CHEMISTRY
Foundation Course

CH – 0001

Dr. Jonathan Agger

Room FARADAY B303 extension 4527

j.agger@umist.ac.uk

An Introduction to General / Inorganic Chemistry

What is CHEMISTRY?

chemistry / ˈkɛmɪstri / *noun.*

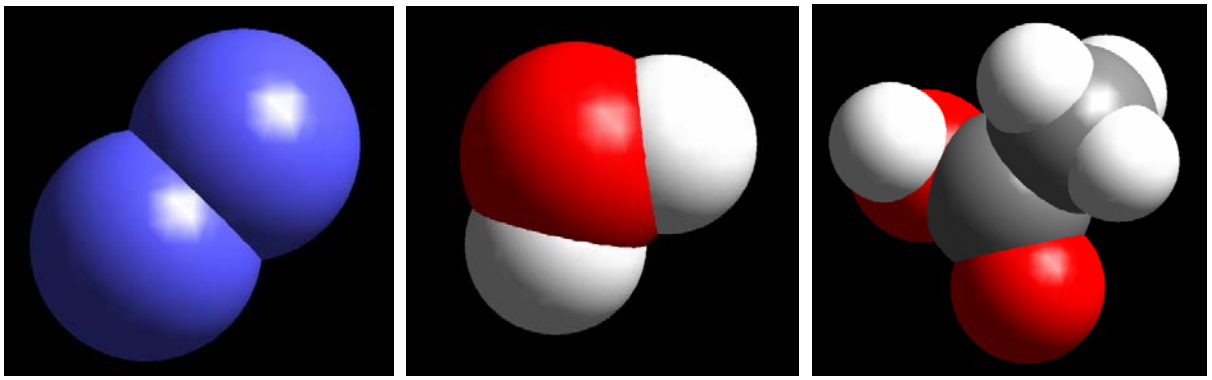
1 (The branch of science that deals with) the investigation of the substances of which matter is composed, and the phenomena of combination and change which they display. [from the Oxford English Dictionary]

Therefore to understand chemistry we need to know what matter is made of.

What is a MOLECULE?

"A molecule is a group of atoms joined together."

e.g.



nitrogen	water	vinegar
N_2	H_2O	CH_3COOH

We must thus understand what atoms are and how they join together to form molecules.

What is in an ATOM?

Atoms initially consist of three types of particle:

- protons symbol p
- neutrons symbol n
- electrons symbol e

	mass (amu)	*charge*
proton	1	+1
neutron	1	0
electron	negligible	-1

amu = atomic mass unit = 1.67265×10^{-27} kg

m_e = mass of electron = 9.10953×10^{-31} kg

m_e is roughly 1000 times smaller…

Atoms contain equal numbers of electrons and protons and are therefore electrically neutral.

$$^{A}_{Z}Li$$

A Mass number - number of protons + neutrons

Z Atomic number - number of protons

The particles were detected experimentally…

Electrons

Joseph John Thomson born 1856 in Manchester.

Awarded Nobel prize for Physics in 1906 for work on electric discharge in gases. Discovered a stream of particles from the cathode which could be deflected by both magnetic and electric fields.

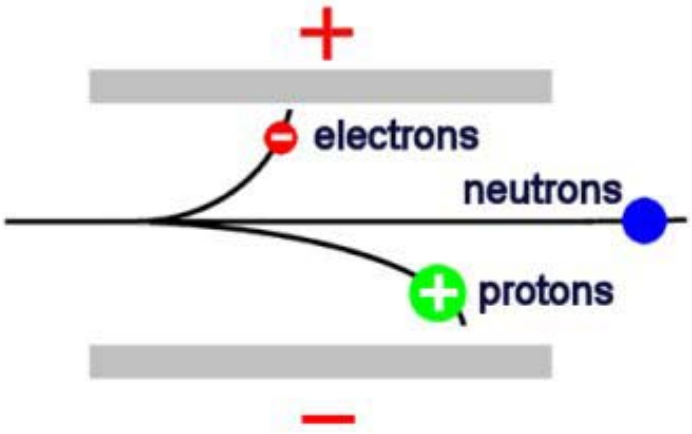
Protons

Thomson also observed a stream of particles from the anode which were oppositely charged to the beam from the cathode.

Neutrons

James Chadwick born 1891 in Cheshire.

