

# Welcome to Chemistry!

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## Introduction

Lecturer: Dr Adrian George (Chemistry room 224; [adrian.george@sydney.edu.au](mailto:adrian.george@sydney.edu.au))

General administration and course structure

- Tutorials and tutorial quizzes (3 quizzes – 15% final mark)
- Laboratory (start week 2, 10 x 3 hr sessions, compulsory – 15% final mark )
- On line research exercise (10% final mark)
- Final exam (3 hours – 60% final mark)

Aim of this chemistry course

- Provide you with a sound foundation on which your studies in the pharmaceutical and molecular sciences are be built.
- Weeks 1-4 will cover atomic structure, types of bonding, molecular shape and equilibrium reactions involving acids and bases.
- Weeks 5-13 will cover organic chemistry; representation and analysis of structure, isomers, chemical transformations and the chemistry of biomolecules.

Resources

- USYD e-learning: [elearning.sydney.edu.au/](http://elearning.sydney.edu.au/)
- First Year Chemistry Web site: <http://firstyear.chem.usyd.edu.au/index.shtml>
- Chemistry Learning Centre: <http://firstyear.chem.usyd.edu.au/learningcentre.shtml>
- Text book: Blackman, Bottle, Schmid, Mocerino and Wille, *Chemistry*, 2011 (John Wiley), (the 2007 edition of this book is also acceptable).

## Nucleogenesis – The origin of the elements

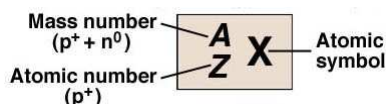
There are four basic sub-atomic particles

Particle	Symbol	Charge	Mass (a.m.u.)
proton	p	+1	1.007276
neutron	n	0	1.008665
electron	e <sup>-</sup>	-1	0.000549
positron*	e <sup>+</sup>	+1	0.000549

\* Not present in stable atoms

The composition of any nucleus is defined by two numbers.

- The atomic number,  $Z$ , is the number of protons in the nucleus.
  - This defines the chemical nature of the atom.
  - It is equal to the total charge on the nucleus.
- The mass number,  $A$ , is the total number of nucleons (protons and neutrons) in the nucleus.



e.g.  $^{12}_6\text{C}$  has an atomic number of 6 and a mass number of 12.

- A nuclide is an atom with a particular mass number and atomic number.
- Nuclei with the same atomic number but different mass numbers are called isotopes.

The *atomic mass of an element* is the weighted average of the atomic masses of each of the *naturally-occurring isotopes*.

e.g. Naturally occurring carbon is 98.89%  $^{12}\text{C}$  and 1.11%  $^{13}\text{C}$ .

The atomic mass of carbon is therefore  $(12.0000 \times 98.89\% + 13.00335 \times 1.11\%) = 12.01$

...but where do the elements come from? Answer: from hydrogen in the stars by a series of nuclear reactions:

The fundamental nuclear reaction is  $^1_1\text{H} + ^1_1\text{H} \rightarrow ^2_1\text{H} + ^0_1\text{e}^+$

followed by  $^2_1\text{H} + ^1_1\text{H} \rightarrow ^3_2\text{He} + \gamma$  and  $^3_2\text{He} + ^3_2\text{He} \rightarrow ^4_2\text{He} + 2\ ^1_1\text{p}$

to give the overall *hydrogen burning reaction*:  $4\ ^1_1\text{H} \rightarrow ^4_2\text{He} + 2\ ^0_1\text{e}^+ + \gamma$

As the star exhausts its hydrogen, it begins *helium burning* and so on to fuse heavier nuclei to form increasingly larger atoms.

e.g.  $^3_2\text{He} + ^4_2\text{He} \rightarrow ^7_4\text{Be} + \gamma$  and  $^7_4\text{Be} + ^1_1\text{p} \rightarrow ^8_5\text{B} + \gamma$

These types of reaction can produce all the elements up to iron. As the fuel in the star is exhausted it expands to form a red giant before dramatically collapsing with release of huge amounts of energy. This is a supernova, which may last only a few weeks, and which shines incredibly brightly and has enough energy to fuse nuclei together to form the heaviest elements before exploding to scatter the matter through interstellar space.

