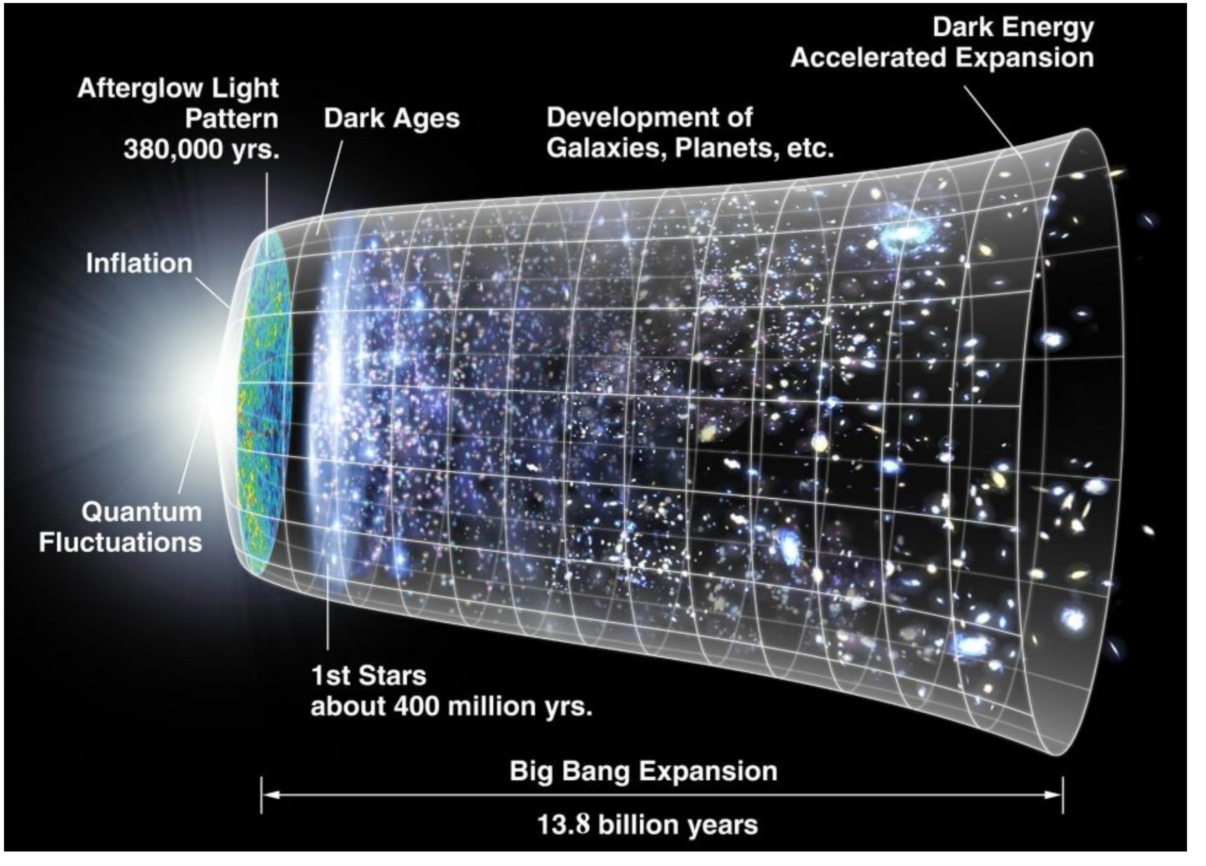
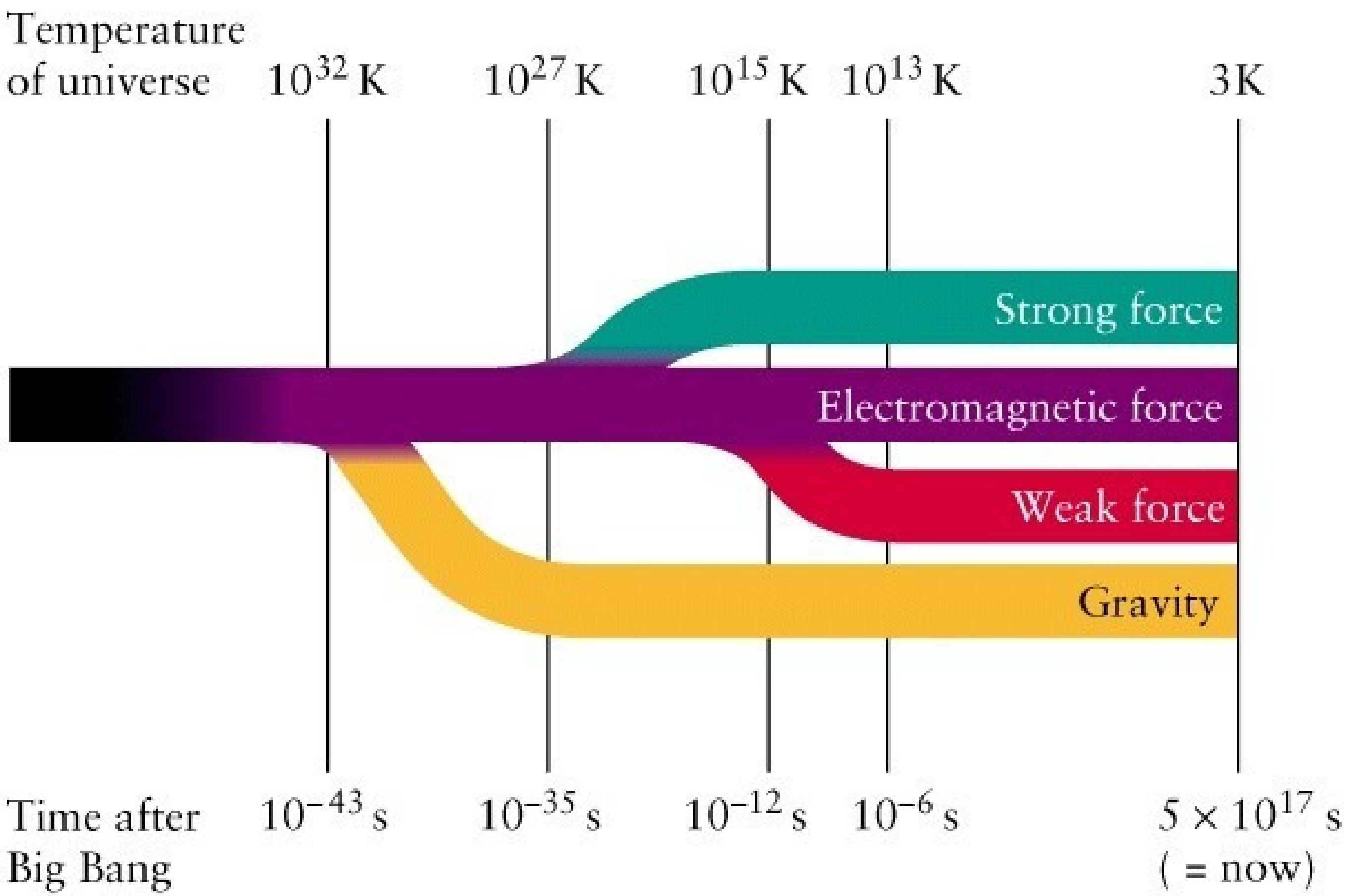
Atoms and Solids



Fundamental interactions



Fundamental interactions

interaction	range	relative strength
1. Gravity	long	1
2. Weak nuclear	short	10^{25}
3. Electromagnetic	long	10^{36}
4. Strong nuclear	short	10^{38}

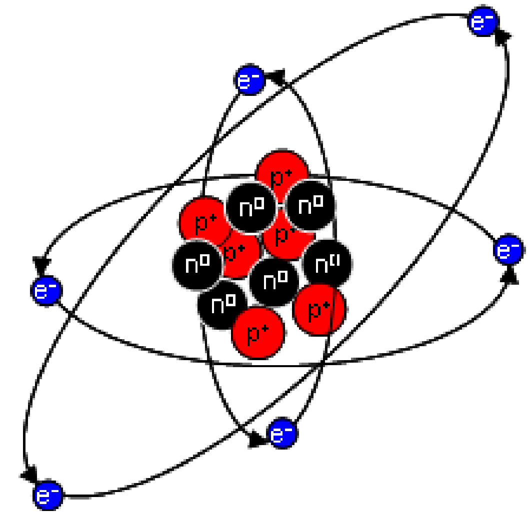
Fundamental interactions

1. Gravity — acts on all objects
2. Weak nuclear — causes unstable atomic nuclei to decay
3. Electromagnetic — between charged objects
4. Strong nuclear — binds protons and neutrons together

- Smallest charge found free in nature: $e=1.6\times10^{-19}$ C
- All charges must be $Q = \pm Ne$ (N integer) → quantization of the charge
- The total charge of the Universe is unchanged → conservation of the charge

Subatomic particles

	mass (kg)	Electric charge (C)
proton	1.67×10^{-27}	1.602×10^{-19}
neutron	1.675×10^{-27}	0
electron	9.11×10^{-31}	$- 1.602 \times 10^{-19}$



- Atoms are normally in a neutral state. Number of protons Z is fixed → defines the element
- Number of neutrons N can vary → isotopes
- When electrons are removed the atom is ionised
- Elements are symbolised with their mass number and atomic number

Example: $^{16}_{8}O$

Mass number A=Z+N

Atomic number Z

Foundation of atomic theory

Non continuity of matter proposed by

- Anaxagoras (c. 510-428 BC)
- Empedocles (c. 490-430 BC)
- Leucippus (~450 BC)
- Democritus (460-370 BC)

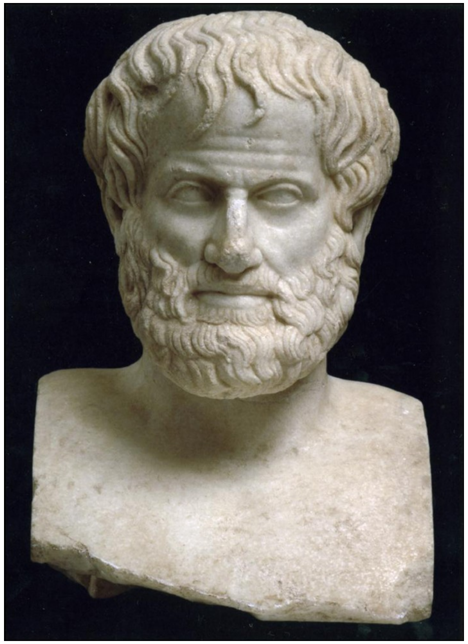
"ἐτεῇ δὲ ἄτομα καὶ κενόν"

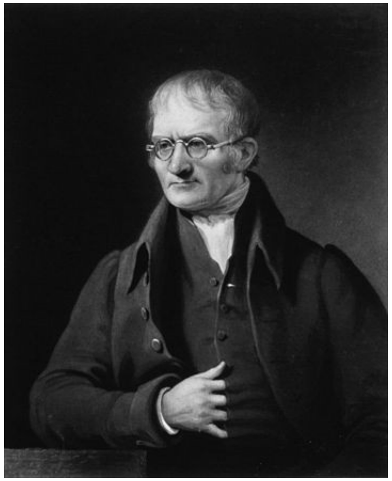
“There are only atoms and void”

Foundation of atomic theory

But Aristotle (384–322 BC) asserted that matter is continuous and consists of the 4 classical elements + aether:

- Earth → solids
- Air → gas
- Water → liquids
- Fire → plasma, heat
- Aether → heavenly bodies

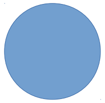




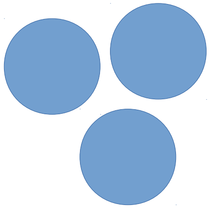
Dalton model

John Dalton (1808) assumed that all elements are made of atoms.