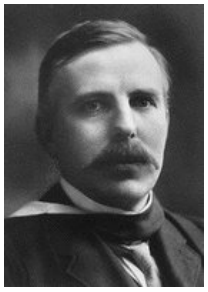
Awarded Nobel prize for Physics in 1935. Bombarded beryllium Be with α-particles ($^4_2$He nuclei). Fast moving, highly penetrating particles were emitted that were unaffected by either magnetic or electric fields.



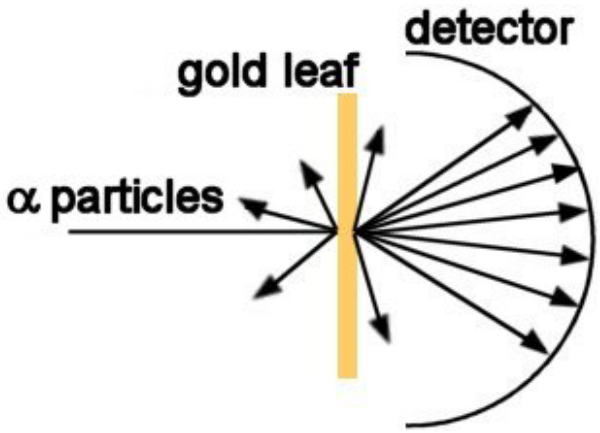
How do these particles make an atom?

Thomson's model

A relatively large, positively charged, amorphous mass, in which much smaller, negatively charged electrons were embedded.



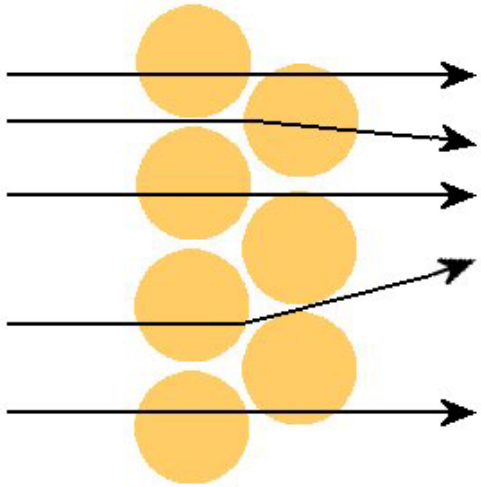
Ernest Rutherford born 1871 in New Zealand. Awarded Nobel prize for Chemistry in 1908. Rutherford reasoned that if this model was correct positively charged α-particles should pass through atoms with very little change in their direction.



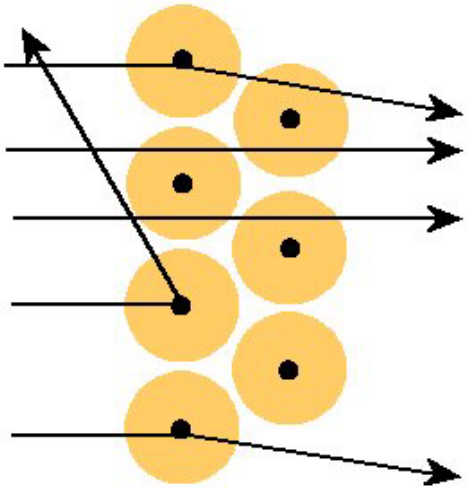
Most α-particles did pass through however, a number were severely deflected…

$\therefore$ Thomson's model was wrong!