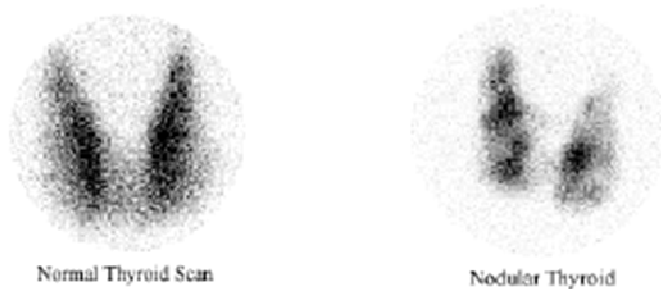
Nucleogenesis produces nuclides that can be stable or unstable. Unstable nuclei decay through a range of mechanisms involving the release of particles  $\{\alpha\ (^4_2\text{He}^{2+}), \beta\ (^0_{-1}\text{e}^-) \text{ or } \beta^+\ (^0_1\text{e}^+)\}$  with high kinetic energy or of  $\gamma$ -radiation. These high-energy products are collectively known as *radioactivity*.

## One application...

Nuclear imaging is useful because it allows us to radiolabel molecules that specifically target organs, molecules or chemical processes for diagnosis or biochemical research.

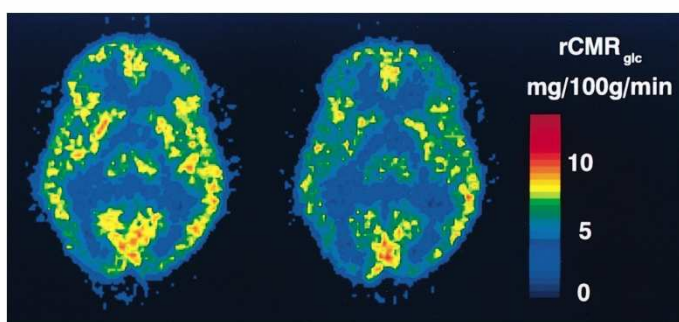
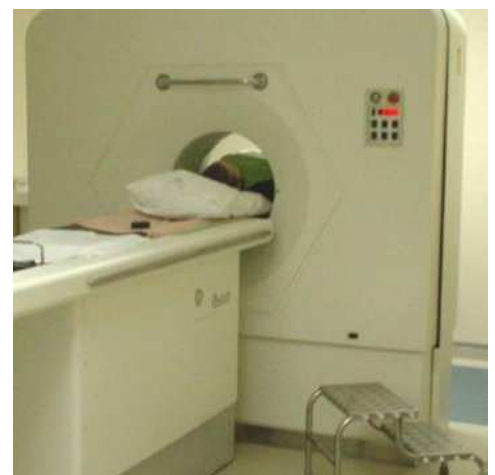
- Isotope used should emit low-energy, highly-penetrating radiation to minimise effective dosage equivalent to patient. In practice this usually means  $\gamma$  radiation.
- Image distribution of radioisotope detected using scintillation counting
  - gamma camera (planar image like an x-ray) or
  - computerised-axial tomography (CAT or CT scan - cross section or three-dimensional reconstruction)
- Images may be a simple gray scale density or pseudo-colour signal. Pseudo colour is especially common in computer-reconstructed imaging.

e.g.  $\gamma$ -camera and image of  $^{131}\text{I}$  (from NaI solution) uptake in a normal (left) and diseased (right) thyroid gland, showing localisation of iodine.



Positron Emitting Isotopes ( $^{11}\text{C}$ ,  $^{18}\text{F}$ ...) are generally formed in a cyclotron, which bombards a stable sample with protons or deuterons. These isotopes are often exploited in the synthesis of organic molecules (drugs, peptides, carbohydrates, steroids, vitamins...) for imaging. As soon as a positron is emitted it collides with an electron, annihilates and two  $\gamma$  rays are formed at  $180^\circ$ . It is the  $\gamma$  rays that are detected.

