

2.12 Electronic Structure

In this chapter we are going to look at electronic structure in atoms. This is actually a very complex area of chemistry because it is very hard, if not impossible, to describe the behaviour of electrons. We work instead with simplified models of the atom. At A-level we use more than one model of the atom.

It is important to realise that in chemistry we are often creating and using models that can explain observed behaviour. These models are often modified over time when new evidence is produced. They are only models though and not reality.

Bohr model

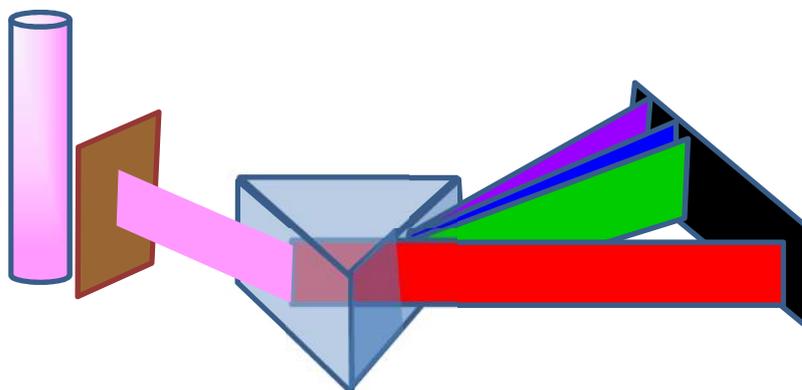
An early model of the atom was the Bohr model. This is named after the Danish scientist Niels Bohr who described it in the early 20th century. This is essentially the model you will be familiar with from GCSE, with a central nucleus and electrons arranged in discrete shells or energy levels around the nucleus. Electrons can only have fixed discrete energies.

Evidence for the Bohr Model

Emission spectra for elements give evidence for Bohr's model

When various elements are heated or electronically excited, they emit light of different colours.

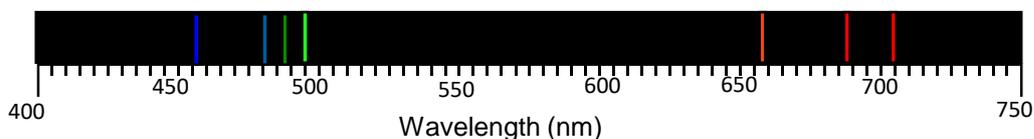
The light is separated into various colours by a spectroscope- an emission spectrum is observed, which appears as a series of lines.



Hydrogen emission spectrum



Strontium emission spectrum

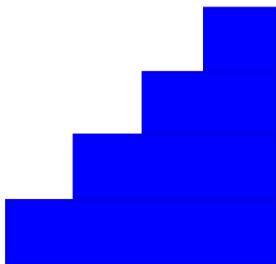


Each element has its own unique line spectra (fingerprint). Elements can be identified by their emission spectra.

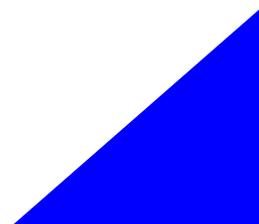
An emission spectra is a series of discrete lines with fixed wavelengths. It is possible for this spectra to appear at wavelengths outside of the visible spectrum of the electromagnetic spectrum.

The line spectra can be used as evidence for the theory that electrons have fixed quantised energy levels

Electrons only have specific discrete energy levels possible (only certain energies are allowed) rather than a continuous range of possible energies.

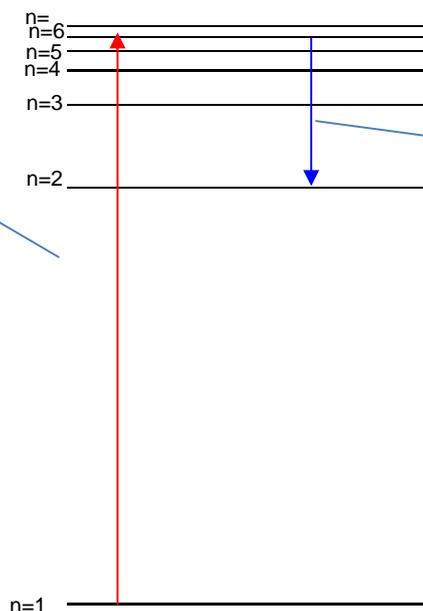


These diagrams represent the difference between discrete and continuous. The steps represent discrete energy levels whereas the ramp shows the idea of a continuous range of energies.



