

The Noble Gases

The Noble Gases (inert gases, Group 0, Group 18 or the helium group) are notoriously unreactive elements ('noble' means unreactive in chemistry) and in their elemental state they exist as monoatomic gases – gases whose 'molecules' are single atoms of the element, since the atoms are reluctant to react with anything, including one-another. This inertness is due to the fact that they have stable outer electron shells, with stable octets of electrons (full s and p subshells) except helium, which has a stable full inner shell. The electronic configurations are:

Helium (He): $1s^2$

Neon (Ne): $1s^2 2s^2 2p^6$

Argon (Ar): $[\text{Ne}] 3s^2 3p^6$

Krypton (Kr): $[\text{Ar}] 3d^{10} 4s^2 4p^6$

Xenon (Xe): $[\text{Kr}] 4d^{10} 5s^2 5p^6$

Radon (Rn): $[\text{Xe}] 5d^{10} 6s^2 6p^6$

Nevertheless, this group does have some interesting chemistry and also exhibit interesting physical properties. Reactivity increases down the group. Often helium is included as the first member of the group.

Helium (He)

Helium is chemically a highly unreactive element. It only forms transient species when electric discharges are passed through a mixture of helium gas and another gaseous element. For example, passing an electric discharge through a mixture of helium and hydrogen forms the transient molecule HHe, which has a very short half-life. HHeF is metastable.

Neon (Ne)

Neon is chemically the most unreactive element. It forms no true compounds, and no neutral molecules. Ionic molecules are known, e.g. $(\text{NeAr})^+$, $(\text{NeH})^+$, $(\text{HeNe})^+$ and Ne^+ .

Argon (Ar)

The unstable argon fluorohydride, HArF, is known. Ar also forms clathrates (see krypton) with water and highly unstable ArH^+ and ArF are known. ArF exists as an excited dimer (excimer) with a half-life of nanoseconds. ArF is thought to be a Rydberg cluster (Rydberg matter) – a state of matter formed with atoms in a very high energy state, but not quite ionised. The electron in such atoms is usually found quite far from the nucleus and can be delocalised into a weak molecular orbital, which decreases the electron energy slightly. Such clusters generally contain less than 100 atoms.

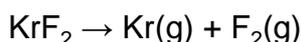
Krypton (Kr)

Krypton is also very unreactive. Some clathrate compounds occur – compounds in which helium atoms are sandwiched or caged in by other molecules without forming any definite chemical bonds with the encaging molecules. For example, $3\text{C}_6\text{H}_4(\text{OH})_2 \cdot 0.74\text{Kr}$, in which some krypton atoms become trapped inside crystals of $\text{C}_6\text{H}_4(\text{OH})_2$ or para-quinol (p-hydroxybenzene, 'para' meaning that the two –OH groups are opposite one-another):



p-hydroxybenzene

KrF_2 is unstable and has the weakest element-fluorine bond energy (50 kJ/mol) known. It decomposes into Kr and F_2 at room temperature (at the rate of about 10% per hour):



The ions KrF^+ and Kr_2F_3^+ are known to form ionic salts with MF_6^- or $\text{M}_2\text{F}_{11}^-$ ions, where M is antimony (Sb), niobium (Nb) or tantalum (Ta), e.g. $\text{KrO}_2\text{F}^+\text{Sb}_2\text{F}_{11}^-$.

Radon (Rn)

RnF_2 has been reported. The RnF^+ ion forms similar salts to the KrF^+ ion. The cost and radioactivity of radon have inhibited a study of its chemistry, which is expected to be diverse.

The chemistry of xenon is discussed below.

Physical Properties

The elements exist as monoatomic gases at room temperature and pressure, but can be solidified at extremely low temperatures, due to weak (induced) van der Waals forces between the atoms, e.g. neon freezes at -249°C , helium at -270°C . The larger the atomic mass, the lower the freezing temperature (as the van der Waals forces are stronger between larger atoms with more electrons to contribute to the inter-atomic attractive forces). The solids have the face-centred cubic (fcc) close-packed arrangement.

Solid xenon is a white crystalline material (fcc) and at high pressures (140 GPa) it switches to a metallic sky-blue solid with a hexagonal close-packed (hcp) structure. In this hcp form, the bonding between the atoms is **metallic** – xenon bonds with itself under these extreme conditions to form a metal!