E.g. tomographic image of a single anatomical level of the brain using  $^{18}\text{F}$ -labelled glucose.



the control, a PET scan of a normal brain

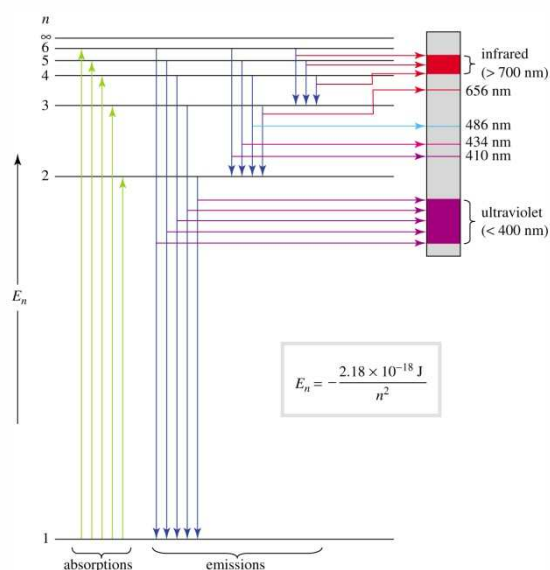
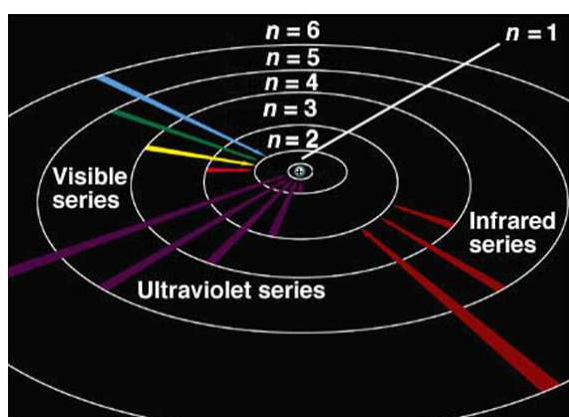
the PET scan of the brain of a volunteer injected with nicotine

colour code indicates rate of glucose metabolism

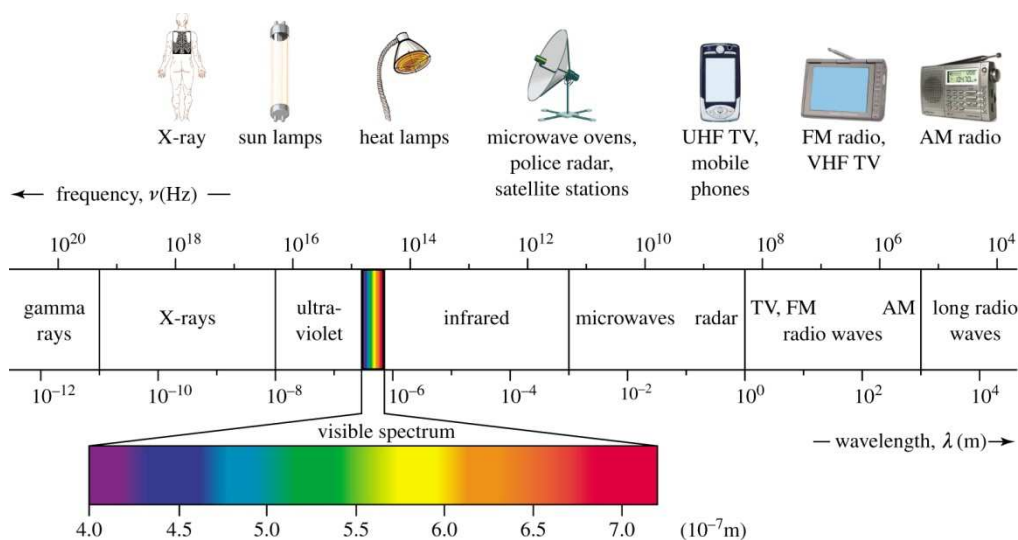
# Atomic Structure

## Historical context

1803	J Dalton	provided evidence for fundamental indivisible particles - atoms
1897	J J Thomson	studied cathode rays - electrons
1909	R A Millikan	measured the charge of an electron ( $1.6 \times 10^{-19}$ C)
1909	E Rutherford	proposed an atom be composed of a small positive nucleus surrounded by a lot of space occupied by the electrons
1913	N Bohr	suggested electrons in an atom were arranged in a series of orbits
1932	J Chadwick	discovers the neutron



