Universidade Federal do Rio de Janeiro
Instituto de Química
Departamento de Química Inorgânica

IQG – 112

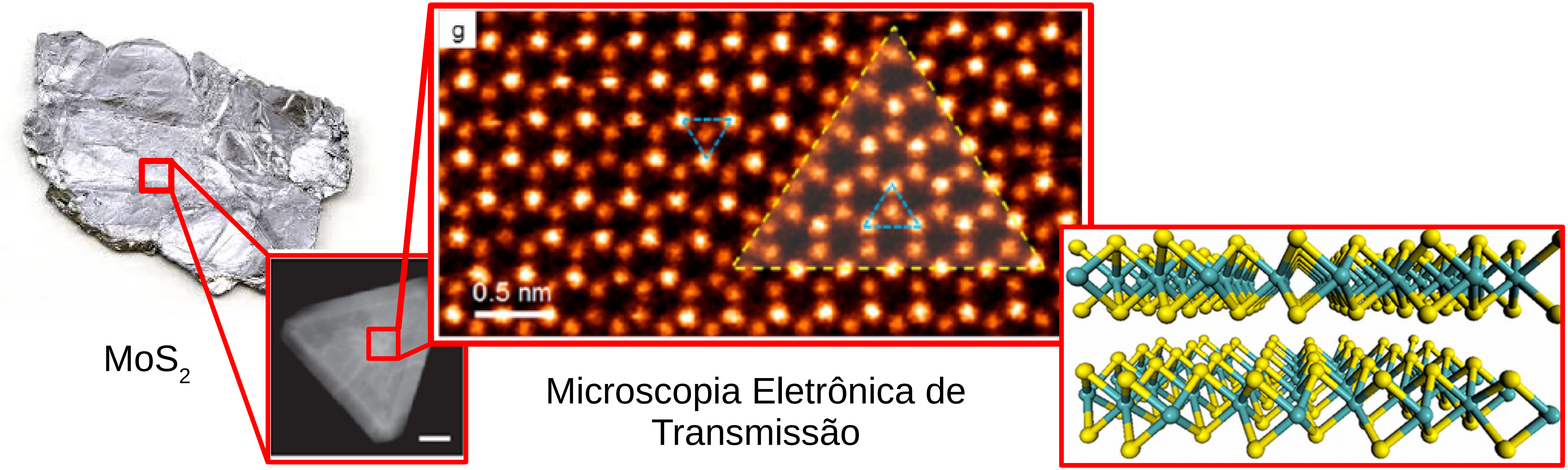
Modelos Atômicos e Espectroscopia

Prof. Daniel Grasseschi

Rio de Janeiro, 21 de agosto de 2018

A matéria é composta de átomos!

Menores partículas de um elemento



MoS_2

Microscopia Eletrônica de Varredura

Microscopia Eletrônica de Transmissão

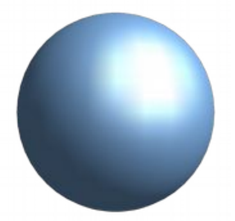
Mo → 145 pm   S → 100 pm

Átomos podem ser manipulados!

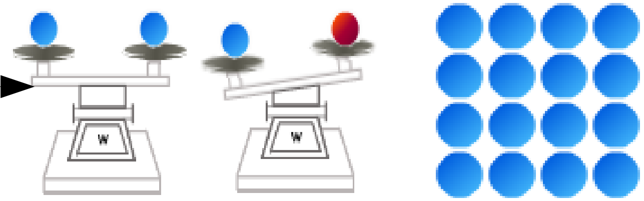
Modelos Atômicos

John Dalton - 1805

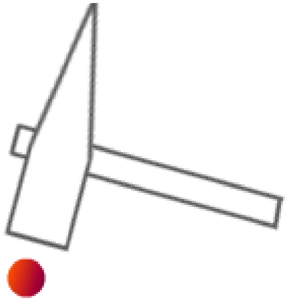
Átomos →Esferas maciças



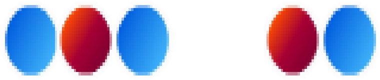
Elementos → Definidos pelo tamanho e massa dos átmos



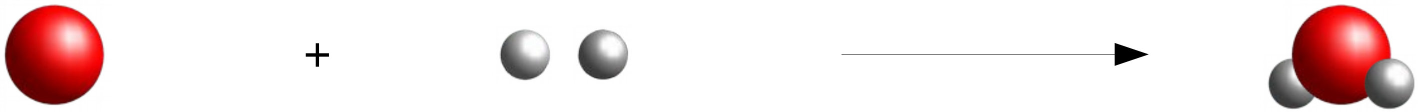
Indivisíveis



Elementos se combinam para formar compostos



Reações química → átomos são rearanjados, combinados ou separados



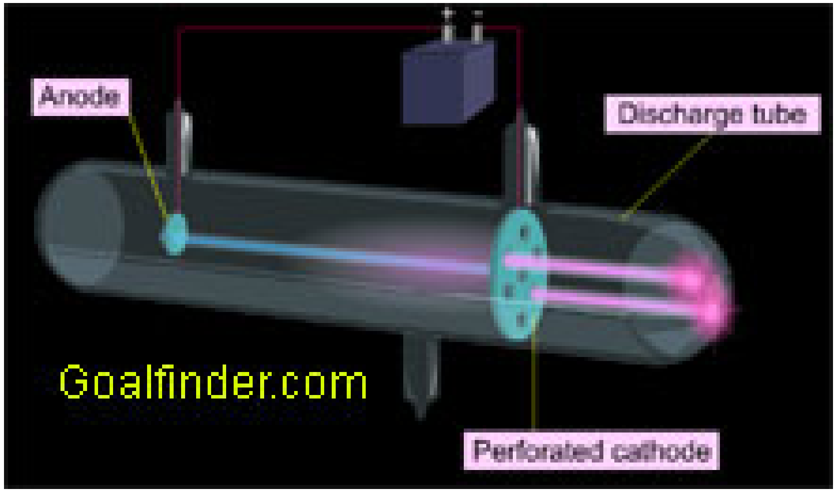
O → 16 unidades de massa

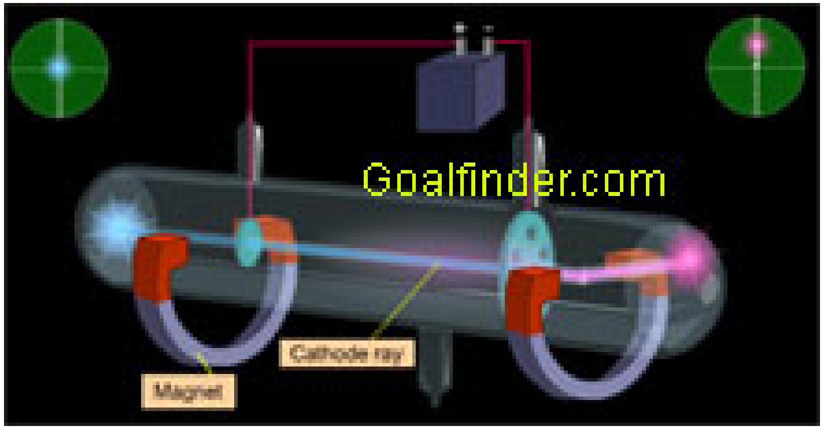
H → 1 unidade de massa cada

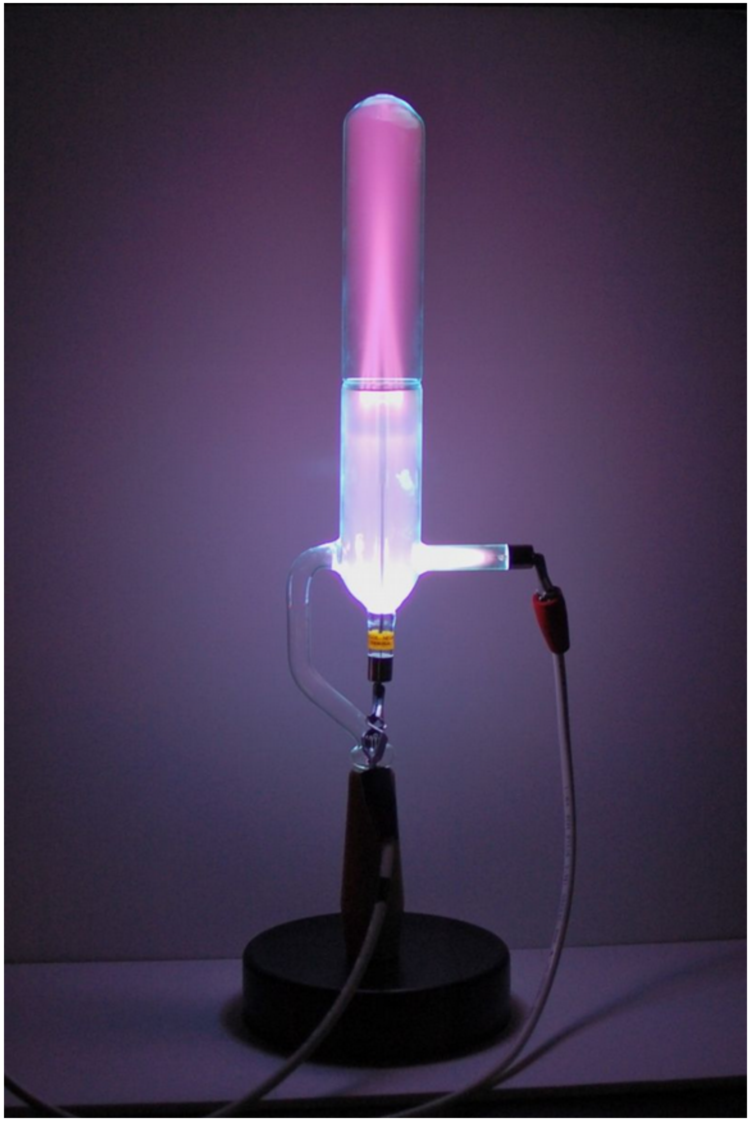
H2O → 18 unidades de massa

Experimento de Goldstaein

1886 → Eugen Goldstein → Tudo de Raios anôdicos


Anode
Discharge tube
Goalfinder.com
Perforated cathode

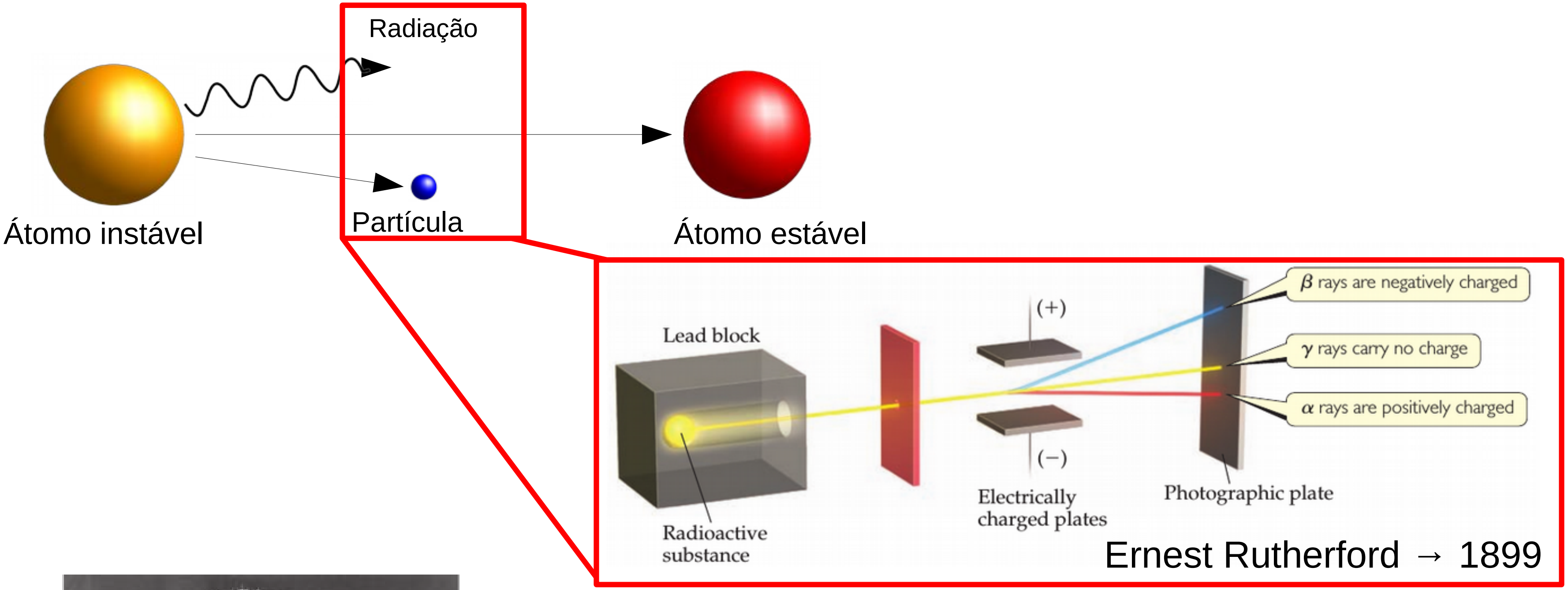

Goalfinder.com
Cathode ray
Magnet



Cargas multiplos de +1,6 x 10-19 C

Partículas Subatômicas

1896 → Bequerel → Radioatividade do Urânio


Radiação
Átomo instável
Partícula
Átomo estável
Lead block
Radioactive substance
(+)
(−)
Electrically charged plates
Photographic plate
β rays are negatively charged
γ rays carry no charge
α rays are positively charged

Ernest Rutherford → 1899

$_{0}\beta^{-1}$

$_{0}\gamma^{0}$

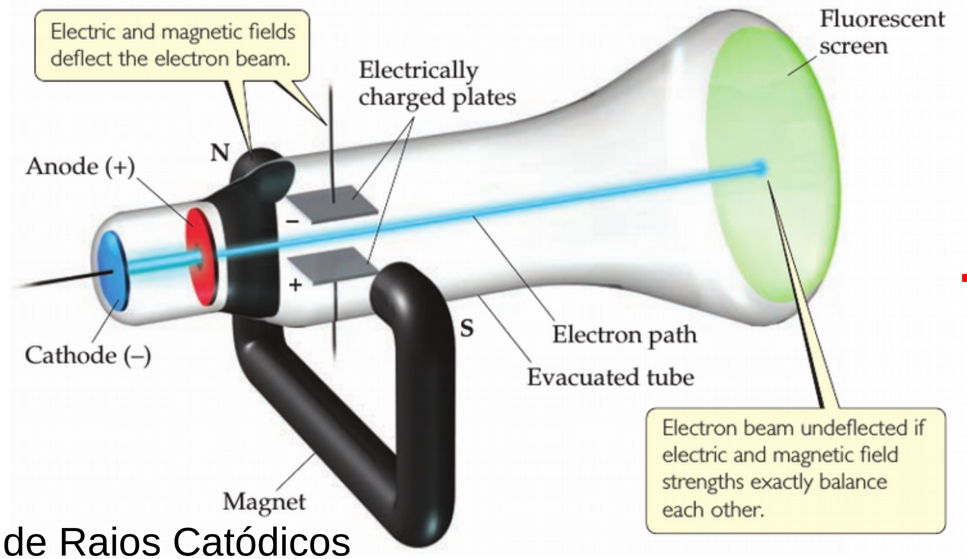
$_{2}^{4}\alpha^{2+}$

Marie Sklodwska Curie

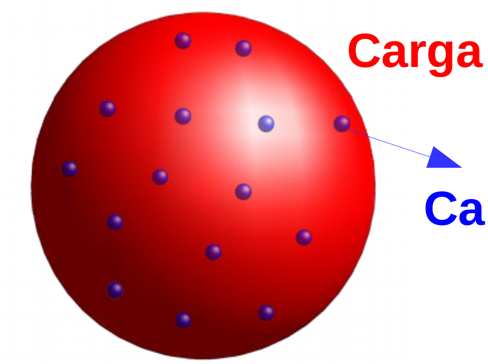
“Cada pessoa deve trabalhar para o seu aperfeiçoamento e, ao mesmo tempo, participar da responsabilidade coletiva por toda a humanidade”.