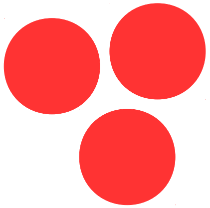
- Atoms are indivisible particles



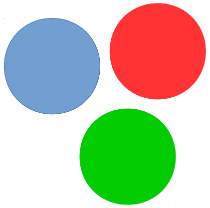
- For a given element all atoms are identical



- For different elements atoms are different



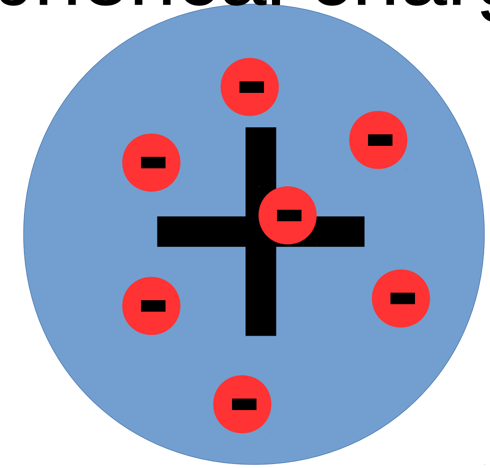
- Compounds are formed by combining atoms



J. J. Thomson’s atomic model

Nobel Prize in Physics 1906
Prize share: 1/1

- Atom is divisible! Spherical symmetry R~10^{-10} m
- Electrons in fixed positions with negative charge and small mass (plum pudding model)
- Electrically neutral → positive spherical charge

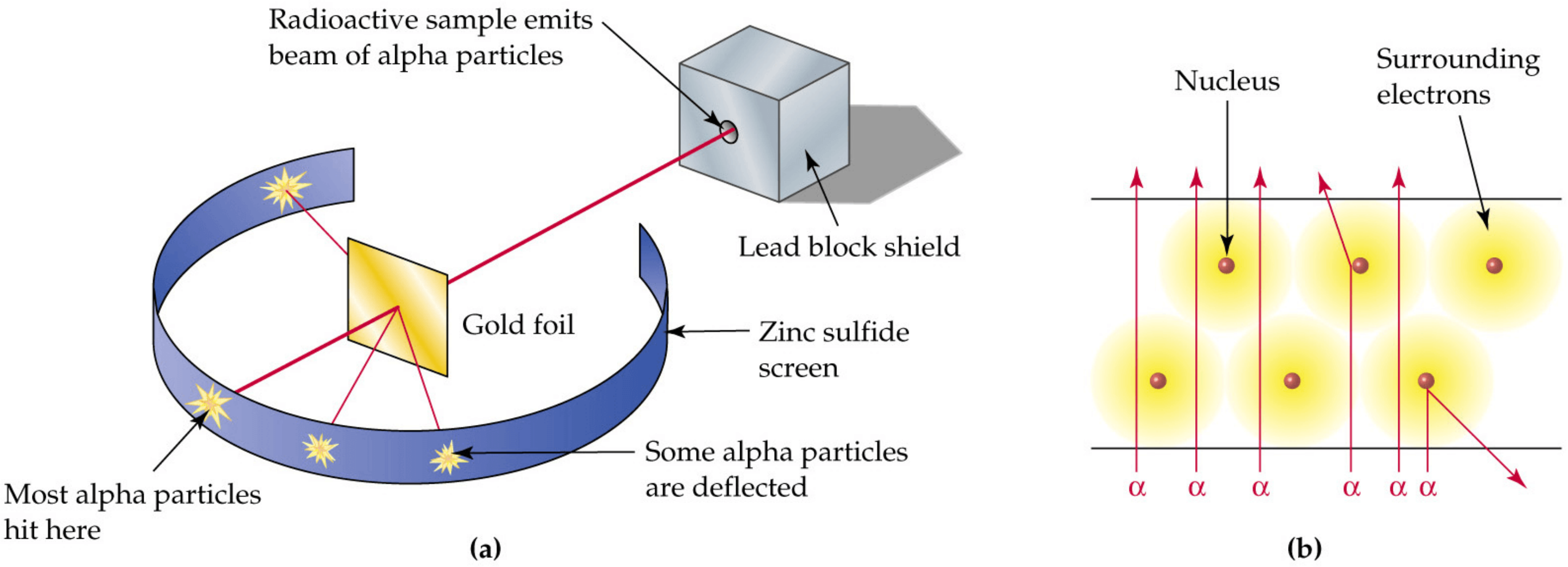


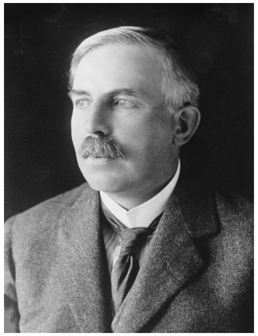
- N_e=(atomic weight)/2
- Light emission → oscillation of e around their equilibrium position

J. J. Thomson’s atomic model

Failure: could not explain the scattering of α-particles in gold foil

- **Rutherford’s experiment (by Geiger and Marsden)**

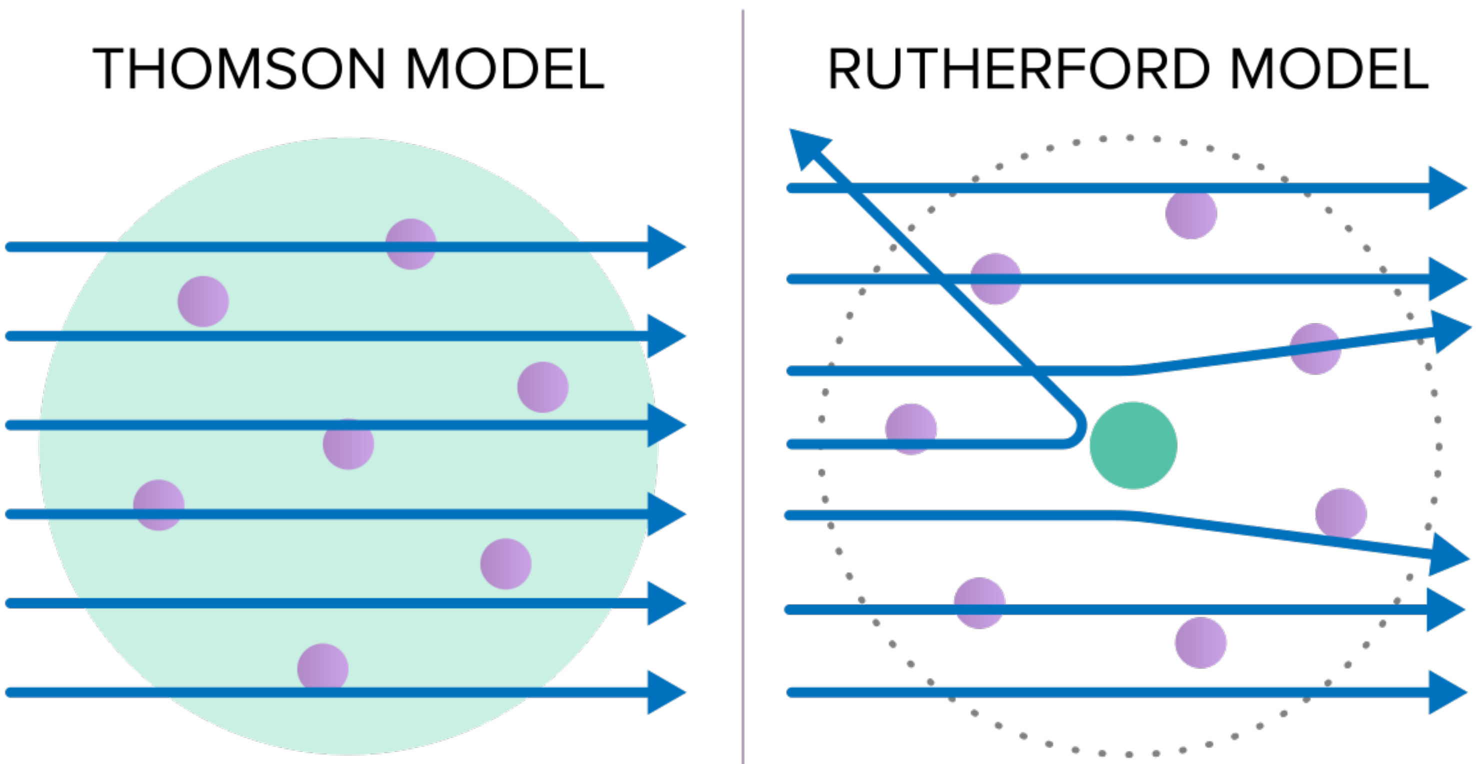




Rutherford's atomic model

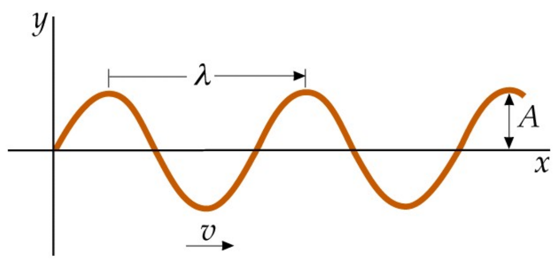
Nobel Prize in Chemistry 1908
Prize share: 1/1