Rutherford's expectation



Actual experimental result

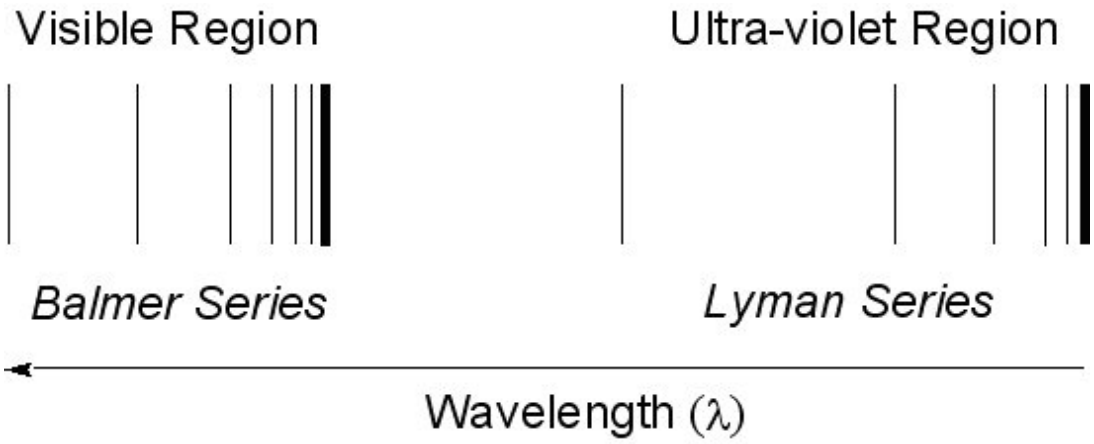


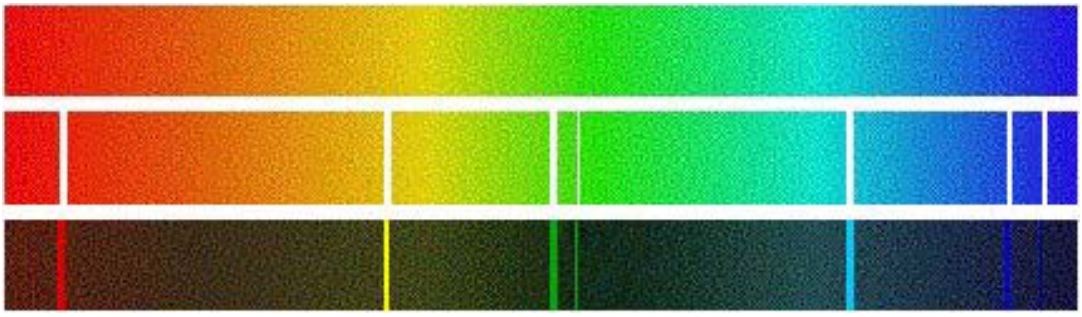
Rutherford's model

The atom is largely empty space with a small but relatively massive positively charged nucleus.

Was Rutherford's model correct?

Excitation of atomic gases causes the emission of electromagnetic radiation with discrete energies. e.g. hydrogen

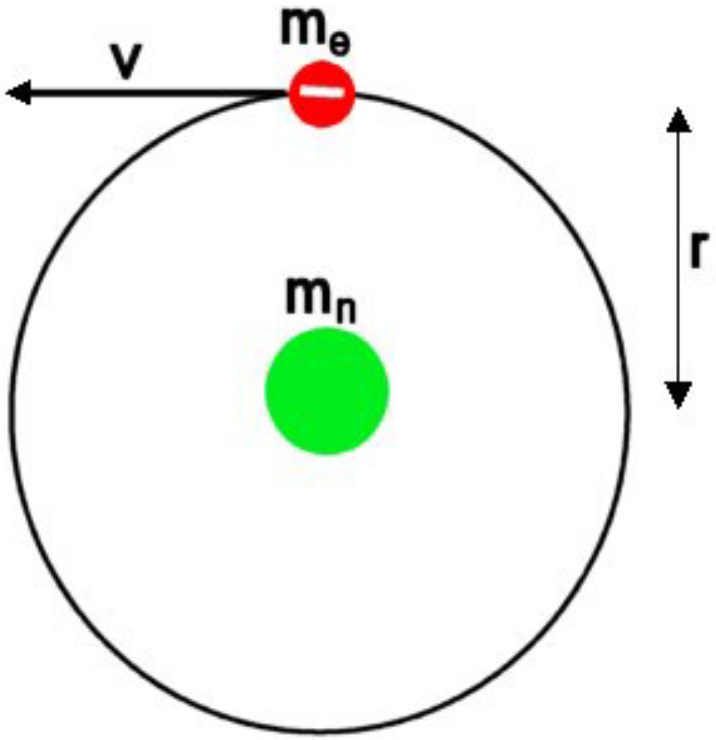




How could Rutherford's model be adapted to explain the atomic emission spectrum of hydrogen?

Bohr's model of the atom

Niels Bohr born 1885 in Copenhagen.
Awarded Nobel prize for Physics in 1922. Proposed the atom consisted of a small, positively charged nucleus around which electrons circulated at certain fixed distances called orbits.



The energy of an electron of mass m_e orbiting a nucleus of mass m_n at distance r with velocity v is given very simply as:

$$E = -\frac{e^2}{2r}$$

where e is the charge on the electron.

Clearly, the orbital energy is a function of *r* and this is VERY important…

i.e. $E = f(r)$

It follows that if any value of *r* is allowed then so is any value of *E*.