O elétron

1897 → J. J. Thomson → Relação carga/massa do elétron → 1.76 x 10^{11} C/kg


Electric and magnetic fields deflect the electron beam.
Electrically charged plates
Fluorescent screen
Anode (+)
N
–
+
Cathode (–)
S
Electron path
Evacuated tube
Electron beam undeflected if electric and magnetic field strengths exactly balance each other.
Magnet

Tubo de Raios Catódicos



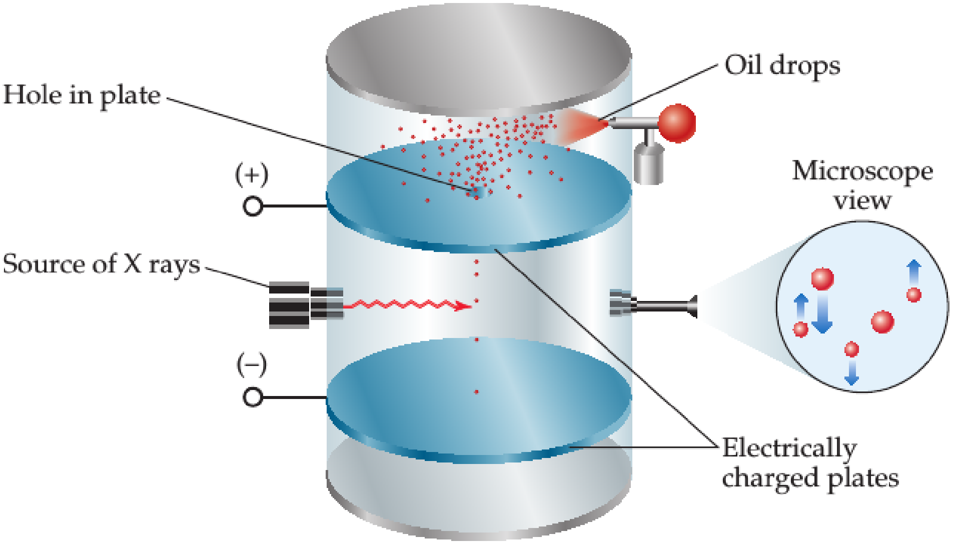
Carga positiva

Carga Negativa

Modelo do Pudim de passas

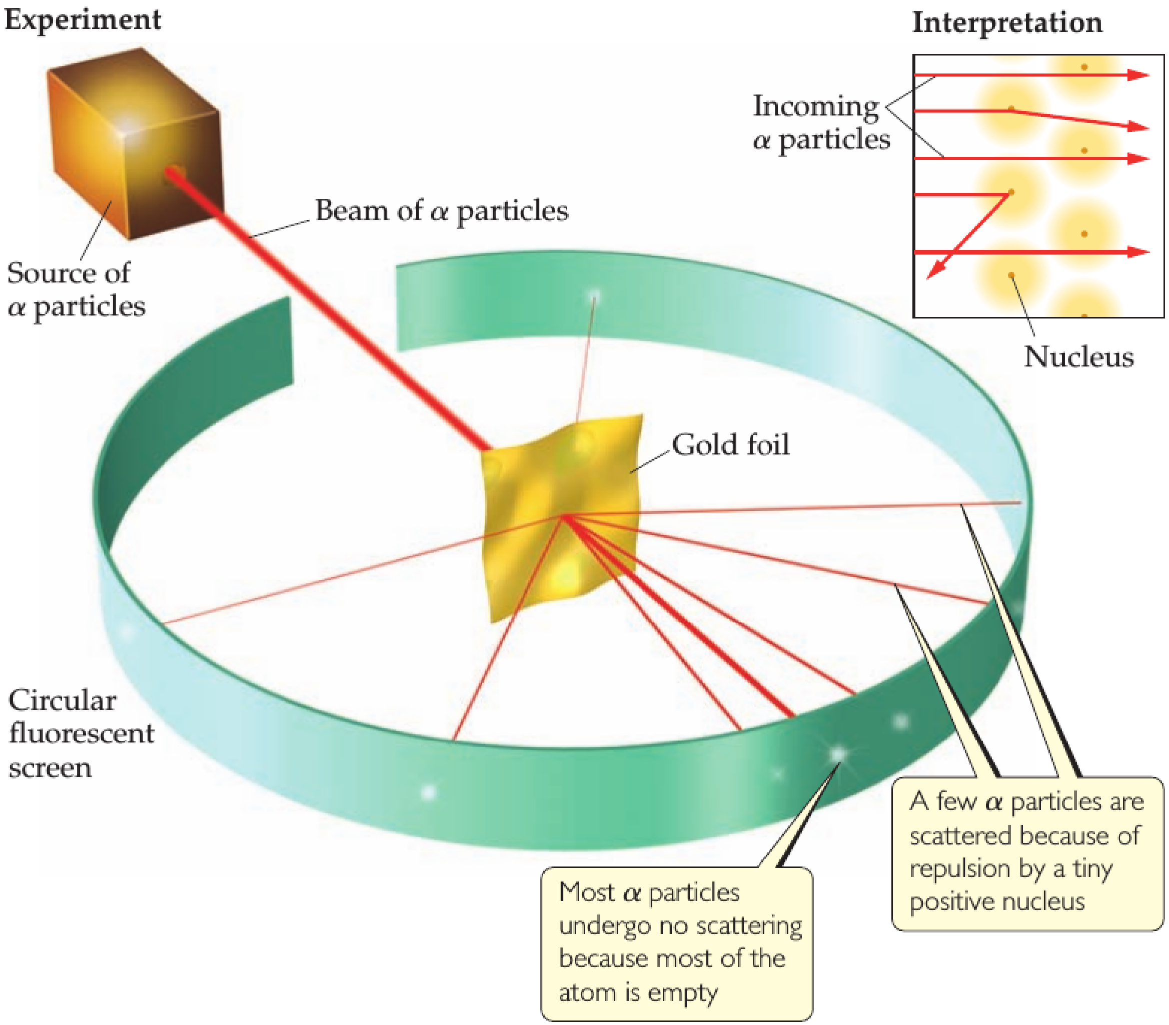
1909 → Robert Milikan → carga do e^- → -1.6 x 10^{-19} C

$$Massa\ do\ elétron = \frac{1.602\,x\,10^{-19}\,C}{1.76\,x\,10^{8}\,C/g} = 9.10\,x\,10^{-28}\,g$$


Hole in plate
Oil drops
(+)
Microscope view
Source of X rays
(–)
Electrically charged plates

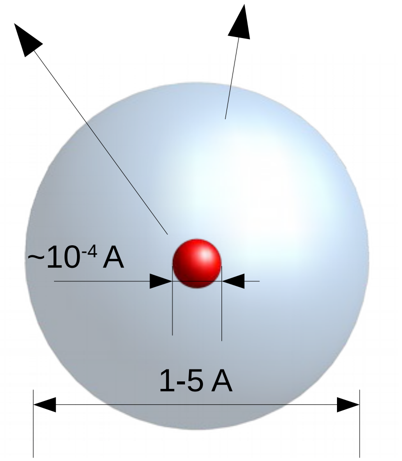
Modelo Nuclear do Átomo

1911 → Ernest Rutherford


Experiment
Interpretation
Source of α particles
Beam of α particles
Incoming α particles
Nucleus
Gold foil
Circular fluorescent screen

A few α particles are scattered because of repulsion by a tiny positive nucleus

Most α particles undergo no scattering because most of the atom is empty



Volume ocupado pelo Núcleo

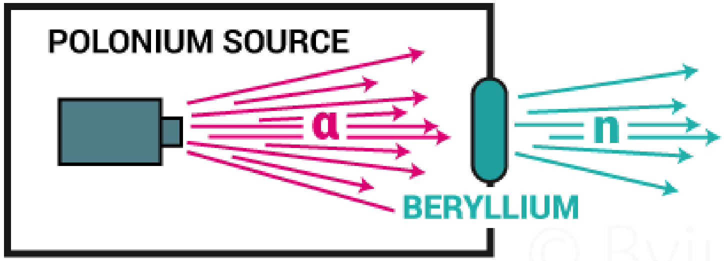
Volume ocupado pelos elétrons

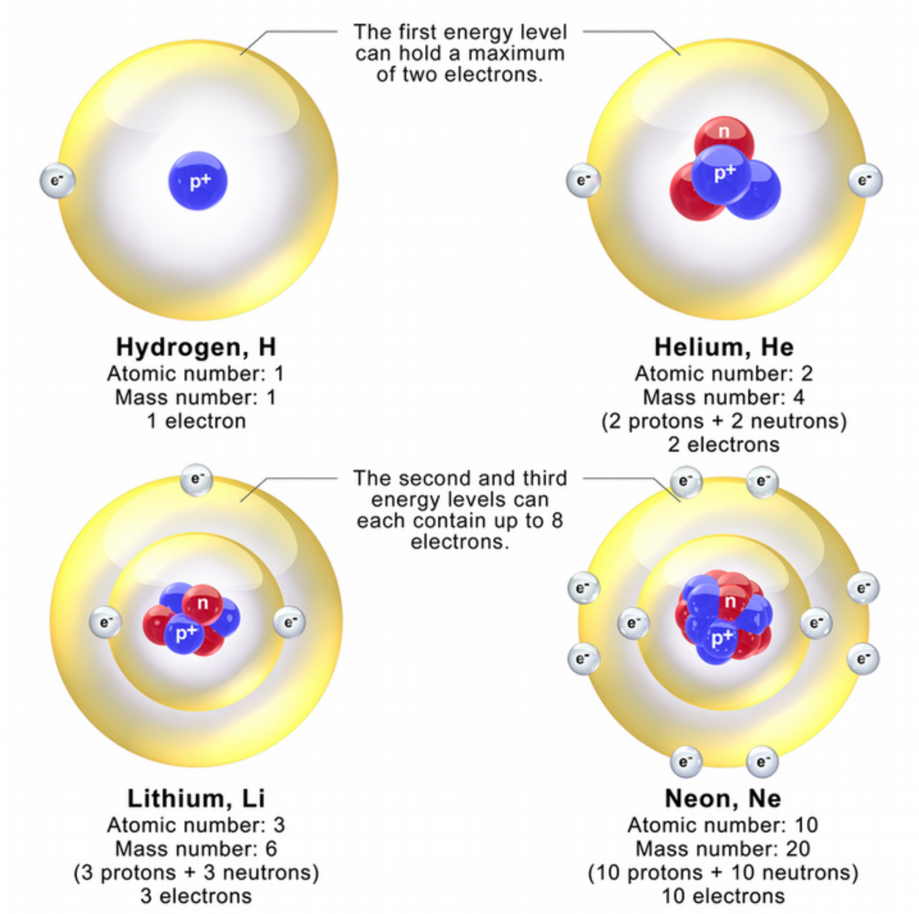
Partículas Subatômicas

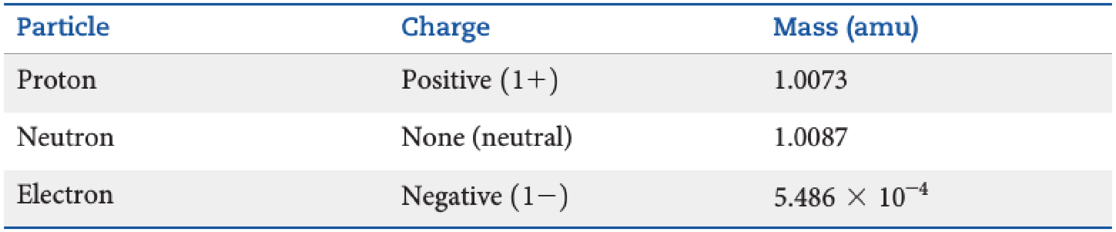
1919 → Enerst Rutherford → descoberta do próton