Discharge tubes. The gases can all be made to fluoresce. In discharge tubes, such as neon lights, the inert gas is at low pressure and several thousand volts are applied across two metallic electrodes. The electric voltage ionises the gas, completing the circuit, and causing the gas to fluoresce (light is emitted by electron transitions in the ions). The characteristic colour of the light produced depends on the element as follows:

Helium (He) pink

Neon (Ne) red-orange

Argon (Ar) violet

Krypton (Kr) white

Xenon (Xe) blue/lavendar

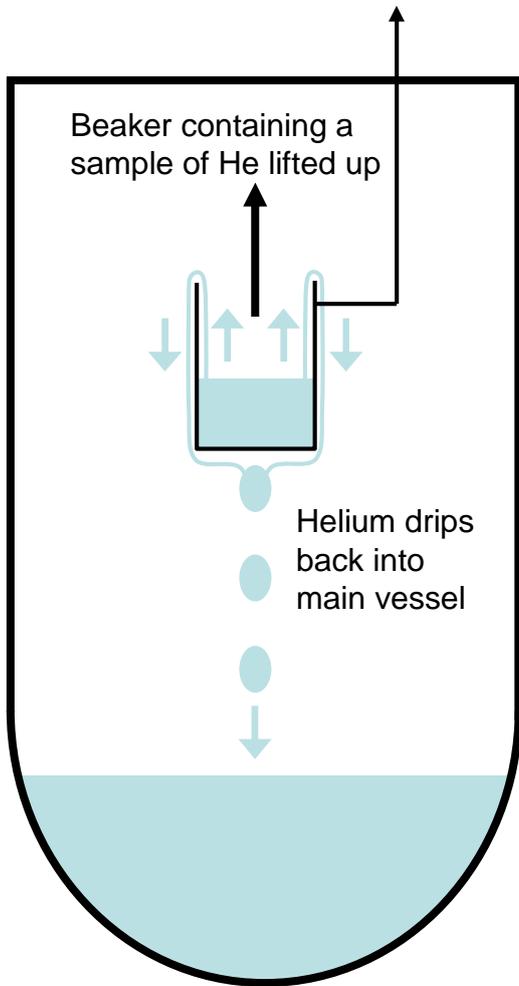
Liquid Helium

Helium liquefies at -269°C (4 K), but on further cooling to 2.17K (the lambda point) the properties of the liquid suddenly change, it becomes a **superfluid**. A superfluid exhibits bizarre properties: it flows **without viscosity** or friction/drag. This enables it to leak from porous containers which would normally contain liquid helium. It also allows a helium superfluid fountain to continue apparently indefinitely, since without friction no energy is lost from the system (but the system must remain cooled below the lambda point). Upon reaching the lambda point the liquid also immediately ceases to boil, since the temperature becomes the same everywhere within the fluid.

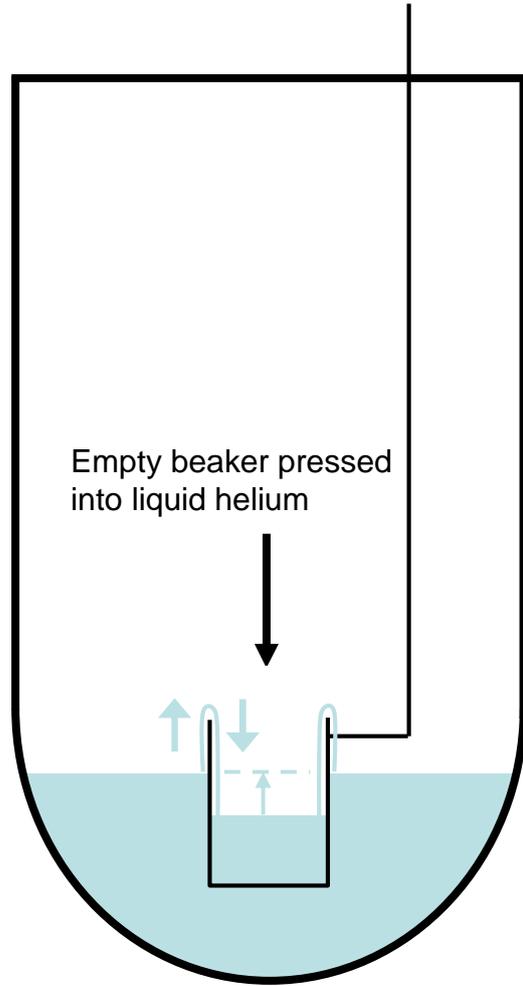
In this superfluid state the atoms of the fluid are behaving cooperatively, as if the whole fluid was a single quantum state. This phenomenon is described by Bose-Einstein statistics and such a fluid is also called a **Bose-Einstein condensate**. Such a state of matter can only be formed by particles called bosons. Particles can be either bosons, which have an integral value of spin (the quantum mechanical equivalent of angular momentum due to rotation of the particle) that is a whole number value such as 0, 1, 2, etc. Fermions have fractional spin. Electrons are fermions with a spin = $\frac{1}{2}$. Protons and neutrons are also fermions with spin $\frac{1}{2}$. Composite particles, like atoms, are also either fermions or bosons. Fermions can, and prefer to, pair in such a way that their spins cancel ($+\frac{1}{2} + -\frac{1}{2} = 0$). Thus, a particle composed of an even number of fermions is a boson, whilst a particle composed of an odd number of fermions is a fermion. A normal atom of hydrogen (hydrogen-1 ^1H) is a boson: it consists of one electron and one proton. An atom of deuterium (D or ^2H , hydrogen-2) consists of one electron, one proton and one neutron, and is a fermion. Similarly, the dominant isotope of helium, helium-4 (^4He) is a boson, consisting of two electrons, two protons and two neutrons. Thus helium-4 will form a Bose-Einstein condensate on cooling.

