EPFL

General Chemistry - Lecture 3
Atoms

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What is the current model of the atom?

(i.e. what does an atom actually look like?)

You don't need to know the theory but should be able to do exercises

Introduction video: https://www.youtube.com/watch?v=FGQseB-pvIg (Sorry for the ads)

The nuclear model of an atom

The **nuclear model** of an atom: a small, positively charged **nucleus** surrounded by a large, mostly empty space containing electrons.

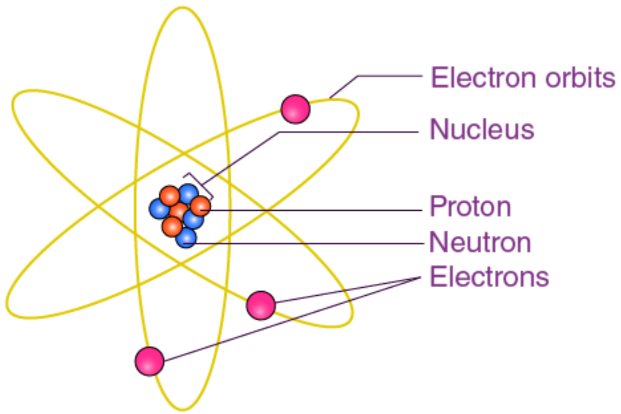
The **nucleus** of an atom contains two particles.

1. **protons** (charge equals +*e*)
2. **neutrons** (uncharged)

The number of protons in the nucleus is different for each element and is called the **atomic number**, ***Z***.

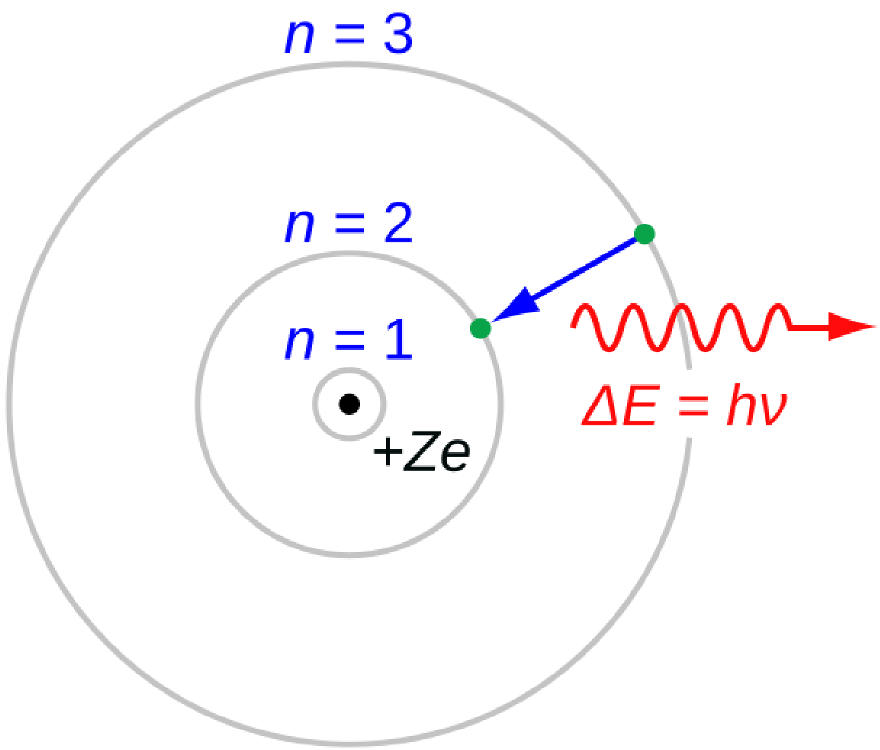
The total charge on an atomic nucleus of atomic number Z is $+Ze$ and, for the atoms to be electrically neutral, there must be Z electrons around it.

The **electrons** define the complex structure of the atoms.



Bohr's model of the atom (1913)

- The **electrons** orbit the nucleus in **orbits or shells** (a circular path for electrons)
- Electrons can **only exist** within those shells
- The first shell (closest to the nucleus) is denoted as **n=1**, then n=2, n=3, etc.
- A shell can hold a maximum of **$2n^2$** electrons
- The shells are located at **specific distances** from the nucleus
- The **energy** of an electron depends on its shell
- The **velocity** (speed) of an electron depends on its shell



The model is great to explain many things, but not, for example, how atoms combine to form molecules

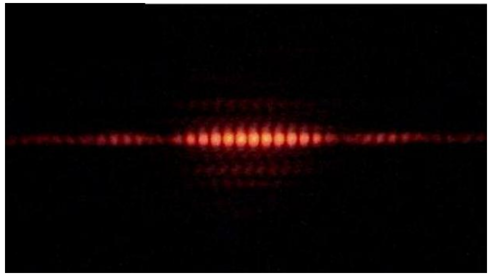
Every object has wave nature when in motion (de Broglie, 1924)

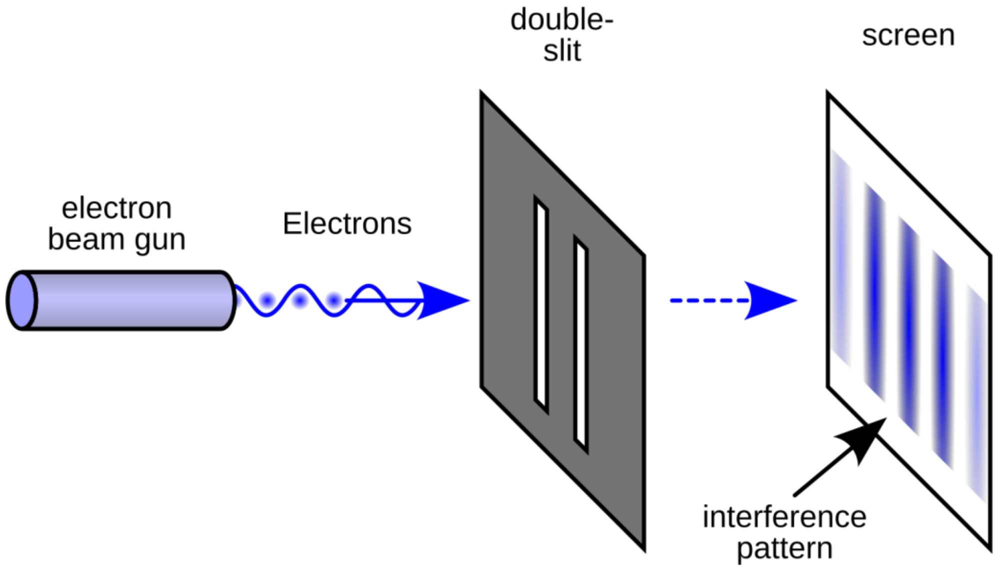
- The **wavelength** of any object is λ= **h / m*v**
  - h is Planck's constant
- For macroscopic objects, the wavelength is negligible (too small)
- It is significant for tiny objects like electrons

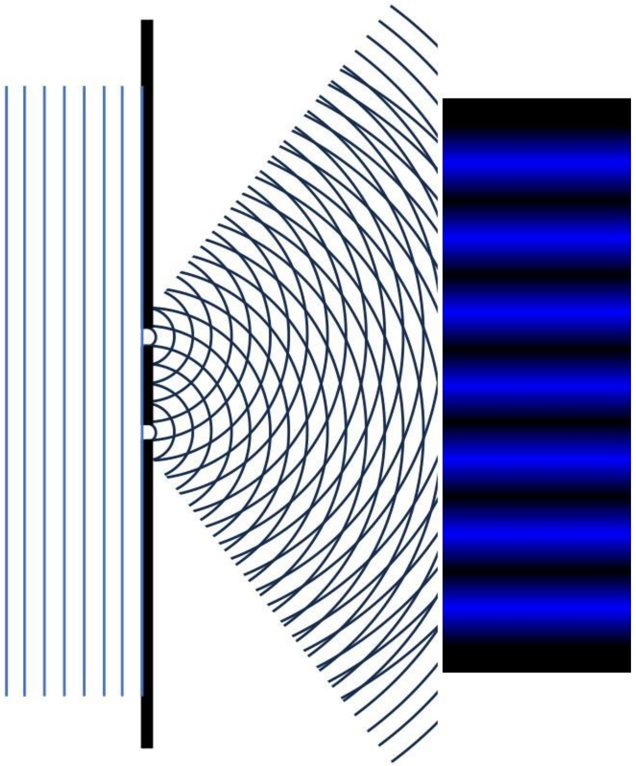
This is the dual nature of matter

- In particle form, we can locate an object, but not in its wave form
- It has been proven through mathematical calculation, but also through the double slit experiment

Double- slit experiment







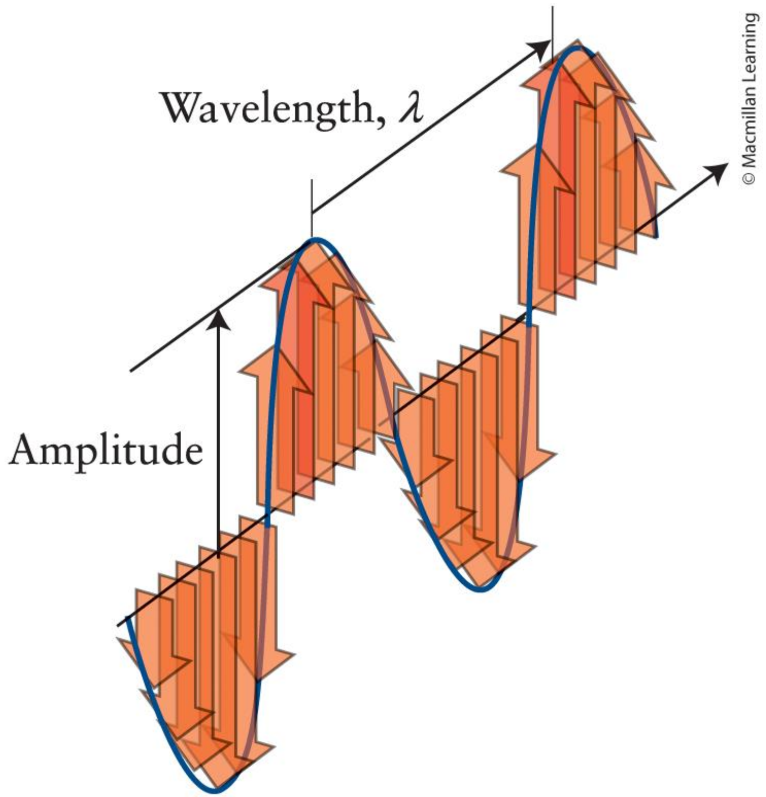
What are waves? The example of light

Light is a form of **electromagnetic radiation,** which is oscillating electric and magnetic fields that travel through space at the speed of light, $c = 3.00 \times 10^{8}\ \mathrm{m \cdot s^{-1}}$.

The **frequency** (in Hz or s^{-1}), ν, of radiation is the number of cycles per second.