Movement of an electron from one level to another results in a change in its energy, ΔE.

An energy change is related to frequency of electromagnetic radiation according to:

$$\Delta E = h\upsilon$$

h = Planck's constant = 6.34×10^{-34} Js

also

$$c = \upsilon\lambda$$

$$\therefore \Delta E = hc / \lambda$$

υ = frequency

c = speed of light = 3×10^{8} ms^{-1}

λ = wavelength

$$\overline{\upsilon} = \frac{1}{\lambda}$$

$\overline{\upsilon}$ = wavenumber

Quantisation of electronic energies.

If all values of E are allowed, then the emission spectrum of hydrogen should be continuous...

This is NOT the case.

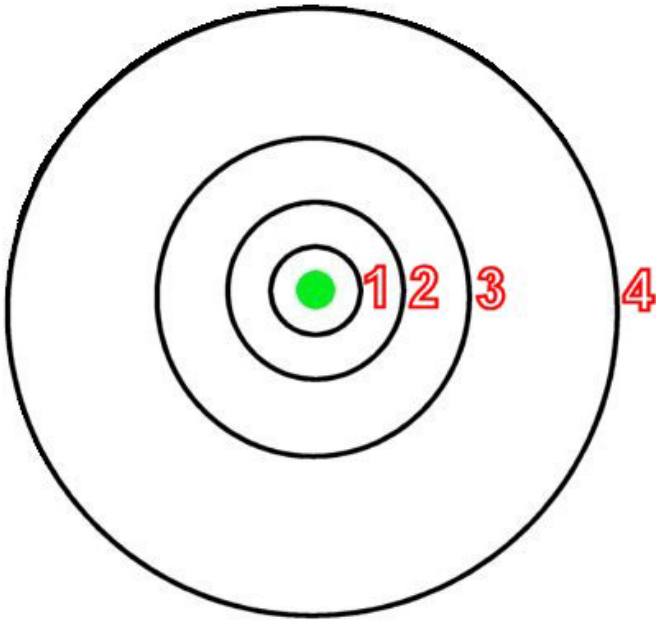
$\therefore$ constraints MUST be placed on the model.

If only certain values of the radius r are allowed, then only certain values of the energy E and hence energy difference ΔE will be allowed.

The restriction of r values implies specific orbits and we describe these orbits as quantised.

Compare quantisation of energy levels with rungs of a ladder. Gravity sees to it that you can only stand on a rung and not between rungs. If we number the rungs of the ladder we obtain quantum levels. The person pictured is on level 4.

Applying the "*ladder principle*" to Bohr's original atom, we get:



But what distance from the nucleus are these quantised levels?

$$r = kn^2$$

r = orbital radius

n - quantum number (an integer 1,2,3,4 etc.)

$$k = \frac{h^2}{4\pi^2 m_e e^2} = 52.918\,\text{pm}$$

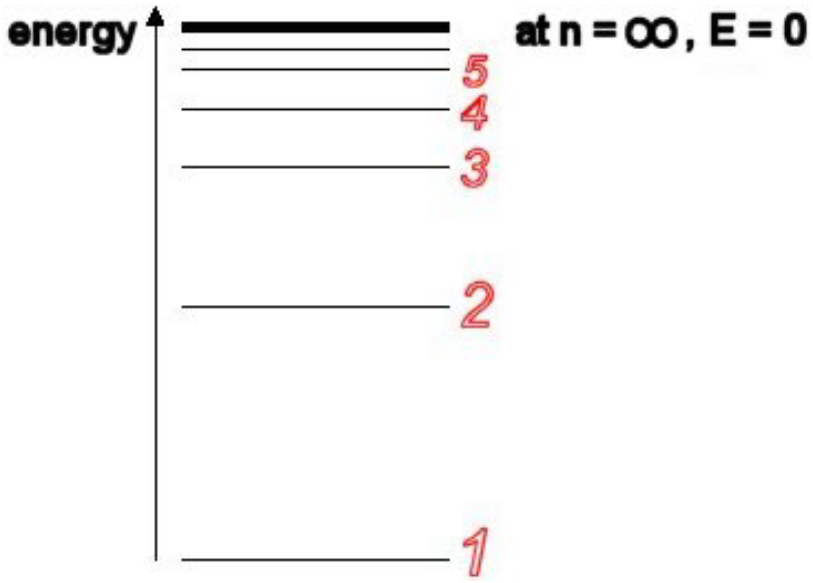
1 pm = 1 picometre = 10^{-12} m or
in layman's terms one million millionth of a m.

