

LEAPS Course: Atomic Structure, Chemical Bonding, Molecular Geometry

Main topics covered:

Atomic structure (what atoms are composed of and how we define their contents)

Chemical bonding (different types of bonding and the effect that has on molecular geometry and molecular interactions)

- **Atoms have internal structure. What is this?**
- We now know this internal structure is composed of a **nucleus** containing

Protons: Mass 1.673×10^{-27} kg

Charge $+1.6 \times 10^{-19}$ C

Neutrons: Mass 1.675×10^{-27} kg

Charge 0

Nuclear size $\sim 10^{-15}$ m across

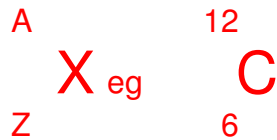
Note distance between nuclei in a molecule is $\sim 10^{-10}$ m

(Orange example)

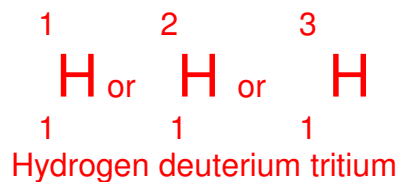
- Around nucleus are **electrons: mass $\sim 9.1 \times 10^{-31}$ kg, charge -1.6×10^{-19} C**
- Mass of electron is **2000 times less than a proton \therefore insignificant in mass terms**
- **Atoms are neutral so must contain equal numbers of protons and electrons**
- Led to idea of **atomic number and mass number**
- Atomic number **$Z =$ no. of protons in atom**

- Mass number A = number of protons and neutrons

- Accepted notation is:



- Atomic number Z = no. of protons in atom
- Z is the same for an element but A can vary
- Isotopes eg



or



- Uranium 235 is fissile and useful but less than 1 % abundance in natural U
- Atomic masses measured by AMUs (atomic mass units)
- By definition (international agreement) Carbon 12 has atomic mass 12 AMU
- $\therefore 1 \text{ AMU} = 1/12$ the mass of Carbon 12
- But in the periodic table the mass of C is 12.01, because elemental carbon is 98.9 % carbon 12 and 1.1 % carbon 13
- Also, even if protons and neutrons were EXACTLY 1 AMU, when forming a nucleus there would not be a whole number for the mass because some mass is released as binding energy to form the nucleus. ($1 \text{ AMU} + 1 \text{ AMU} \neq 2 \text{ AMU}$ in a nucleus)
- Example (nuclear binding energy)

For any element we should be able to calculate its mass eg $^{19}_9\text{F}$

9 protons and 10 neutrons

The known mass of an H atom is 1.007825 amu

$$\therefore 9 \times 1.007825 \text{ amu} = 9.070425 \text{ amu}$$

The mass of 1 neutron is 1.008665 amu

$$\times 10 = 10.08665 \text{ amu}$$

$$10.08665 + 9.070425 = 19.15708 \text{ amu}$$

However, measured mass is 18.9984 amu

\therefore there is a mass defect of 0.1587 amu

This mass was released as energy, calculate this using $E = mc^2$ (or $\Delta E = (\Delta m)c^2$)

Since $1 \text{ kg} = 6.022 \times 10^{26} \text{ amu}$

$$1 \text{ J} = 1 \text{ kgm}^2/\text{s}^2$$

$$\underline{-0.1587 \text{ c}^2} = -2.37 \times 10^{-11} \text{ J}$$

$$6.022 \times 10^{26}$$

= energy released when one ^{19}F nucleus is formed, but nuclear binding energy expressed per mole.

$$\Delta = (-2.37 \times 10^{-11} \text{ J}) (6.022 \times 10^{23}/\text{mol})$$

$$= -1.43 \times 10^{13} \text{ J mol}$$

$$\text{or } -1.43 \times 10^{10} \text{ kJ mol}$$

- $6.022 \times 10^{23}/\text{mol}$ is Avogadro's number. Number of atoms/ molecules per mole. Huge number, 1 mole of marbles covers the Earth 50 miles thick. 1 mole of pounds could give each person in the world £1 m per day for 275000 years.