Characteristics of a wave include the **amplitude** (the height above center line), the **wavelength**, λ, (the peak-to-peak distance), and the **intensity**, or brightness (square of the amplitude)

$$\nu = \frac{c}{\lambda}$$

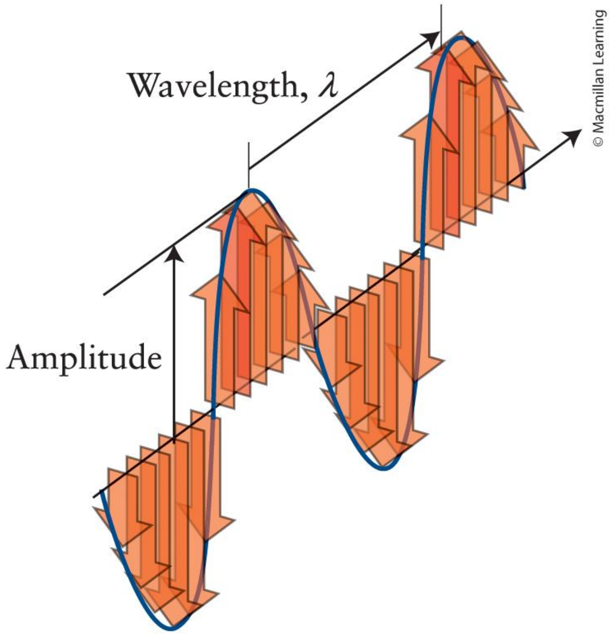


Wavelength x frequency = speed of light

For your information

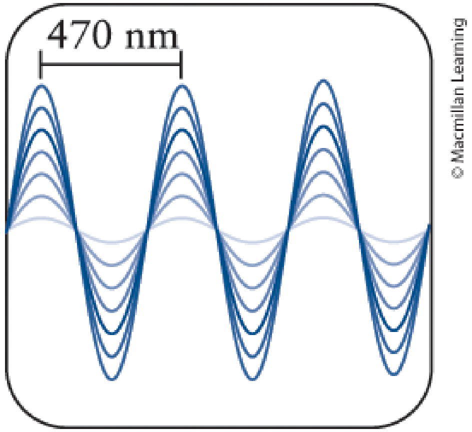
Radiation type	Frequency (10^{14} Hz)	Wavelength (nm, 2 sf)
x-rays and γ-rays	$\geq 10^3$	≤ 3
ultraviolet	8.6	350
visible light		
violet	7.1	420
blue	6.4	470
green	5.7	530
yellow	5.2	580
orange	4.8	620
red	4.3	700
Infrared	3.0	1000
microwaves and radio waves	$\leq 10^{-3}$	$\geq 3 \times 10^6$

*The values listed here are representative values within the range corresponding to each region.

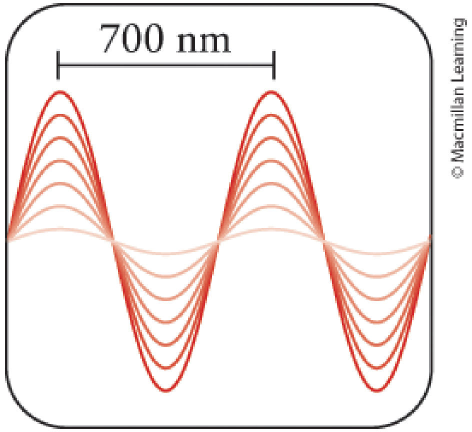


Wavelength and frequency are inversely proportional

A shorter wavelength, λ, corresponds to a higher frequency, ν, and vice versa.



Blue light has $\lambda\downarrow$, $\nu\uparrow$



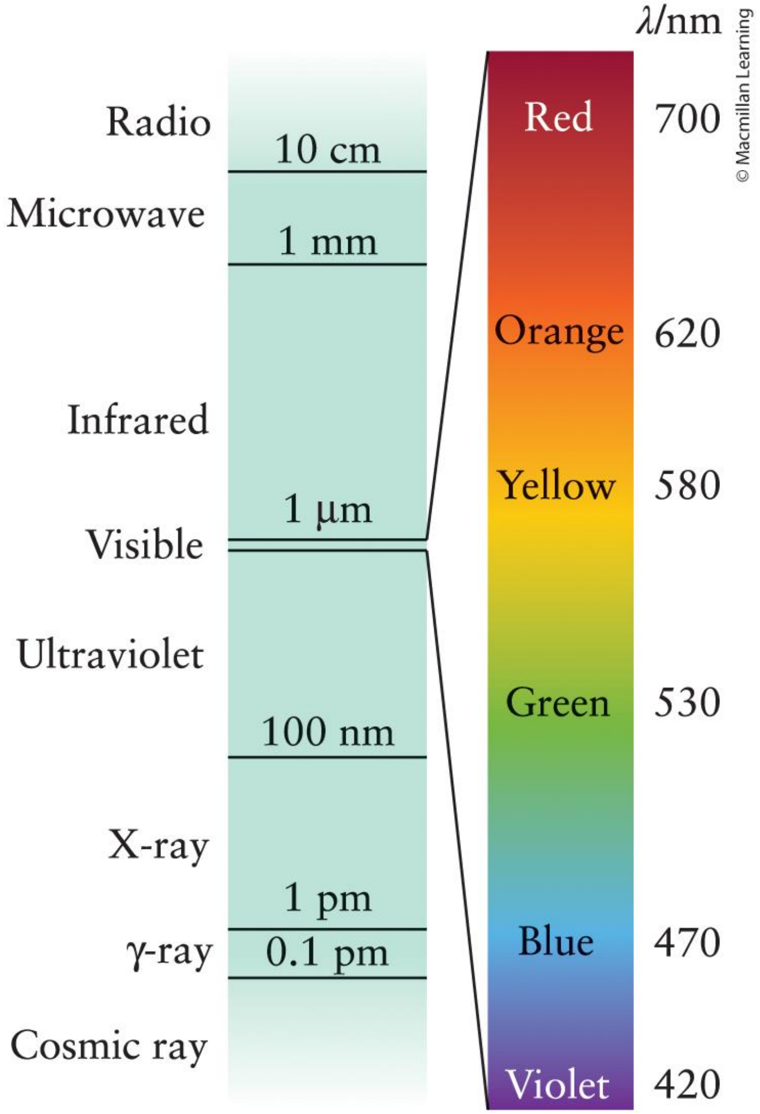
Red light has $\lambda\uparrow$, $\nu\downarrow$

The electromagnetic spectrum

Visible light – visible to the human eye

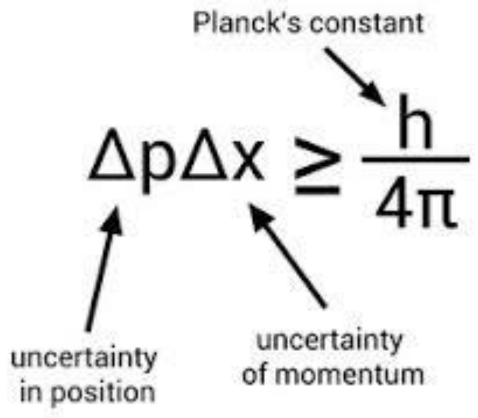
Ultraviolet radiation – higher frequency than violet

Infrared radiation – lower frequency than red; felt as heat



The uncertainty principle (Heisenberg, 1927)

- It is **not possible** to measure both the **position and the momentum** of a subatomic particle at a given time
- **Momentum = mass * velocity**
- This is a **fundamental property** of nature
- We cannot determine precise values but we can make **approximations** (probabilities)



This probability framework leads to the quantum model of atoms

Probability and Schrödinger (1926)

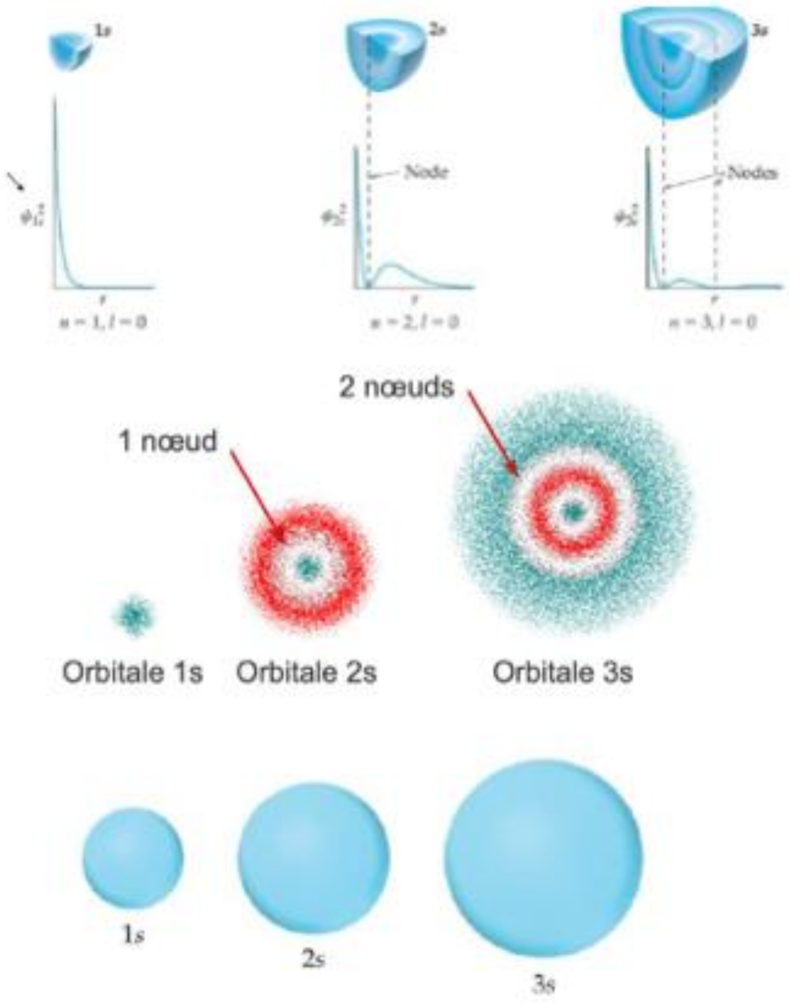
- Erwin Schrödinger replaced the trajectory of a particle with a wavefunction, Ψ.
- He provided a complete set of equations describing **energy** as a **wave-particle** and developed the Schrödinger equation.

