow A^-(g)$$

Another property that greatly influences the chemical behavior of atoms is their ability to accept one or more electrons. This property is called ***electron affinity,*** which is *the negative of the energy change that occurs when an electron is accepted by an atom in the gaseous state to form an anion.*

$$X(g) + e^- \longrightarrow X^-(g) \qquad (8.2)$$

Consider the process in which a gaseous fluorine atom accepts an electron:

$$F(g) + e^- \longrightarrow F^-(g) \qquad \Delta H = -328 \text{ kJ/mol}$$

The electron affinity of fluorine is therefore assigned a value of +328 kJ/mol. The more positive is the electron affinity of an element, the greater is the affinity of an atom of the element to accept an electron. Another way of viewing electron affinity is to think of it as the energy that must be supplied to remove an electron from the anion. For fluorine, we write

$$F^-(g) \longrightarrow F(g) + e^- \qquad \Delta H = +328 \text{ kJ/mol}$$

Ionization Energy
IE = ΔH (electron ejection)

$$A(g) \rightarrow A^+(g) + e^-(g) \quad I = E(A^+,g) - E(A,g)$$

The **first ionization energy**, I_1, is the energy required to remove the least tightly bound electron from the neutral atom, the **second ionization energy**, I_2, is the energy required to remove the least tightly bound electron from the resulting cation, and so on. Ionization energies are conveniently expressed in electronvolts (eV), but are easily converted into kilojoules per mole by using 1 eV = 96.485 kJ mol^{-1}. The ionization energy of the H atom is 13.6 eV, so to remove an electron from an H atom is equivalent to dragging the electron through a potential difference of 13.6 V.