$$^{14}N + \alpha \rightarrow {}^{17}O + p$$

1923 → James Chadwick → decoberta do neutron


POLONIUM SOURCE
α
n
BERYLLIUM

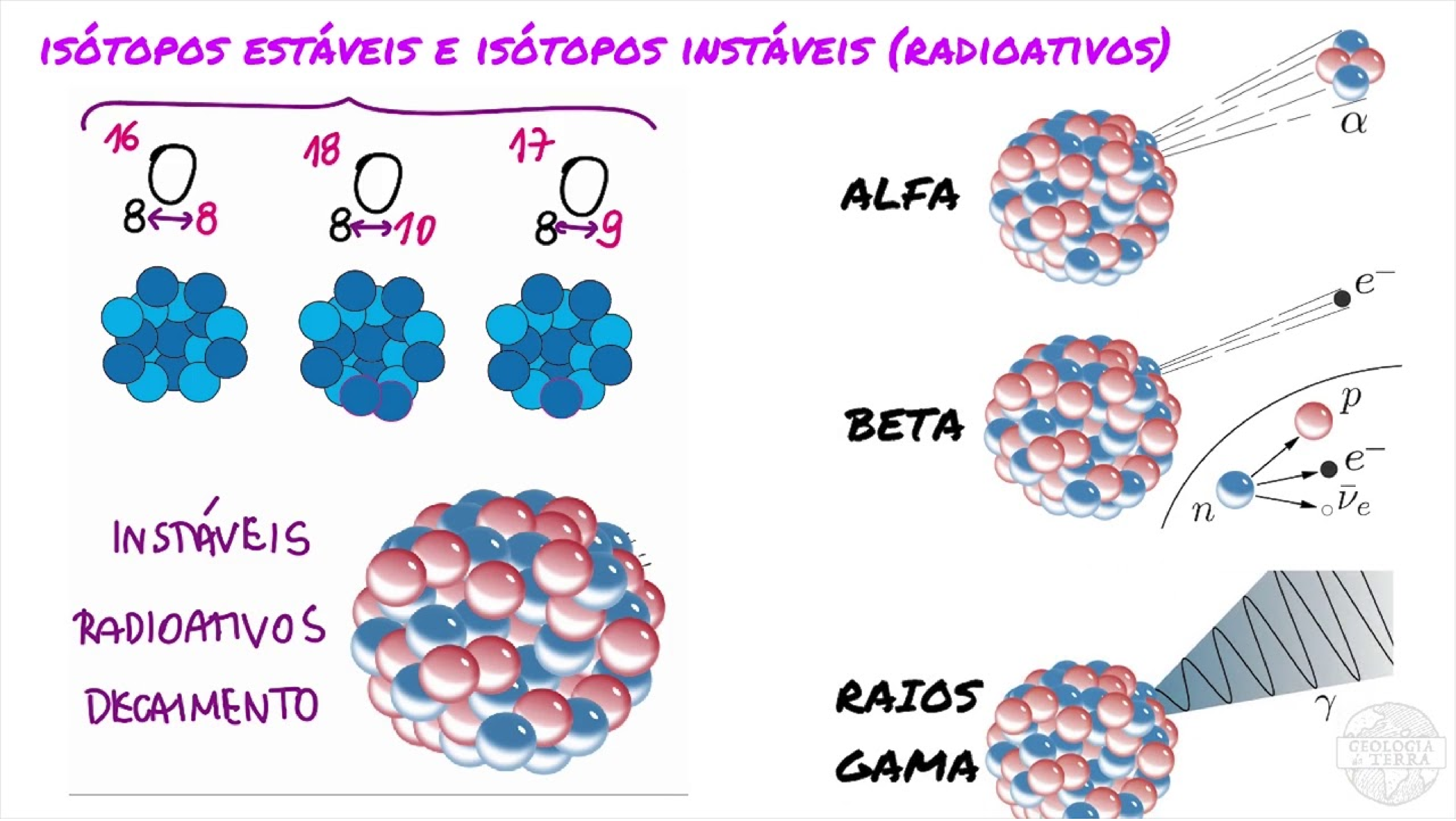

The first energy level can hold a maximum of two electrons.
p+
n
e-
Hydrogen, H
Atomic number: 1
Mass number: 1
1 electron
Helium, He
Atomic number: 2
Mass number: 4
(2 protons + 2 neutrons)
2 electrons
The second and third energy levels can each contain up to 8 electrons.
Lithium, Li
Atomic number: 3
Mass number: 6
(3 protons + 3 neutrons)
3 electrons
Neon, Ne
Atomic number: 10
Mass number: 20
(10 protons + 10 neutrons)
10 electrons



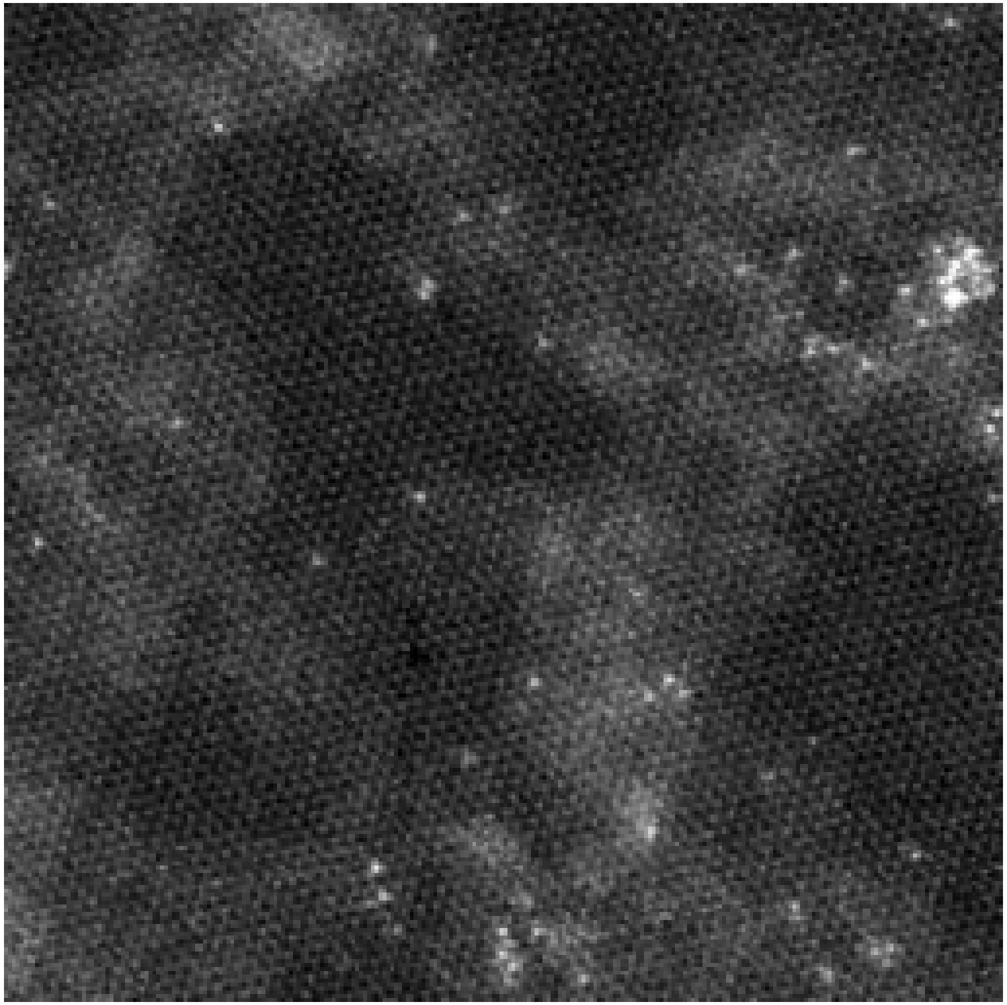
Particle	Charge	Mass (amu)
Proton	Positive (1+)	1.0073
Neutron	None (neutral)	1.0087
Electron	Negative (1−)	5.486×10^{-4}

→ Modelo próton-núcleo → Heisenber

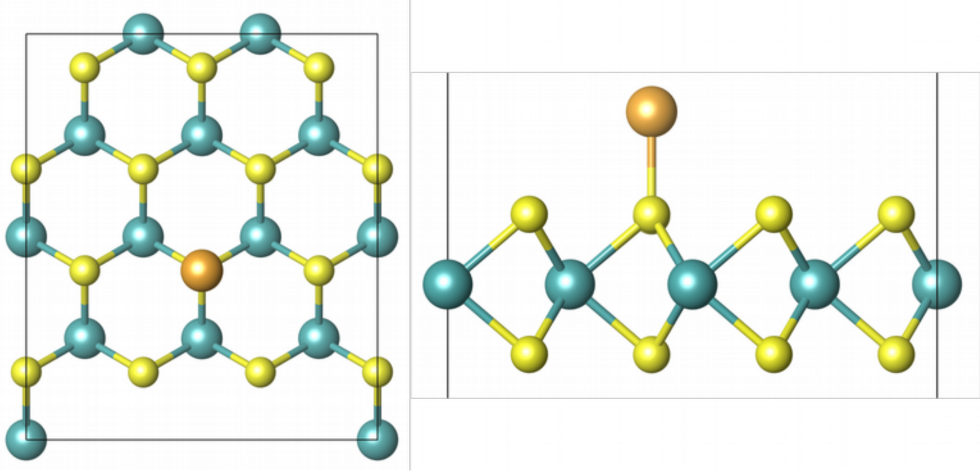
Isótopos


ISÓTOPOS ESTÁVEIS E ISÓTOPOS INSTÁVEIS (RADIOATIVOS)
16 O 8↔8
18 O 8↔10
17 O 8↔9
INSTÁVEIS
RADIOATIVOS
DECAIMENTO
ALFA
α
BETA
e−
p
e−
n
ν̄e
RAIOS GAMA
γ
GEOLOGIA da TERRA

Enxergando átomos!



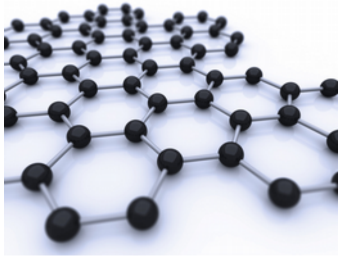
Microscopia Eletrônica de Alta Resolução!

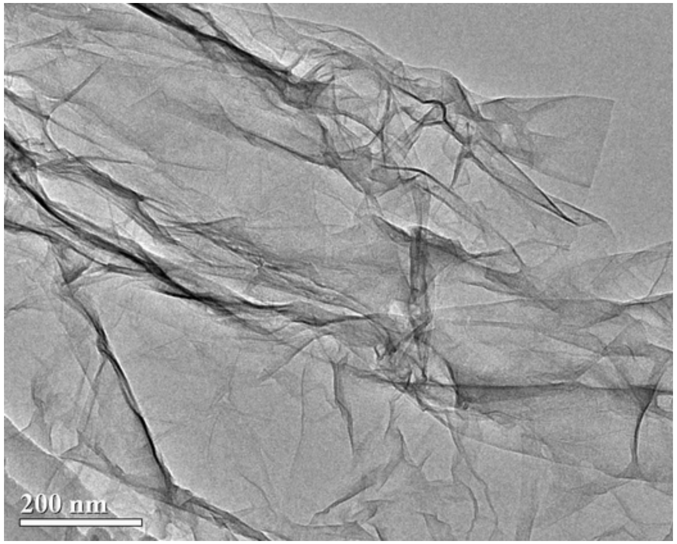


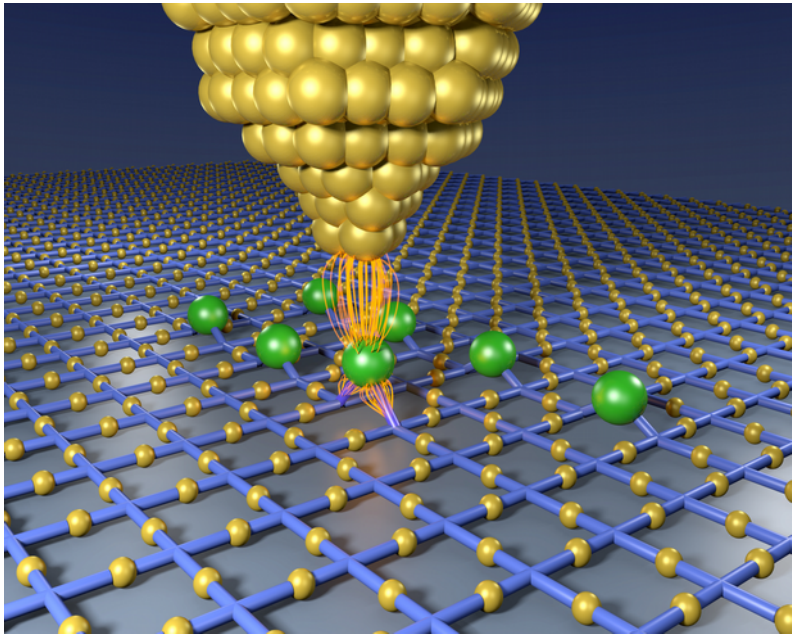
$MoS_2 + Au$

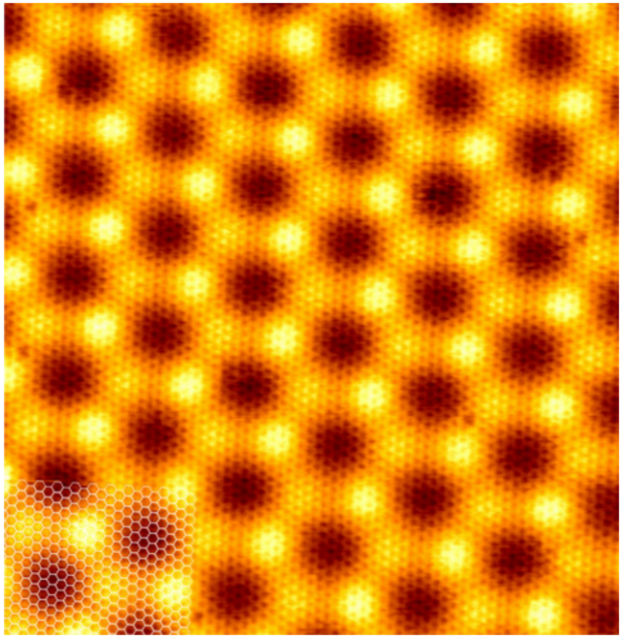
Enxergando átomos!