The diagram below represents the different energy levels that electrons in an atom have and how lines on an emission spectrum are formed

1. By absorbing specific energies from heat or light, an electron can move to a higher energy level. The atom is then in an excited state



2. The atom is unstable at the higher energy level and so the electron drops back down to a lower energy level. When the electron falls to a lower energy level it will emit photons of exactly that energy difference.

3. As the electron falls from higher to lower energy level, E_6 to E_2 , so a photon of light is emitted with frequency, ν , given by the equation :
$$\Delta E = E_6 - E_2 = h \times \nu$$

(where h is Planck's constant with the value of $6.63 \times 10^{-34} \text{ J Hz}^{-1}$)

4. Transfers of electrons between different energy levels will result in different lines on an emission spectrum

Bohr proposed the above idea of energy levels by studying the emission spectrum of hydrogen. He labelled the energy levels with a number which he called the **principle quantum number, n**. The energy level closest to the nucleus that is lowest in energy is labelled $n=1$. The energy levels are also called **shells**.

Planck's Equation

This equation used above links the frequency of the energy emitted with the energy difference between the different energy levels.

$$\Delta E = h\nu$$

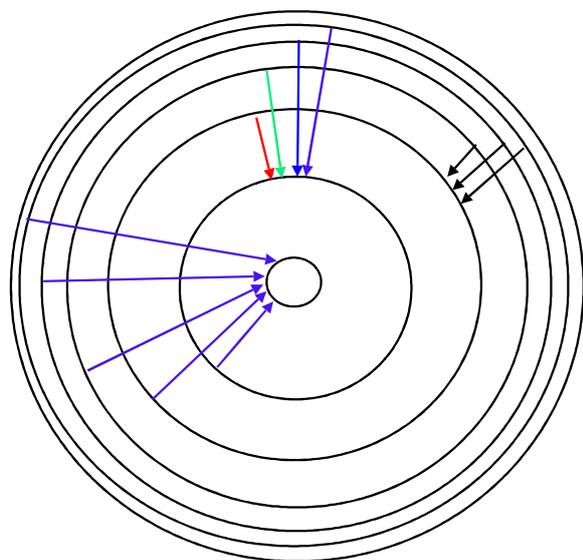
ν = frequency of light emitted (unit s^{-1} or Hz)

h = Planck's constant $6.63 \times 10^{-34} \text{ (J s)}$

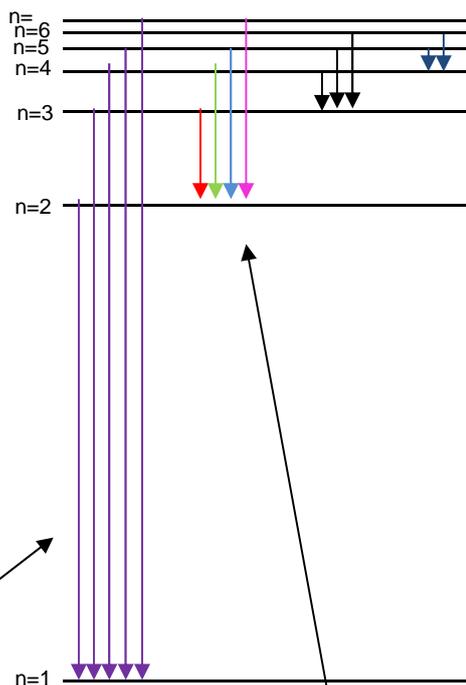
ΔE = energy difference between energy levels (J)

The Hydrogen Spectrum

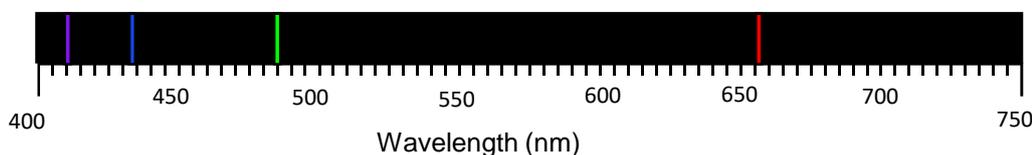
The hydrogen emission spectrum consists of several series of lines that exist in the ultra-violet, visible and infra-red regions of the electromagnetic spectrum.