For information only

$$\overbrace{-\frac{\hbar^2}{2m}\nabla^2\Psi}^{\text{KE}} + \overbrace{V\Psi}^{\text{PE}} = E\Psi$$

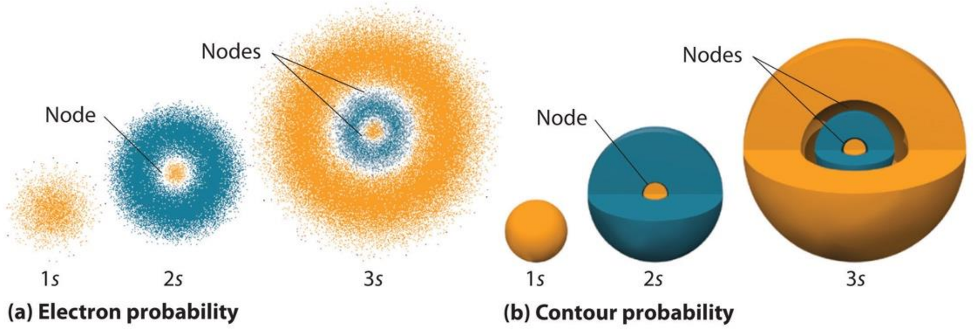
Probability and Schrödinger (1926)

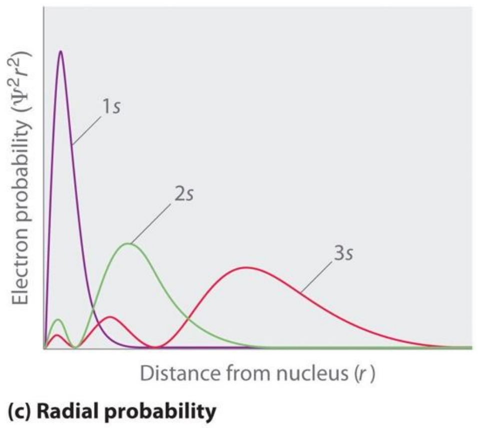
- When function is 0, the probability of finding electron is 0
- When function peaks, highest probability of finding electrons
- Simplified representation (spheres) is the envelope that contains 95% probability to find the electron



Probability and Schrödinger (1926)

- This **equation** to describe how electrons behave in a quantum system (i.e. the atom)
- Electrons are in electron clouds that are a **representation of the wave function** (Schrödinger's equation)
- The electron can be detected **anywhere within its wave function**, but more **likely** in specific areas



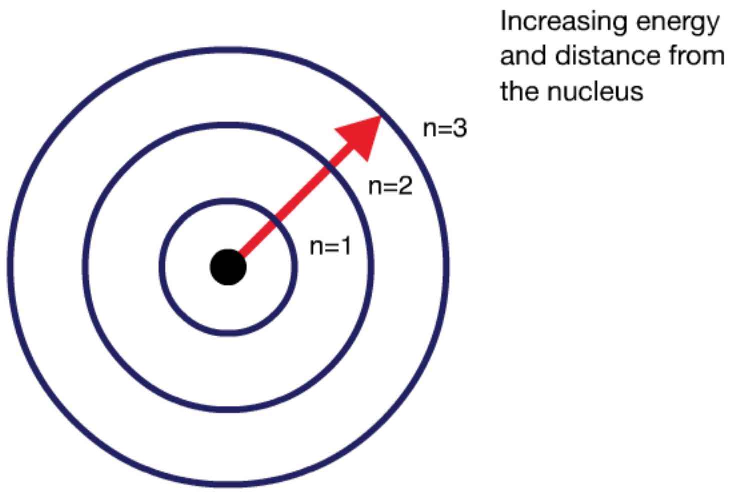


Probability and Schrödinger (1926)

- When the **Schrödinger's equation** is solved for an atom, a **set of values** emerges to explain electron behaviour: n, l, m_l and m_s
- These are the **quantum numbers**, which provide information about an electron in an atom, such as size, position, shape, energy, orientation and spin

Shells

- Shells are denoted by the number **‘n’**, called the **principal quantum number**
- Similar to Bohr’s number of orbit, but here it determines the **size of the electron cloud**
- Always **positive integers** (=nombres entiers positifs)
- The **size** of the electron cloud increases with the n (i.e. the highest probability to find an electron is further from the nucleus)
- The **number of electrons** in an atom increases with its number of shell (number of electrons = $2n^2$)

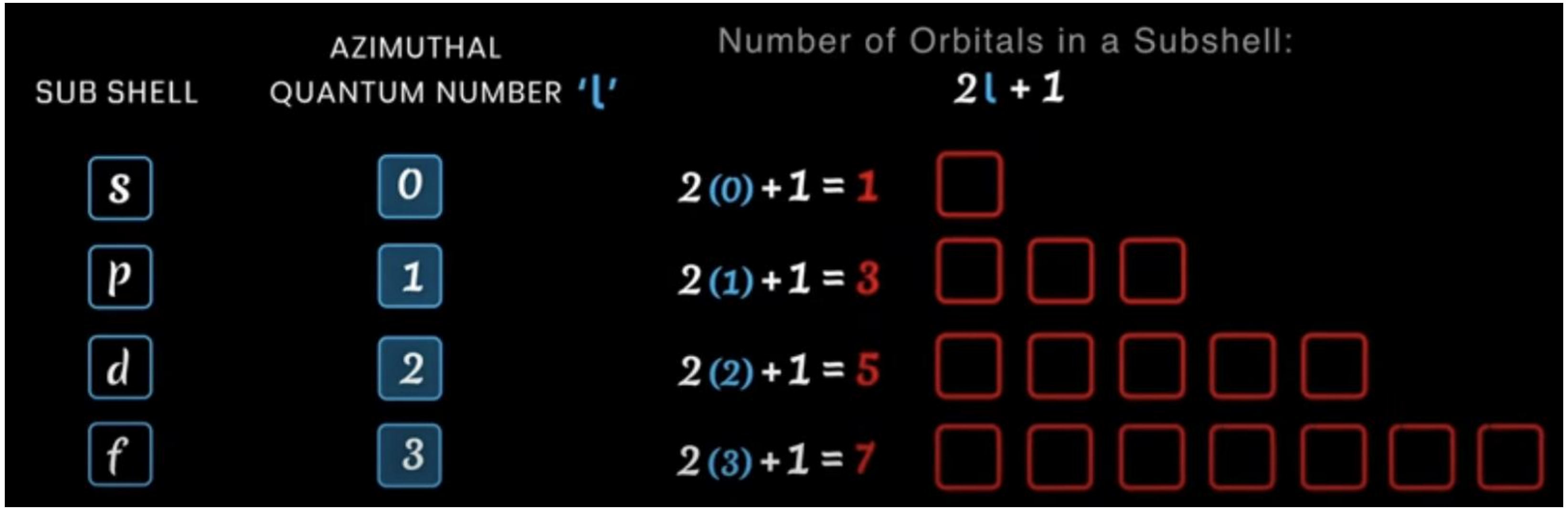


Subshells

- Each shell is divided into **subshells**, denoted by ‘**l**’, the **Azimuthal quantum number**
- Subshells are **s, p, d or f**
- A shell **n=1** has only 1 subshell **s; l = 0**
- A shell **n=2** has 2 subshells **s and p; l = 0, 1**
- A shell **n=3** has 3 subshells **s, p and d; l = 0, 1, 2**
- A shell **n=4** has 4 subshells **s, p, d and f; l = 0, 1, 2, 3**
- So, if n=1, 2, 3, 4, …, l= 0,…, (n-1) (remember the house floor analogy)

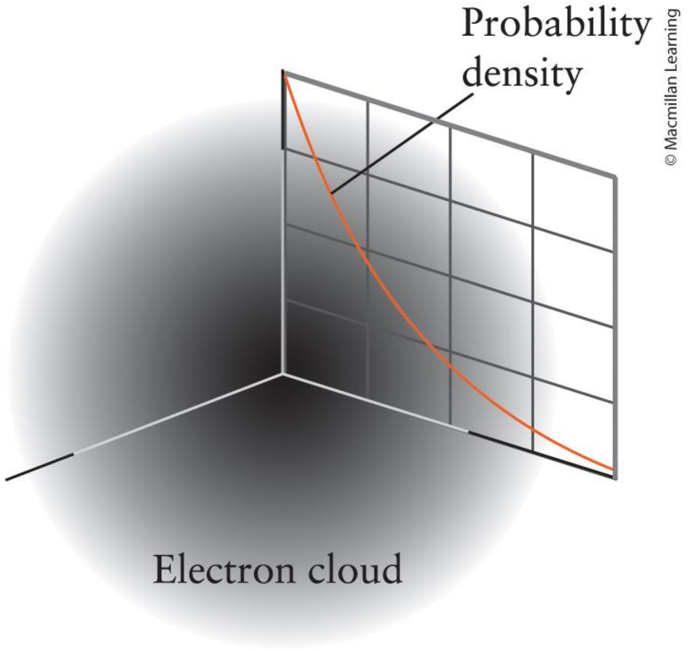
Orbitals

- Each subshell is divided into **orbitals**, denoted by ‘m_l’, the **Magnetic quantum number**
- The location where an electron is most likely to be found
- The **number of orbitals** in a subshell is given by **2l+1**
- Each orbital can hold **2 electrons** – this fits with Bohr’s model
- (remember the house room analogy)

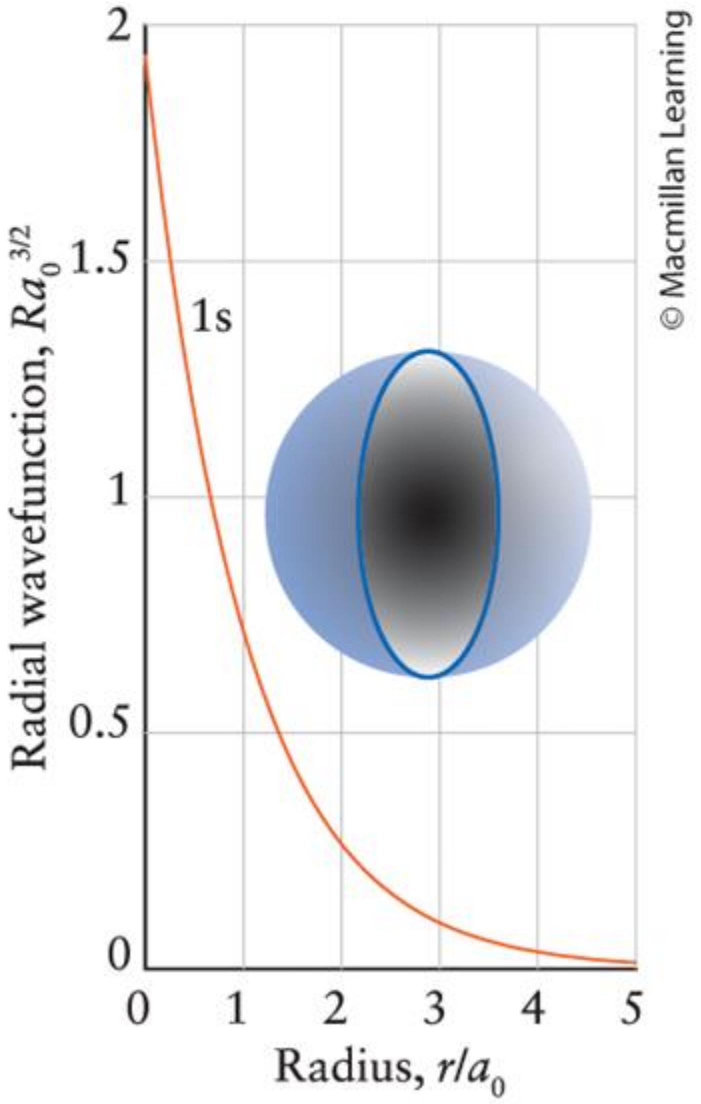


Orientation of the electrons

- The magnetic quantum number describes the orientation of orbitals within a subshell
- It can take values from –l to +l, including 0
- For a **s** subshell, **l=0 and m_l=0**; this means that there is **only one possibility** for the orbital
  - Ex: hydrogen atom: the electron cloud surrounds the nucleus in all directions