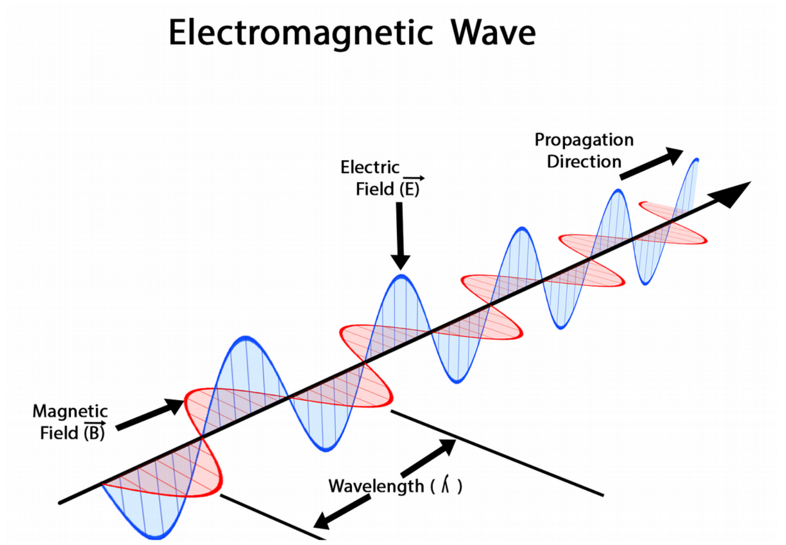
- A positive nucleus with e orbiting in circle
- Scattering of α-particles from the gold (Au) nucleus is due to Coulomb force ($F=kZ_1Z_2e^2/r^2$)



Electromagnetic waves

- Maxwell unified existing laws of electricity and magnetism
- Light is an electromagnetic wave (coupled oscillating electric and magnetic field) that travels with speed $c=2.998 \times 10^8$ m/s in vacuum

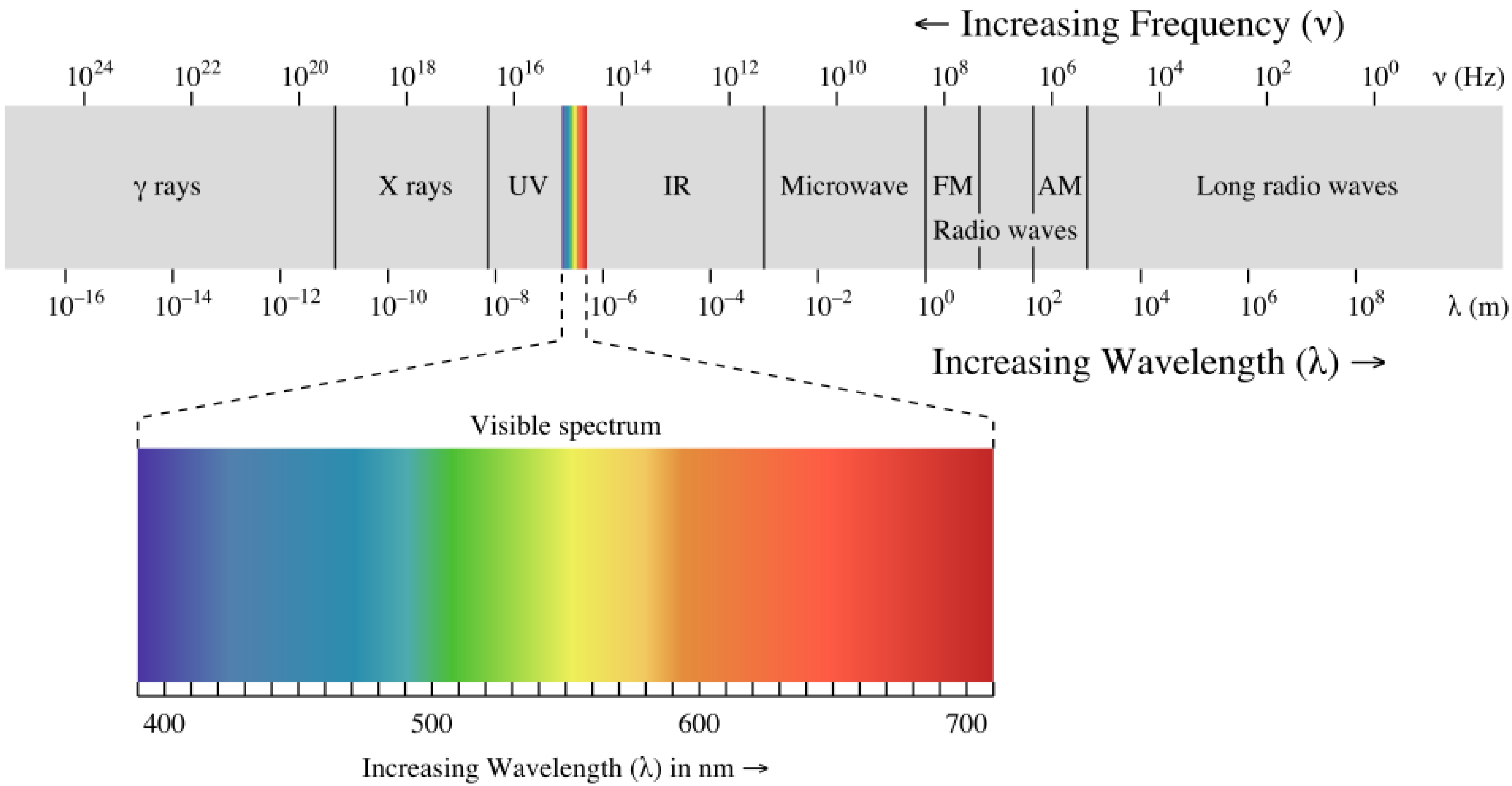




Wave properties:

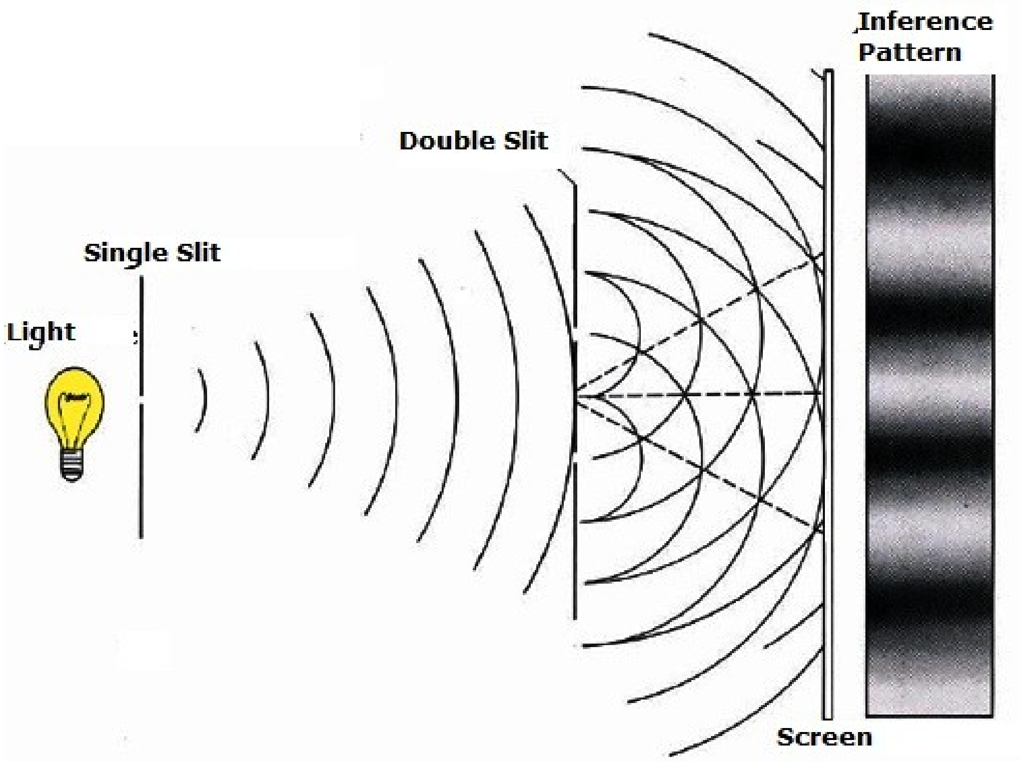
- **Amplitude A**: maximum displacement
- **Period T**: Time to make a complete oscillation ($T=1/\nu$)
- **Wavelength** λ: distance between two consecutive maxima
- **Energy:** $E \propto A^2$
- **constant speed:** $c=\lambda\nu$

Electromagnetic spectrum



Wave nature of light

- Thomas Young demonstrated the wave nature of light with the double slit experiment (1801). Maxwell later developed the electromagnetic theory (1865).

