

CH158 A2: Professor Peter Sadler : Atoms and orbitals

Please use textbooks to supplement the notes below.

Recommended reading: Housecroft & Constable 'Chemistry', 3rd Ed. 200
Chapter 3 (Atoms and atomic structure), pages 79-117

Revision 1

SI Units

metre (m) - distance

kilogram (kg) - mass

second (s) - time

kelvin (K) - temperature

Ampere (A) - current

mole (mol) - amount of substance

"The **mole** is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12"

Avogadro's Number = the number of atoms or molecules per mole of a substance

= $6.022\ 141\ 99 \times 10^{23}$

(Italian chemist and physicist Amadeo Avogadro, 1776-1856)

Multipliers

kilo (k) = 10^3 ; mega (M) = 10^6 ; giga (G) = 10^9 ; tera (T) = 10^{12}

deci (d) = 10^{-1} ; centi (c) = 10^{-2} ; milli (m) = 10^{-3} (one thousandth) ;

micro (μ) = 10^{-6} (one millionth) ; nano (n) = 10^{-9} ; pico (p) = 10^{-12} ; femto (f) = 10^{-15} ;

atto (a) = 10^{-18}

Angstrom (\AA) = a metric unit of length = 0.1 nanometre (0.1 nm) or 10^{-10} metre

Atom = particle indivisible during chemical reactions

Element = atoms of the same atomic number

Atom = **nucleus** (positive charge) + **electrons** (negative charge)

Atomic number = number of **protons** in the nucleus = number of electrons (atoms are neutral - no overall charge)

Electrons have an *electric charge* of -1.6022×10^{-19} coulomb,

a *mass* of 9.11×10^{-31} kg

Proton = nuclear particle with positive charge equal to that of electron

$+1.6022 \times 10^{-19}$ coulomb

mass 1.6726×10^{-27} kg

Mass of proton is about 1836x that of electron

diameter of about 1.5×10^{-15} m (1.5 fm)

Neutron = particle in nucleus, about same mass as proton but no charge

1.6749×10^{-27} kg (slightly more than a proton)

A neutron consists of two down quarks and one up quark.

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Mass number = total number of protons and neutrons in the nucleus

Protons are spin-1/2 fermions and are composed of three quarks, making them baryons. The two up quarks and one down quark of the proton are also held together by the strong nuclear force, mediated by gluons.

Protons and neutrons are both nucleons, which may be bound by the nuclear force into atomic nuclei.

Nuclide = particular nucleus characterised by atomic number and mass number

Superscript = mass number; subscript = atomic number

e.g. ${}^6_6\text{C}$ an **isotope** of carbon with 6 protons and 6 neutrons in the nucleus

Isotope = atoms with same atomic number but different mass numbers

(same number of protons, same number of electrons, but different number of neutrons)

There are 2 naturally occurring **isotopes of hydrogen**:

${}^1_1\text{H}$ Protium 99.985% ${}^2_1\text{H}$ Deuterium 0.015%

The third known isotope of hydrogen is ${}^3_1\text{H}$ Tritium (radioactive, β^- emitter, half-life 12 years)

1903 Dalton : atomic weight

Atomic weight = average atomic mass for naturally occurring element, in atomic mass units

One atomic mass unit (amu) = exactly $1/12^{\text{th}}$ of the mass of ${}^{12}_6\text{C}$ (arbitrarily assigned a mass of exactly 12 amu)

Calculation of atomic weight

Multiply each isotopic mass by fractional abundance and sum values

e.g. atomic weight of hydrogen = $0.99985 \times 1.007825 + 0.00015 \times 2.0140 = 1.007976$

Periodic table = arrangement of elements by order of atomic number

1869 Mendeleev: arrangement of elements by mass

Period = elements in a horizontal row

Group = elements in one column (18 groups)

Group 1 (IA) = alkali metals

Group 2 (IIA) = alkaline earth metals

Groups 3-12 contain the transition elements and the lanthanide elements

Group 17 (VIIA) = halogens

Group 18 (VIIIA) = inert gases

Groups of the periodic table

Numbered 1 to 18 from left to right

Elements in the same group usually have similar chemical properties, e.g.