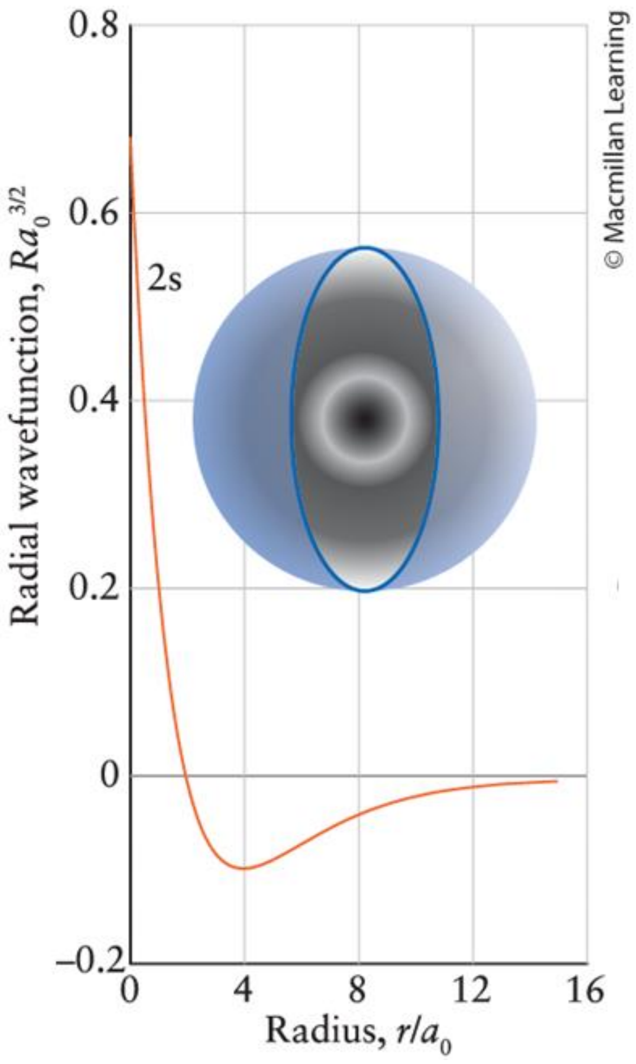
The 1s-orbital



The 1s orbital contains **zero** radial nodes.

$n = 1$
$l = 0$

The 2s-orbital

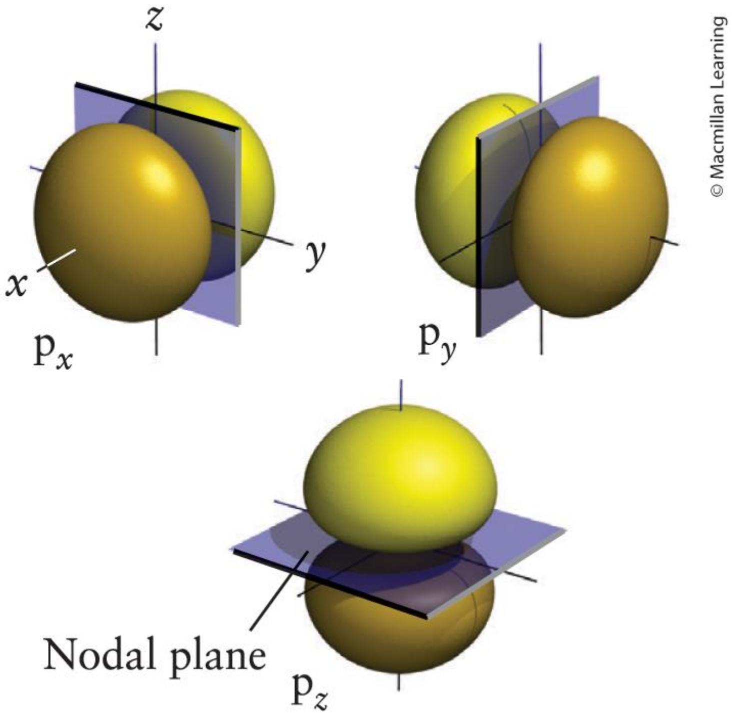


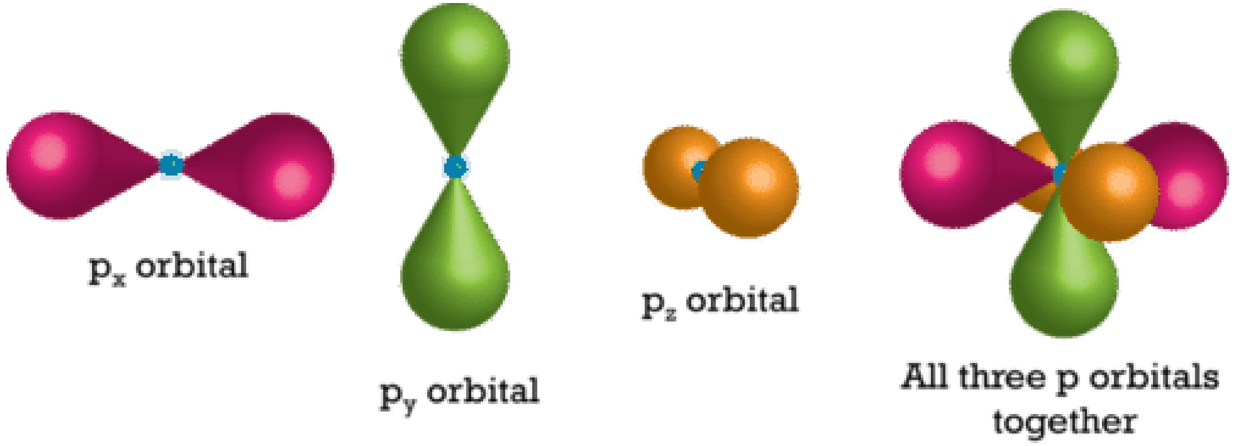
The 2s orbital contains **one** radial node.

n = 2
l = 0

Orientation of the electrons

- For a **p** subshell, **l=1, so m_l= -1, 0, +1**; these numbers represent the positions and orientation of the orbitals in 3D (along an x, y, z axis centered on the nucleus)
- The center is called node (probability to find an electron is 0) and each side is called a lobe

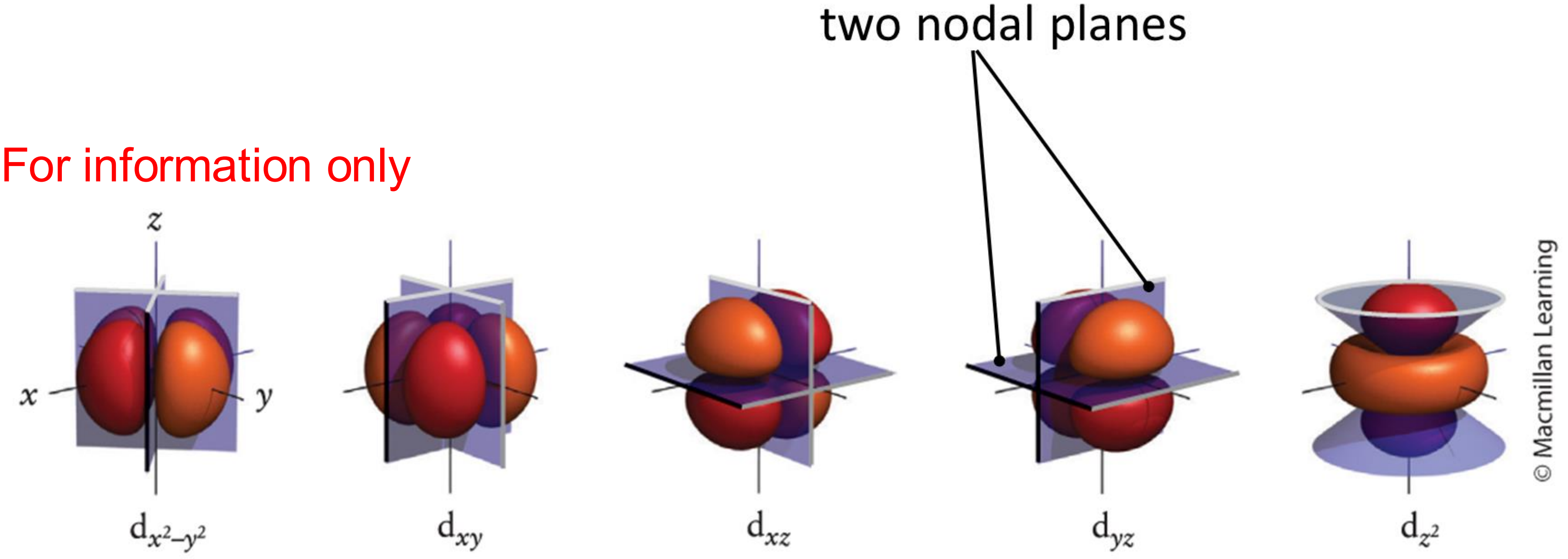




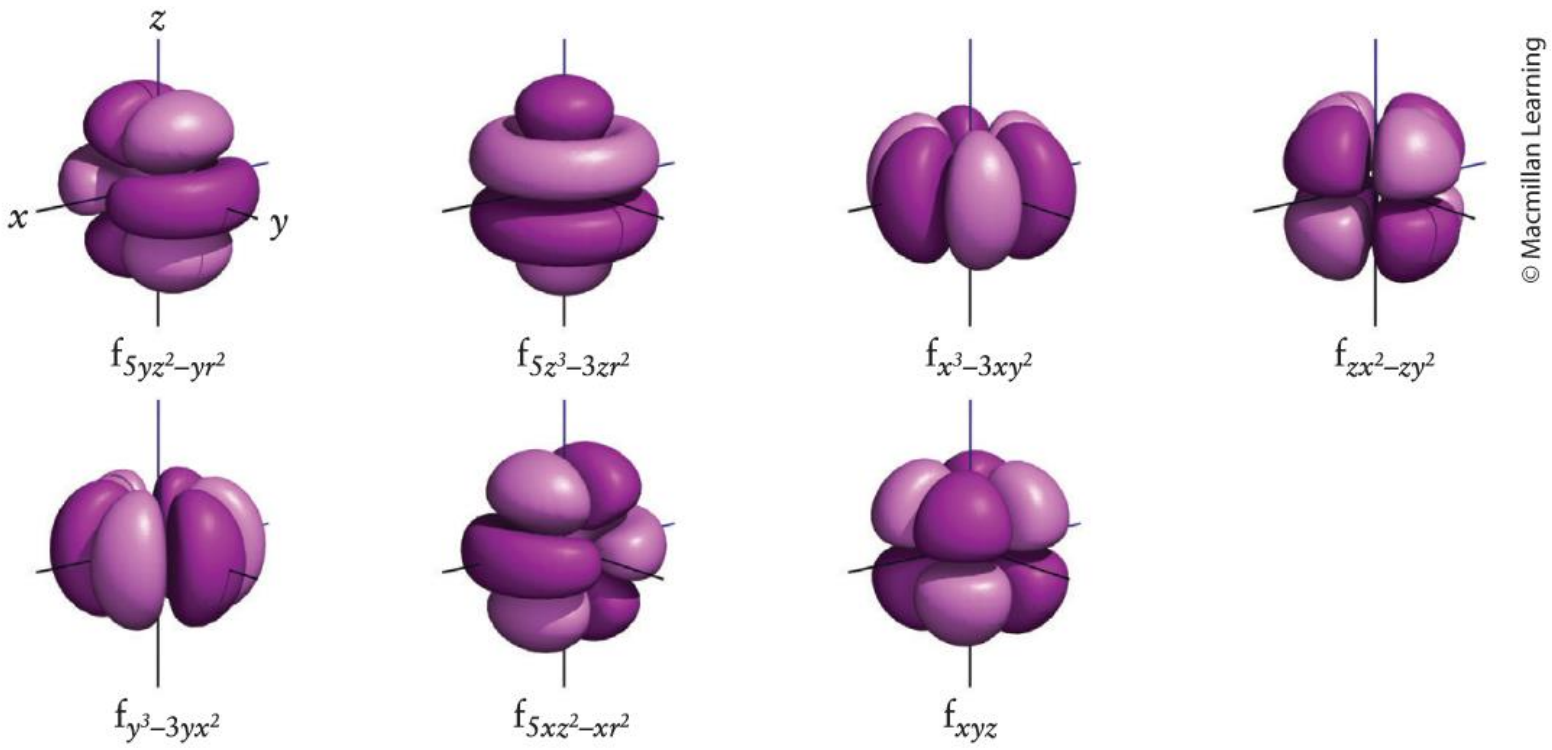
Orientation of the electrons

- For a **d** subshell, **l=2, so m_l= -2, -1, 0, +1, +2**; these numbers represent the positions and orientation of the orbitals in 3D (along an x, y, z axis centered on the nucleus)
- The center is called node (probability to find an electron is 0) and each side is called a lobe
- Higher subshells have even more complex shapes