Grafeno





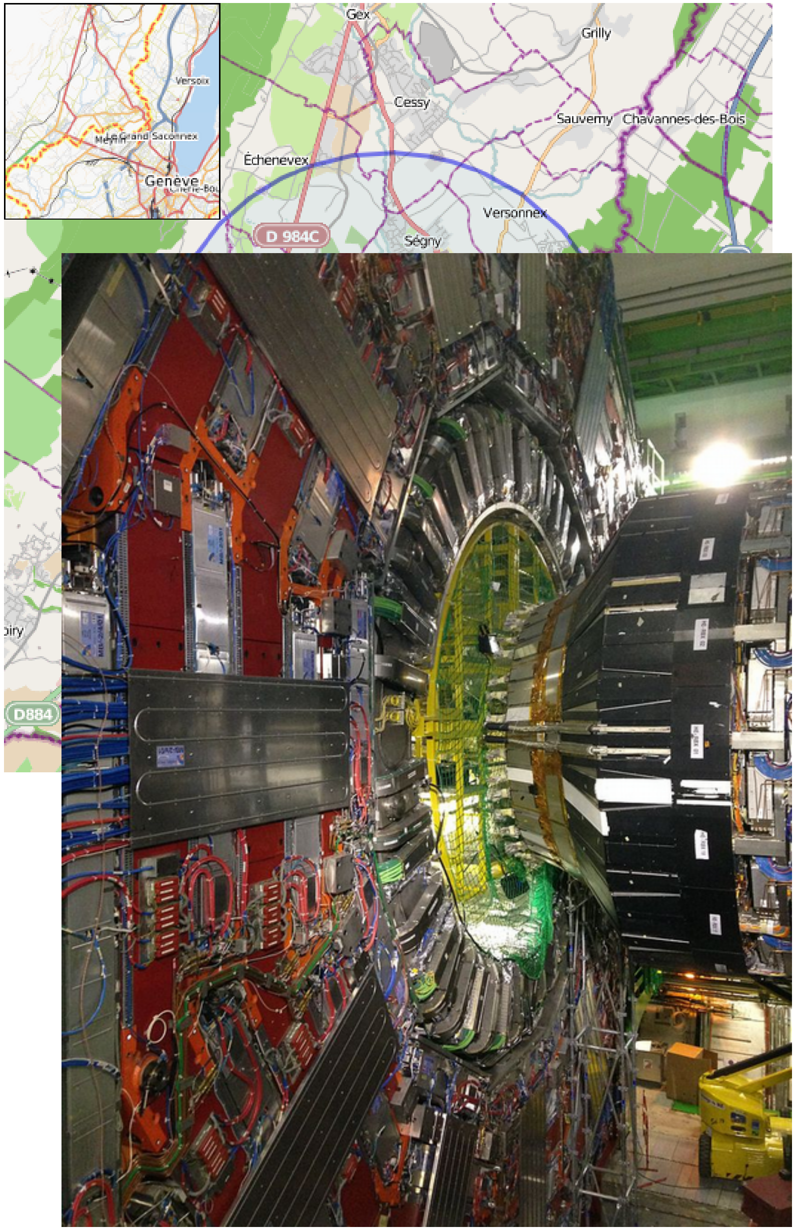


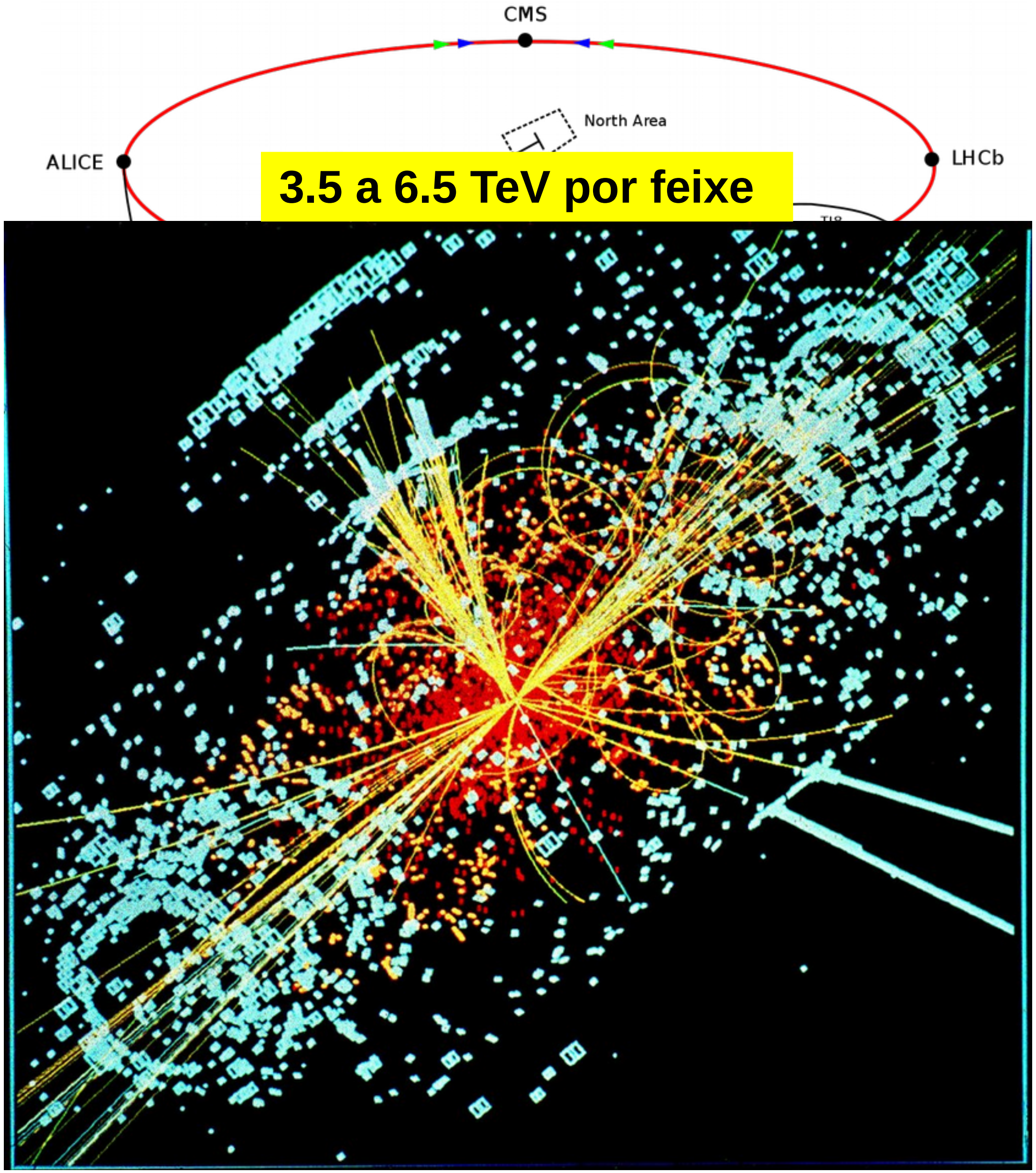


Microscopia de Força Atômica

Partículas Subatômicas

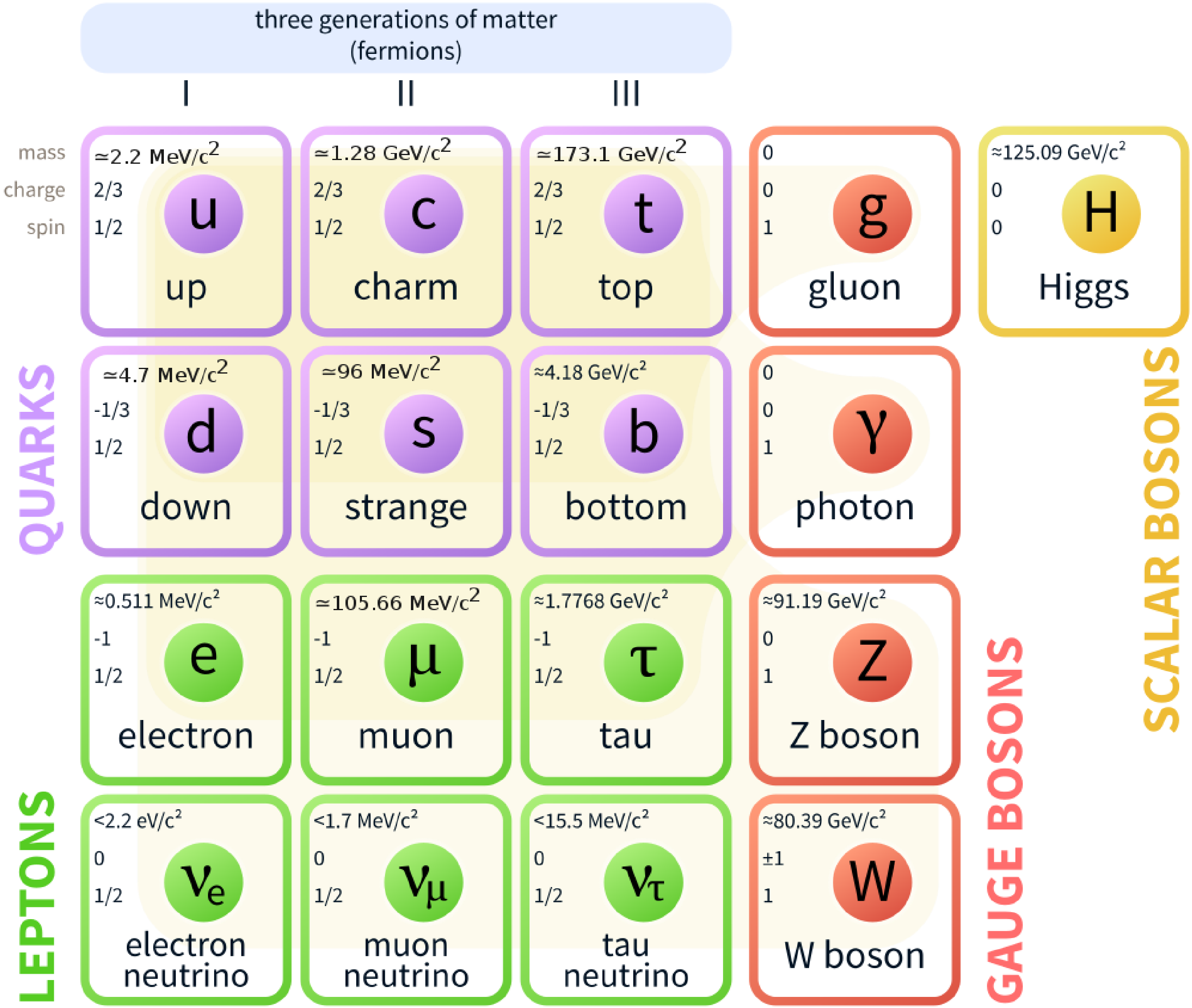
The Large Hadron Collider -CERN


Gex
Grilly
Cessy
Sauverny
Chavannes-des-Bois
Échenevex
Versonnex
Ségny
D 984C
D884
Versoix
Meyrin
Le Grand Saconnex
Genève


CMS
North Area
ALICE
LHCb
TI8

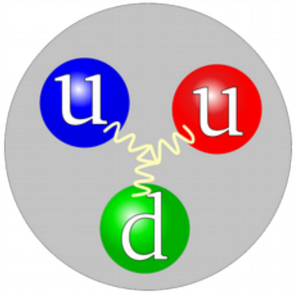
3.5 a 6.5 TeV por feixe

Standard Model of Elementary Particles

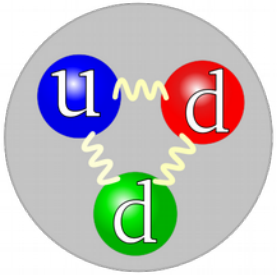


three generations of matter (fermions)

	I	II	III		
mass charge spin	≃2.2 MeV/c^2 2/3 1/2 u up	≃1.28 GeV/c^2 2/3 1/2 c charm	≃173.1 GeV/c^2 2/3 1/2 t top	0 0 1 g gluon	≃125.09 GeV/c^2 0 0 H Higgs
QUARKS	≃4.7 MeV/c^2 -1/3 1/2 d down	≃96 MeV/c^2 -1/3 1/2 s strange	≃4.18 GeV/c^2 -1/3 1/2 b bottom	0 0 1 γ photon	SCALAR BOSONS
	≃0.511 MeV/c^2 -1 1/2 e electron	≃105.66 MeV/c^2 -1 1/2 μ muon	≃1.7768 GeV/c^2 -1 1/2 τ tau	≃91.19 GeV/c^2 0 1 Z Z boson	
LEPTONS	<2.2 eV/c^2 0 1/2 ν_e electron neutrino	<1.7 MeV/c^2 0 1/2 ν_μ muon neutrino	<15.5 MeV/c^2 0 1/2 ν_τ tau neutrino	≃80.39 GeV/c^2 ±1 1 W W boson	
				GAUGE BOSONS	