This distance is known as the Bohr, a_0.

It follows that as the radii of the atomic orbitals are quantised then the energies of the orbitals are also quantised as $E = f(r)$.

$$E_n = \frac{-2\pi^2 m_e e^4}{n^2 h^2}$$

Unlike a ladder, the energy levels are not evenly spread as $E \propto 1/n^2$.

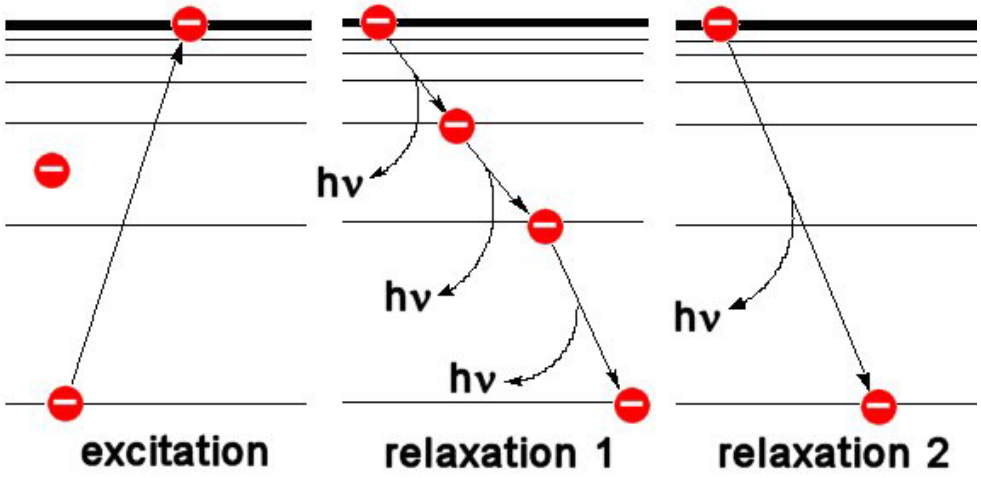


The model is supported by experimental evidence:

Hydrogen only emits electromagnetic radiation of specific wavelength / frequency after excitation, indicating that only discrete energy levels exist.

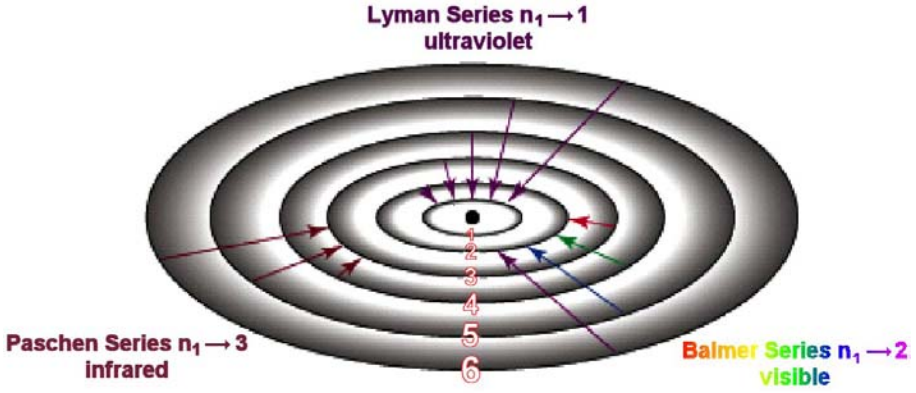
The hydrogen emission spectrum

Why does the emission spectrum of hydrogen consist of many series of lines?



Once excited, an electron does not have to move directly to the ground state. It may jump down via intermediate levels. Each "jump" results in an emission of electromagnetic energy, $h\nu$.

Overall a series of lines are observed which correspond to the following transitions:



i.e. series of transitions terminating at a particular energy level.

Each set of transitions was named after its discoverer…

Transition	Series	Region
$n_2 = 1$	Lyman	ultraviolet
$n_2 = 2$	Balmer	visible
$n_2 = 3$	Paschen	infrared
$n_2 = 4$	Brackett	
$n_2 = 5$	Pfund	

Each set of lines is readily calculated using the Rydberg equation:

$$\bar{\upsilon} = R_H\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$\bar{\upsilon}$ = transition wavenumber

R_H = Rydberg hydrogen constant
= 1.09737×10^5 cm^{-1}

n_1 = the quantum number FROM which the transition occurs

n_2 = the quantum number TO which the transition occurs

Quantum mechanics.