## Electromagnetic radiation



Electromagnetic radiation travels at the speed of light ( $c = 3.00 \times 10^8 \text{ m s}^{-1}$ ) and is characterised by a wavelength ( $\lambda$ , lambda) and a frequency ( $\nu$ , nu). The higher the frequency, the shorter the wavelength.

Wavelength x frequency = speed of light

$$\lambda \nu = c = 3.00 \times 10^8 \text{ ms}^{-1}$$

**Example:** A radio station transmits at a wavelength of 2.84 m. Calculate the frequency.

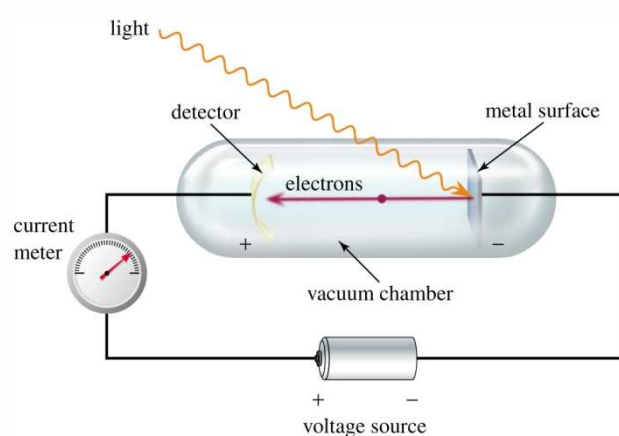
$$\begin{aligned} \nu &= c / \lambda &= 3.00 \times 10^8 \text{ ms}^{-1} / 2.84 \text{ m} &= 1.056 \times 10^8 \text{ s}^{-1} \\ & & &= 106 \text{ MHz} \\ & & &(\text{this is the radio station 2JJJ}) \end{aligned}$$

**Question:** The yellow colour of a sodium street light has a wavelength of approximately 590 nm ( $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$ ). What is the frequency of this light? (**Ans:**  $5.1 \times 10^{14} \text{ Hz}$ )

**Photoelectric effect:** If light strikes the surface of a metal in a vacuum, electrons are given off. Einstein interpreted this as indicating that light is composed of 'packets of energy' or *photons*.

All electromagnetic radiation may have the same speed but the energy is different and directly proportional to frequency. The higher the frequency (the shorter the wavelength), the higher the energy. Energy = Planck's constant  $\times$  frequency

$$E = h\nu \quad h = 6.626 \times 10^{-34} \text{ Js}$$



**Example:** What is the energy associated with the radiation transmitted by 2JJJ?

$$E = h\nu = 6.626 \times 10^{-34} \text{ Js} \times 106 \times 10^6 \text{ s}^{-1} = 7.02 \times 10^{-26} \text{ J}$$

and for one mole of radiation

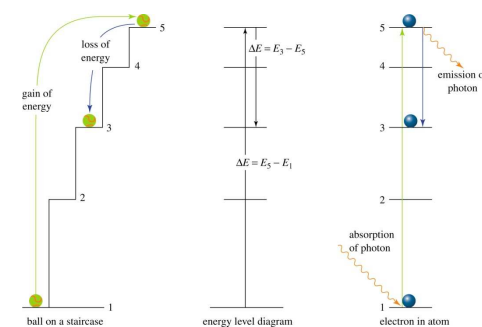
$$E = 7.02 \times 10^{-26} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 0.0423 \text{ J mol}^{-1}$$

**Question:** Calculate the energy associated with one *photon* and a mole of photons of UV-B light with a wavelength of 320 nm. (**Ans:**  $6.21 \times 10^{-19} \text{ J}$  and for 1 mole  $374 \text{ kJ mol}^{-1}$ )