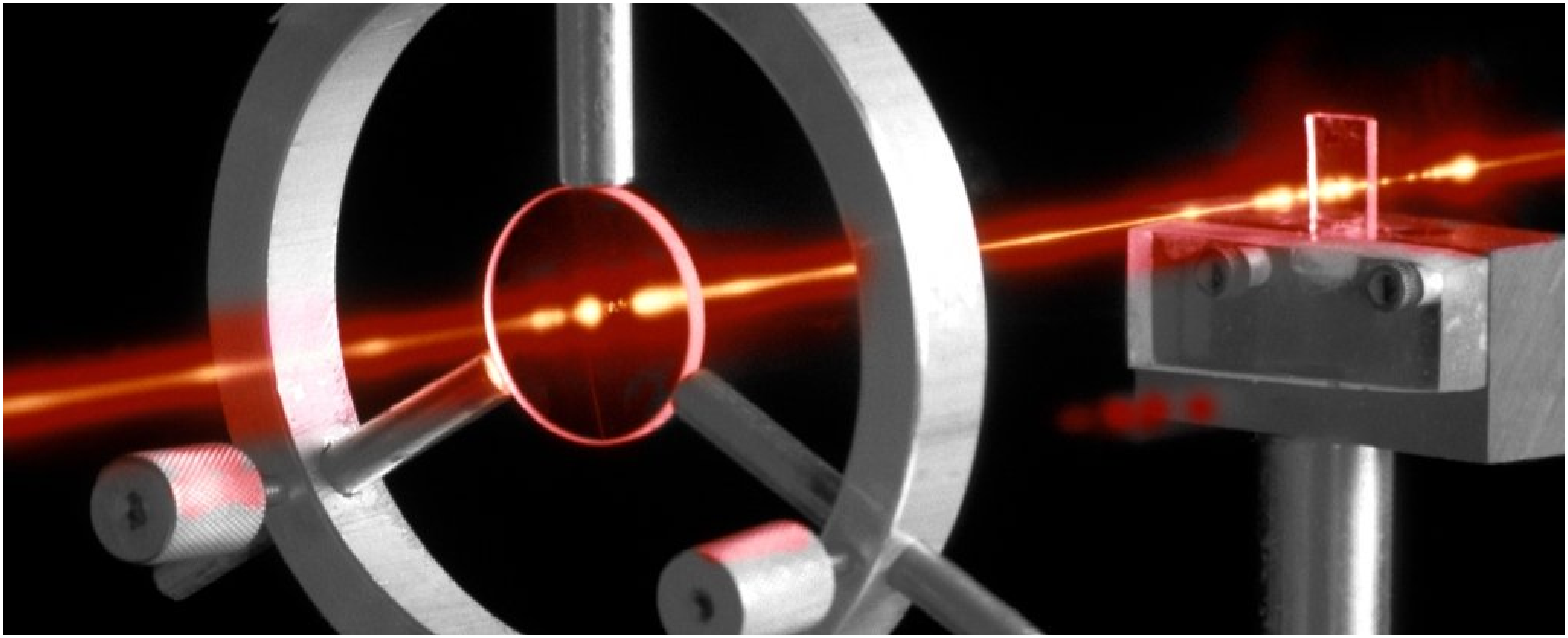
Próton



Neutron

Espectroscopia

Estuda a interação da luz com a matéria

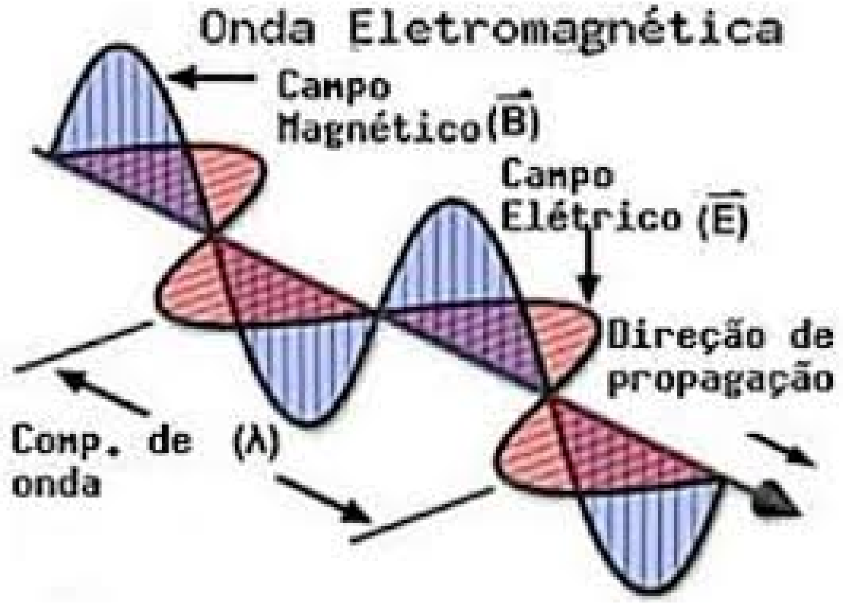


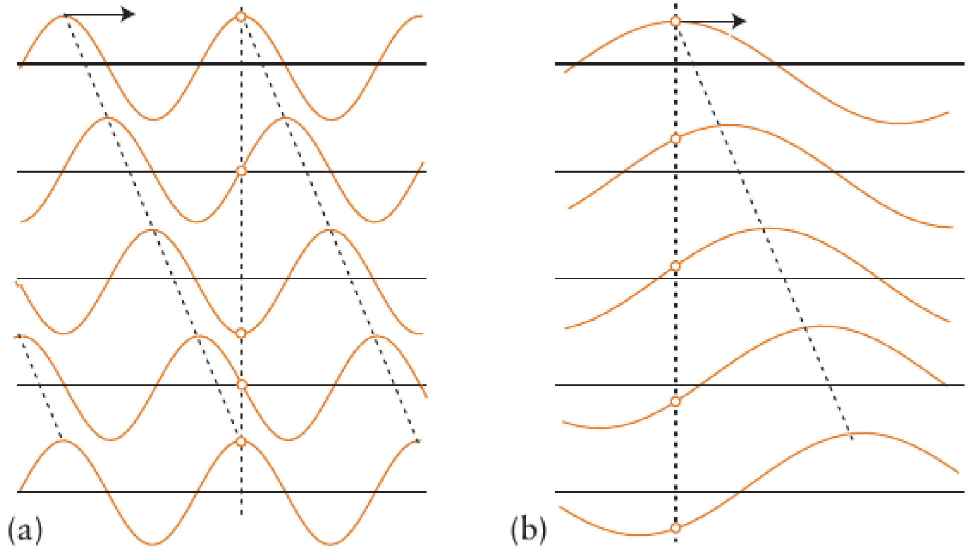
Luz

1672 → Isaac Newton desenvolve a óptica geométrica → luz vista como partícula

1678 → Christian Huygens → Explica a refração da luz → teoria ondulatória da luz

Séc. XIX → T. Young, A. Fresnel, Maxwell → luz como ondas eletromagnéticas

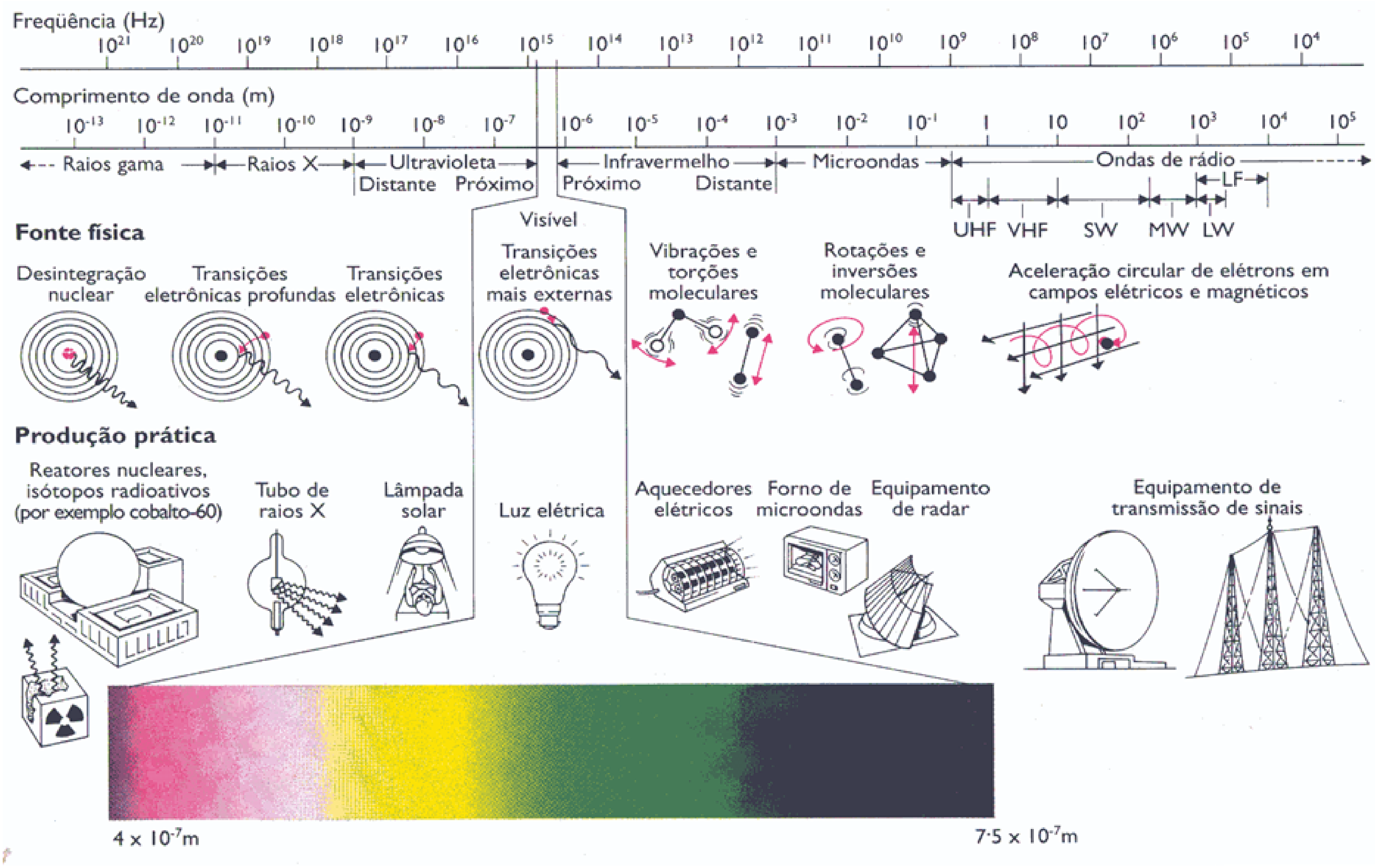

Onda Eletromagnética
Campo Magnético ($\vec{B}$)
Campo Elétrico ($\vec{E}$)
Direção de propagação
Comp. de onda
(λ)



Oscilação de um elétron sob influencia da luz

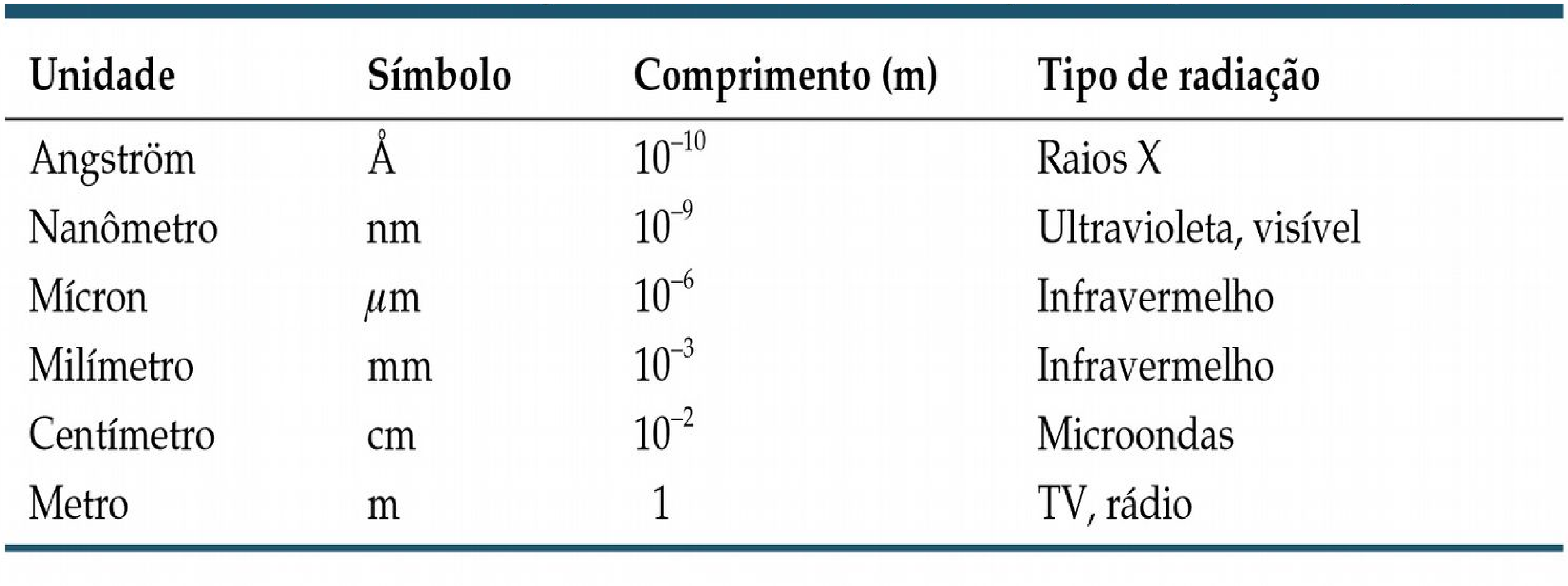
$$\lambda \, . \, \nu = c$$

Espectro Eletromagnético


Freqüência (Hz)
10^{21} 10^{20} 10^{19} 10^{18} 10^{17} 10^{16} 10^{15} 10^{14} 10^{13} 10^{12} 10^{11} 10^{10} 10^{9} 10^{8} 10^{7} 10^{6} 10^{5} 10^{4}
Comprimento de onda (m)
10^{-13} 10^{-12} 10^{-11} 10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1 10 10^{2} 10^{3} 10^{4} 10^{5}
Raios gama
Raios X
Ultravioleta
Distante
Próximo
Infravermelho
Próximo
Distante
Microondas
Ondas de rádio
LF
UHF
VHF
SW
MW
LW
Visível
Fonte física
Desintegração nuclear
Transições eletrônicas profundas
Transições eletrônicas
Transições eletrônicas mais externas
Vibrações e torções moleculares
Rotações e inversões moleculares
Aceleração circular de elétrons em campos elétricos e magnéticos
Produção prática
Reatores nucleares, isótopos radioativos (por exemplo cobalto-60)
Tubo de raios X
Lâmpada solar
Luz elétrica
Aquecedores elétricos
Forno de microondas
Equipamento de radar
Equipamento de transmissão de sinais
4×10^{-7}m
$7{\cdot}5 \times 10^{-7}$m

Espectro Eletromagnético

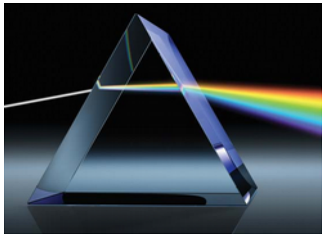
Tabela 3 – Unidades de comprimentos de nos comuns para radiações eletromagnéticas



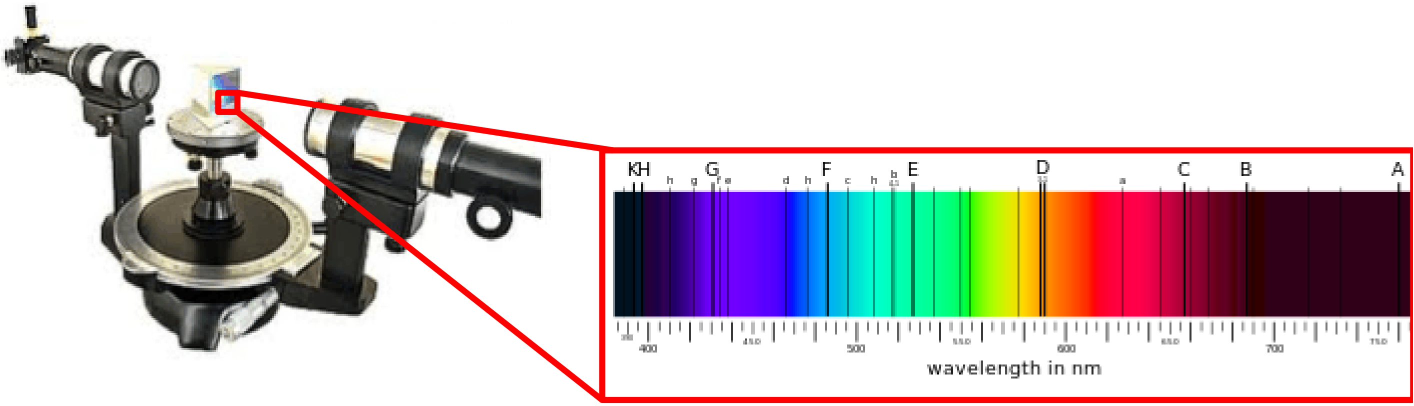
Unidade	Símbolo	Comprimento (m)	Tipo de radiação
Angström	Å	10^{-10}	Raios X
Nanômetro	nm	10^{-9}	Ultravioleta, visível
Mícron	μm	10^{-6}	Infravermelho
Milímetro	mm	10^{-3}	Infravermelho
Centímetro	cm	10^{-2}	Microondas
Metro	m	1	TV, rádio