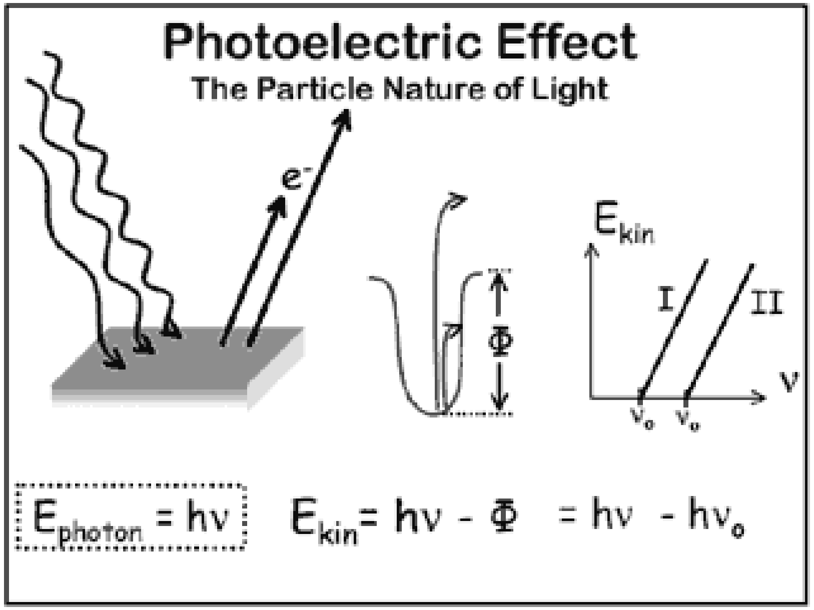


Particle nature of light

- Albert Einstein explained the photoelectric effect (1905) assuming light is a particle, a photon of energy E=hv

Planck's constant $h=6.626 \times 10^{-34}$ J s

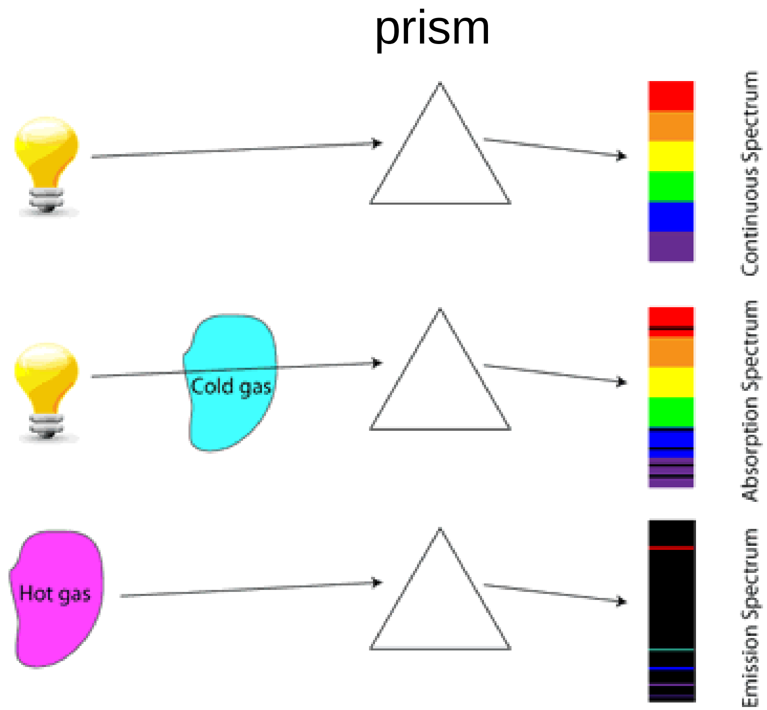
Nobel Prize in Physics 1921
Prize share: 1/1



UC Berkeley's Digital Chem1A

Atomic spectra

- Kirchhoff and Bunsen discovered that every atom has a characteristic spectrum.
- Balmer suggested an empirical formula for the wavelength



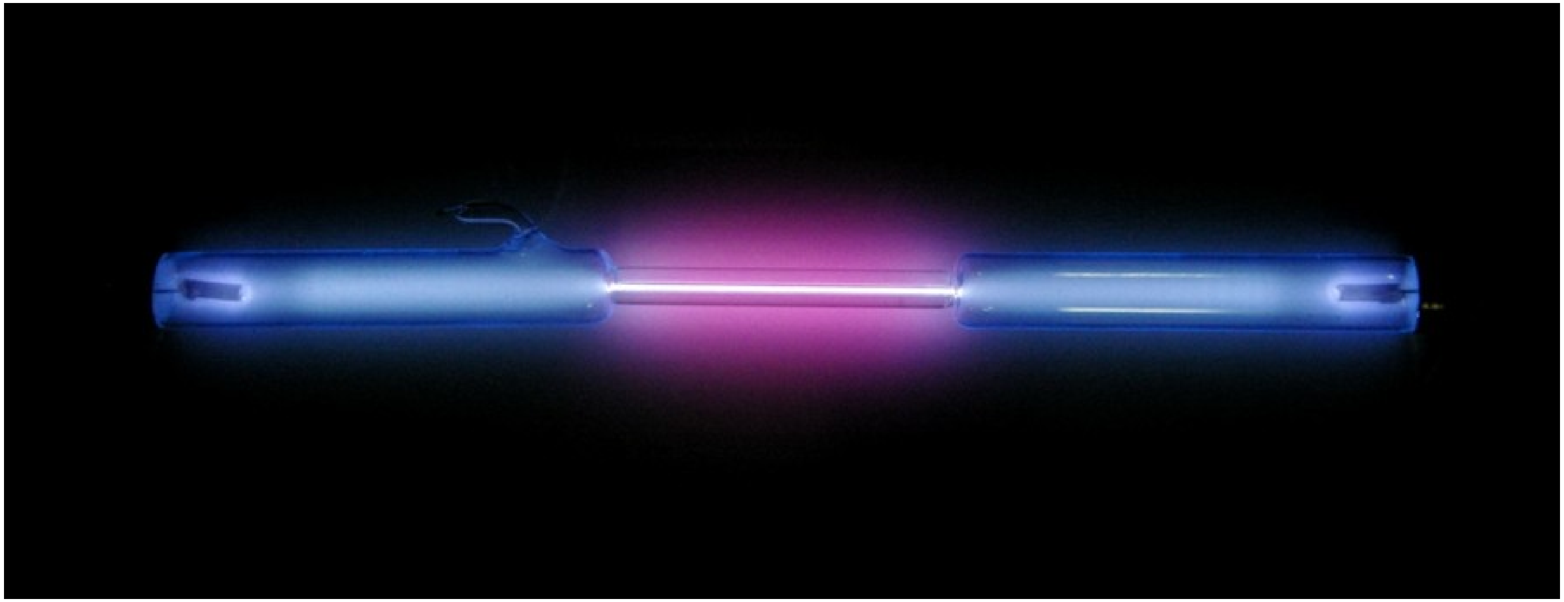
$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, \ldots$$

R_H: Rydberg constant

$R_H = 1.0973731568527 \times 10^{7}\ m^{-1}$

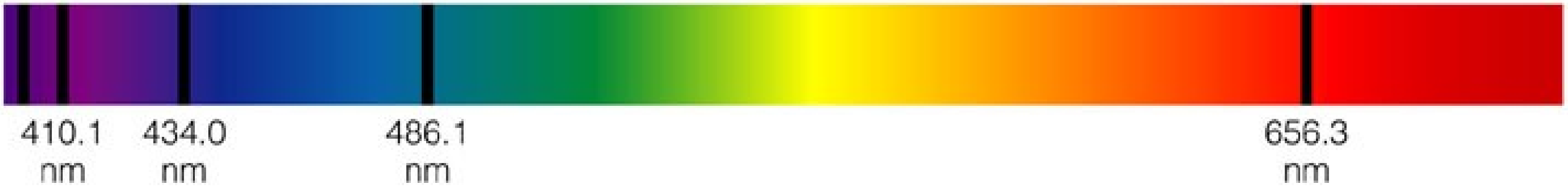
Failures of Rutherford's model

- Could not explain the atomic spectra of gases



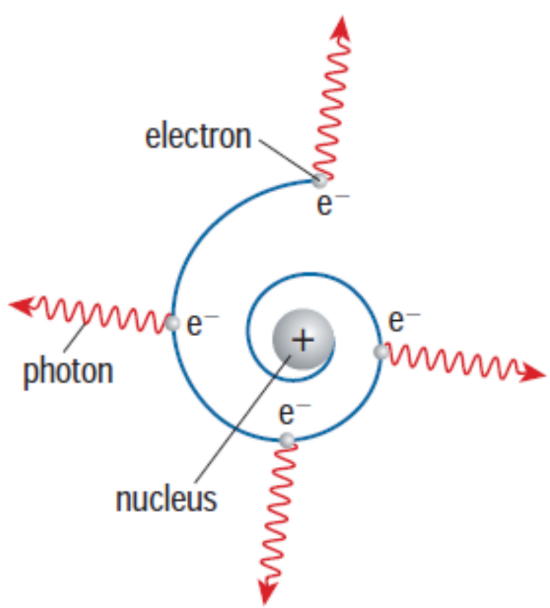
Hydrogen emission spectrum

Hydrogen absorption spectrum



Failures of Rutherford's model

- According to Maxwell's theory an e accelerating around the nucleus would emit electromagnetic radiation and loose energy → collapse of the atom in ~ 10^{-12} s



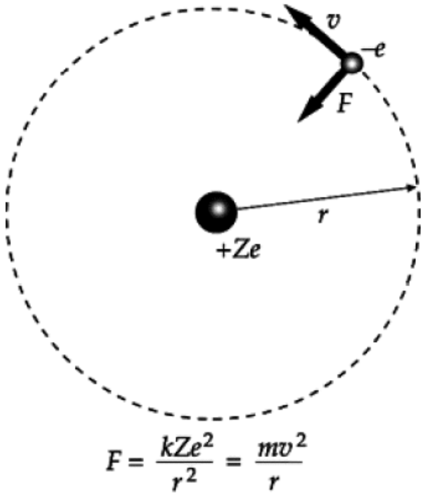
Bohr's model

Nobel Prize in Physics 1922
Prize share: 1/1

- Niels Bohr developed a semiclassical model (1913) to explain the emission spectra of the H atom.
- An electron of charge -e orbiting the nucleus

potential energy

$$U = \frac{kq_1 q_2}{r} = \frac{k(Ze)(-e)}{r} = -\frac{kZe^2}{r}$$



$$F = \frac{kZe^2}{r^2} = m\frac{v^2}{r}$$

$$K = \frac{1}{2}mv^2 = \frac{1}{2}\frac{kZe^2}{r} \qquad E = K + U = -\frac{1}{2}\frac{kZe^2}{r}$$

Bohr's model

- From classical electromagnetic theory (Maxwell) such an atom would be unstable. If e accelerates → it should radiate electromagnetic energy of frequency $\nu = 1/T$

  Bohr's postulates:

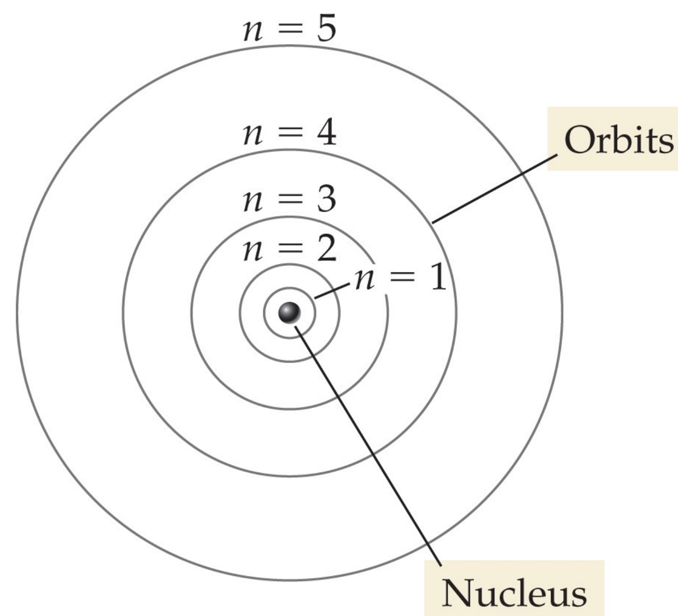
1) *The electron in the hydrogen atom can move only in certain nonradiating, circular orbits called stationary states. The angular momentum of the e in a stable orbit is*

$$L = m\upsilon r = n\hbar$$

$$n = 1, 2, 3, \ldots$$

$$\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34}\ \mathrm{Js}$$

$$E_n = -\frac{me^4}{2\hbar^2}\frac{1}{n^2} = -\frac{13.6}{n^2}$$

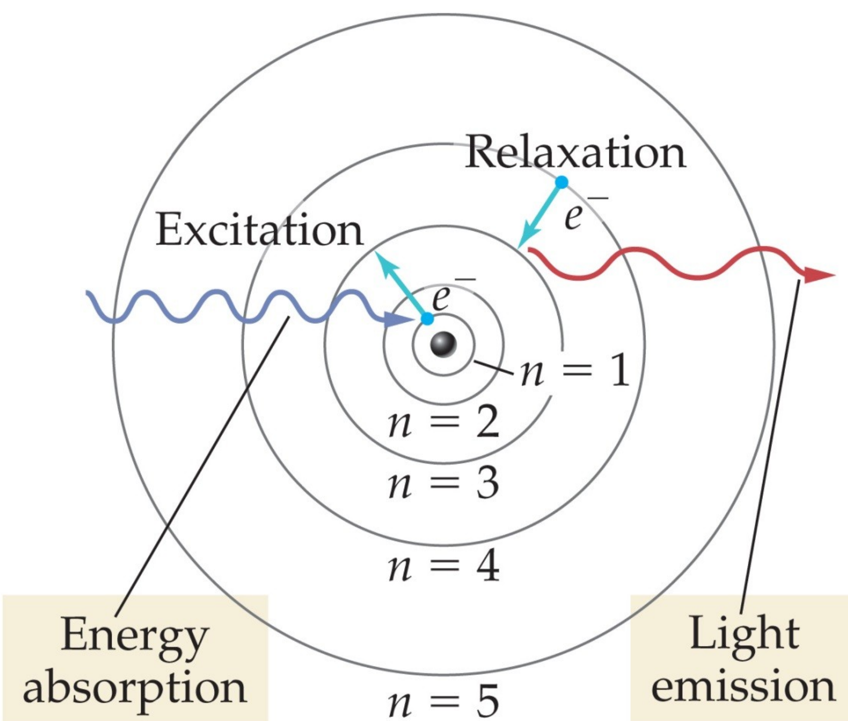


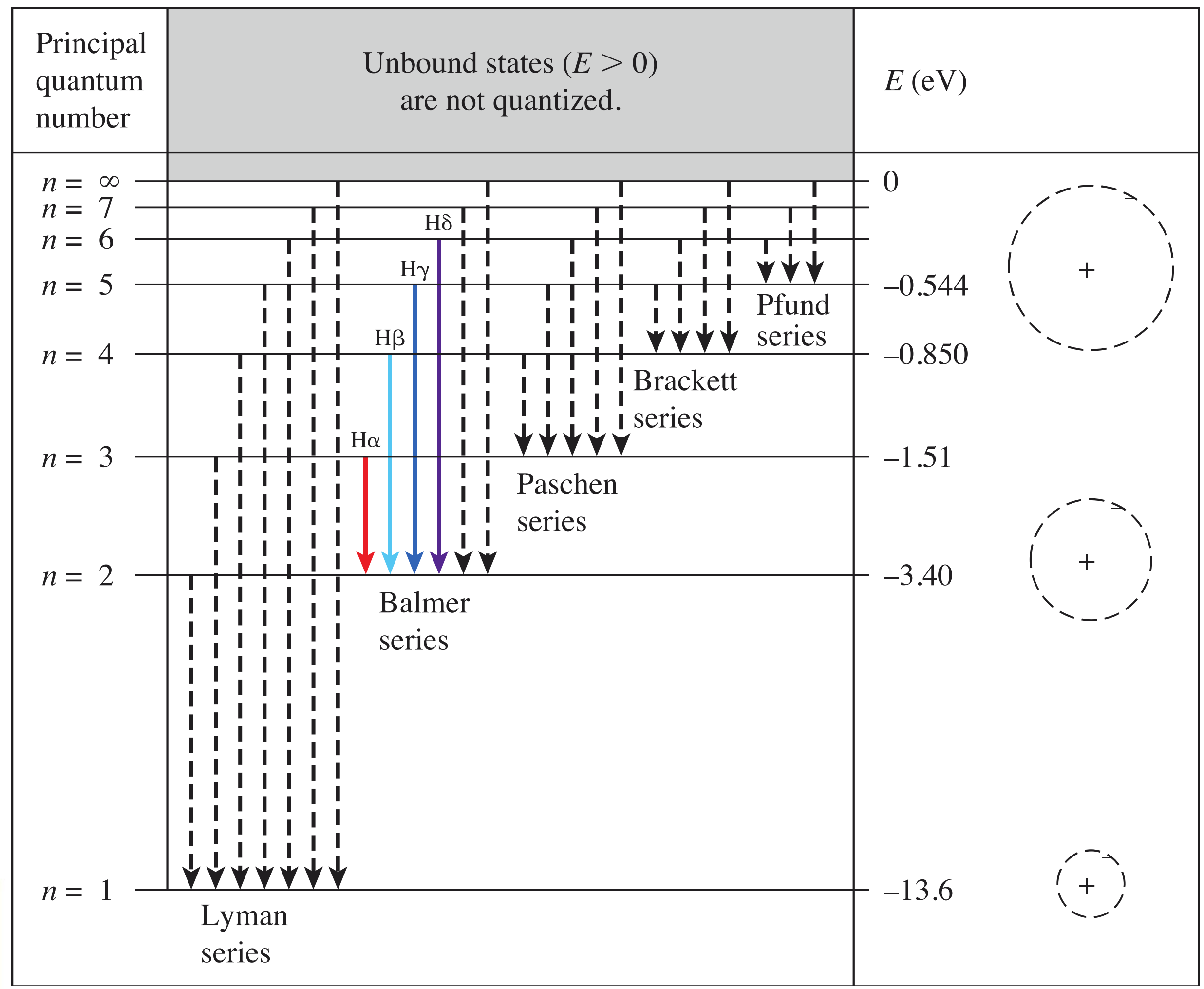
Bohr's model

Bohr's postulates:

2) *The frequency of the emitted radiation during a transition is given by* $\nu = \frac{E_i - E_f}{h}$

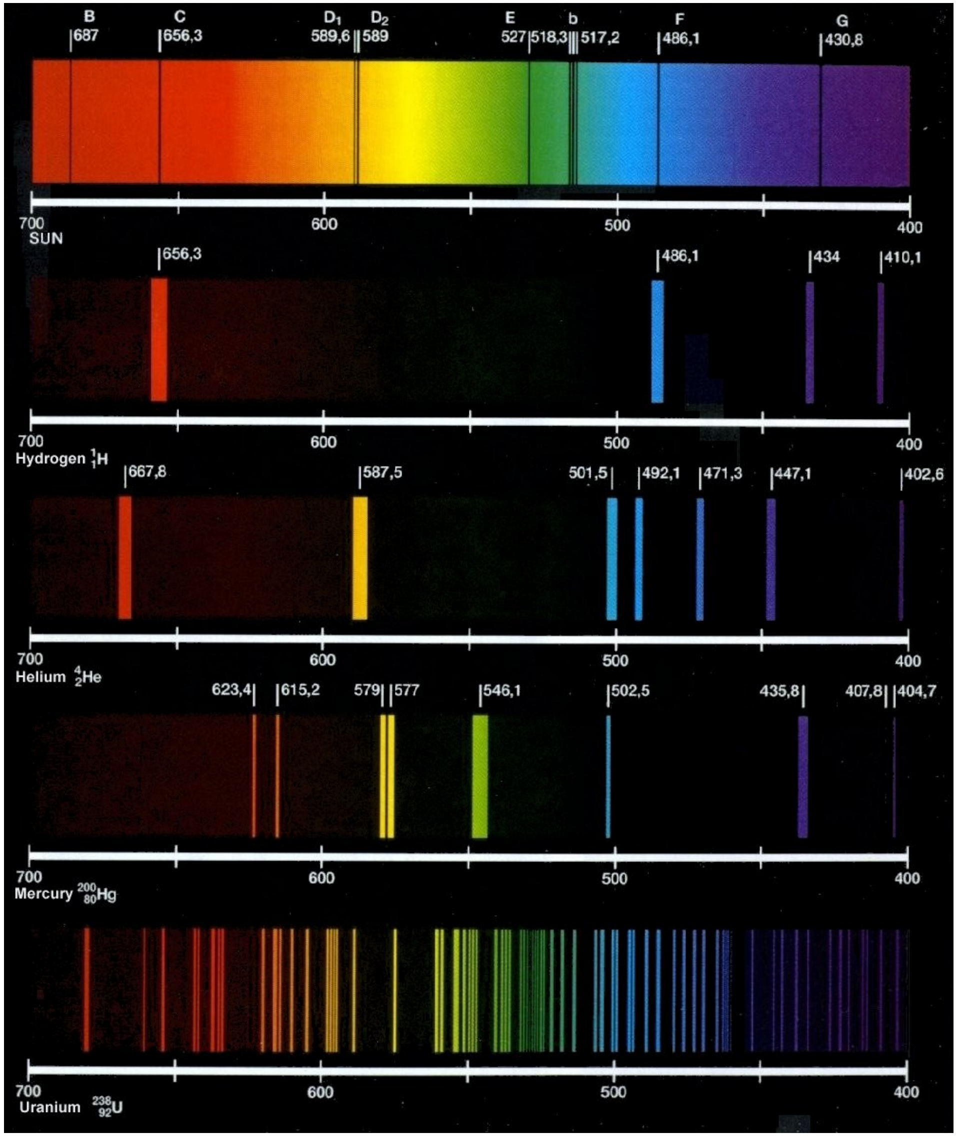
$$E_n = -\frac{me^4}{2\hbar^2}\frac{1}{n^2} = -\frac{13.6}{n^2}$$