## The atomic spectrum of hydrogen

Light emitted from a hydrogen arc lamp is composed of only a few lines:

- Only light of certain energy is emitted
- The pattern of lines is unique to hydrogen
- Suggests the process emitting light in the atom is *quantised*
- The electron in the atom may possess only certain energies



Energy of the hydrogen atom orbits is inversely proportional to the square of the orbit number

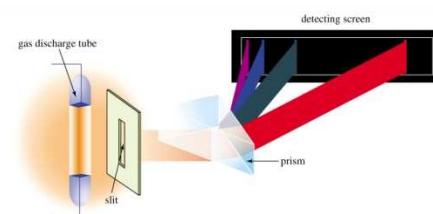
$$E = -E_R(1/n^2) \quad E_R = 2.18 \times 10^{-18} \text{ J}$$

(More generally,  $E = -E_R(Z^2/n^2)$  where  $z$  = atomic number of the element. But this formula only works for species with one electron (eg  $\text{He}^+$ ,  $\text{Li}^{2+}$ ). See later (p10) for more information.)

The difference in energy between the orbits is the same as the energy of light emitted when an electron moves from a higher to a lower orbit.

$$\text{As} \quad \Delta E = E_{\text{final}} - E_{\text{initial}}$$

$$\text{then} \quad \Delta E = -2.18 \times 10^{-18} \text{ J} (1/n_{\text{final}}^2 - 1/n_{\text{initial}}^2)$$



**Example:** Calculate the wavelength of light emitted when an electron moves from the  $n = 3$  to the  $n = 2$  orbit of a hydrogen atom.

$$\begin{aligned} \Delta E &= -2.18 \times 10^{-18} \text{ J} (1/2^2 - 1/3^2) \\ &= -3.03 \times 10^{-19} \text{ J} \quad (\text{minus indicates light emitted}) \end{aligned}$$

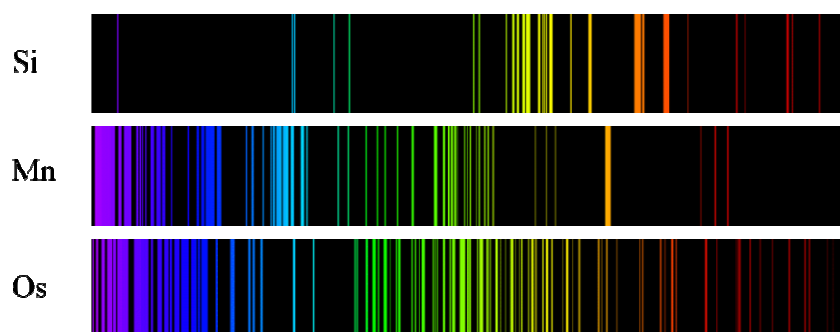
$$\text{now} \quad E = h\nu \text{ and } \nu = c/\lambda$$

$$\begin{aligned} \text{so} \quad \lambda &= hc/E = (6.626 \times 10^{-34} \text{ Js}) (3.00 \times 10^8 \text{ ms}^{-1}) / (3.03 \times 10^{-19} \text{ J}) \\ &= 656 \text{ nm} \quad (\text{red light}) \end{aligned}$$



**Question:** Calculate the energy required (in  $\text{kJ mol}^{-1}$ ) to completely remove an electron from a hydrogen atom. (Hint: this corresponds to an electron going from  $n = 1$  to  $n = \infty$ ).

However, many atomic emission spectra are much more complex than expected from the Bohr model of the atom. (<http://chemistry.bd.psu.edu/jircitano/periodic4.html>)



## A wave - mechanical model

Light has a dual nature and the de Broglie equation relates wavelength to momentum

$$\lambda = h/mv$$

Heisenberg Uncertainty Principle

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

Schrödinger Equation

$$\hat{H}\psi = E\psi$$

This can only be solved if various boundary conditions are applied. That is, the waves must be *standing waves* that are

- continuous
- single valued
- multiples of a whole number of half wavelengths

There are then discrete solutions that represent the energy of each electron orbital. The coordinates of the orbital are given by *quantum numbers*.