Espectros Atômicos

1672 → Dispersão da luz branca →

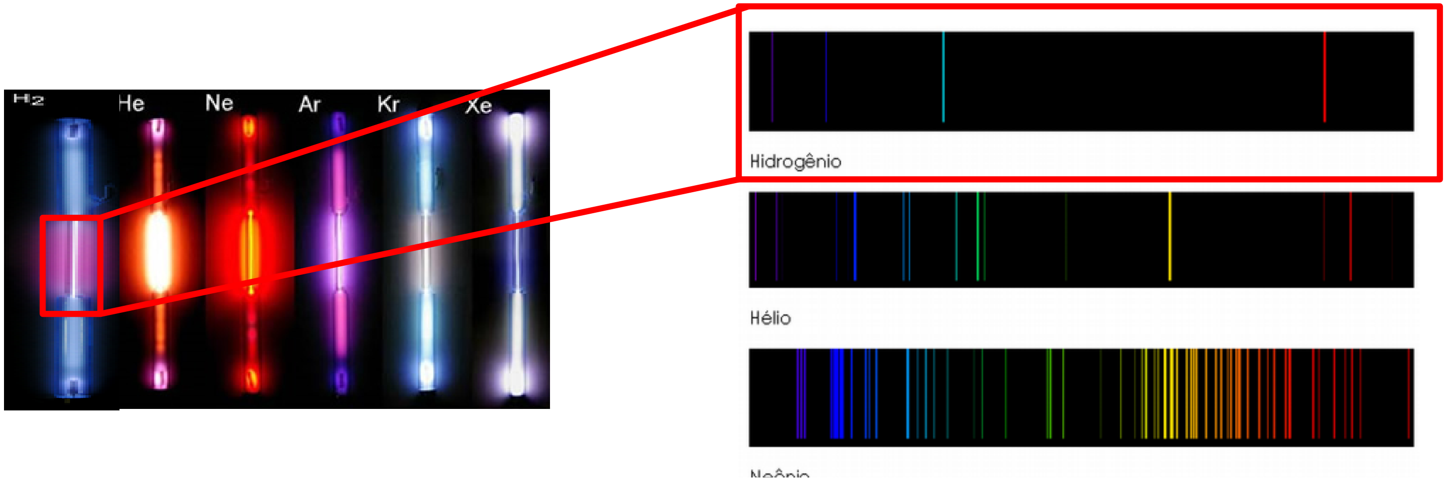


1814 → Fraunhofer →


KH
G
F
E
D
C
B
A
400
450
500
550
600
650
700
750
wavelength in nm

Linhas de Fraunhofer

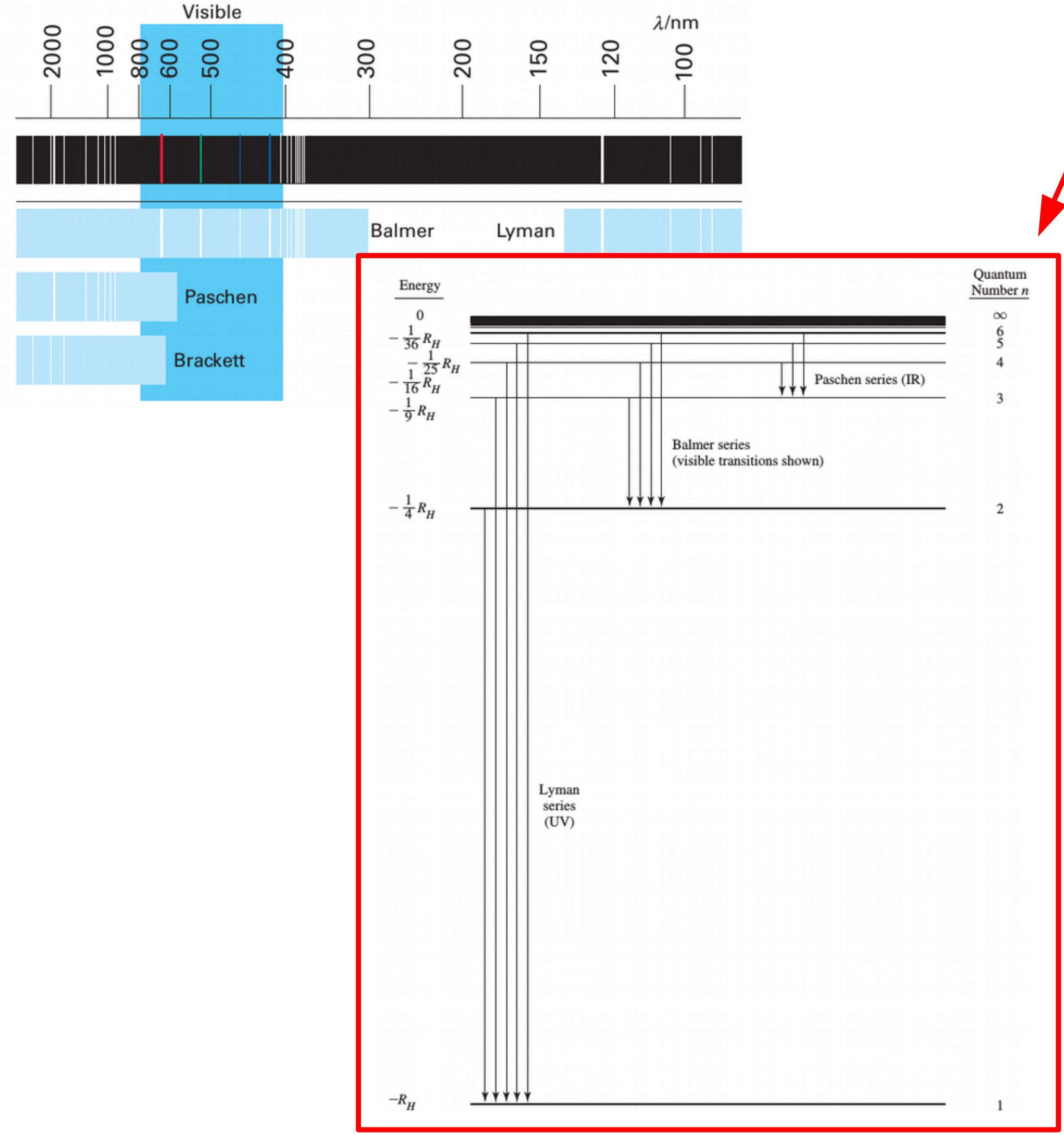
1859 → Kirchhoff e Bunsen → correspondência entre as linhas de Fraunhofer e a emissão de elementos quando aquecidos


H2
He
Ne
Ar
Kr
Xe
Hidrogênio
Hélio
Neônio

Característico de cada elemento

Espectros Atômicos

Espectro do Hidrogênio


Visible
λ/nm
2000
1000
800
600
500
400
300
200
150
120
100
Balmer
Lyman
Paschen
Brackett
Energy
0
$-\frac{1}{36}R_H$
$-\frac{1}{25}R_H$
$-\frac{1}{16}R_H$
$-\frac{1}{9}R_H$
$-\frac{1}{4}R_H$
$-R_H$
Quantum Number n
∞
6
5
4
3
2
1
Paschen series (IR)
Balmer series (visible transitions shown)
Lyman series (UV)

$$E = \boxed{R}\left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right)$$

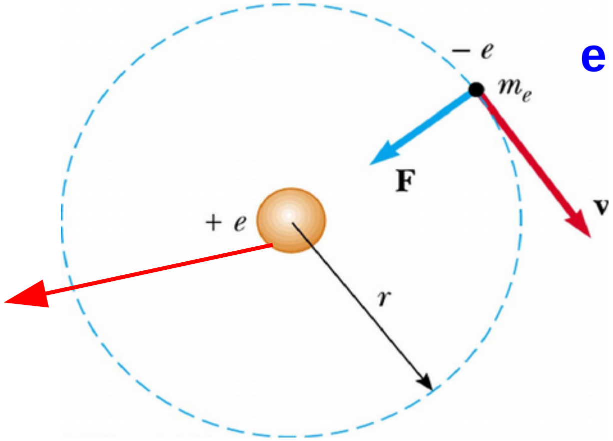
Constante de Rydberg

$$R = \frac{2\pi^2\mu Z^2 e^4}{(4\pi\varepsilon_0)^2 h^2}$$

Primeira aparição do conceito de quantização de energia

O átomo de H

H → 1 próton + 1 elétron



e → orbitas circulares

Núcleo Fixo

$$F = \frac{e^2}{4\pi\epsilon_0 r^2}$$

Força de Coulomb

$$F_{centrifuga} = \frac{m_e v^2}{r}$$

Elétron está sendo acelerado → emissão de radiação

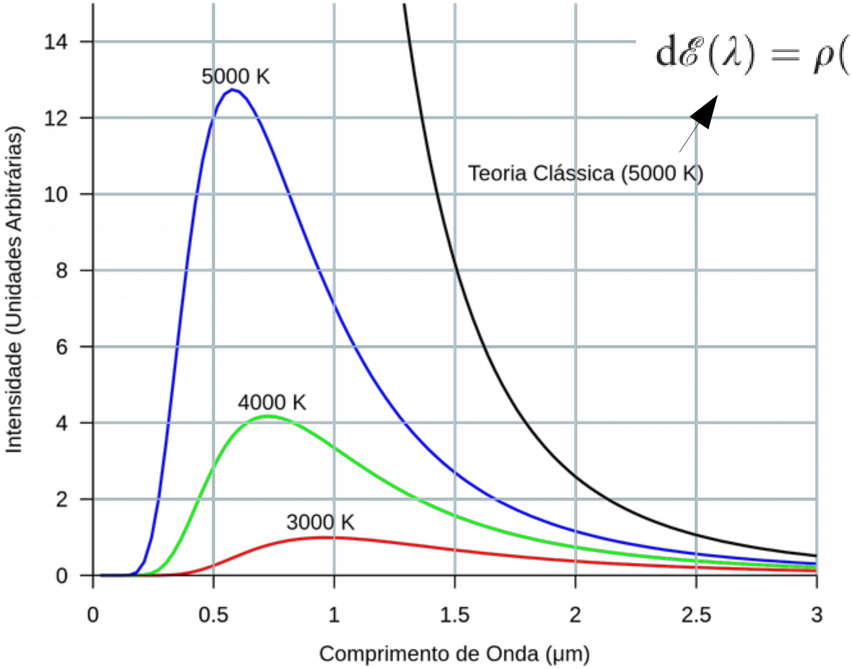
Orbital em espira em direção o núcleo → colisão elétron-núcleo

Física Claśica → não explica a estrutura do átomo e o perfil dos espctros de emissão

Princípios de Mecânica Quântica

Explica a estrutura da matéria e suas interações com o meio

Radiação do corpo negro → Radiação emitida por um corpo aquecido



$$d\mathscr{E}(\lambda) = \rho(\lambda)\,d\lambda \qquad \rho(\lambda) = \frac{8\pi kT}{\lambda^4}$$

1900 → Max Plank
Radiação emitida → oscilações dos eletrons do material **→ assumem energias discretas**

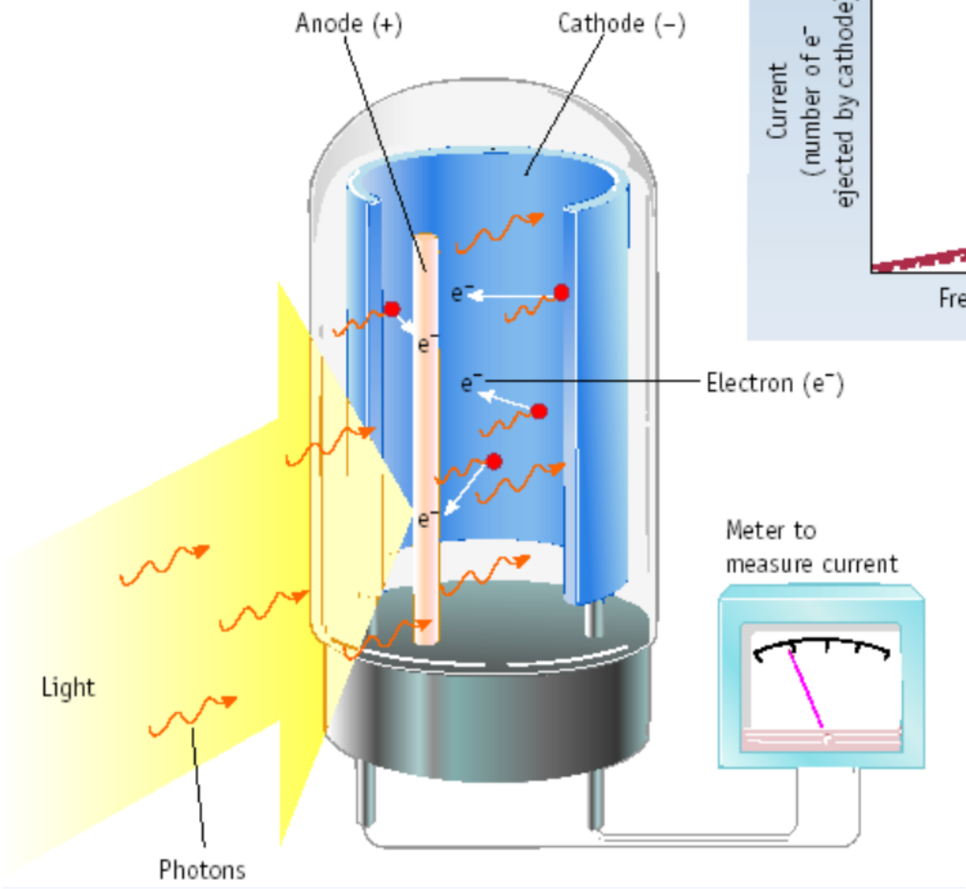
E = nhν

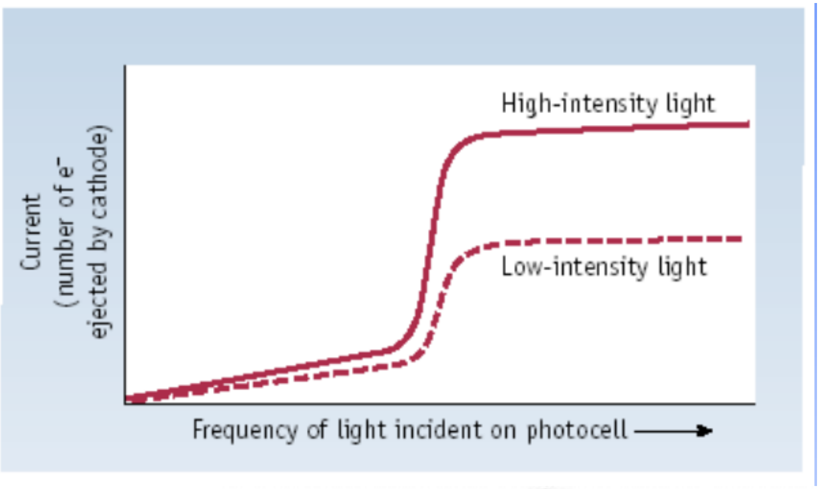
Energia do Oscilador
Frequência

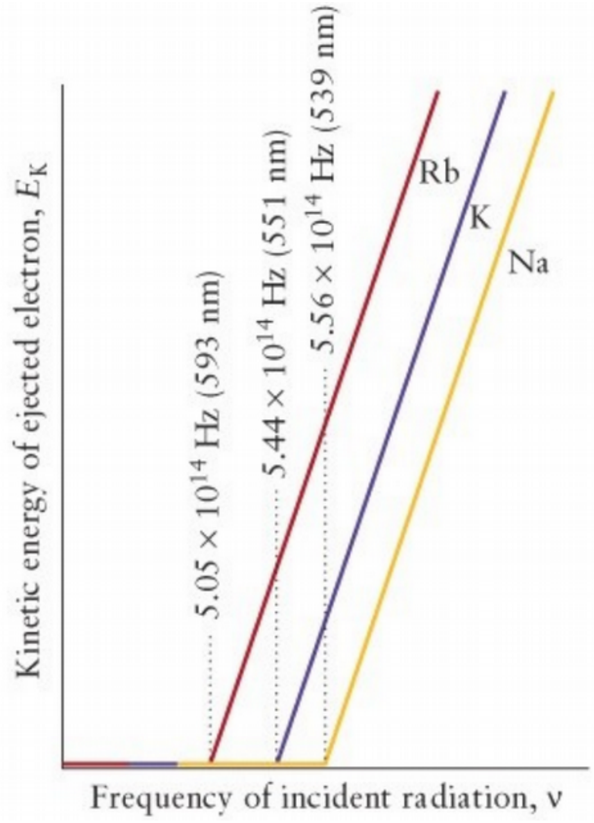
$$\rho(\lambda) = \frac{8\pi hc}{\lambda^5}\,\frac{e^{-hc/\lambda kT}}{1 - e^{-hc/\lambda kT}}$$

