The Configuration of Electrons in Atoms: Shells and Subshells

Evidence was found towards the end of the 19th century that electrons existed. Particularly following the cathode ray tube experiments of Dr J. J. Thompson, by 1909 it was known that electrons were negatively charged particles with a tiny mass. Soon after this the nuclear atom\(^1\) was proposed by Rutherford, in which the vast majority of the mass of an atom is in a small positively-charged nucleus and the electrons are in a ‘cloud’ around the nucleus. Evidence about the configuration of electrons in an atom came from two sources; ionisation energies and emission spectra. In his document the development of our understanding of the electron and its configuration inside the atom is explored, by relating it to experimental evidence.

**Cathode Ray Tube Experiments**

Our initial understanding about electrons emerges from the study of cathode rays. At low pressures, gases conduct well (eg fluorescent lights). In an evacuated glass vessel, containing a cathode, (ie a negatively charged plate) and an anode (a positively charged plate). A voltage is applied across the plates and this heats up the cathode so that thermionic (electron) emission occurs. The cathode rays are electrons that are repelled by the negative plate and are attracted by the positive plate, accelerated through the vacuum. A phosphorescent material (which causes scintillations when struck by electrons) is used to coat the far end of the vessel, so that the electrons can be detected.

If a magnet is brought close to the vessel then the beam of particles is deflected; the nature of the deflection indicating that the cathode rays are negatively charged. In 1897, in the cathode ray experiment\(^2\), Dr J. Thomson was able to calculate the charge to mass \((e/m)\) ratio by measuring the deflection of a narrow beam of cathode rays in both electric and magnetic fields. Let \(\theta_E\) be the angle of deflection when an electric field is imposed and let \(\theta_B\) be the angle of deflection when a magnetic field is imposed. In the case when \(\theta_E = \theta_B\)

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\frac{e}{m} = \frac{E \theta_E}{B^2 I},
\]

and it was found that \(\frac{e}{m} = -1.76 \times 10^8 \text{ C/g}\).

Thompson found that the \(e/m\) value did not change for the cathode rays when different gases and different metals for the electrodes were used. It followed that all materials used as cathodes contained this same particle, and the cathode-ray particles had a minute mass of only 1/1837 of the mass of a hydrogen atom. Thomson called them **electrons** (the name suggested earlier by Stoney for the ‘units of electricity’).

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\(^1\) The Discovery of the Nuclear Atom

\(^2\) Cathode Ray Tube Experiment
Ionisation Energies of Elements

The ionisation energies of elements are the energies required to remove electrons from the elements. The first ionisation energy\(^3\) is the energy required to remove the first electron from the element, or more accurately the energy required to remove one mole\(^4\) of electrons from one mole of gaseous atoms in order to produce one mole of gaseous ions, each with a charge of +1.

The graph below shows the first ionisation energy of the first 20 elements.

As you move across a period of the periodic table\(^5\) the 1\(^{st}\) ionisation generally energy increases. As you move down a group of the periodic table the 1\(^{st}\) ionisation energy decreases.

The successive ionisation energies of sodium are shown in the following graph.

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\(^3\) First Ionization Energy
\(^4\) The Mole and Avogadro’s Number
\(^5\) Atomic Structure and the Periodic Table
The graph shows the general increase in energy required to remove each electron and shows the marked increase when a new shell is reached.

**Emission Spectra of the Elements**

The light emitted by the elements, for example during burning or through discharge through a gas, is a characteristic ‘fingerprint’ of the element concerned. The analysis of the emission spectra of the emitted light informs us of the configuration of electrons in atoms.

**Flame test**

When an element is supplied with energy they may emit light. This can be observed simply when an element is burned and this is called the flame test\(^6\). The following table shows the flame colour of a number of metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Flame Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>Yellow</td>
</tr>
<tr>
<td>Barium</td>
<td>Green</td>
</tr>
<tr>
<td>Copper</td>
<td>Blue/Green</td>
</tr>
<tr>
<td>Potassium</td>
<td>Lilac</td>
</tr>
<tr>
<td>Calcium</td>
<td>Brick Red</td>
</tr>
</tbody>
</table>

Similarly, when an electric charge is discharged through a gas in a gas discharge tube then the light emitted is characteristic of the gas. If the light emitted from the flame test or the gas discharge tube is passed through a prism to separate out the different frequencies of light emitted, a set of coloured lines is observed called an **emission line spectrum**.

Each element has its own atomic emission spectrum\(^7\), that is unique to that element. In the late 19th century it was found that the hydrogen emission spectrum had lines in the ultra-violet and infra-red areas of the spectrum (as well as the visible spectrum). Three such sets of lines were discovered:

- The **Balmer series**: lines in the visible spectrum
- The **Lyman series**: lines in the ultraviolet region of the spectrum
- The **Paschen series**: lines in the infrared region of the spectrum

The analysis of the emission spectra of atoms gives us information about the configuration of electrons in an atom. For example the hydrogen atom has one electron, which may occupy the

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\(^6\) [Flame Test](#)

\(^7\) [Atomic Emission Spectrum](#)
lowest energy state possible, also called the ground state. The lone electron may be excited by an input of energy and move to a higher energy level. When an excited electron relaxes back to its ground state or to a lower energy level, the excess energy is lost by emission of radiation (visible, infra-red or ultra-violet light) with a certain energy value equal to the difference in energy between the two energy levels.

The frequency of radiation emitted from an element can tell us the energy difference between the different energy levels (or shells). Since particular frequencies are emitted, this can be explained by the theory that the electrons in an atom can only occupy fixed energy levels (or shells). From the hydrogen emission spectrum, Niels Bohr proposed an electronic structure of the hydrogen atom (the simplest case since hydrogen contains only one electron), based on electrons occupying a shell structure.