The much rarer isotope helium-3 (^3He) consists of two electrons, two protons and one neutron and is a fermion. Our discussion so far relates to ^4He , however, at even lower temperatures of a few milliKelvins ^3He also forms a Bose-Einstein condensate, since ^3He atoms form pairs, called **Cooper pairs** which behave as bosons as each pair contains an even number of fermions. In a Cooper pair, the temperature is low enough to allow weak quantum mechanical interactions between a pair of fermions, that are normally swamped by thermal vibrations, to become dominant. These interactions are attractive. In many metals cooled to very low temperatures, electrons pair-up into Cooper pairs due to weak attraction resulting from the exchange of phonons. (A phonon is a pseudo-particle and quanta of crystal vibrations, which are standing waves confined inside the crystal and so their energy is necessarily quantised). These Cooper electron pairs are responsible for superconductivity.

Most bizarrely since the fluid is frictionless it can **flow uphill** and will do so whenever this allows it to lose gravitational potential energy and finally flow to a lower point! If a beaker half-full of He-superfluid is withdrawn from the bulk, then the liquid in the beaker will return to the bulk liquid in the vessel beneath by flowing up over the sides of the beaker, in a thin film, and dripping from the bottom of the beaker back into the bulk fluid. (See diagram below).



Superfluid helium will flow uphill over the sides of a beaker to move down with gravity!

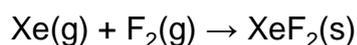


Superfluid helium will flow uphill over the sides of a beaker to move down with gravity! In this case it will move up and over the sides of the empty beaker until the level of fluid in the beaker is the same as that in the main vessel.

Xenon (Xe)

Xenon has quite a rich chemistry, forming a variety of compounds with the most reactive elements, such as fluorine and oxygen. These compounds are unstable, often explosive and producing hazardous products such as HF. It reacts by expanding its octet. The fluorides are stable colourless/white solids at room temperature. Even with fluorine, reactions are reluctant and require harsh conditions and a catalyst:

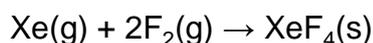
Xenon difluoride (xenon(II) fluoride), a white solid:



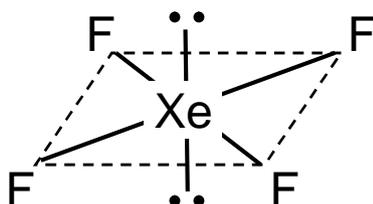
(1:4 ratio of Xe:F₂, passed through a Ni tube at 400°C)



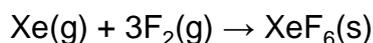
Xenon tetrafluoride (xenon(IV) fluoride), a white solid:



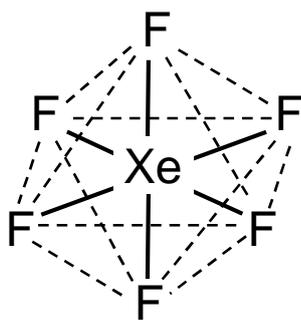
(1:5 ratio of Xe:F₂, heated for 1h at 13 atm in a Ni can at 400°C)