Princípios de Mecânica Quântica

1905 → A. Einsten → Efeito Fotoelétrico


Anode (+)
Cathode (–)
e⁻
e⁻
e⁻
e⁻
Electron (e⁻)
Meter to
measure current
Light
Photons

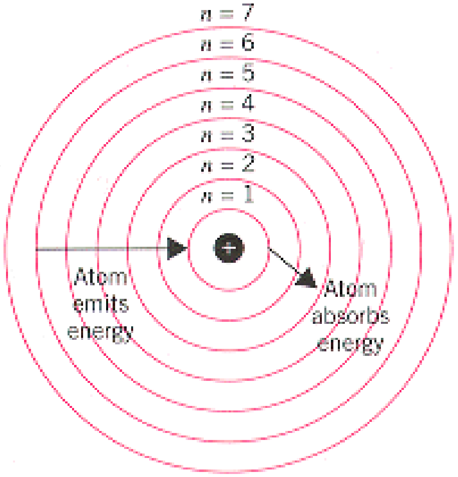




Teoria de Bohr para o átomo de H

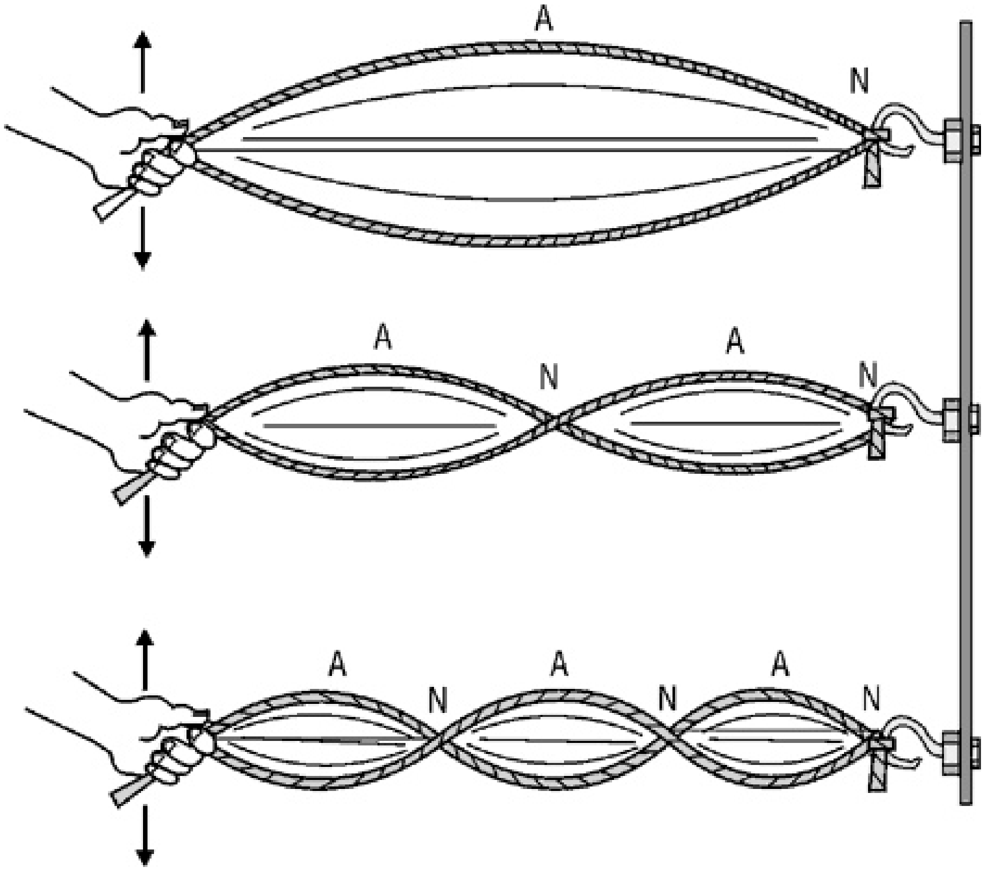
1911 → Niels Bohr

- O eletron apresenta uma orbita estacionária



$n = 7$
$n = 6$
$n = 5$
$n = 4$
$n = 3$
$n = 2$
$n = 1$
Atom emits energy
Atom absorbs energy

- Elétrons se comportam como ondas estacionárias

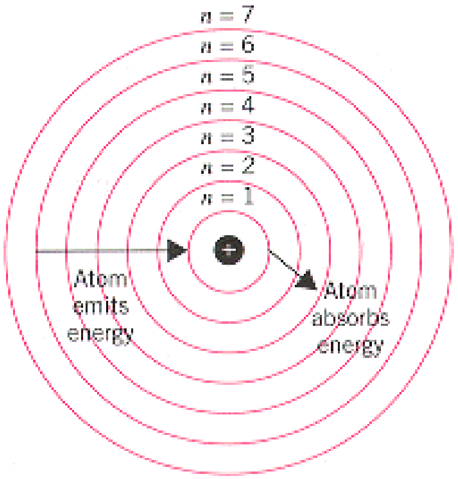


A
N
A
N
A
N
A
N
A
N
A
N

Teoria de Bohr para o átomo de H

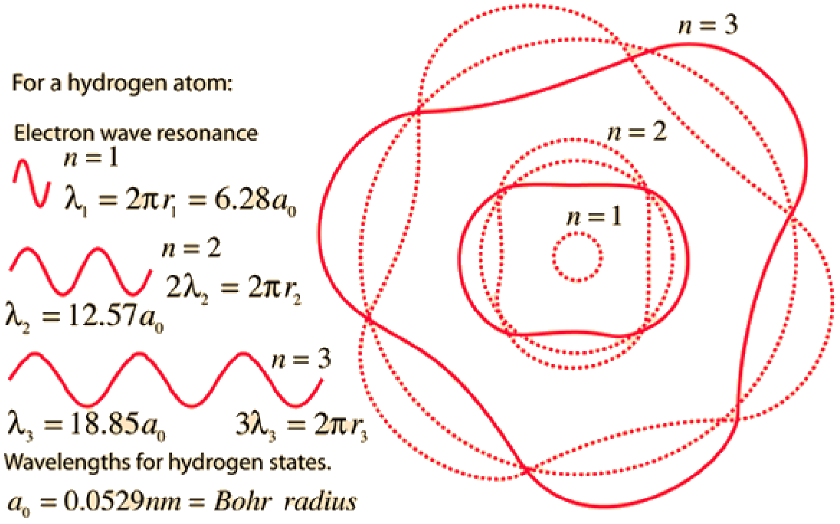
1911 → Niels Bohr

- O eletron apresenta uma orbita estacionária


n = 7
n = 6
n = 5
n = 4
n = 3
n = 2
n = 1
Atom emits energy
Atom absorbs energy

- Elétrons se comportam como ondas estacionárias

$$2\pi r = n\lambda$$


For a hydrogen atom:
Electron wave resonance
n = 1
λ₁ = 2πr₁ = 6.28a₀
n = 2
2λ₂ = 2πr₂
λ₂ = 12.57a₀
n = 3
λ₃ = 18.85a₀
3λ₃ = 2πr₃
Wavelengths for hydrogen states.
a₀ = 0.0529nm = Bohr radius
n = 3
n = 2
n = 1

Dualidade Onda x Partícula

Relação de de Broglie

1923 – 1923 → L. de Broglie: Partículas também apresentam propriedades ondulatórias