For information only



The 7 f-orbitals



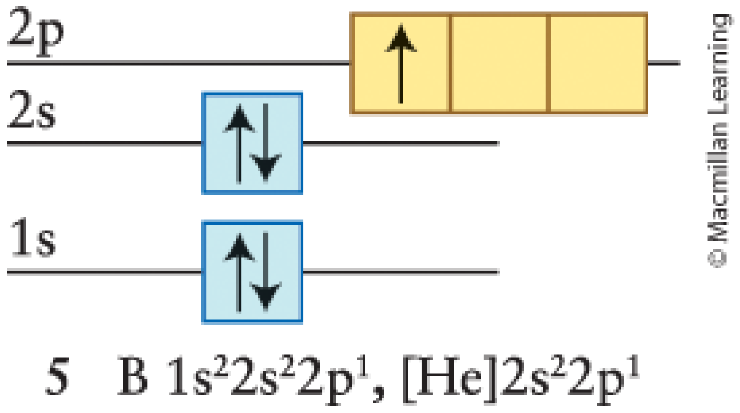
n = 4, 5, …
l = 3
m_l = +3, +2, +1, 0, −1, −2, −3

Dark and light shades denote different signs of the wavefunction.

Each contains three nodal planes.

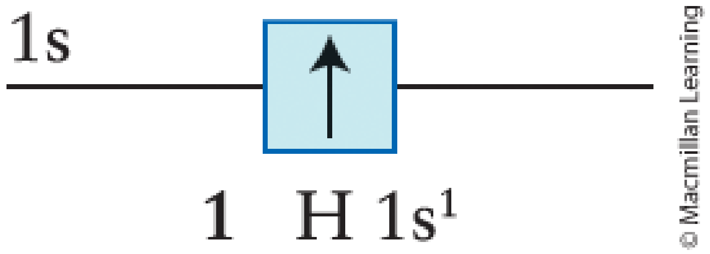
Electronic configuration of atoms

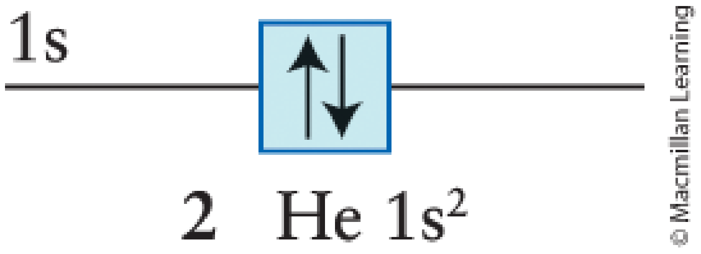
- Describes how electrons are distributed in the different orbitals
- Energy level n is described by a number
- Orbital type l is described by a letter
- Exponent is the number of electrons in a given orbital
- Can also be drawn in quantum cases



Electrons configuration and 4 quantum numbers for H and He

Electrons have two spin states: spin ↑ (up) and spin ↓ (down)





He in its ground state has a **closed shell**.

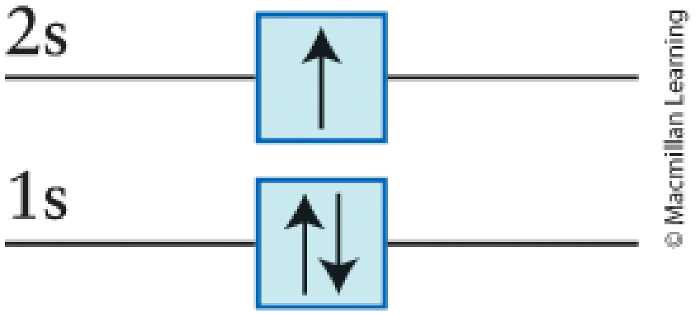
1*s* electron (n, l, m_l, m_s)

- 1, 0, 0, (+½ or −½)

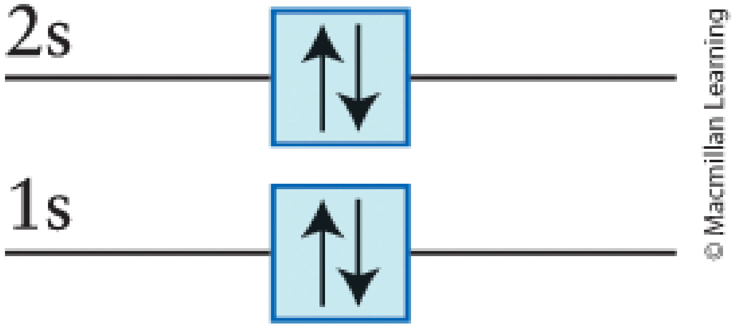
1*s* electrons (n, l, m_l, m_s)

- 1, 0, 0, +½
- 1, 0, 0, −½

Electrons configuration and noble gas electron configuration



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



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

1*s* electrons (n, l, m_l, m_s)

- 1, 0, 0, +½
- 1, 0, 0, −½

2*s* electron*

- 2, 0, 0, +½

1*s* electrons (n, l, m_l, m_s)

- 1, 0, 0, +½
- 1, 0, 0, -½

2*s* electrons

- 2, 0, 0, +½
- 2, 0, 0, −½

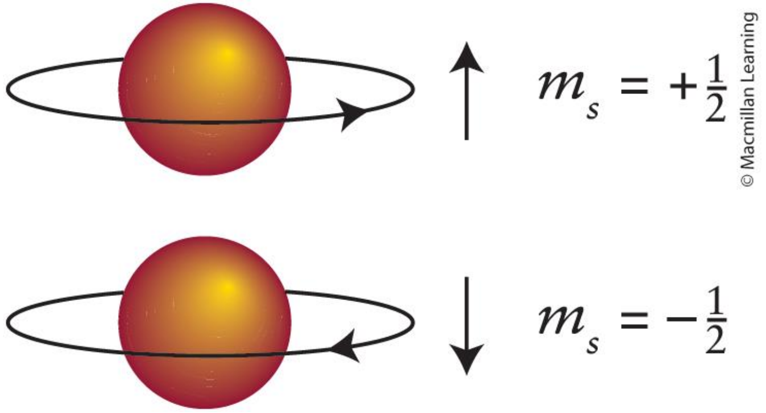
Aufbau principle: building up

Example of the carbon atom (1)

- Has 6 electrons
- The 2 first electrons fill the first shell (n=1), which has one (s) subshell, containing one spherical orbital
- Once the first shell is full, the electrons begin to fill higher energy levels
- The second shell (n=2) has 2 subshells (s and p). The s subshell has one orbital and the p subshell, 3.
- Two of the remaining electrons fill this 2s orbital. The 2 remaining electrons will begin to fill the 2p orbitals – how?

The spin (Pauli, 1925)

- The Pauli exclusion principle: **no two electrons in an atom can have the same quantum numbers**
  - In a 2px orbital:
    - n =2
    - l =1
    - m_l = -1
    - But it can hold 2 electrons… there is a fourth quantum number



- The Spin quantum number is denoted by m_s
- In any orbital, 2 electrons must have opposite spins, that means that the two electrons in the same orbital will differ only in their spin
- Spin quantum number (m_s) of +1/2 or -1/2

Electronic configuration of atoms (rules)

- Electrons are spread into shells (n=1,2,3,…) and subshells (s,p,d,…)
- They have to be filled starting from low to high energy (Aufbau principle)

  1s < 2s < 2p < 3s < 3p < 4s < 3d <…
- Pauli exclusion rule: in an atom, there cannot be two electrons defined by the same 4 quantum numbers
- Hund rule: the most stable arrangement corresponds to the maximum of parallel spins

Example of the carbon atom (2)

- Hund's rule: **each of the three p-orbitals gets one electron before any orbital gets a second**
- **Electrons in singly occupied orbitals always have the same spin** (either all up or down). This reduces electron-electron repulsion and makes the atom more stable