## Quantum numbers

The Principal Quantum Number: n      n = 1, 2, 3 ...

- Describes the size and extent of the orbital
- The larger the value of n, the bigger & the higher energy the orbital

The Angular Momentum Quantum Number: l      l = 0, 1, 2 ... (n-1)

- Describes the shape of the orbital
- e.g. if n = 2; l = 0 or 1

l = 0	s orbital
l = 1	p orbital
l = 2	d orbital
l = 3	f orbital

The Magnetic Quantum Number:  $m_l$

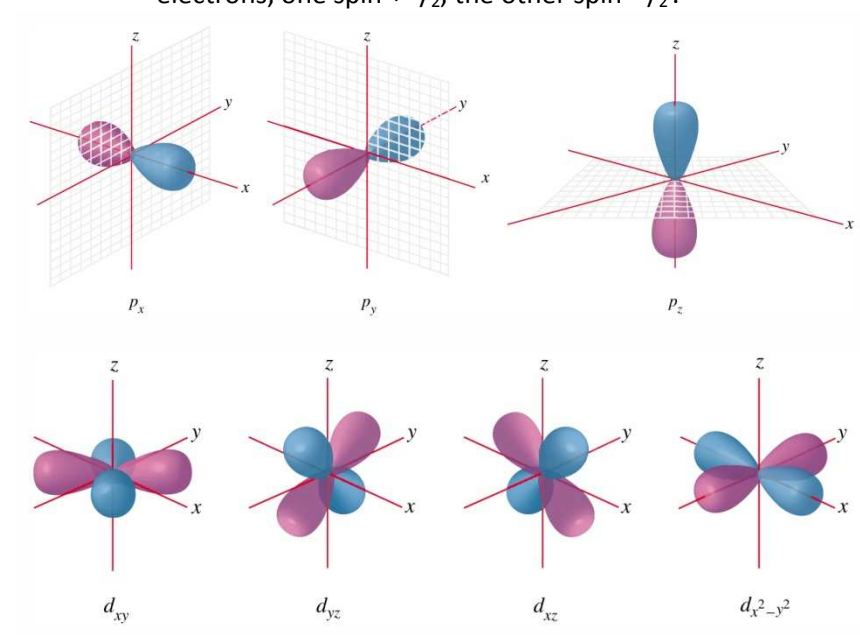
$$m_l = -l, -(l-1) \dots 0 \dots (l-1), l$$

- Describes the orientation of the orbital
- e.g. if  $l = 0$ ;  $m_l = 0$  (s orbital)  
 if  $l = 1$ ;  $m_l = -1, 0, +1$  ( $p_x, p_y, p_z$  orbitals)  
 if  $l = 2$ ;  $m_l = -2, -1, 0, +1, +2$  ( $d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$  orbitals)

The Spin Quantum Number:  $m_s$

$$m_s = +\frac{1}{2}, -\frac{1}{2}$$

- Describes the spin of the electron
- Each orbital, uniquely described by  $n, l$  and  $m_l$ , may contain a maximum of two electrons, one spin  $+\frac{1}{2}$ , the other spin  $-\frac{1}{2}$ .