- group 1 alkali metals : form +1 ions (cations)

- group 2 alkaline earth metals : form +2 ions (cations)

- groups 4 -11 transitions metals : form coloured compounds, undergo redox reactions

- group 17 halogens : form -1 ions (anions)

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1900 Max Planck : electromagnetic radiation (light) is quantised

- radiation emitted or absorbed in discrete amounts

$$E = h\nu$$

E = energy, ν = frequency

h = Planck's constant (6.626×10^{-34} J s)

Frequency and wavelength of electromagnetic radiation related by

$$c = \lambda \nu$$

c = speed of light (3×10^8 m/s; 670,616,629.2 miles per hour)

1901 Photoelectric effect

- light exhibits characteristics of waves and particles at different times

When a metallic surface is exposed to electromagnetic radiation above a threshold frequency

(which is specific to the surface of the material), the photons are absorbed and current is produced

1905 Albert Einstein's mathematical description in 1905 of how the photoelectric effect was caused by absorption of quanta of light (now called photons)

1909 Geiger-Marsden Rutherford experiment : gold foil experiment

- some alpha particles (He^{2+} , helium nuclei) deflected through angles much larger than 90° ; some scattered back toward the source

- Rutherford concluded that atoms contain a very small (compared with size of the atom) positive charge, which can repel alpha particles if comes close enough

1911 Rutherford model of atom

Electrons move in circular orbits around positively-charged nucleus

- classical picture, electrons obey Newton's Laws of motion, electrons would plunge into nucleus, orbits could not be maintained

- difficult to solve equations for many electrons, cannot explain some spectroscopic observations

Wave mechanical (quantum mechanical) model of an atom

1913 Bohr's quantized model of atom

For H, electron moves round nucleus in orbit of discrete energy

- other orbits possible with discrete energies

1924 de Broglie: matter can show characteristics of waves

de Broglie relation: λ (wavelength) = h (constant) / [m (mass) x v (velocity)]

Electrons move fast and have associated wavelengths of about 1 pm - electrons can be diffracted by crystals

A ball travelling at 60 miles per hour (27 m per second) has an associated wavelength of 10^{-34} cm!! - not detectable

Light can show characteristics of particles (photons): E (energy) = h (constant) x ν (frequency)

1926 Schrödinger wave equation

$$H\psi = E\psi$$

H = Hamiltonian operator

Ψ = wave function – an eigenfunction

Describes behaviour of electron in region of space of atom = atomic orbital (defined by 3 quantum numbers n , l and m_l)

E = energy – an eigenvalue

Operator working on a function = (scalar quantity) \times (original function)

We describe electrons by *wave functions* : square of the wave functions tells us the probability of finding the electron at a point in space

$$\Psi = \Psi_{\text{radial}} \times \Psi_{\text{angular}} = R \times A$$

Ψ_{radial} is dependent on n and l : gives distance information

Radial distribution function = $4\pi r^2 R(r)^2$

Gives probability of finding electron in spherical shell of radius r and thickness dr (radius measured from nucleus)

$R(r)$ means that R is a function of r (the radius, distance of the electron from the nucleus)

Note that wavefunction R can have positive and negative values, but R^2 only positive values

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1927 Heisenberg's uncertainty principle : product of uncertainty in position and uncertainty in momentum (mass x velocity) of a particle can be no smaller than Planck's constant divided by 4π
 $(\Delta x)(\Delta p) \geq h/4\pi$

The more precisely you know the position, the less precisely you know the momentum

Electron has wave-like properties, cannot know exactly position and momentum at same time

Hence talk of *probability* of finding electron at point in space: determined from ψ^2
 (square of wave function)