Example of the oxygen atom

- Has 8 electrons

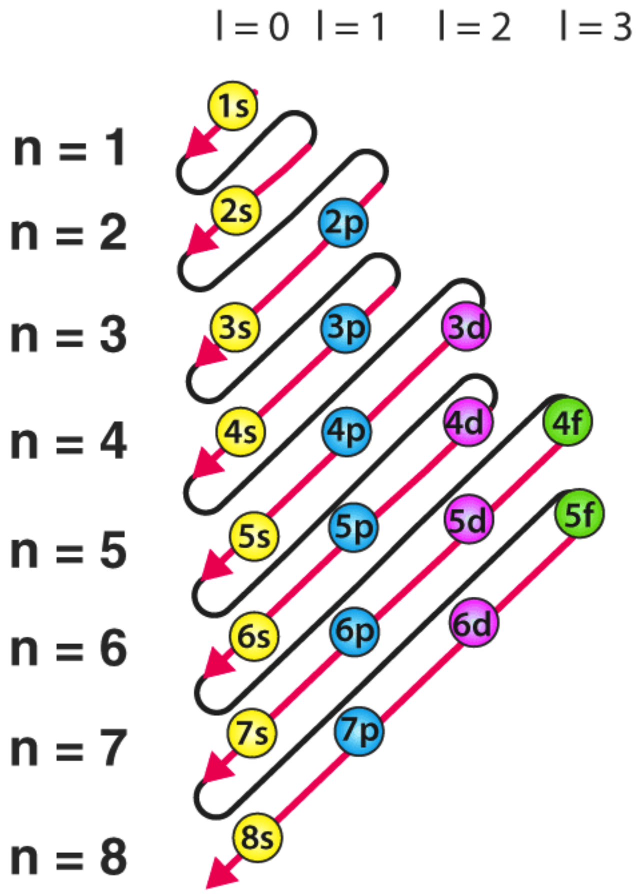
Example of the potassium atom

- Has 19 electrons

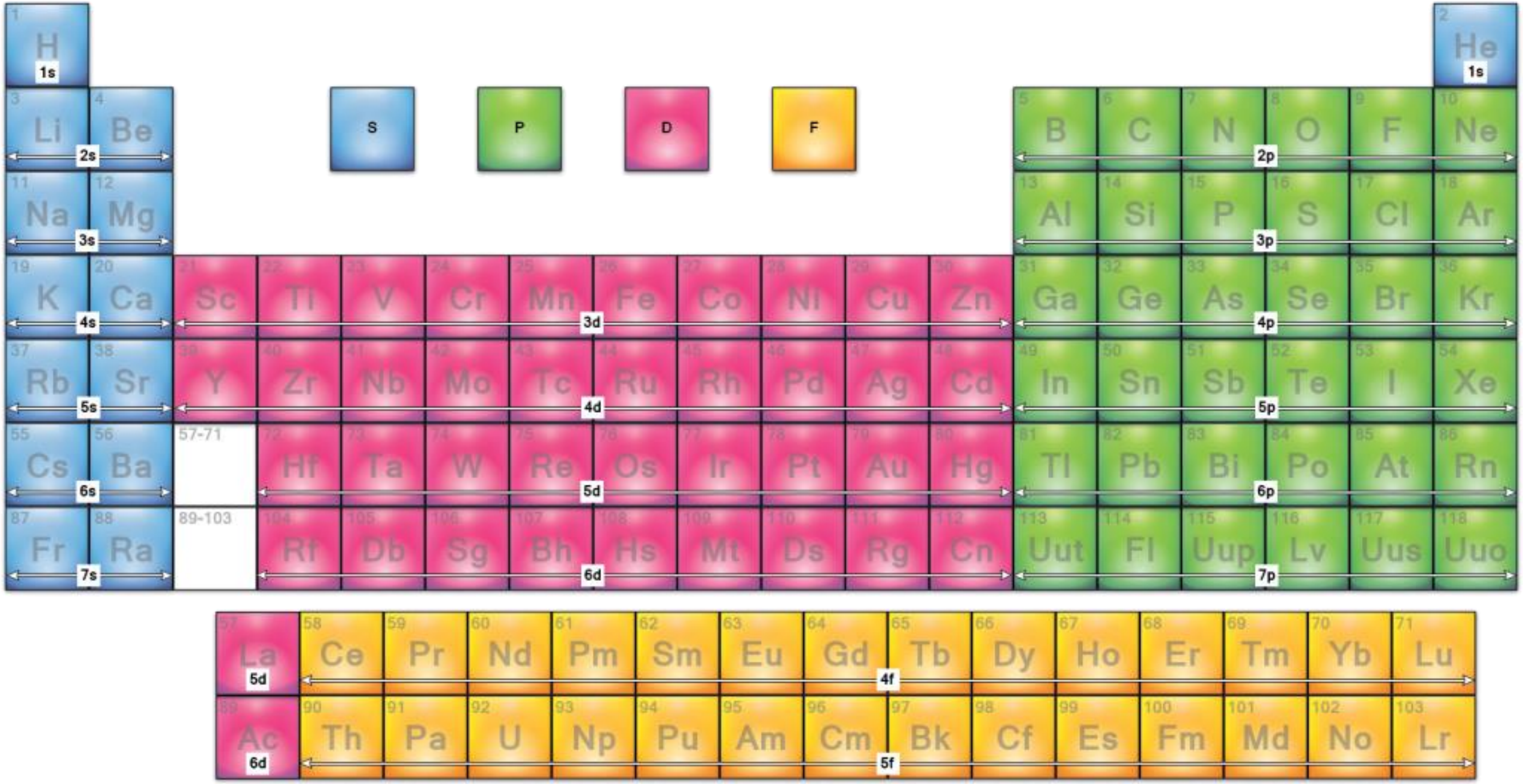
Madelung's rule and Aufbau principle

- Electrons are spread into shells (n=1,2,3,…) and subshells (s,p,d,…)
- They have to be filled starting from low to high energy (Aufbau principle)

  1s < 2s < 2p < 3s < 3p < 4s < 3d <…
- Electrons fill orbitals in order of increasing **n+l** value
  - 1s orbital 1+0=1
  - 2s orbital 2+0=2
  - 2p orbital 2+1=3
  - 3s, 3p, 3d; 3, 4 and 5 respectively
  - What is the n+l value of a 4s orbital? 4+0 = 4, which is lower than 3d
- The electrons start filling the fourth shell before the third shell is fully occupied

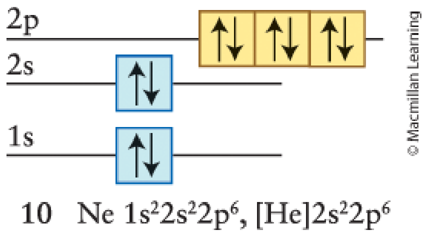


Periodic table and orbitals

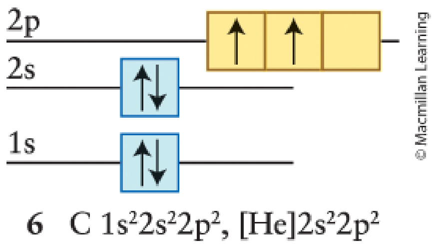


Valence electrons and filled shells

- Stability (meaning non-reactive or low energy) is based on filled shells. In other words, atoms tend to stop reacting once they get a filled shell = Noble Gas Electron Configuration

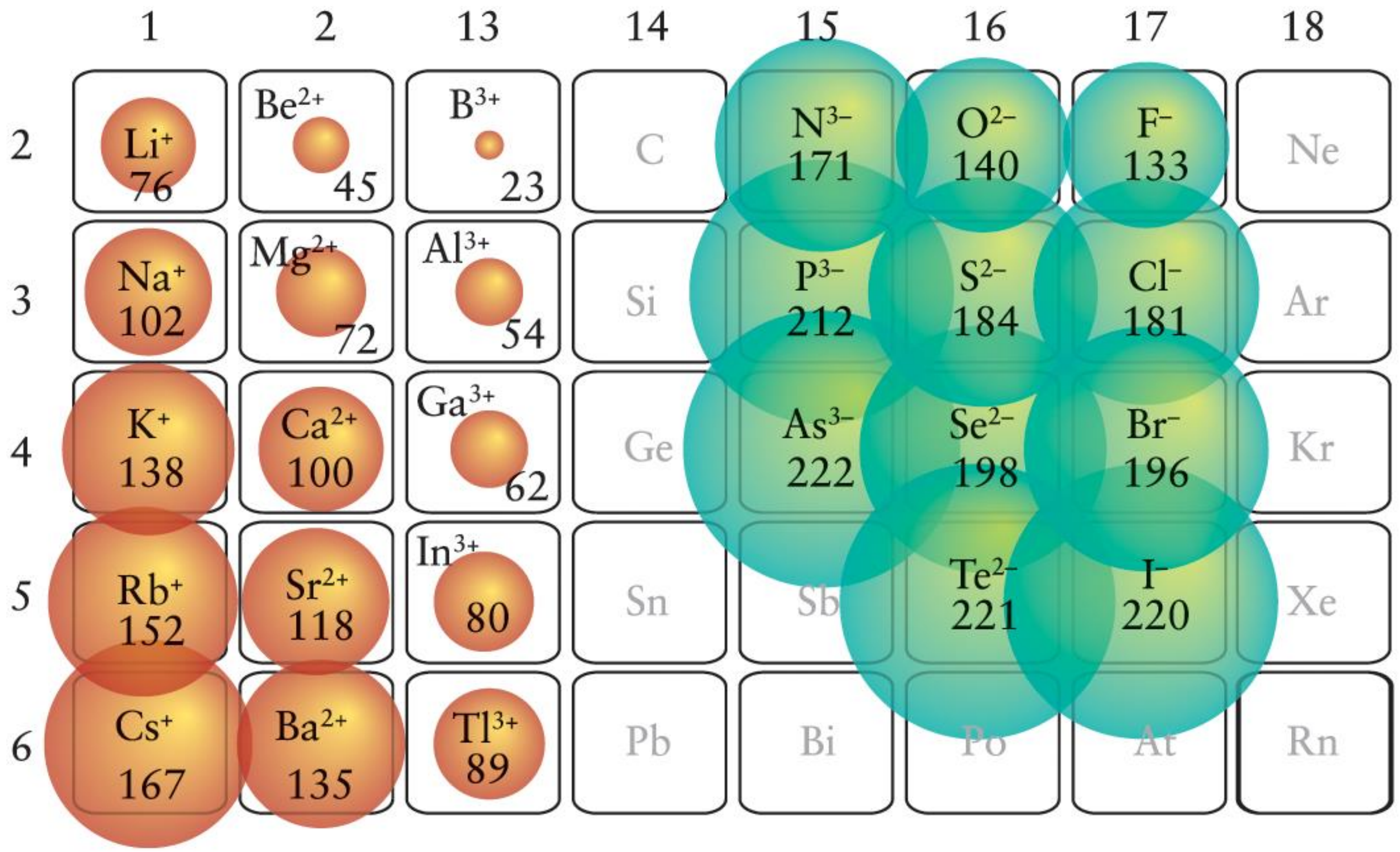


- Valence electrons occupy the external shell (highest n)
- They determine the chemical reactivity of the atom



Valence electrons and filled shells

All atoms want a filled shell (noble gases (group 14) electron configuration). They gain and lose electrons to do so.



Summary: Solving Schrödinger's equation

- Solving Schrödinger's equation give orbitals defined by 3 integers $\Psi(n, l, m_l)$ called quantum numbers
- To fully define an electron in an orbital, we need an additional quantum number, the spin (m_s)
- This qualitative description is sufficient to explain the electronic configuration and the chemical reactivity of most elements

Summary: Electron quantum numbers in atoms

Three quantum numbers are needed to specify each wavefunction: n, l, and m_l.

Name	Symbol	Values	Specifies	Indicates
principal	n	1, 2, . . .	shell	size
orbital angular momentum*	l	0,1, . . . , n – 1	subshell: l = 0, 1, 2, 3, 4, . . . s, p, d, f, g, . . .	shape
magnetic	m_l	l, l – 1, . . . , – l	orbitals of subshell	orientation
spin magnetic	m_s	+½, –½	spin state	spin direction

* Also called the azimuthal quantum number.