Bohr's model achieves excellent correlation with experimental data for hydrogen but breaks down for heavier elements. Therefore it is clearly flawed…

Louis de Broglie born 1892 in France.
Awarded Nobel prize for Physics in 1929. de Broglie proposed that the electron should be treated as a wave leading to the current view of electronic wave-particle duality and the birth of quantum mechanics.

The comparison between electrons in an atom and planets in a solar system was no longer reasonable...

This hypothesis led to the development of quantum mechanics and subsequently the Schrodinger wave equation.

This equation predicts the probability of finding an electron at a given point and provides a measure of the electron density about an atom of hydrogen.

It also predicts shapes for the various atomic orbitals inhabited by electrons.

Atomic Orbitals

Each atomic orbital is defined by three quantum numbers:

the principle quantum number

the azimuthal or orbital quantum number

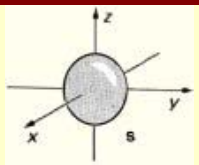
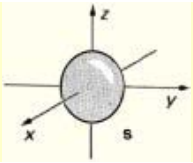
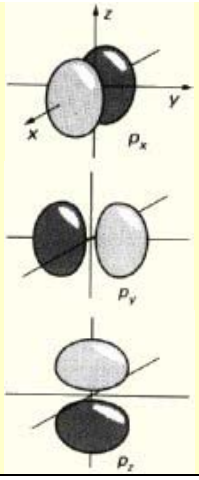
the magnetic quantum number:

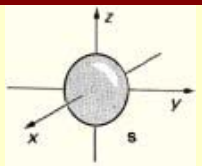
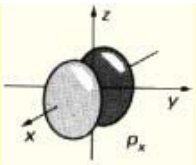
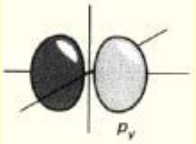
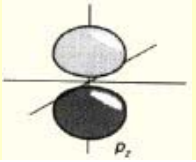
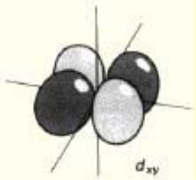
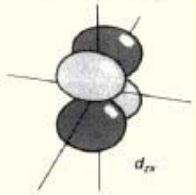
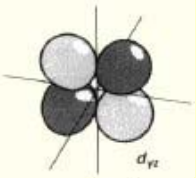
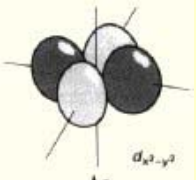
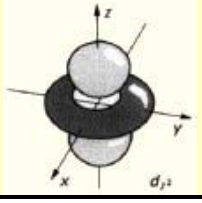
Quantum number	*Symbol*	*Allowed values*	*Significance*
principle	n	1,2,3,4…	orbital number
orbital	l	0,1,2…(n-1)	orbital type
magnetic	m_l	+l...-l	degeneracy

The orbitals are classified using a standard nomenclature which includes energy level and orbital type.

e.g. 1s, 3p, 5d, 6f...

The quantum numbers and corresponding orbital shapes are as follows:

n	*l*	m_l	*orbital*	*Orbital shape*
1	0	0	1s	
2	0	0	2s	
2	1	+1	$2p_x$	
2	1	0	$2p_y$	
2	1	-1	$2p_z$	

n	*l*	m_l	*orbital*	*Orbital shape*
3	0	0	3s	
3	1	+1	$3p_x$	
3	1	0	$3p_y$	
3	1	-1	$3p_z$	
3	2	+2	$3d_{xy}$	
3	2	+1	$3d_{zx}$	
3	2	0	$3d_{yz}$	
3	2	-1	$3d_{x^2-y^2}$	
3	2	-2	$3d_{z^2}$	

So how do the electrons fit into all this?

The Pauli Exclusion Principle

Wolfgang Pauli born 1900 in Austria.

Awarded Nobel prize for Physics in 1945 for the exclusion principle:

"No two electrons in the same atom may have the same set of quantum numbers"

Electrons possess a fourth quantum number called the spin quantum number:

Spin quantum number s ±1/2

What is spin?

Spin is necessary for quantum mechanical calculations. Electrons are magnetic, they may either lie with or against a magnetic field.