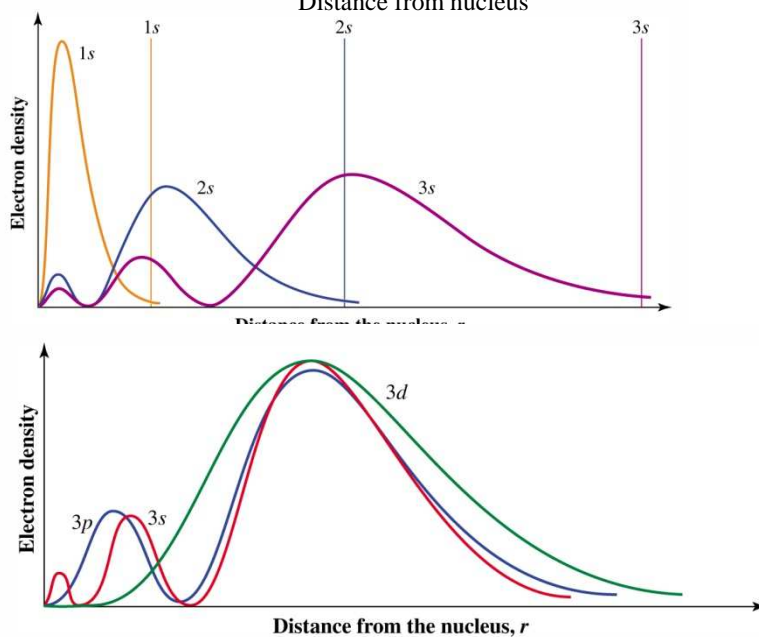
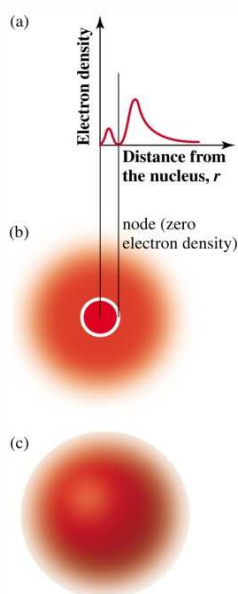
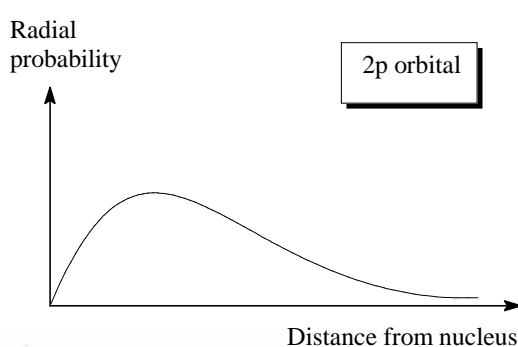
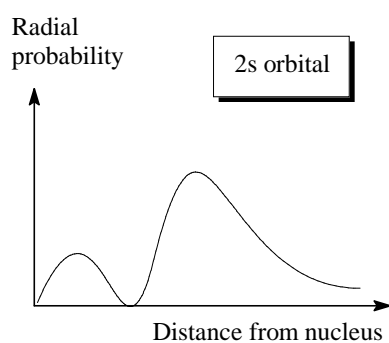
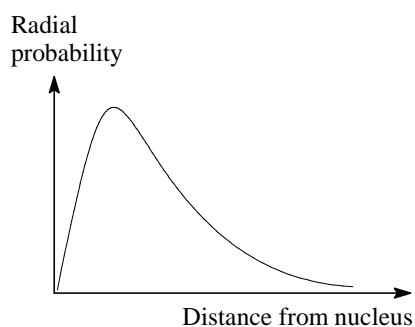
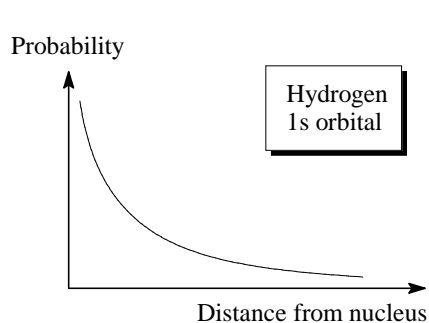


**Question:** Complete the table:

Shell, $n =$	1	2		3			4			
Sub-shell, $l =$	0	0	1							
Description	s	s	p							
Maximum no. of electrons in sub-shell	2	2	6							
Total electrons	2	8								



Remember: this model treats electrons as waves not particles and so its distribution relative to the nucleus of an atom is a region not a point. Moreover the Heisenberg Uncertainty principle means we can only locate an electron in terms of probability.



**Question:** How many *spherical* nodes (point at which the electron density falls to zero excluding start and end) do the following orbitals have?