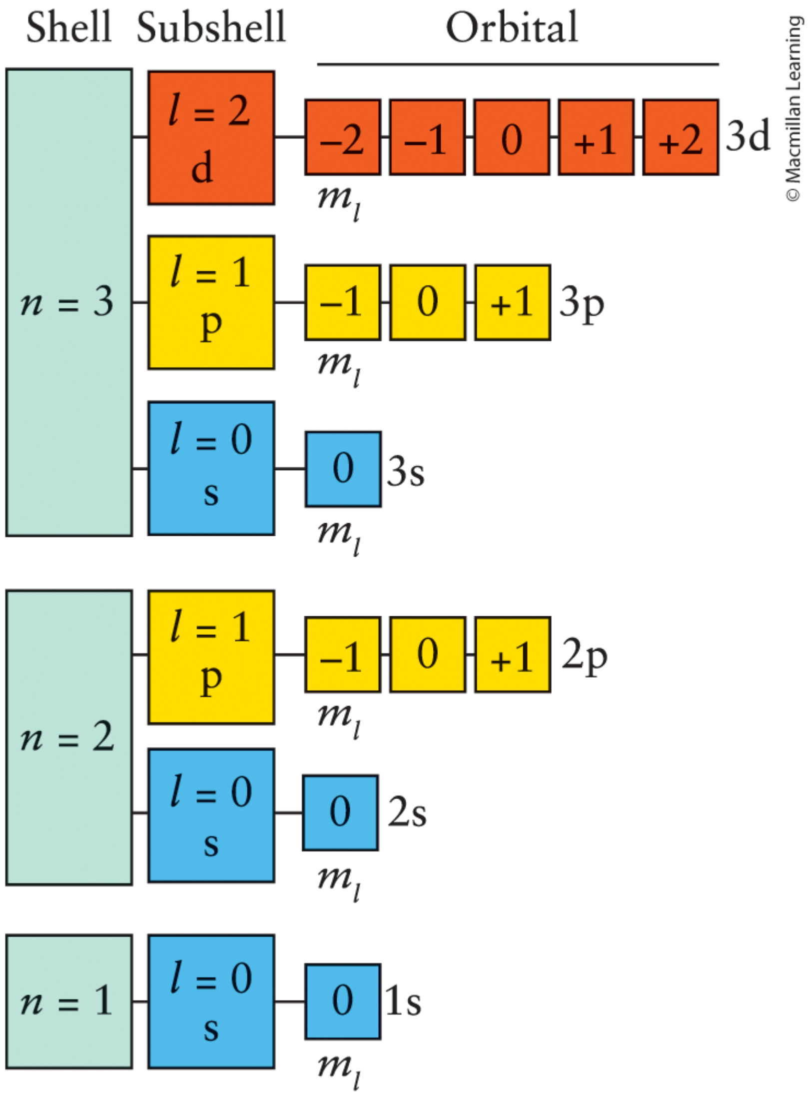
Pauli exclusion principle:
No two electrons in the same atom have the same four quantum numbers.

Summary: Allowable combinations of quantum numbers

$n = 1, 2, \ldots$

$l = 0, 1, 2, 3, 4, \ldots (n - 1)$
s, p, d, f, ….

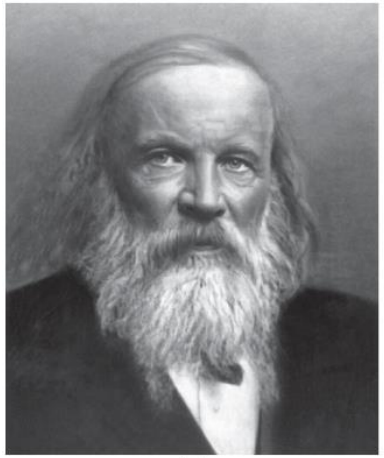
$m_l = l, (l - 1), \ldots, -l$



Quantum model of the atom

- Describes electrons in an atom
- Explains chemical bonding between atoms (next week!)

Development of the periodic table



(a)

Dmitri
Mendeleev

(b)

Lothar
Meyer

(a): RIA Novosti/Science Source. (b): Smithsonian Institution Libraries/Science Source.

Observed the **periodic** nature of elements, then arranged elements in order of increasing **atomic mass.**

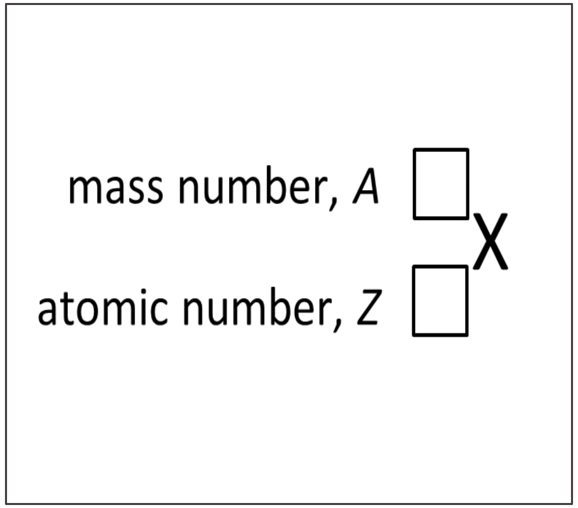
They were able to accurately **predict** properties of undiscovered elements.

The nuclear model (reminder)

- The nucleus contains positively charged **protons**, neutral **neutrons** and is surrounded by negatively charged **electrons**

Particle	Symbol	Charge	Mass/kg
electron	e^-	−1	9.109×10^{-31}
proton	p	+1	1.673×10^{-27}
neutron	n	0	1.675×10^{-27}

- The **negative** charge of the electron cancels the **positive** charge of the proton (the atom is electrically neutral)
- The **atomic number Z** of an element represents the number of **protons** in the nucleus of one atom of this element
- The **mass number A** represents the number of **protons and neutrons** in a nucleus

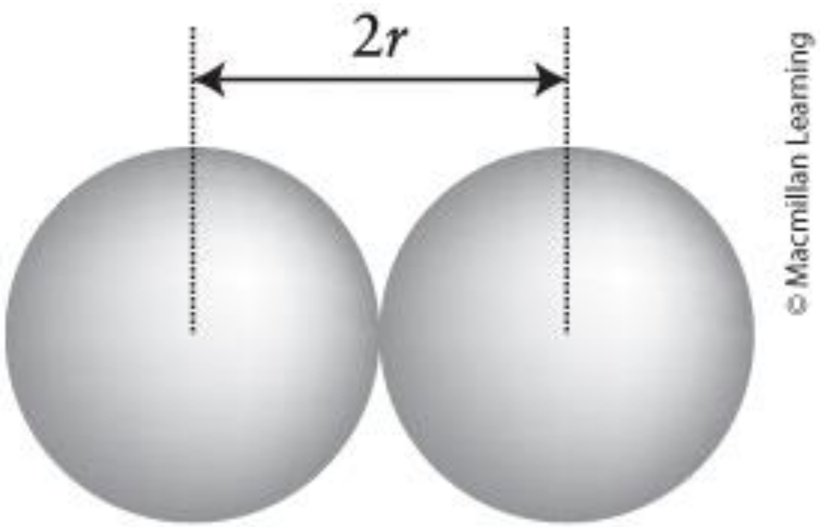


Periodic trends

- **Atomic radius**
- Ionisation energy and electronic affinity
- Electronegativity

Atomic radius

- Half-distance between neighbouring atoms (experimental using X-ray, diffraction)