One set of lines, called the Lyman series, appear in the ultraviolet part of the spectrum. Bohr proposed that each of these lines was caused by an electron returning from a higher energy level back to energy level $n = 1$



Another set of lines, that appear in the visible spectrum called the Balmer series, are due to electrons returning to the $n=2$ energy level from a higher energy level.

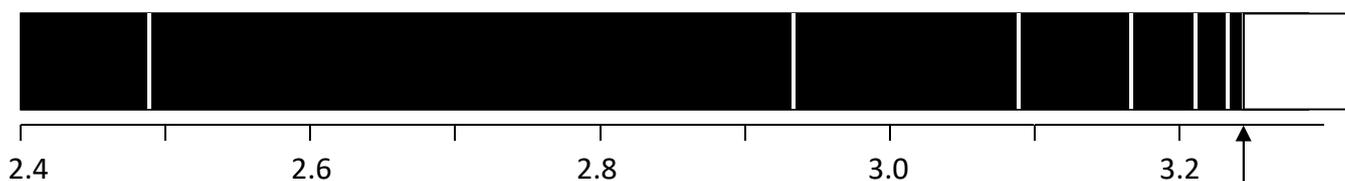


The Balmer series

Convergence limit

The spectrum below is the Lyman Series for Hydrogen.

Frequency/ 10^{15} Hz



The lines formed at the continuum are due to the energy drop, $\Delta E = E_{\infty} - E_1$. This is the equivalent to the energy required to ionise the atom and remove the electron from the atom.

Using Planck's equation we can calculate an ionisation energy for hydrogen from the convergence frequency of the Lyman series

$$\begin{aligned} \text{ionisation enthalpy, } \Delta E &= h \times \nu \\ &= 6.63 \times 10^{-34} \times 3.27 \times 10^{15} \\ &= 2.17 \times 10^{-18} \text{ joules} \end{aligned}$$

The lines converge at the frequency of 3.27×10^{15} Hz. Here the lines get so close together that they form a continuum.

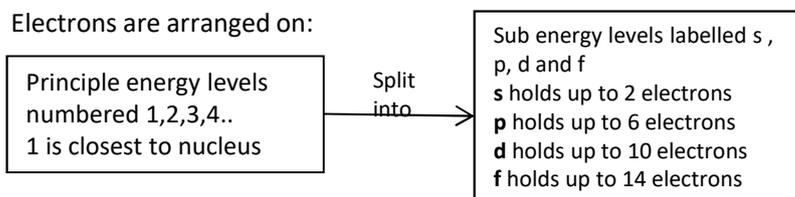
Sub shells

The emission spectra for atoms with more electrons than hydrogen become more complicated. There are many more lines than can be explained just by transfers of electrons between the main energy levels. The idea of sublevels or subshells was proposed to explain the existence of the extra lines.

For the shell $n=1$ there is one sub shell labelled the 1s

For the shell $n=2$, there are two sub shells labelled 2s and 2p. The 2p is higher in energy than the 2s

For the shell $n=3$, there are three sub shells labelled 3s, 3p and 3d



Principle level	1	2	3	4
Sub-level	1s	2s, 2p	3s, 3p, 3d	4s, 4p, 4d, 4f

The letters used to label the sub shells came from the nature of the lines that appeared in the sodium line emission spectrum

S was labelled the **sharp** series

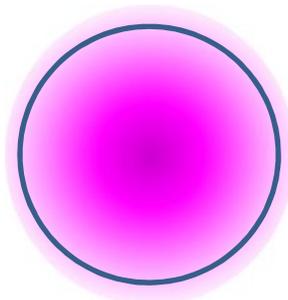
P was labelled the **principle** series

D was labelled the **diffuse** series

Into Wave mechanics

Within a few years of Bohr's model of the atom with fixed shells of electrons, scientists came to realise the nature of electronic structure was much more complicated. Bohr's model cannot explain fully line spectra for atoms more complicated than hydrogen. Bohr also assumed that the electron was a solid particle of matter.