- Now need to consider the **electronic structure** of the atom
- So far considered as a **particle with specific mass**
- Realised that electron **could also be thought of as a wave**
- Let us compare the **properties of particles and waves**

Particles	Waves
Specific mass, energy and momentum – discrete or quantised	Diffract, refract, are continuous Have amplitude and phase Can constructively or destructively interfere

Overhead of constructive and destructive interference.

- **Electron has mass but can be diffracted**
- We think of **light** as a wave, but **can be thought of as a particle** since a **photon** of light has a specific energy:

$$E = h\nu$$

Where h = Planck's constant and ν = frequency

$$c = \nu\lambda = 2.988 \times 10^8 \text{ ms}^{-1}$$

- Frequency defined as the number of waves that pass through a particular point each second
- For light frequency is related to wavelength by speed of light.
- So for example, if light of $\nu = 5.09 \times 10^{14} \text{ s}^{-1}$ we can calculate wavelength λ

$$(c = \nu\lambda)$$

$$\text{Or } \lambda = c/\nu = 3 \times 10^8 \text{ ms}^{-1} / 5.09 \times 10^{14} \text{ s}^{-1}$$

$$= 5.89 \times 10^{-7} \text{ m or } 589 \text{ nm}$$

- Remember also that $E = hc/\lambda$
- **De Broglie Relation (1923)**: Since an electron can exhibit the characteristics of a wave de Broglie in 1923 reasoned that an **electron will have an associated wavelength**. He put forward an equation known as the de Broglie relation.

$$\lambda = h/mv$$

λ = wavelength, h = Planck's constant, m = mass, v = velocity

- So if we know how fast an electron is going (**velocity of electron**) we can calculate its **wavelength**.

$$\text{So if } v = 1 \times 10^6 \text{ ms}^{-1}$$

$$\text{Then } \lambda = 6.626 \times 10^{-34} \text{ Js} / (9.1 \times 10^{-31} \text{ kg}) \times (1 \times 10^6 \text{ s}^{-1})$$

$$= 7.28 \times 10^{-10} \text{ m}$$

$$= 7.28 \text{ \AA}$$

{ \AA = \AA ngstrom- common unit for measuring bond lengths (range 0.7 – 3.0 \AA)}

- However, de Broglie relation applies to an electron in a **force free environment**, **not the case for an electron in an atom** where it is **influenced by the nucleus**
- So in **1926**, **Schrödinger** developed a theory for the **wave properties of electrons in atoms**, come to be known as **Quantum Mechanics**
- This addresses the failings in Bohr's Theory, although we had a pretty good shot at it.
- In Bohr's Theory the electron was thought to be orbiting the nucleus, like the Earth orbits the Sun)

- However, this cannot be so because we would need to know the position of the electron at all times, and exactly how long it would take to reach the next position in its orbit (as we do for the Earth orbiting the Sun)
- In 1927, Heisenberg showed it is impossible to know simultaneously with absolute precision both the position and speed of an electron. This is the Heisenberg Uncertainty Principle which takes the form:

$$(\Delta x)(m\Delta v) \geq h/4\pi$$

Δx = uncertainty in the position

Δv = uncertainty in the velocity, h = Planck's constant

- Example: what is the error in velocity if the uncertainty in position is 0.1 \AA ($1 \times 10^{11} \text{ m}$)

$$\Delta v \geq (h/4\pi)/m \Delta x = 5.25 \times 10^{-35} / 9.1 \times 10^{-42} \geq 5.8 \times 10^6 \text{ ms}^{-1}$$

- However, although we cannot make precise statements about position and velocity we CAN make statistical statements about the electron. For example we can calculate the probability of finding an electron in a hydrogen atom using a wave function Ψ and Ψ^2 gives the probability of finding an electron in a region of space. There is a greater probability of finding the electron near the nucleus but there is no definite boundary as in the Bohr atom. Using Ψ^2 we can draw a surface boundary diagram within which there is a 90 % probability of finding an electron. For a hydrogen atom it would look like this {diagram}
- This is a diagrammatic representation of a solution of the Schrödinger equation and we call this an orbital (in the above case an s orbital). To understand orbitals, their energies, and shapes we need to know about quantum numbers (QNs). According to quantum mechanics each electron in an atom is described by 4 quantum numbers.