Atomic line spectra

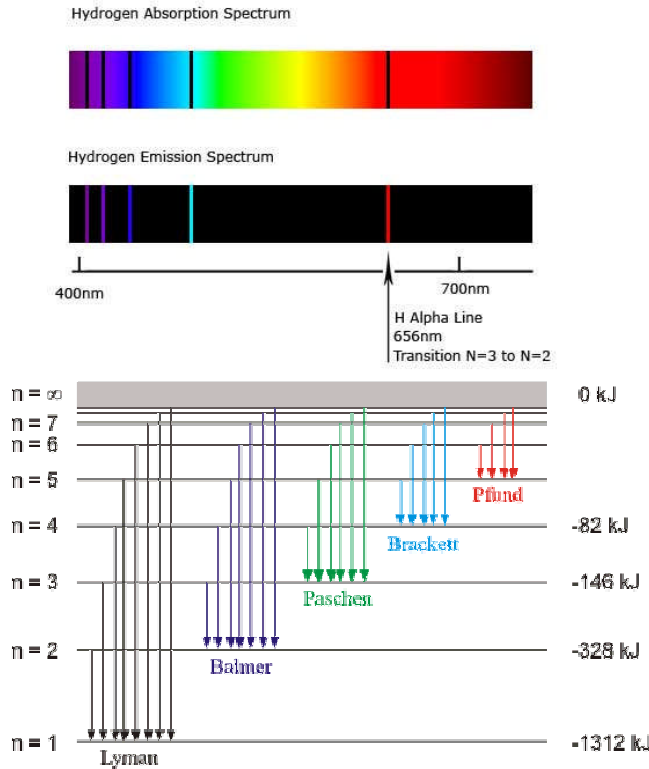
When atoms are *excited* (given energy, e.g. by heat or electrical discharge) they emit light.

The light emitted has specific wavelengths (not all wavelengths).

This suggests that electrons have specific energy levels - they can be excited to higher energy levels (less strongly bound) and then emit light as they lose energy and drop down to a lower energy level. Energy is emitted in discrete packets (quanta); the energy is *quantized*.

Emission spectrum of hydrogen

Electric current passed through glass tube containing hydrogen gas at low pressure: tube gives off blue light. Light is passed through a prism narrow bands of bright light are observed against a black background.



Absorption and emission spectra

Ground state – electrons in lowest energy arrangement

Absorption of electromagnetic radiation – electrons promoted to an excited state (higher energy state)- **absorption spectrum**

In terms of frequency ($E = h\nu$): $\nu_2 \leftarrow \nu_1$

Excited state is transient – electron falls back to ground state producing an **emission spectrum**

$\nu_2 \rightarrow \nu_1$

Selection rules

Principal quantum number

$\Delta n = 0, \pm 1, \pm 2, \pm 3, \pm 4, \dots$

Orbital quantum number

$\Delta l = +1$ or -1 (Laporte selection rule; change in angular momentum by one unit)

Lyman series: ultraviolet region

$n' \rightarrow 1, 3 \rightarrow 1, 4 \rightarrow 1$)

Balmer series: visible region

$(3 \rightarrow 2, 4 \rightarrow 2, 5 \rightarrow 2)$

Paschen (IR), Brackett (far IR), Pfund (far IR)

Rydberg equation

Frequencies of lines in Lyman, Balmer, Paschen and other series

For $n' \rightarrow n$ transition where $n' > n$

$\nu = R (1/n^2 - 1/n'^2)$

ν = frequency in Hz (s^{-1})

R = Rydberg constant for hydrogen = 3.289×10^{15} Hz

Note use of wavenumbers = reciprocal of wavelength ($\bar{\nu} = 1/\lambda$)

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Quantum numbers

Every electron has a unique set of 3 **quantum numbers** which characterise the atomic orbital and a 4th quantum number related to the magnetism of the electron (spin)

Principal quantum number : $n = 1, 2, 3, \dots$

Describes the *energy* of the electron; orbitals with same n value belong to same **shell**

Orbital (angular momentum) quantum number : $l = 0$ to $n-1$

(determines the *shape* of the orbital; also called azimuthal quantum number)

$l = 0$: s orbital

$l = 1$: p orbital

$l = 2$: d orbital

$l = 3$: f orbital

Magnetic quantum number : m_l : $-l$ to $+l$

Describes the *orientation* of the orbital in space

e.g. $l = 1$, $m_l = -1, 0, +1$

-these orbitals have the same shape but different orientations in space

Spin quantum number : m_s

- can have two possible values $+1/2$ and $-1/2$ (like a little bar magnet - can align for or against a magnetic field), sometimes indicated by an up arrow (\uparrow) and a down arrow (\downarrow)