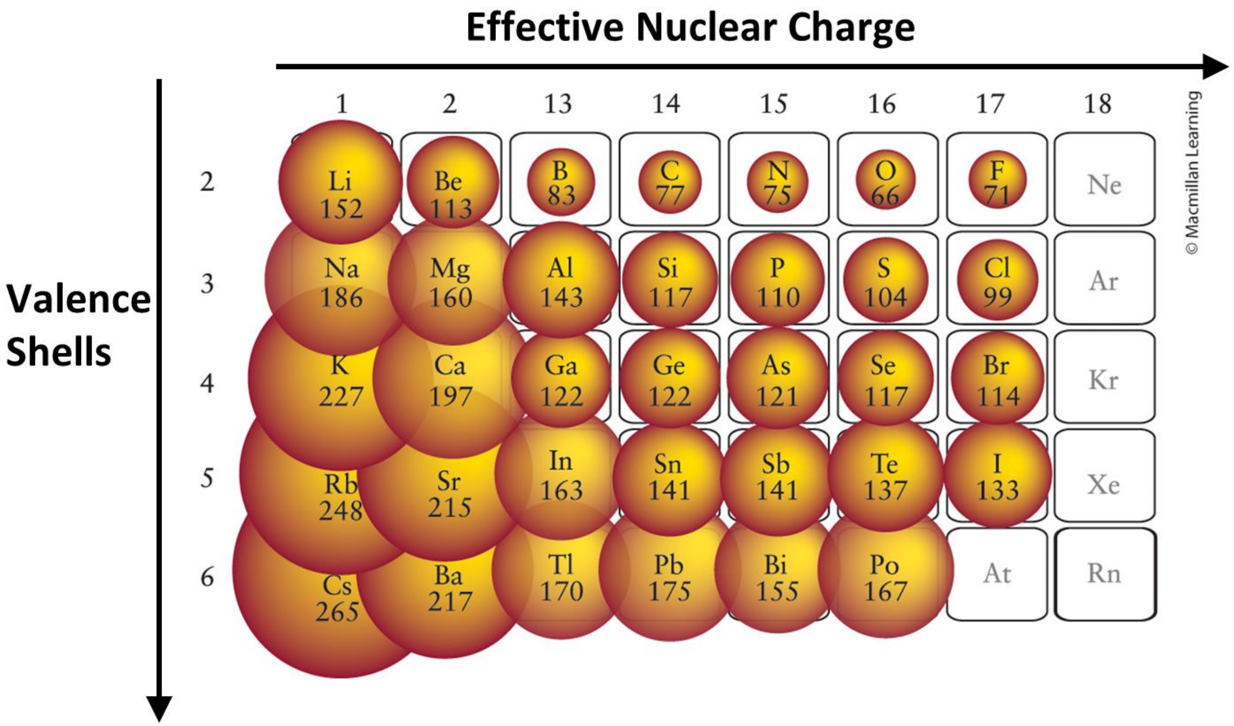


1 Atomic radius

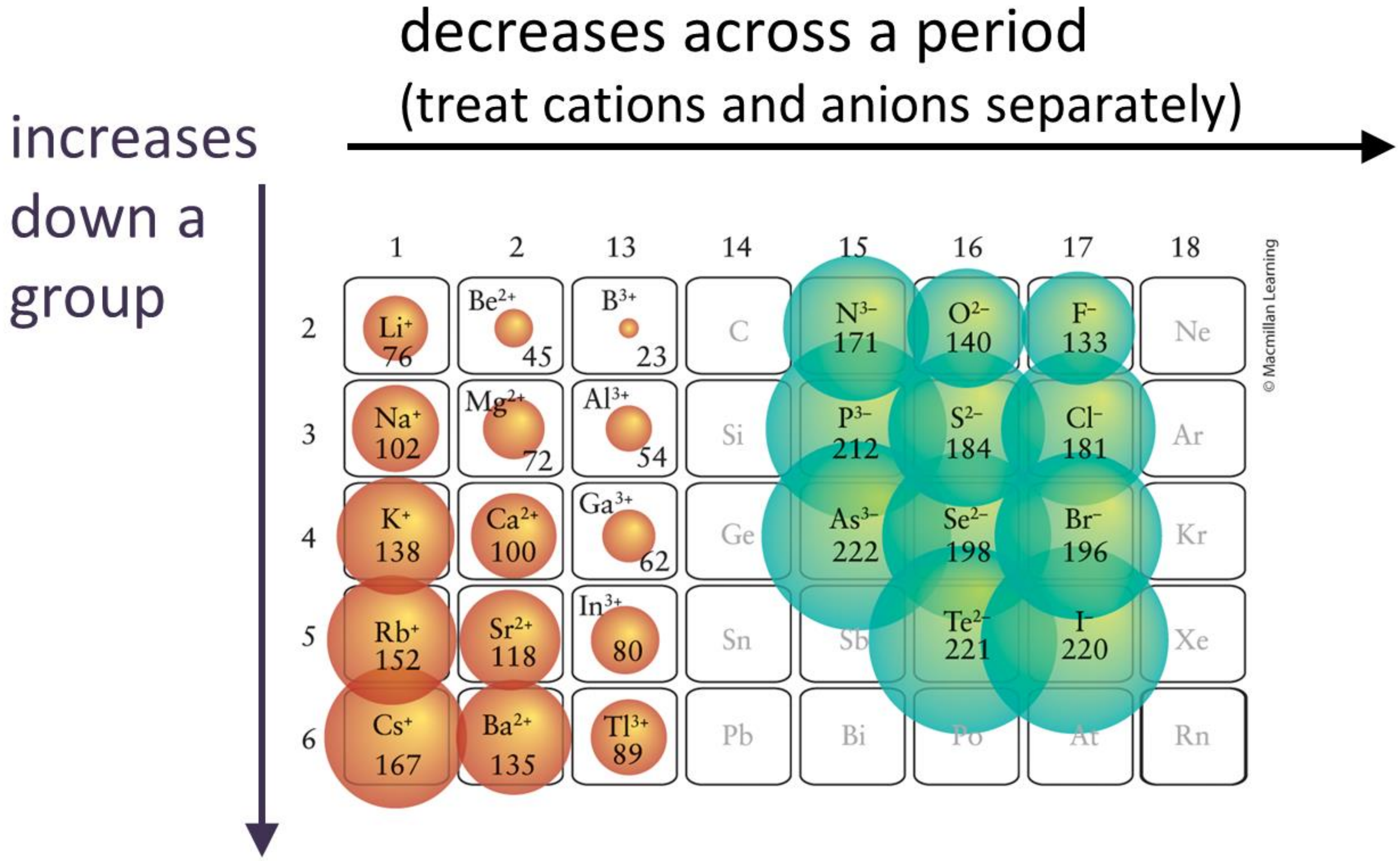
Atomic radius

- Adding more **shells increases** the distance from the electrons to the nucleus; it also **decrease** the effect the nucleus has on the outer electrons.

- The **effective nuclear charge** on valence electrons increases across a period as there are more protons that pull the electrons inward. Result: Atomic radius decreases across a period.



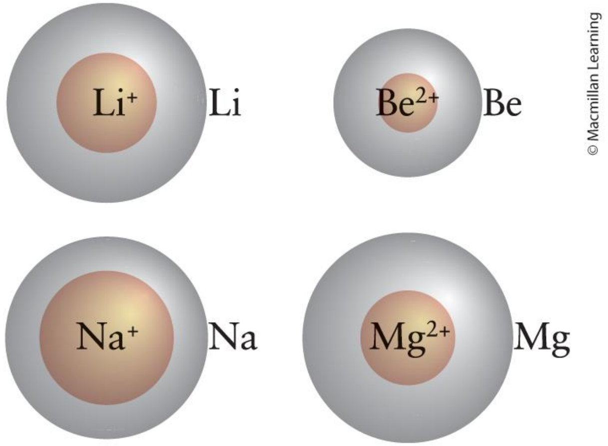
What about ions?



Ionic radius explained

atom → cation

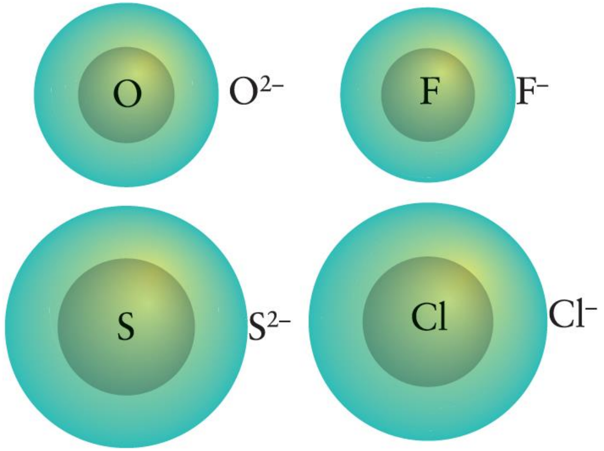
radius decreases



Removing electrons:
- Loss of a shell
- Higher "+Z" in nucleus draws e^- in.

atom → anion

radius increases



More electrons weakens +Z nuclear electrostatic attraction and at the same time an increase in e^- to e^- repulsions.

Periodic trends

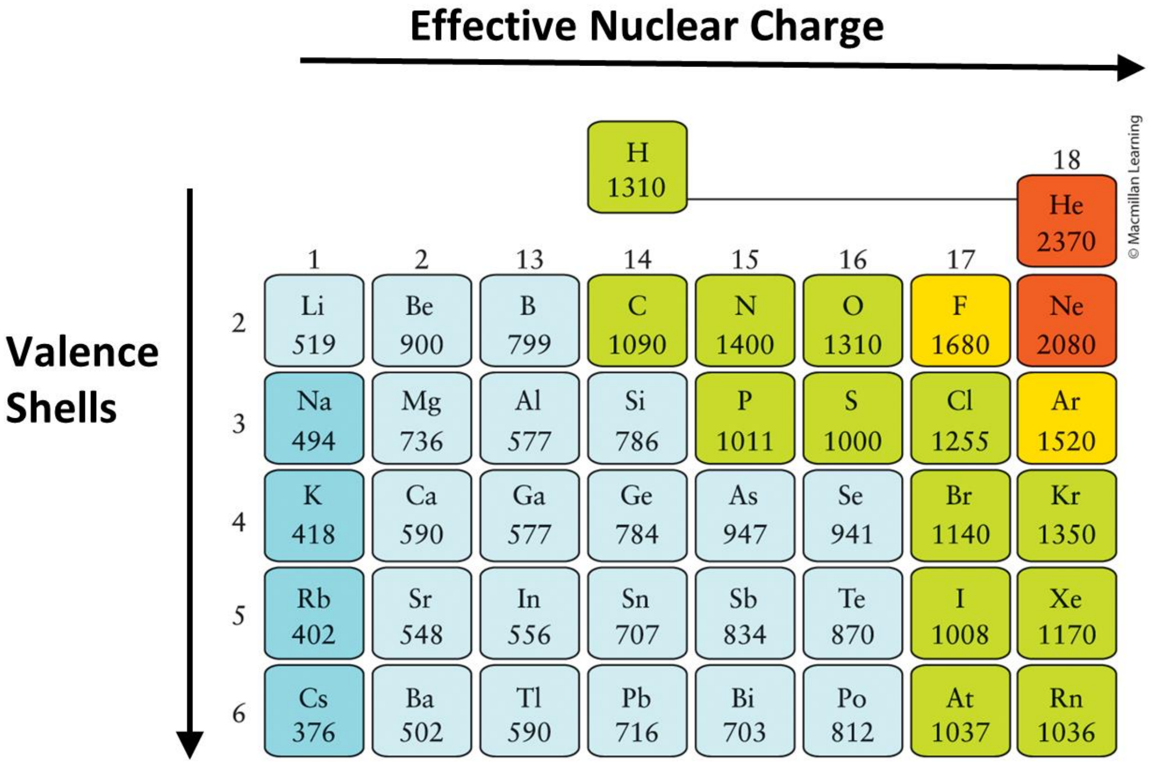
- Atomic radius
- **Ionisation energy and electronic affinity**
- Electronegativity

Ionization energy (IE)

Minimum energy needed to remove an electron from an atom.

- Decreases from the top to the bottom of a group: It becomes easier and easier to remove electrons as shells are added.

- Increases along a period

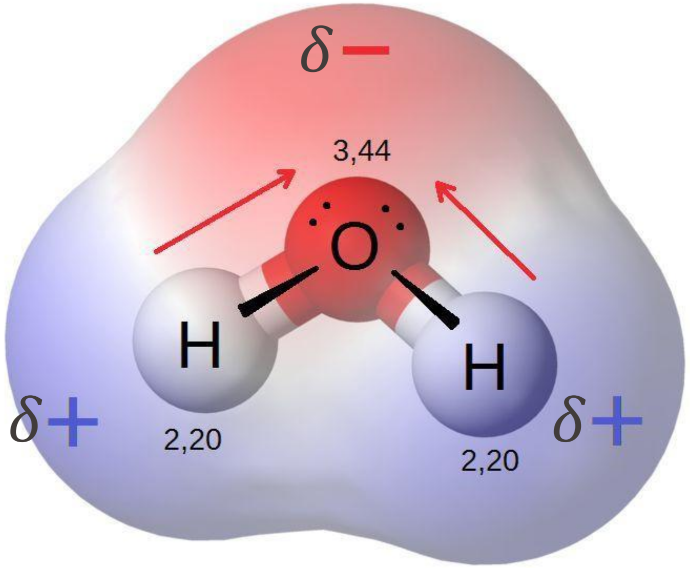


Periodic trends

- Atomic radius
- Ionisation energy and electronic affinity
- **Electronegativity**

Electronegativity

- Power of an atom to **attract electrons** when it is engaged in a chemical bond
- Arbitrary scale proposed by **Pauling** (0-4)
- 2 atoms with the **same** electronegativity share electrons equally
- If electronegativity is **different**, the electrons are localized on the most electronegative atom



Electronegativity

Electronegativity of the Elements

1 H 2.20																	2 He no data
3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98	10 Ne no data
11 Na 0.93	12 Mg 1.31											13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16	18 Ar no data
19 K 0.82	20 Ca 1.00	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.88	28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96	36 Kr 3.00
37 Rb 0.82	38 Sr 0.95	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.16	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66	54 Xe 2.6
55 Cs 0.79	56 Ba 0.89	57-71	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Tl 1.62	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2	86 Rn no data
87 Fr 0.7	88 Ra 0.89	89-103	104 Rf no data	105 Db no data	106 Sg no data	107 Bh no data	108 Hs no data	109 Mt no data	110 Ds no data	111 Rg no data	112 Cn no data	113 Nh no data	114 Fl no data	115 Mc no data	116 Lv no data	117 Ts no data	118 Og no data

Low — High

57 La 1.10	58 Ce 1.12	59 Pr 1.13	60 Nd 1.14	61 Pm 1.13	62 Sm 1.17	63 Eu 1.2	64 Gd 1.2	65 Tb 1.22	66 Dy 1.23	67 Ho 1.24	68 Er 1.24	69 Tm 1.25	70 Yb 1.1	71 Lu 1.27
89 Ac 1.1	90 Th 1.3	91 Pa 1.5	92 U 1.38	93 Np 1.36	94 Pu 1.28	95 Am 1.3	96 Cm 1.3	97 Bk 1.3	98 Cf 1.3	99 Es 1.3	100 Fm 1.3	101 Md 1.3	102 No 1.3	103 Lr no data

Periodic trends

Isolated Atom	Molecule	Metal?	Redox?
Low ionisation energy	Low electronegativity	High metallic character	Strong reducing power (tendency to give electrons)
High ionisation energy	High electronegativity	Non-metallic character	Strong oxidizing power (tendency to take electrons)

Homework

- Check next week’s videos

EPFL

Have a beautiful day !

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RESPECT