- Louis de Broglie, in 1924, proposed that electrons can act like waves as well as a particle. This was called **wave-particle duality**.
- In 1927 Werner Heisenberg proposed his '**Uncertainty Principle**' which stated that it was impossible to measure both the position and velocity of an electron at the same time. The path of an electron cannot therefore be determined. It is uncertain. Therefore a circular specific "orbit" for an electron, such as that proposed by Bohr, cannot occur.
- In 1926 Erwin Schrödinger derived an equation using wave mechanics that predicts the probabilities of an electron's location. It gives a model of an atom using the mathematics of waves. The solution to this equation gives 3-D regions of probability of where an electron might be found. These regions are called **atomic orbitals**.
- Schrödinger's equation still uses the ideas of principle or main energy levels and the s,p,d sub levels mentioned above. Orbitals are drawn representing 90% probability of finding an electron. There are different shapes for the s p and d orbitals.



Each orbital has its own approximate, three dimensional shape.

It is not possible to draw the shape of orbitals precisely.

They do not have exact boundaries but are fuzzy.

They are often called 'charge-clouds'.

The outer blue circle represents the boundary of about 90% probability of finding an electron

Shapes of Orbitals

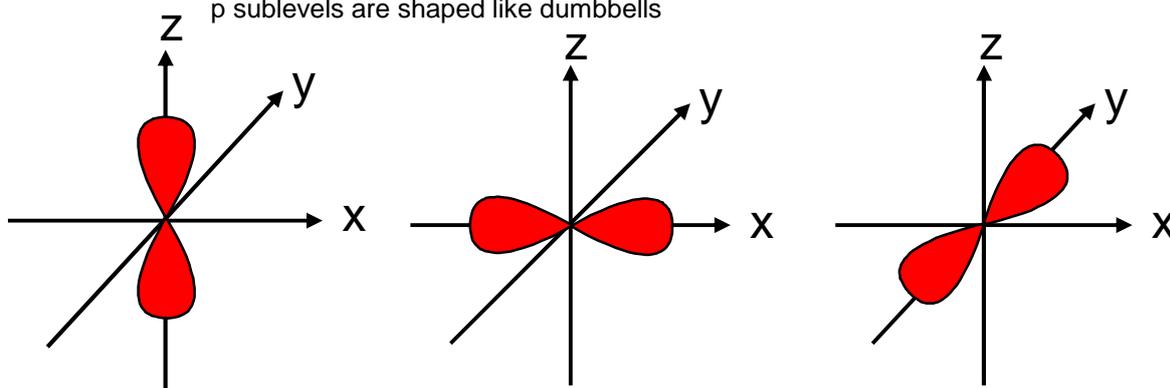


There are different shapes for the s p and d orbitals.

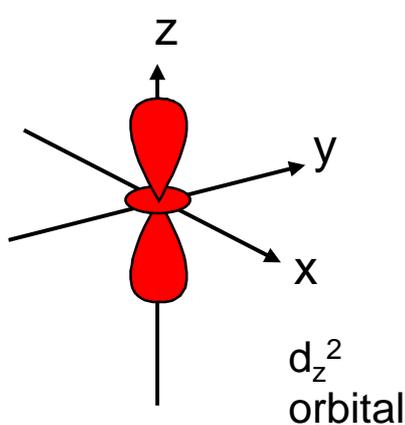
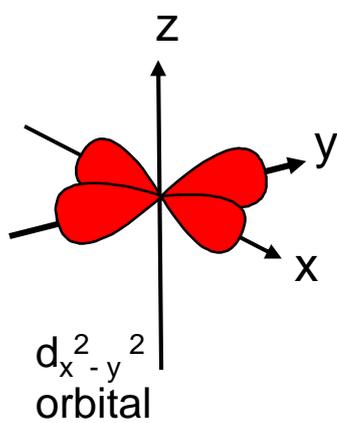
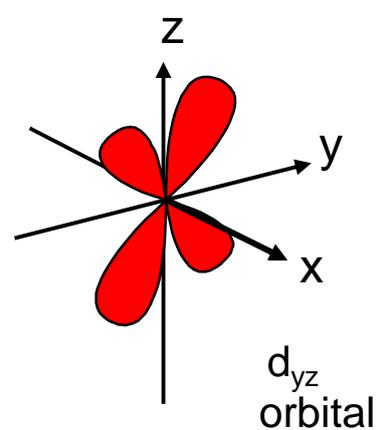
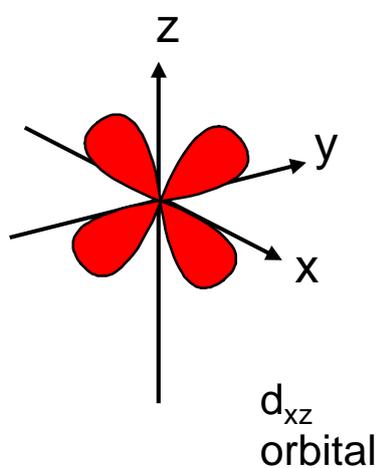
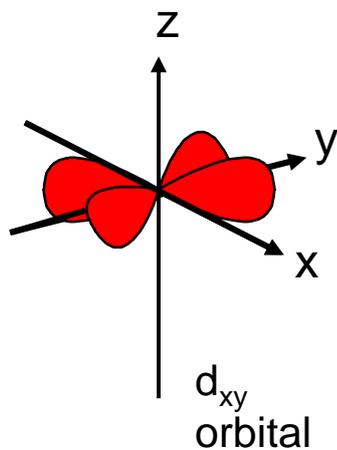
Orbitals hold up to 2 electrons of opposite spin