Quantum number	Description	Specifies	Values
n	principal QN	energy	1,2,3 etc
l	angular mom. QN	shape	0,1,2,3 (s,p,d,f) 0 to (n-1)
m _l	magnetic QN	orientation	-l to +l
m _s	spin QN	orientation of spin axis	+1/2, -1/2

- These are:
- n = principal quantum number = specifies energy = has values 1, 2, 3 etc.
- l = angular momentum quantum number = specifies shape = has letters s, p, d, f = values 0, 1, 2, 3 (s = 0, l = 1 etc.)
- m_l = magnetic quantum number = specifies orientation = has values +l to -l, so for an s orbital m_l = 0. {see diagram}
- For a p orbital m_l = +1, 0, -1, so there are 3 p orbitals {see diagram} p_x, p_y, p_z.
- Fourth quantum number is m_s = spin quantum number = specifies orientation of spin axis = values +1/2, -1/2
- So in the H atom we have 1 proton, 1 electron, therefore n = 1 and l = 0 = s
- This is therefore an s orbital
- Configuration of this electron is written as 1s¹
- How do we build up electrons in orbitals?
- For 1s (or any orbital!) can only have 2 electrons, m_s = +1/2 or -1/2
- Thus for 1s we have 1s¹ (half-filled) and 1s² (full)
- There are no other solutions for n = 1 (l must equal only 0), so we go on to n = 2

- Electrons going into an orbital must obey the **Pauli Exclusion Principle**
- This states 'No 2 electrons in an atom can have the same 4 quantum numbers'
- So for a **1s orbital**, 1 electron has $n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$, the other has $n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$
- This is the electron's 'address'
- To reiterate, because there are only 2 possible values of m_s an orbital can hold no more than 2 electrons (with different m_s values)
- So we build atoms by filling orbitals with electrons {show periodic table diagram}:

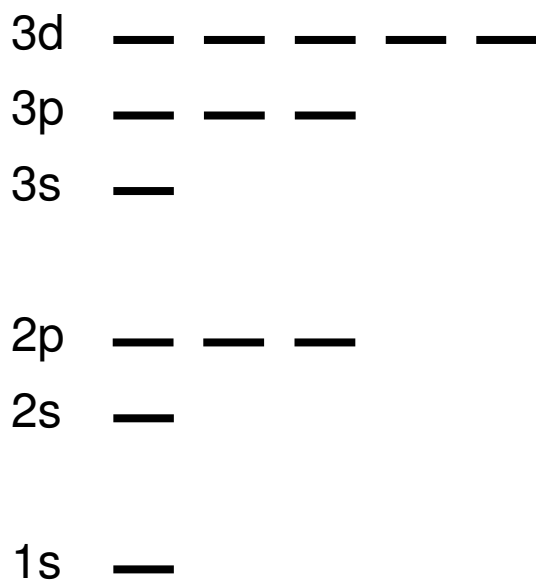
type of orbital	l value	no. of m_l values	no. of orbitals	no. of electrons
s	0	1	1	2
p	1	3	3	6
d	2	5	5	10

- This accounts for the number of columns in the various blocks of the periodic table
- Building an electron configuration in an atom follows the Aufbau Principle
- Order corresponds mostly to increasing energy of the subshells
- This is the pattern

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p

- Order arises because of the following effects
 1. The inner electrons (the 'core') are held closer by the +vely charged nucleus
 2. The outer electrons are partly shielded by the 'core' and \therefore not so tightly held
 3. The effect of shielding is greater for d then p then s (For electrons in 3rd shell:
3p shielded by 3s 3d shielded by 3s/3p)

- Because electrons in 3s shield electrons in 3p from the nucleus, additional energy needed to maintain electrons in 3p orbital. Because both 3s/3p shield 3d from nucleus, even more energy needed to maintain electrons in 3d orbital.
- This explains why 2s is below 2p (lower in energy) and why 4s is below 3d.
- So for H there is one electron and the ground state is $\therefore 1s^1$
- Examples:
 1. Be $4e^- 1s^2 2s^2$
 2. O $8e^- 1s^2 2s^2 2p^4$
 3. Ne $10e^- 1s^2 2s^2 2p^6$ (filled shell)
 4. P $15e^- 1s^2 2s^2 2p^6 3s^2 3p^3$ (or [Ne] $3s^2 3p^3$)
- Electronic configs develop the patterns seen in the periodic table