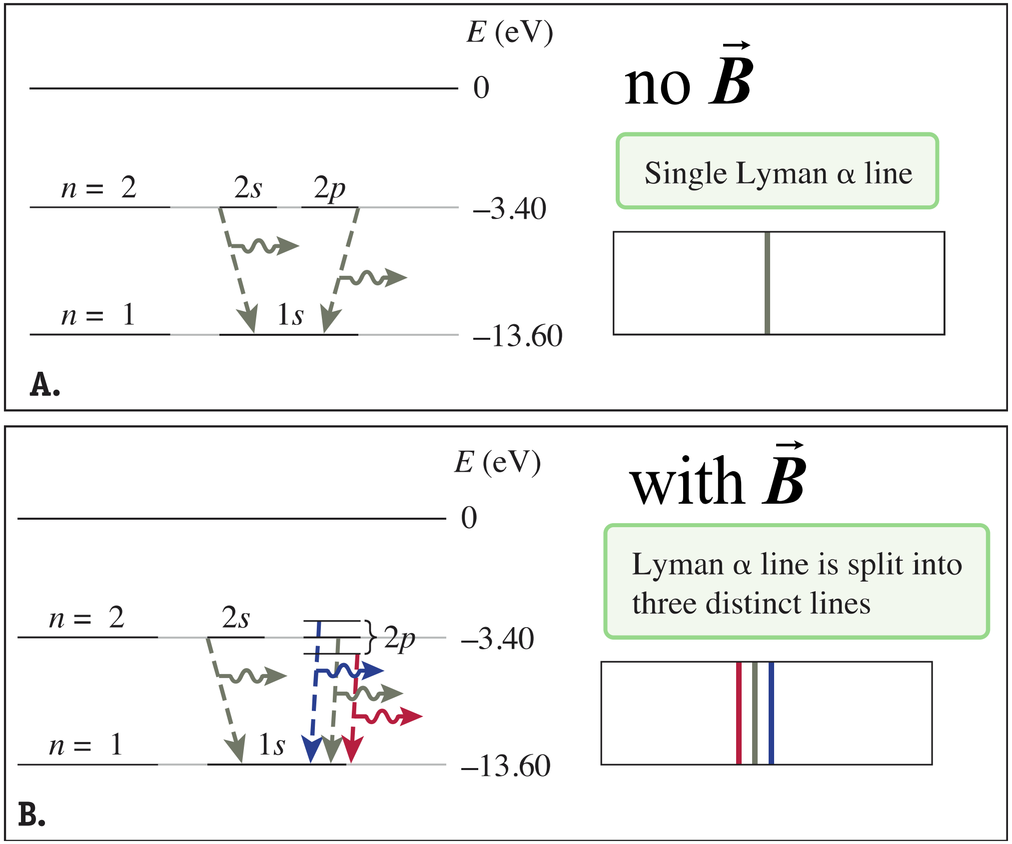
Bohr's model shortcomings

- Can only explain the emission spectrum of hydrogen, not of complex atoms



Bohr’s model shortcomings

- Could not explain the fine structure of H and Zeeman effect (split of spectral lines of some atoms into three when a magnetic field is applied)



De Broglie: the wave-like electron

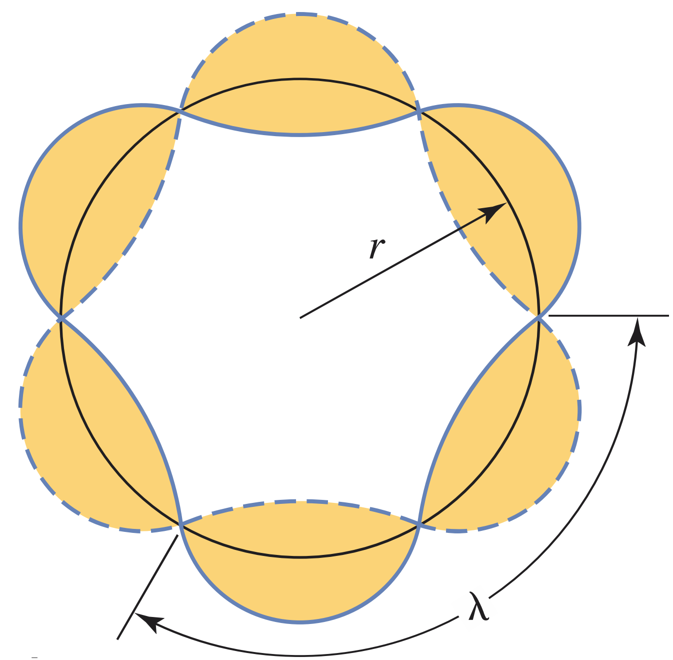
- Louis de Broglie described the electron as a wave → wave-particle duality

Nobel Prize in Physics 1929
Prize share: 1/1

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

$$m_e v = \frac{L}{r} = \frac{n\left(h/2\pi\right)}{r}$$

$$\lambda = \frac{h}{nh} 2\pi r = \frac{2\pi r}{n}$$



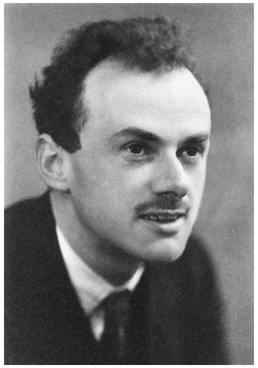
Heisenberg uncertainty principle

Werner Karl Heisenberg determined that it is fundamentally impossible to know precisely both the velocity and position of a particle at the same time

Nobel Prize in Physics 1932
Prize share: 1/1

$$\Delta x\left(m\Delta \upsilon\right)\geq\frac{h}{4\pi}$$

Schrödinger equation



- Schrödinger
Nobel Prize in Physics 1933
Prize share: 1/2

- Dirac
Nobel Prize in Physics 1933
Prize share: 1/2

Erwin Schrödinger formulated the wave equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+U(x)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

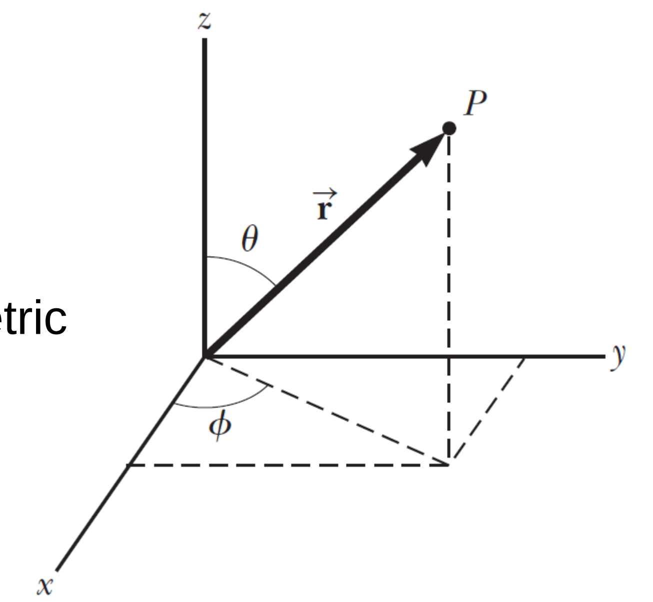
Ψ is the electron wavefunction

The probability density to find the electron in a small length dx at position x and time t $P(x,t)=|\Psi(x,t)|^2$

This equation asserts that an electron in an atom cannot be considered as a particle having an orbit with a definite radius. Instead, there is a probability of an electron being at certain spatial positions → electron cloud

Time-independent Schrödinger equation

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+U\Psi=E\Psi$$



$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$

Potential energy is spherically symmetric for the Hydrogen atom

$$\Psi(r,\theta,\varphi)=R(r)Y(\theta,\varphi)$$

Wave function with 3 quantum numbers n,l,m

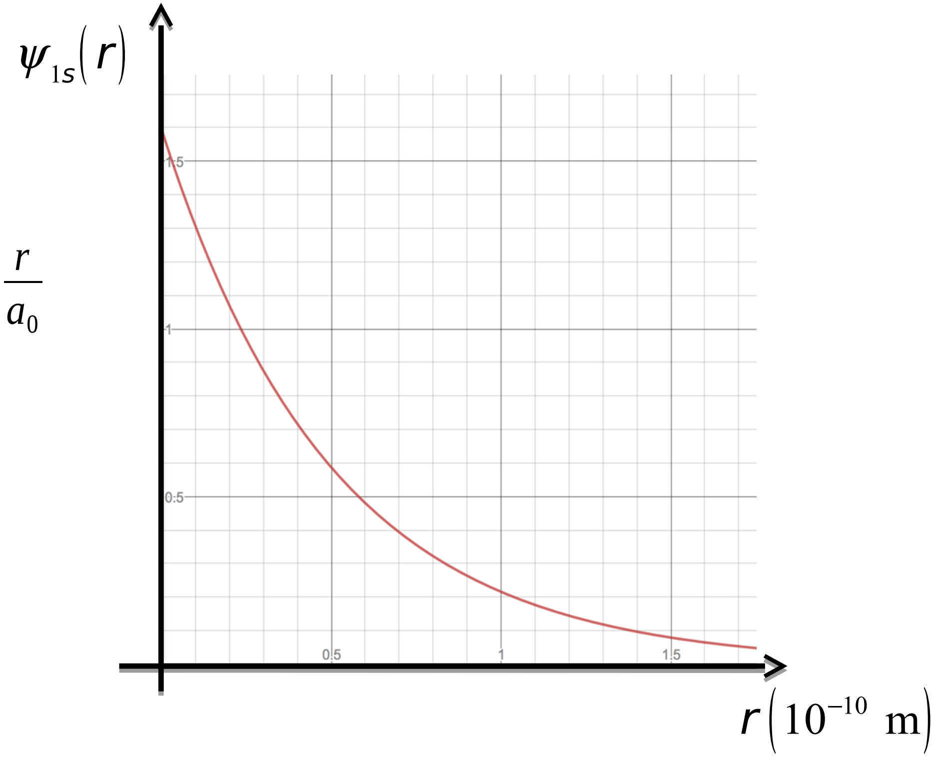
$R(r)$ Radial function

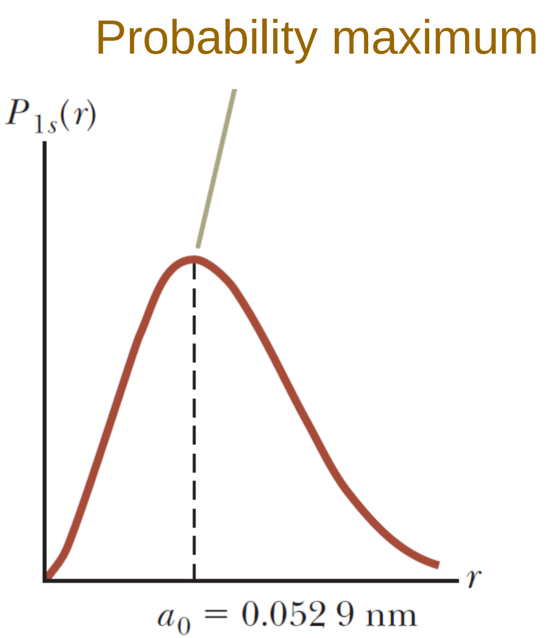
$Y_l^m(\theta,\varphi)$ Spherical harmonics