s sublevels are spherical

p sublevels are shaped like dumbbells



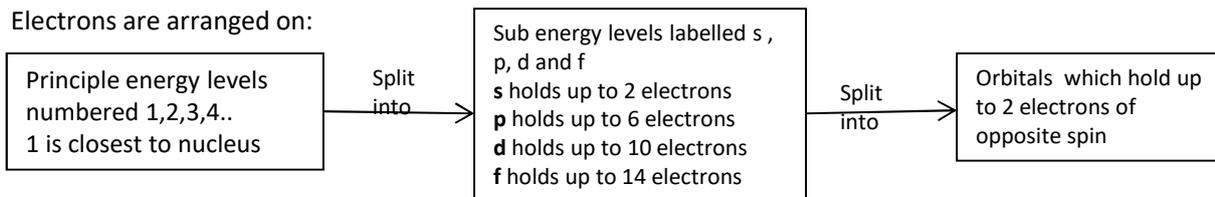
The three 2p orbitals.



The shapes and labels of the five 3d orbitals.

Describing Electronic Structure

Electrons are arranged on:



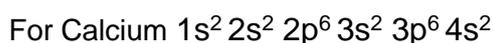
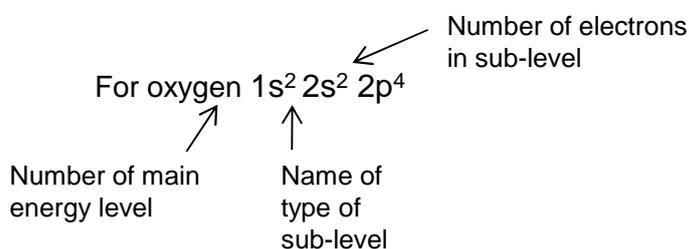
Principle level	1	2	3	4
Sub-level	1s	2s, 2p	3s, 3p, 3d	4s, 4p, 4d, 4f

An atom fills up the sub shells in order of increasing energy (note 3d is higher in energy than 4s and so gets filled after the 4s)

$1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p$

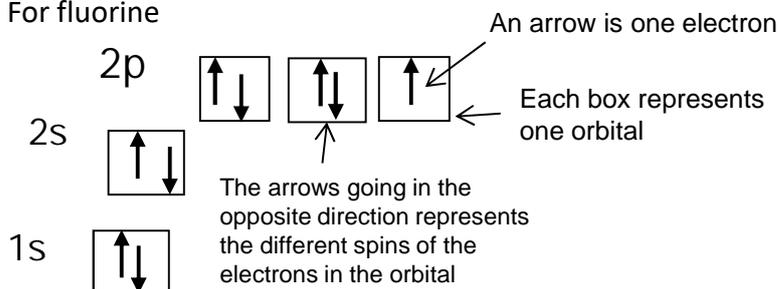
This is called the building up (Aufbau) principle