onda

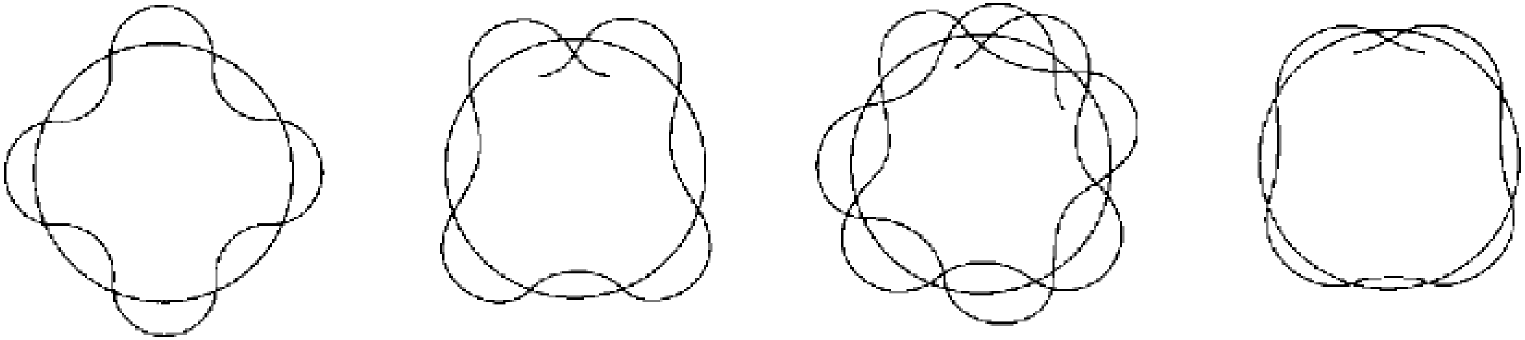
$$\lambda = \frac{h}{p}$$

partícula

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

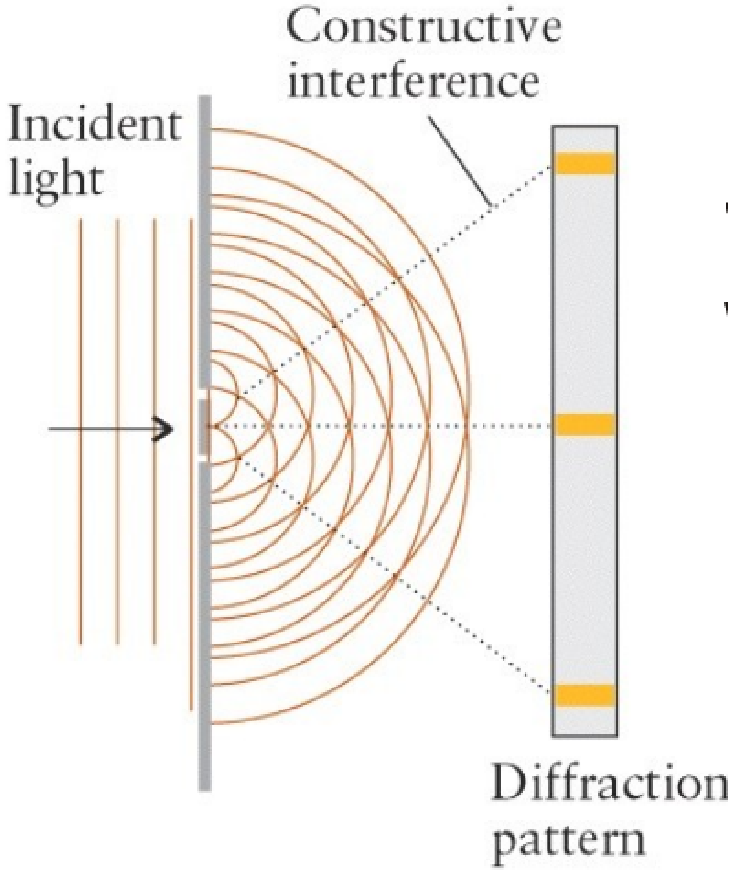
de Broglie : $\nu \longrightarrow E$

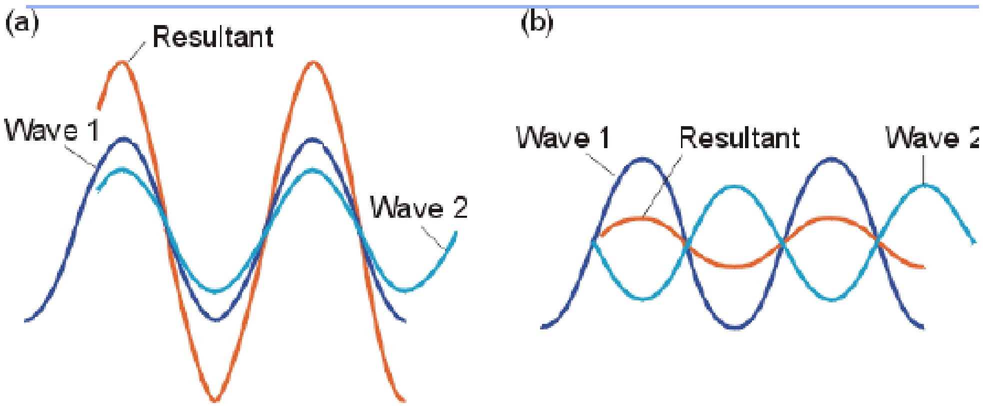
: $\lambda \longrightarrow p$

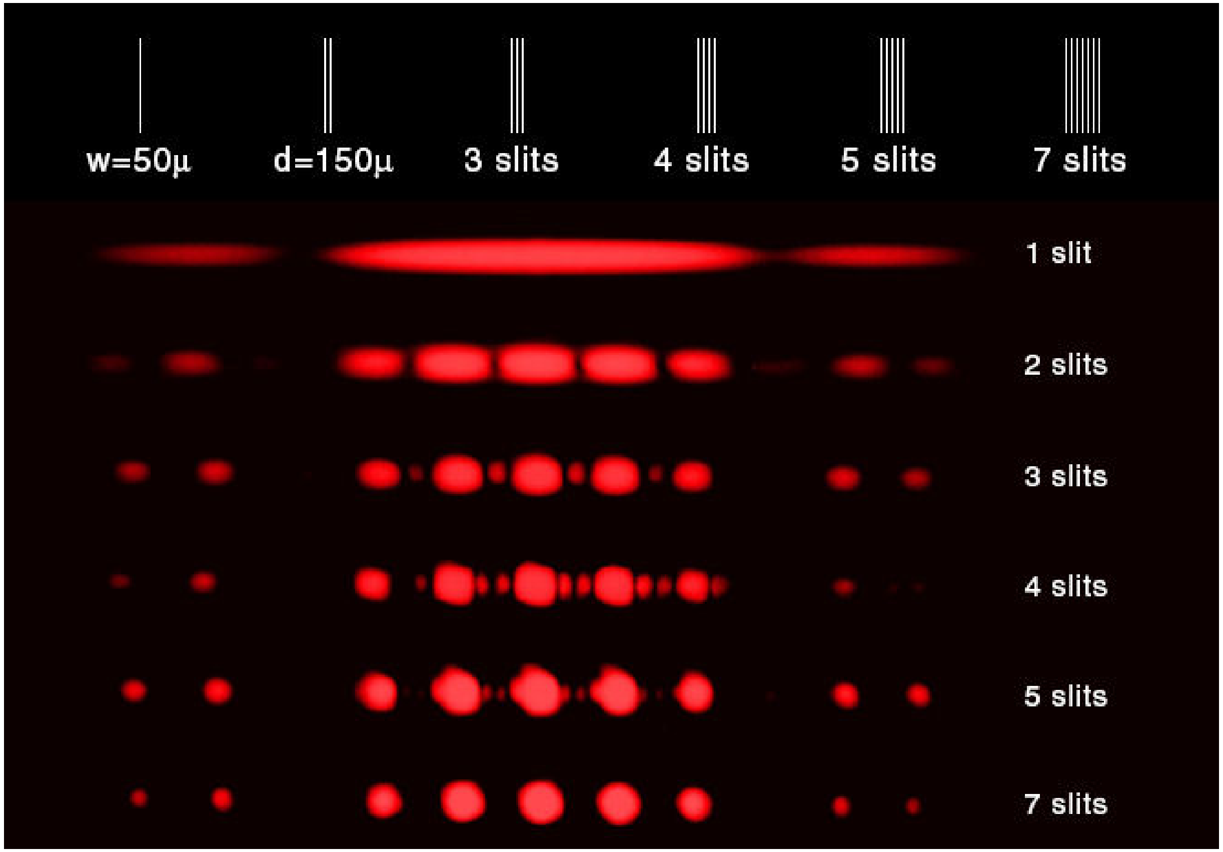


Dualidade Onda x Partícula

Difração da luz

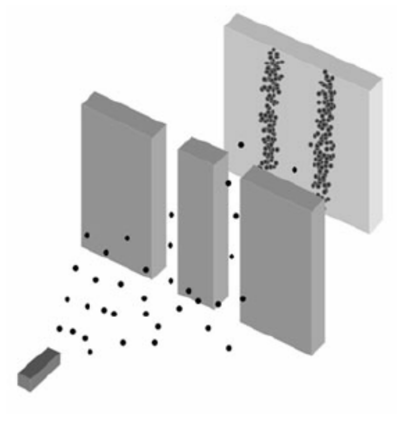

Constructive interference
Incident light
Diffraction pattern

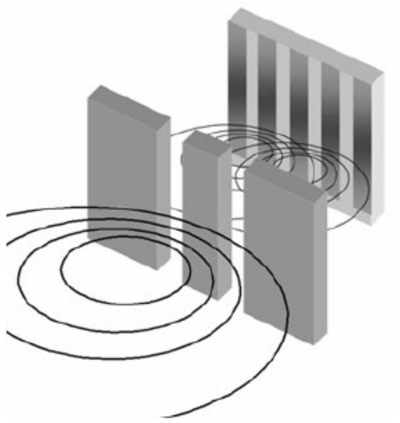

(a)
Resultant
Wave 1
Wave 2
(b)
Wave 1
Resultant
Wave 2

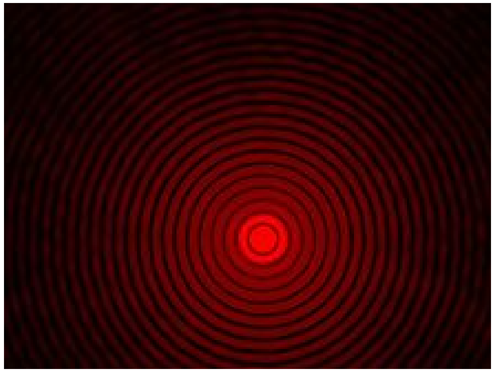

w=50μ
d=150μ
3 slits
4 slits
5 slits
7 slits
1 slit
2 slits
3 slits
4 slits
5 slits
7 slits

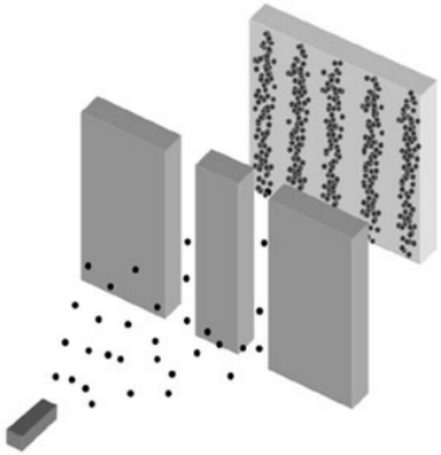
Dualidade Onda x Partícula

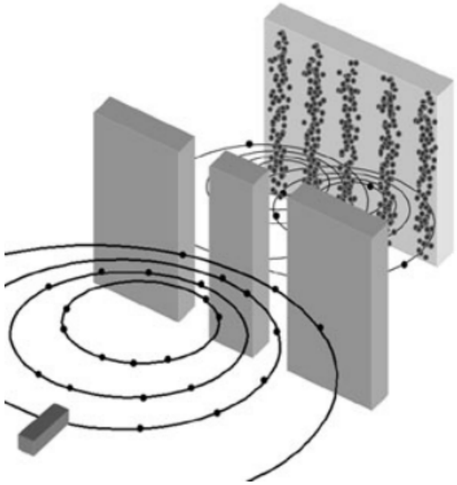
Experimento de Dupla Fenda

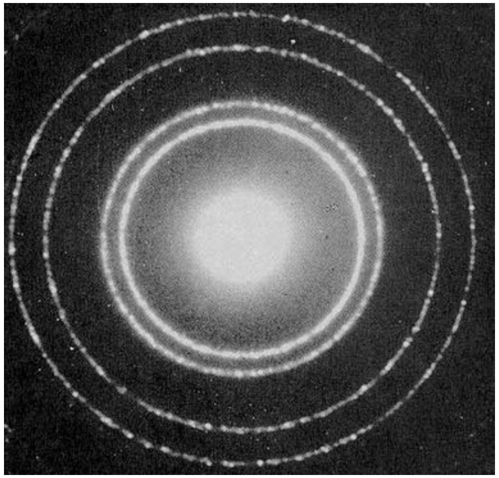

Partículas


Onda

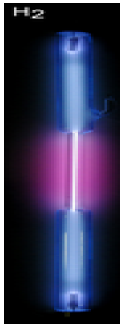


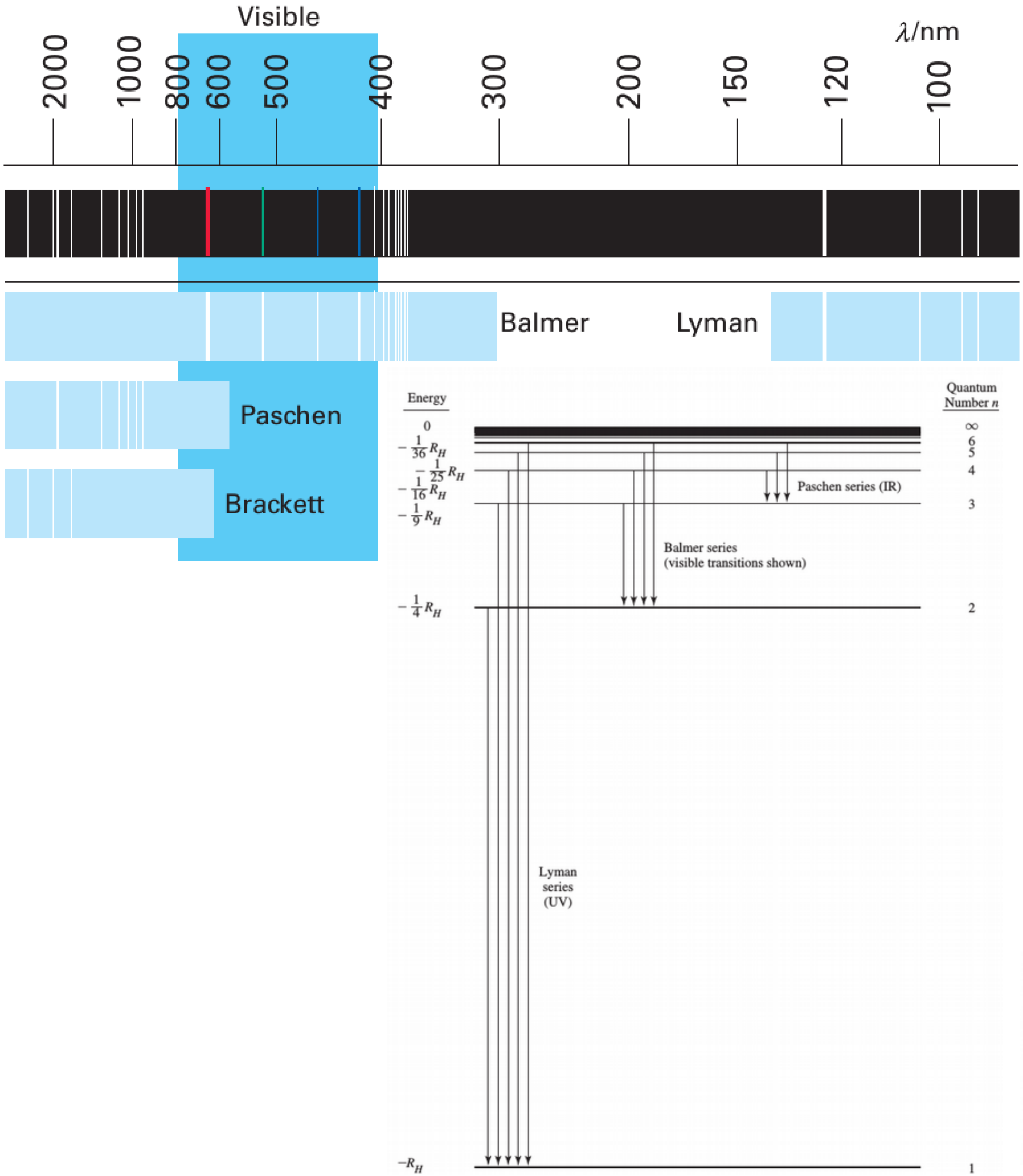

Elétrons


Onda de Elétrons



Teoria de Bohr para o átomo de H




Visible
λ/nm
2000
1000
800
600
500
400
300
200
150
120
100
Balmer
Lyman
Paschen
Brackett
Energy
0
−1/36 R_H
−1/25 R_H
−1/16 R_H
−1/9 R_H
−1/4 R_H
−R_H
Quantum Number n
∞
6
5
4
3
2
1
Paschen series (IR)
Balmer series (visible transitions shown)
Lyman series (UV)

$$\tilde{\nu} = \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) R_\mathrm{H}$$

$n_1 = 1, n_2 = 2, 3, \ldots$	Lyman series, ultraviolet
$n_1 = 2, n_2 = 3, 4, \ldots$	Balmer series, visible
$n_1 = 3, n_2 = 4, 5, \ldots$	Paschen series, infrared
$n_1 = 4, n_2 = 5, 6, \ldots$	Brackett series, far infrared
$n_1 = 5, n_2 = 6, 7, \ldots$	Pfund series, far infrared
$n_1 = 6, n_2 = 7, 8, \ldots$	Humphreys series, far infrared

Teoria de Bohr para o átomo de H

Por exemplo: se o elétron move-se de n_i = 3 para n_f = 1, temos:

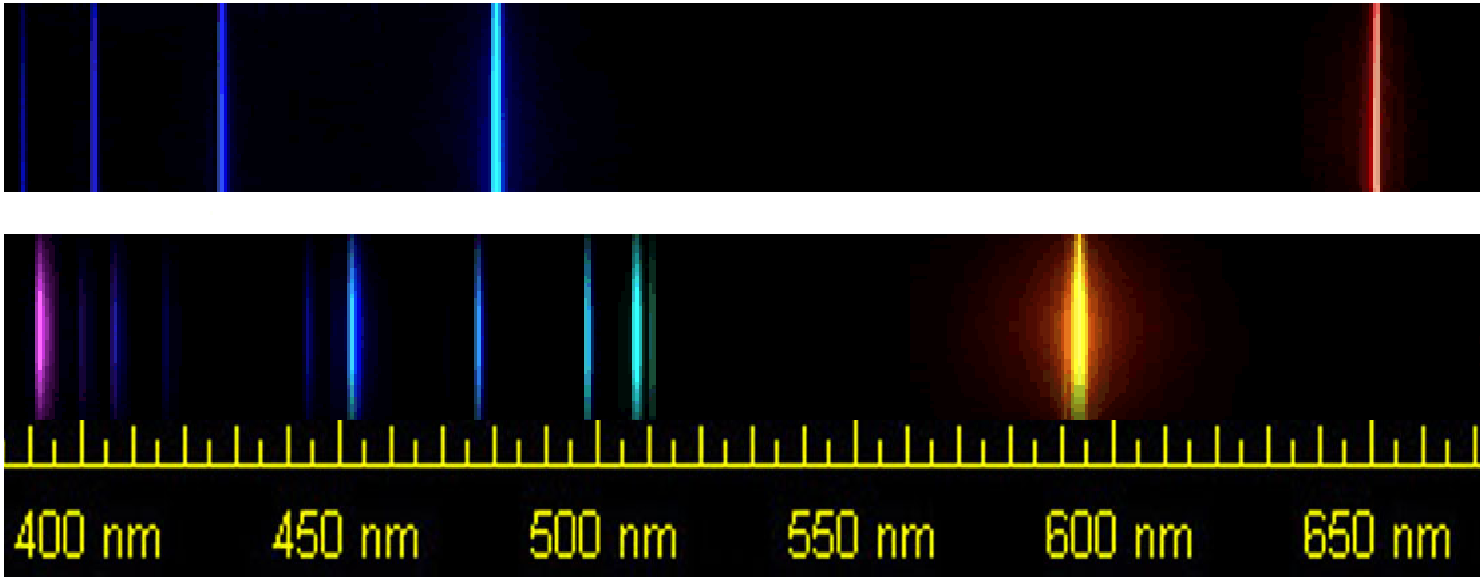
$$\Delta E = (\text{- }2{,}18 \text{ x } 10^{-18} \text{ J})\left(\frac{1}{1^2} - \frac{1}{3^2}\right) = (\text{- }2{,}18 \text{ x } 10^{-18} \text{ J})\left(\frac{8}{9}\right) = \text{ - }1{,}94 \text{ x } 10^{-18} \text{ J}$$

Sabendo a energia para o fóton emitido, podemos calcular sua freqüência ou seu comprimento de onda. Para o comprimento de onda, temos:

$$\lambda = \frac{c}{\nu} = \frac{hc}{\Delta E} = \frac{(6{,}63 \text{ x } 10^{-34} \text{ Js})(3{,}00 \text{ x } 10^{8} \text{ m/s})}{1{,}94 \text{ x } 10^{-18} \text{ J}} = 1{,}03 \text{ x } 10^{-7} \text{ m}$$

O sentido do fluxo de energia é indicado quando se diz que o fóton de comprimento de onda 1,03 x 10^{-7} m foi emitido.

Espectro do He atômico



Exercício!

Baseado no modelo de Bohr proponha uma equação para explicar o espectro de He^+. Discuta se essa aproximação é válida par o átomo de He.