Orbital	1s	2s	2p	3s	3p	3d	4s
No of nodes	0	1	0				

The energy of an orbital is affected by the nuclear charge and the occupancy of the orbital and hence the atoms of different elements give a unique atomic emission spectrum.

In the hydrogen atom the energy of the sub-shells (*s*, *p*, *d*...) are degenerate (the same energy) for a given shell (*n* = 1, 2, 3...).

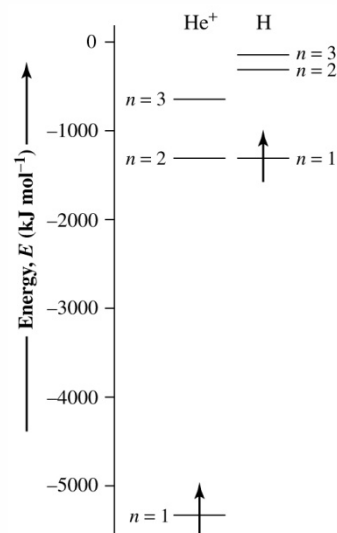
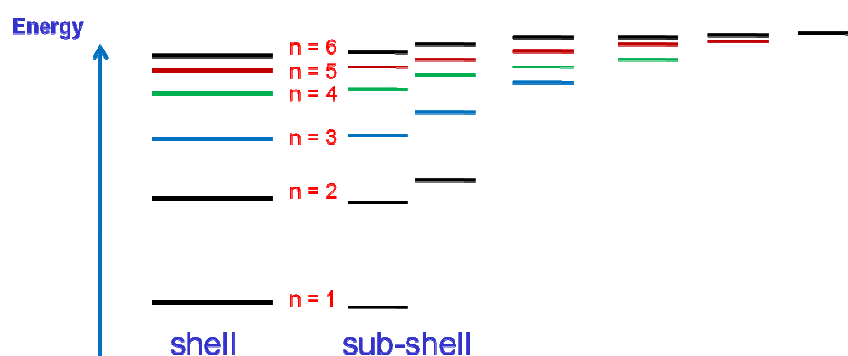
In ions with only one electron ( $\text{He}^+$ ,  $\text{Li}^{2+}$  ...) this is also true and the energy of the shell may be calculated using:

$$E = -E_R Z^2 (1/n^2) \quad Z^2 = \text{atomic number}$$

In all other cases the energy of the sub-shells are no longer degenerate. This gives rise to an atomic emission spectrum that is much more complex than the Bohr model predicted.

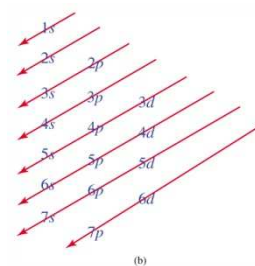
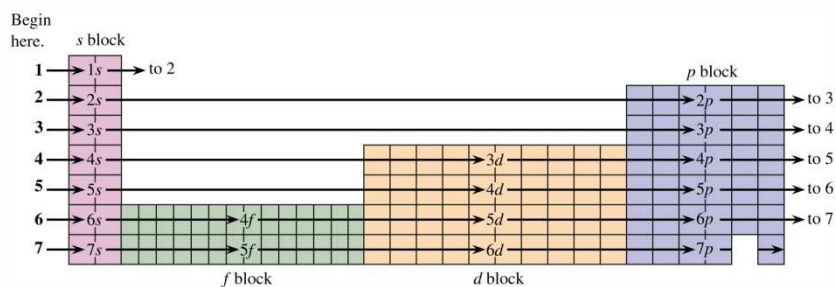
The order in which the sub-shells are filled becomes important with the orbital energy increasing in the order:

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



When determining the ground state electron configuration of an atom, there are three rules:

- Pauli exclusion principle - no two electrons can have an identical set of four quantum numbers. i.e. there are a maximum of 2 electrons in any one orbital.
- Aufbau principle - fill up low energy orbitals before high energy ones.
- Hund's rule - orbitals with the same energy (i.e. the same sub-shell) have the maximum number of unpaired electrons.



**Question:** Write the electron configuration of the following elements: Li, Be, B, C, Ne, Na, Al, V, Ga.