Writing electronic structure using letters and numbers



Using spin diagrams

For fluorine



No one orbital or box can hold more than two electrons. This is called the Pauli exclusion principle

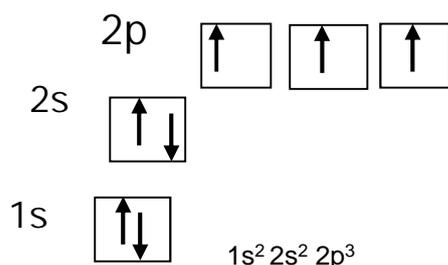
When filling up sub levels with several orbitals, fill each orbital singly before starting to pair up the electrons



This uses Hund's Rule:

Electrons organise themselves so that as far as possible they remain unpaired, occupying the maximum number of sub-level orbitals possible.

For nitrogen



Electronic structure for ions

When a positive ion is formed electrons are lost from the outermost shell
Mg is $1s^2 2s^2 2p^6 3s^2$ becomes Mg^{2+} is $1s^2 2s^2 2p^6$

When a negative ion is formed electrons are gained
O is $1s^2 2s^2 2p^4$ becomes O^{2-} is $1s^2 2s^2 2p^6$

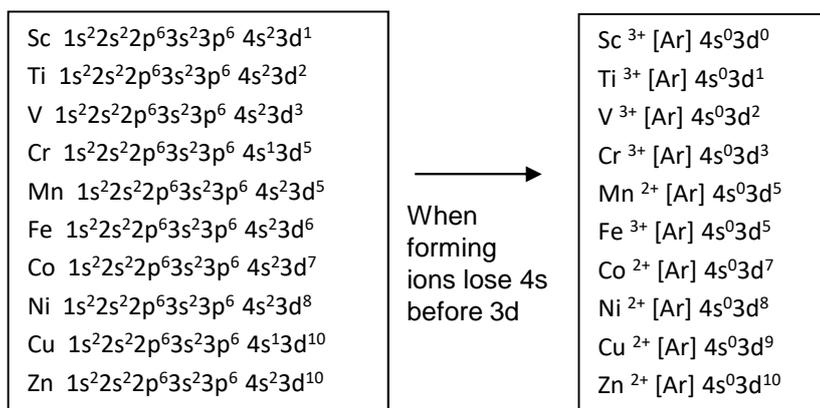
Electronic structure of d-block elements

The electronic structure of the d-block has some complications. As mentioned earlier, conventionally we say that 4s fills before 3d and so we write them in that order. There is, however, disagreement in the scientific community about whether this is true.

If you look at the electronic structures below you will see both Chromium and copper have an unusual arrangement in having a half filled d sub shell.

You will also see that when d block elements form ions they lose the 4s electrons first.

You may find if you research different reasons for these observations. It may well be many of the reasons are false and we have to accept that some things in chemistry don't neatly follow patterns we can explain. You do need to learn these electronic structure though!



Electronic Structure for elements H to Kr

H $1s^1$

He $1s^2$

Li $1s^2 2s^1$

Be $1s^2 2s^2$

B $1s^2 2s^2 2p^1$

C $1s^2 2s^2 2p^2$

N $1s^2 2s^2 2p^3$

O $1s^2 2s^2 2p^4$

F $1s^2 2s^2 2p^5$

Ne $1s^2 2s^2 2p^6$

Na $1s^2 2s^2 2p^6 3s^1$

Mg $1s^2 2s^2 2p^6 3s^2$

Al $1s^2 2s^2 2p^6 3s^2 3p^1$

Si $1s^2 2s^2 2p^6 3s^2 3p^2$

P $1s^2 2s^2 2p^6 3s^2 3p^3$

S $1s^2 2s^2 2p^6 3s^2 3p^4$

Cl $1s^2 2s^2 2p^6 3s^2 3p^5$

Ar $1s^2 2s^2 2p^6 3s^2 3p^6$

K $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

Ca $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Sc $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

Ti $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$

V $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

Cr $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

Mn $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

Fe $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Co $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$

Ni $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$

Cu $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Zn $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

Ga $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

Ge $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$

As $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$

Se $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$

Br $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

Kr $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$