Radial Probability density: $P(r) = 4\pi r^2|\psi|^2$

Solutions for Hydrogen atom

1s Hydrogen wavefunction: $\Psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$

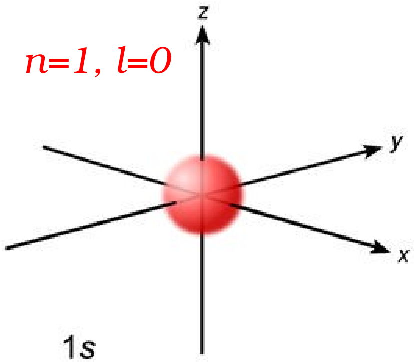




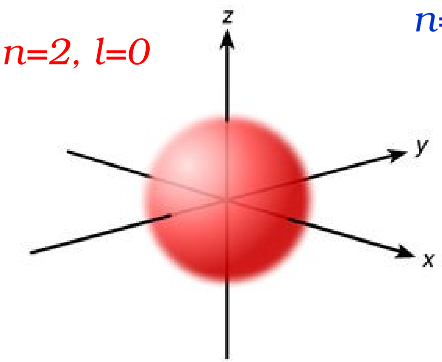
1s Radial probability density: $P_{1s}(r) = \left(\frac{4r^2}{a_0{}^3}\right) e^{-2r/a_0}$

Atomic orbitals

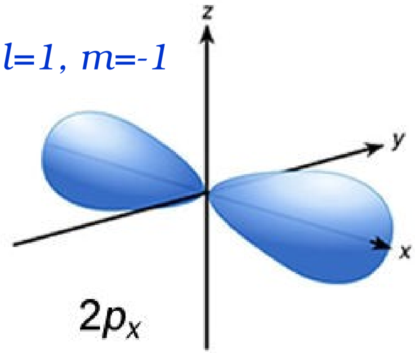
n=1, l=0



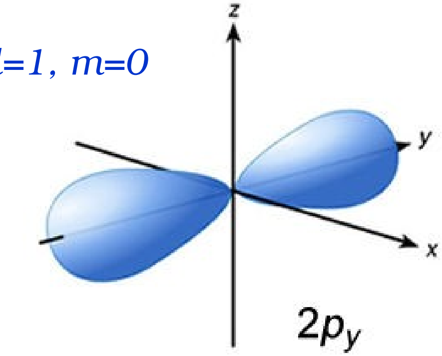
n=2, l=0



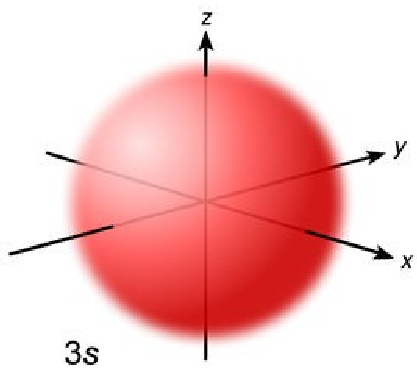
n=2, l=1, m=-1



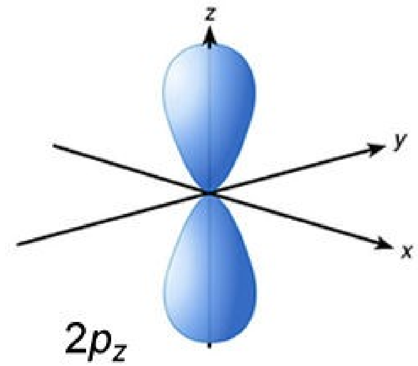
n=2, l=1, m=0



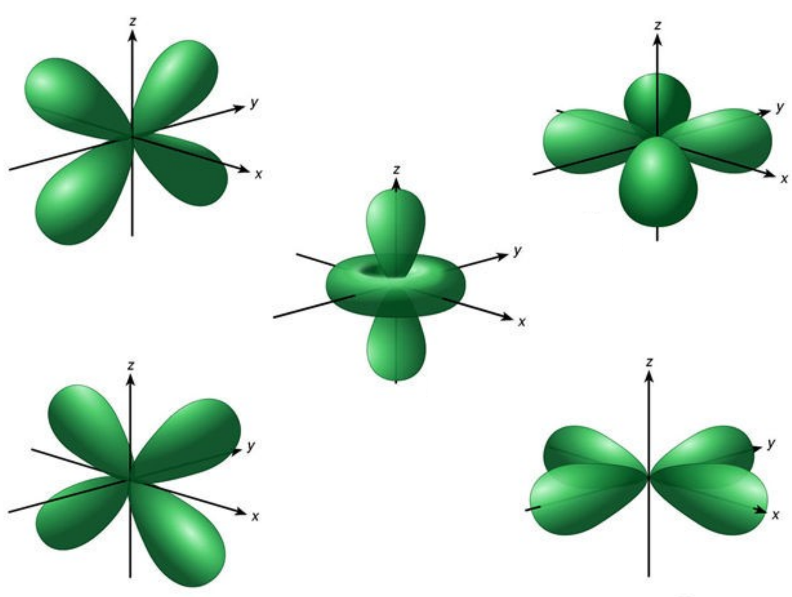
n=3, l=0



n=2, l=1, m=+1



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



Quantum numbers

The three coordinates that come from Schrödinger's wave equations are the principal (n), angular (l), and magnetic (m) quantum numbers. These quantum numbers describe the size, shape, and orientation in space of the orbitals on an atom.

n: Principal quantum number
values: n = 1,2,3,…
(also called K, L, M, N,…)

→

- related to "*the radii of the orbits*".
- Determines the size
- Energy states with the same n form a *shell*.

l: Orbital quantum number
values: l = 0,…, n-1
(also called s, p, d, f, g, …)

→

- related to the angular momentum.
- Determine the shapes
- Energy states with the same l form a *subshell*.

m: Magnetic quantum number
values: m = -l,…, l

→

- Is related to the spatial orientation.
- Determines the orientation
- Energy does not depend on m unless there is an external magnetic field.

ALSO a fourth quantum number **s**: spin quantum number
values: s = -1/2,1/2

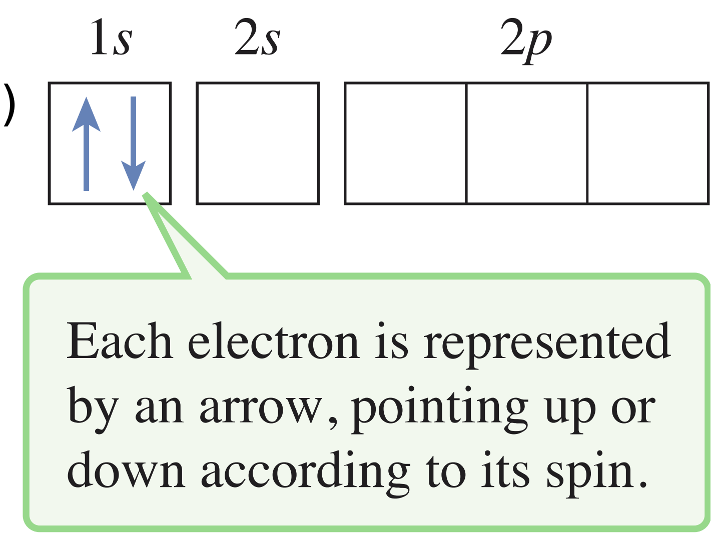
The Pauli exclusion principle

In 1925, Wolfgang Pauli discovered a rule, known as the Pauli exclusion principle, for determining the number of electrons in filled shells of an atom.

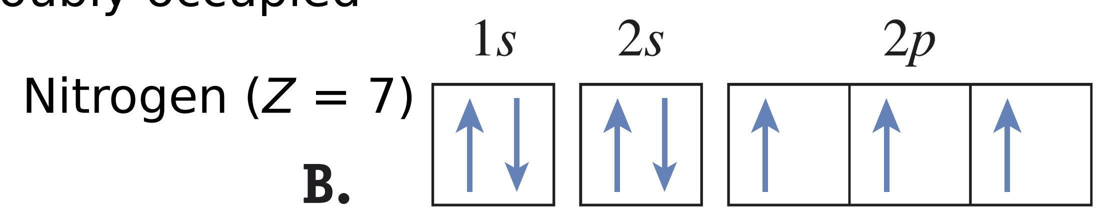
It states that two or more indistinguishable or identical particles with spin one–half can not be in the same quantum state.

Helium (Z = 2)

A.