Each orbital can hold two electrons with opposite spins ($\uparrow\downarrow$)

Atomic orbitals

Picture of the region of space in which there is a high probability of finding the electron

Atomic orbitals have definite shapes

1s orbital

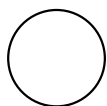
Radial part $R(r) = 2e^{-r}$

Angular part $A(\theta, \phi) = 1/2\sqrt{\pi}$

2p_x orbital

Radial part $R(r) = (1/2\sqrt{6})re^{-(r/2)}$

Angular part $A(\theta, \phi) = \sqrt{3}(\sin \theta \sin \phi)/2\sqrt{\pi}$



s



p_x

p_y

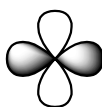
p_z



d_{xy}

d_{xz}

d_{yz}



d_{x²-y²}



d_{z²}

Note that the wavefunction has a sign: positive = shaded, negative = white

Each 2p orbital has two lobes. There is a planar node normal to the axis of the orbital (e.g. 2p_x orbital has a yz nodal plane).

Nodes

At a radial node the radial distribution function = zero.

Therefore layers of electron density like an onion.

1s orbital, no nodes; 2s orbital; 1 radial node, 3s has 2 nodes, 4s has 3 nodes.

2p, no nodes; 3p 1 node; 4p 2 nodes

3d, no nodes; 4d, 1 node; etc

Effect of electrons on each other

A 2s electron screens or shields a 2p electron from the nuclear charge

2s electrons are more penetrating than 2p electrons

Similarly 3d orbitals are higher in energy than 3p, which are higher than 3s

At Sc 3d electron becomes lower in energy than 4s and 3d shell then fills up (first transition series)

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Aufbau Principle

Aufbau is a German word meaning 'building up'

Orbitals are filled in order of energy with the lowest energy orbitals being filled up first

Hund's Rule

Electrons singly occupying orbitals in a degenerate set have the same (parallel) spins.

Pairing of electrons in an orbital cannot begin until each orbital in a set contains one electron.

Pauli Exclusion Principle

No two electrons in an atom can have exactly the same set of the four quantum numbers n , l , m_l , and m_s .

Each orbital can accommodate a maximum of two electrons with different m_s values.

Assigning quantum numbers to electrons

Carbon : 6 electrons $1s^2 2s^2 2p^2$

e.g. for the one of the 2p electrons: $n = 2$, $l = 1$, $m_l = +1$, $m_s = 1/2$

The 2nd shell can hold a total of 8 electrons (two in the 2s orbital, and three in 2p orbitals with $m_l = +1, 0$ or -1 , and 2 electrons in each with $m_s = 1/2$ or $-1/2$)

Ground state electronic configurations

The octet rule

Total number of electrons required to fill the 2s and 2p, or 3s and 3p orbitals. Very stable configuration of inert gases Ne and Ar

Attained by accepting or donating electrons (forming anions or cations), or sharing electrons (covalent bonds)

Extension is the **18-electron rule**: filling the ns , np and nd sub-shells

Usual order of atomic orbitals (lowest energy first):

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 5d \sim 4f, 6p$

Capital	Low-case	Greek Name	English
A	α	Alpha	a
B	β	Beta	b
Γ	γ	Gamma	g
Δ	δ	Delta	d
E	ϵ	Epsilon	e
Z	ζ	Zeta	z
H	η	Eta	h
Θ	θ	Theta	th
I	ι	Iota	i
K	κ	Kappa	k
Λ	λ	Lambda	l
M	μ	Mu	m
N	ν	Nu	n

Ξ	ξ	Xi	x
O	o	Omicron	o
Π	π	Pi	p
P	ρ	Rho	r
Σ	σ	Sigma	s
T	τ	Tau	t
Υ	υ	Upsilon	u
Φ	ϕ	Phi	ph
X	χ	Chi	ch
Ψ	ψ	Psi	ps
Ω	ω	Omega	o