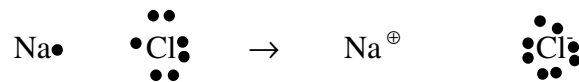
{use this template to fill configs for select atoms}

- eg He, Ne, Ar, Kr, Xe are noble gases and all have filled shells
- Helium $1s^2$ – filled $n = 1$ shell
- Neon (see above)
- Krypton $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
- This helps to explain the chemistry of the elements since most reactions drive towards a noble gas configuration.
- Take Na for an example $1s^2 2s^2 2p^6 3s^1$. Sodium chemistry is dominated by $Na^+ = 1s^2 2s^2 2p^6$ (Neon shell)
- Electrons outside a filled noble gas shell are called valence electrons {circle Na $3s^1$ }
- These electrons dominate chemical reactivity.
- When building up electron configurations we must also consider Hund's Rule: 'The lowest energy arrangement of electrons in a subshell is obtained by putting electrons into separate orbitals of the subshell with parallel spins'
- {draw 3 degenerate p orbitals and fill with 3 electrons – see above}
- this is because the energy required to pair the spins is greater than for parallel spins in different orbitals
- So that concludes the atomic structure part of the course...

Chemical Bonding (the last major section of the course)

- cover different types of bonding, ionic, covalent, representation, molecular geometry as a result of bonding to form molecules, intermolecular forces
- The 'Ionic Bond'

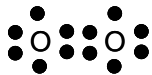
- 'a chemical bond formed by the electrostatic attraction between positive and negative ions'
- It forms between 2 atoms when one (or more) electrons are transferred between valence shells
- Cations (+ve)
- Anions (-ve)
- A large number of ions together form a solid
- E.g. Na ([Ne] 3s¹) + Cl ([Ne] 3s² 3p⁵) → Na⁺ ([Ne]) + Cl ([Ar])
- We can simplify the way we write this using Lewis electron-dot symbols



- The Covalent Bond
- 'formed by the sharing of a pair of electrons between atoms'
- Sharing these electrons leads to stability, e.g H₂ which we can draw using Lewis representation thus:

e.g. H• + •H H:H (Now both H atoms have a filled n = 1 shell)

- We can also have multiple bonds eg O₂



- O=O, here the O atoms each have a filled shell (the octet rule)


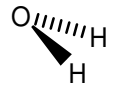

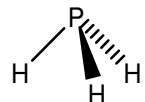
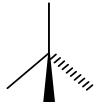
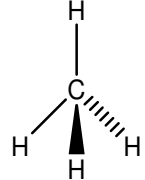
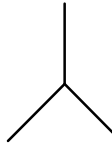
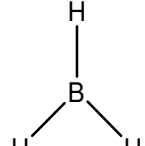
- Molecular Geometry

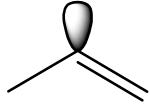
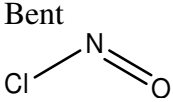
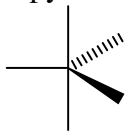
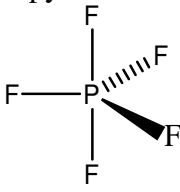
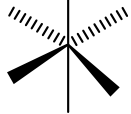
V S E P R

Valence shell electron pair repulsion Theory

- Helps predict shapes of molecules and ions by placing valence shell electron pairs bonding in lone pairs as far apart as possible

{mention satisfying the octet rule for each of the examples}

Molecule	No of lone pairs	No of atoms attached to central atom	Overall shape including lone pair	Shape including bonds only
CO ₂	0	2 (double)	Linear	Linear O = C = O
H ₂ O	2	2	Tetrahedral  (angle between bonds = 105°)	Bent 
PH ₃	1	3	Tetrahedral  (angle = 107°)	Pyramidal 
CH ₄	0	4	Tetrahedral  (angles = 109° for a perfect tetrahedron)	Tetrahedral 
BH ₃	0	3	Trigonal planar  angles = 120°	Trigonal planar 
			Trigonal	

NOCl	1	2	 angle between bonds around 118°	Bent 
PF ₅	0	5	Trigonal bipyramidal  angles 120° and 90°	Trigonal bipyramidal 
SF ₆	0	6	Octahedral  all angles 90°	Octahedral 