Hund's rule: Every orbital in a subshell is singly occupied before any are doubly occupied



Nobel Prize in Physics 1945
Prize share: 1/1

How to write electron configurations

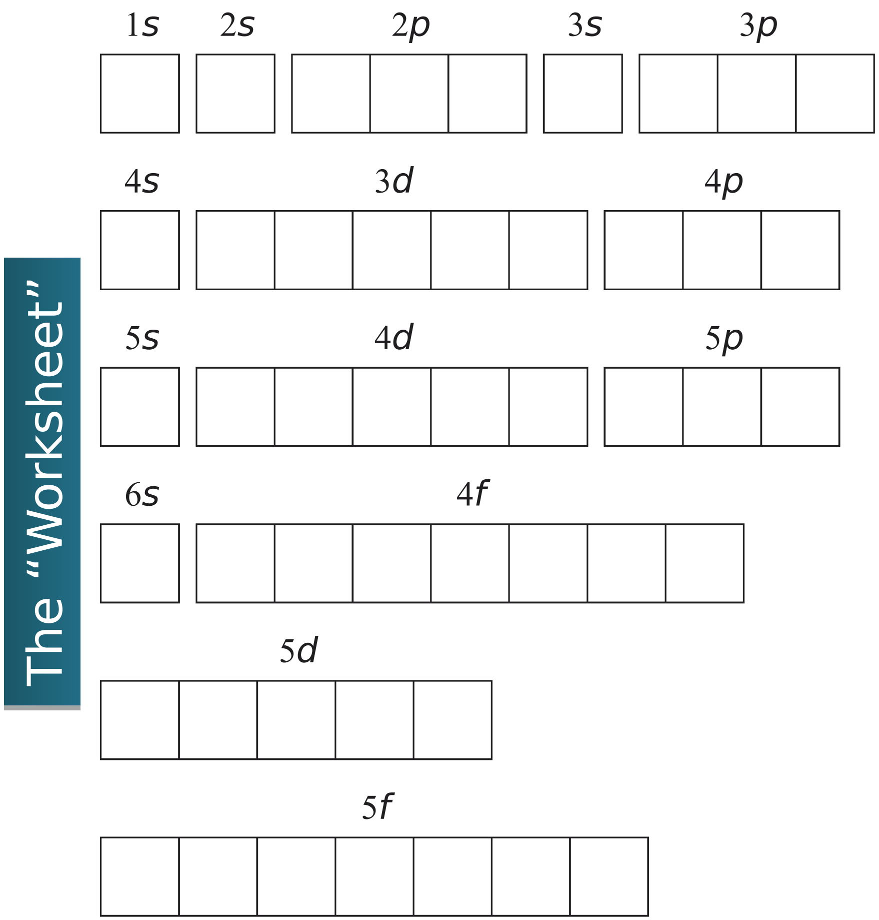
- maximum number of electrons that can fit in an energy level is: $\mathbf{2n^2}$
- Aufbau principle: Orbitals with lower energy filled first
- Pauli's exclusion principle: Two electrons cannot have the same 4 quantum numbers → each orbital (defined by n, l and m) can only have two electrons, corresponding to s=1/2 and s=-1/2.
- Hund's rule: As energy does not normally depend on m, there can be several orbitals with the same energy (degenerate). These orbitals are filled so that there is one electron on each level (all with the same spin) before more electrons fill that level (maximum multiplicity).
- Madelung rule: The states crossed by the same arrow have same n + l value. The arrow direction indicates the order of filling states.

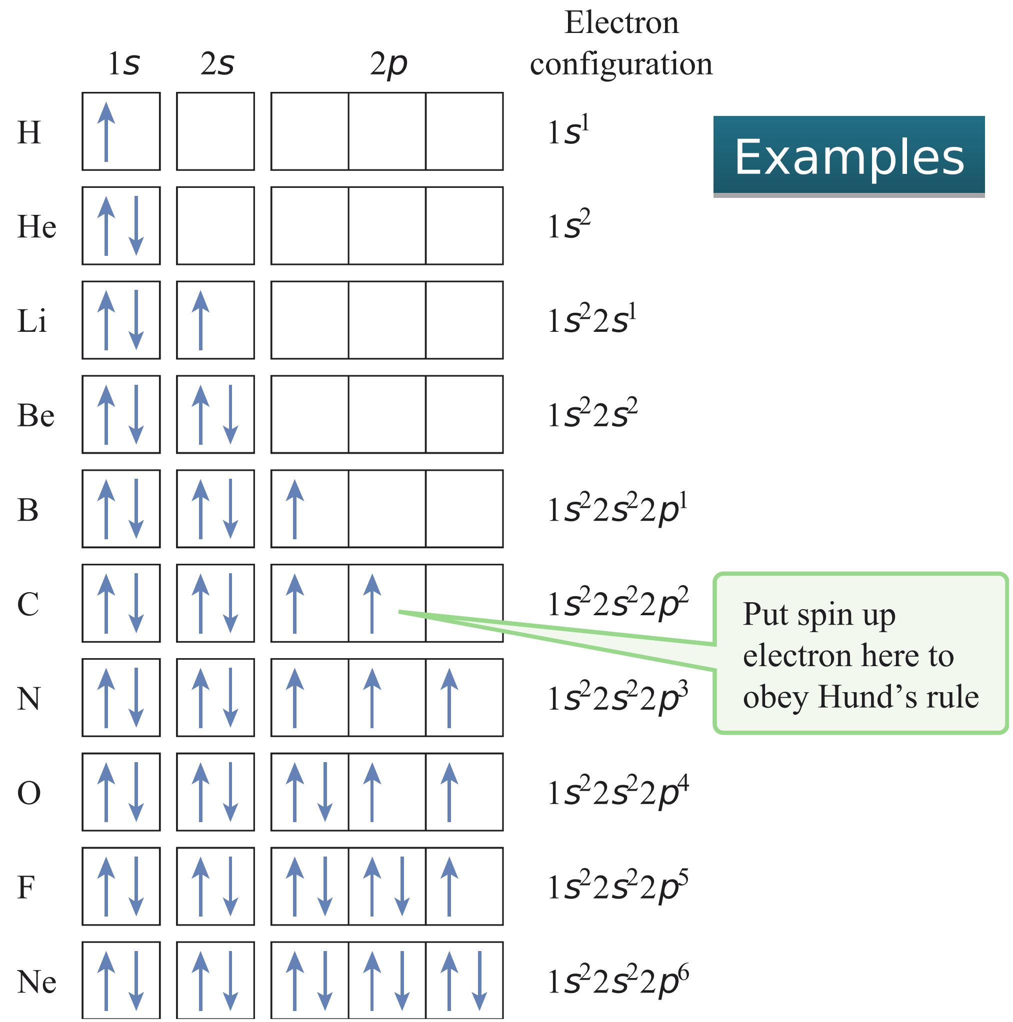
  This rule has exceptions...

$\mathbf{1s^2}$
$\mathbf{2s^2\ p^6}$
$\mathbf{3s^2\ p^6\ d^{10}}$
$\mathbf{4s^2\ p^6\ d^{10}\ f^{14}}$
$\mathbf{5s^2\ p^6\ d^{10}\ f^{14}\ g^{18}}$

$[_{18}Ar]$: $1s^2\ 2s^2\ p^6\ 3s^2\ p^6$

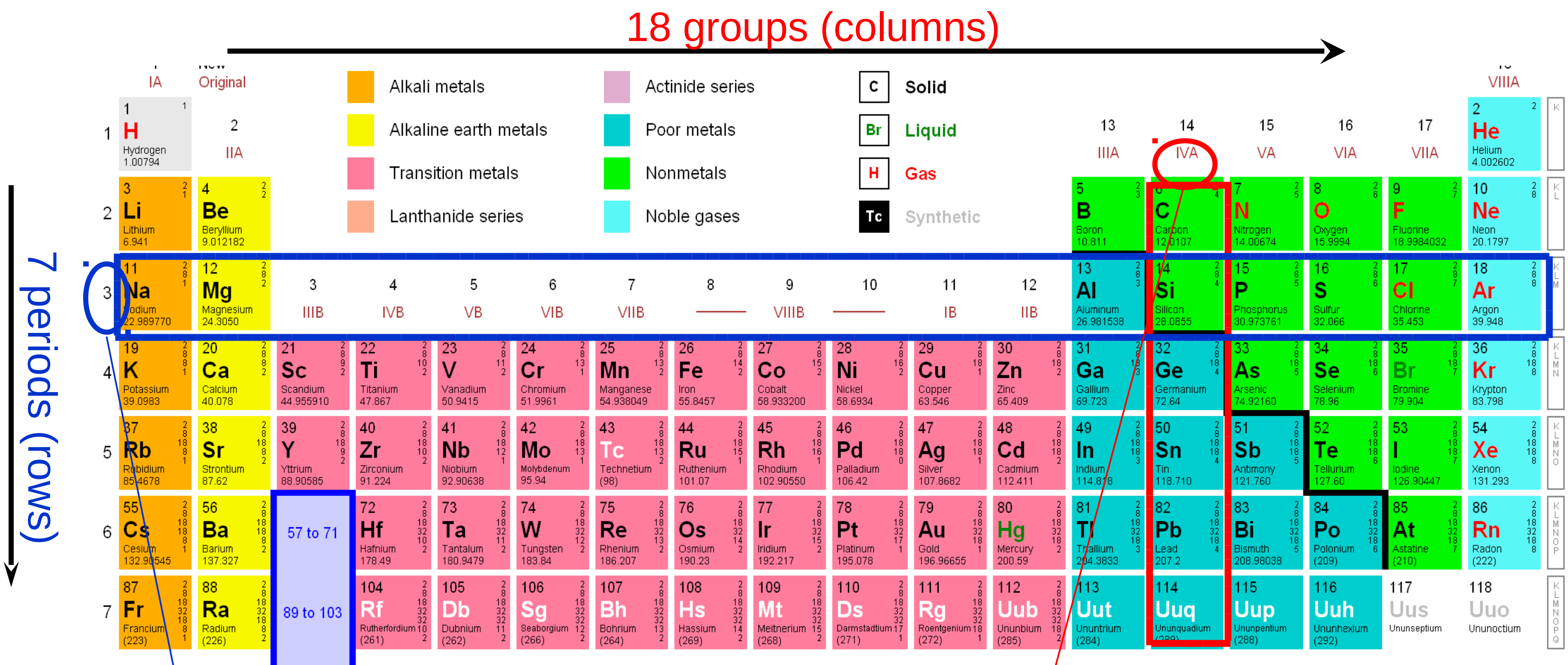
How to write electron configurations





The periodic table

- The electron configuration is related to where an element is located on the periodic table.



In elements in period 3, the last shell filled with electrons (called valence shell) is n=3.

In elements in group IVA, the number of electrons on the valence shell is 4.