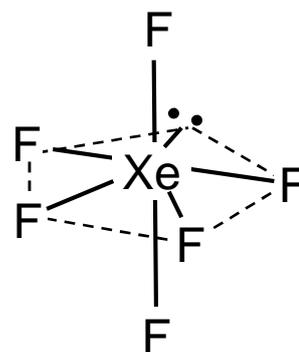
Xenon hexafluoride (xenon(VI) fluoride), a white solid (polymeric), readily sublimates to a yellow vapour (m.p. = 49.25, b.p. = 75.6°C) and forms (XeF₆)₄ molecules in solution:



(Heat Xe in excess F₂ at 200 atm)

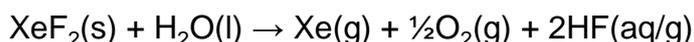
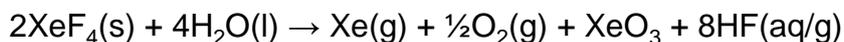
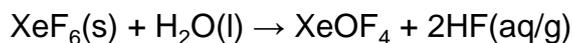


The basic shape of XeF₆ is octahedral (left) but the octahedron is distorted, due to the presence of a 7th electron-pair (a lone pair) which is close to the Xe nucleus and so does not affect the designated shape, but distorts it – right (8 electrons from Xe + 6 from 6F = 14 electrons = 7 pairs).

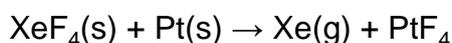
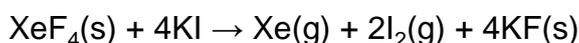


Note that in these structures, xenon has expanded its octet to accommodate more electrons (vacant d-orbitals contribute to the formation of the molecular orbitals).

The fluorides all react with water, splitting the water molecules (hydrolysis):

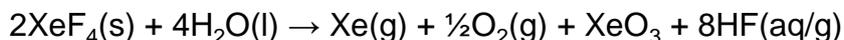


The fluorides are all strong oxidising and fluorinating reagents (the HF produced on reaction with water is a highly reactive fluorinating agent) e.g.



Xenon oxides

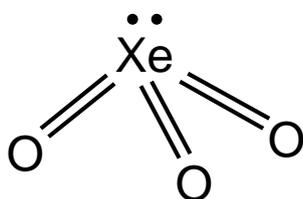
Xenon trioxide (a colourless/white crystalline solid) is produced by hydrolysis of XeF_4 or XeF_6 :



XeO_3 reacts with water to form xenon hydroxide:

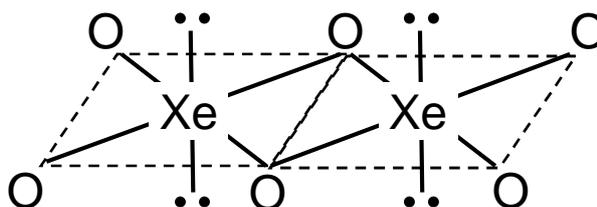


XeO_3 reacts with the oxyfluoride, XeOF_4 to form xenon dioxide (a yellow solid):



Xenon trioxide

Xenon dioxide forms a chain with square planar units:

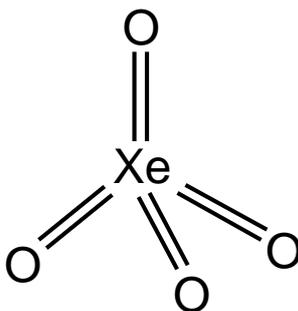


Xenon trioxide is unstable above 25°C and in contact with organic materials, tending to decompose explosively into Xe and O².

Xenon tetroxide, XeO₄, is highly unstable, decomposing explosively into xenon and fluorine at room temperature (or above – 35.9°C):

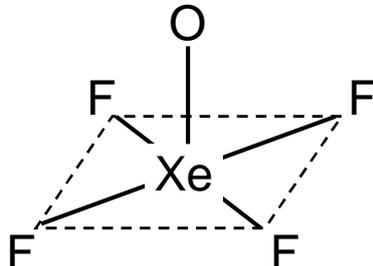
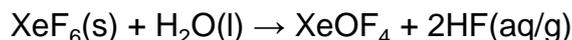


It is a yellow solid below -36°C.

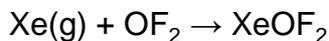


Oxyfluorides

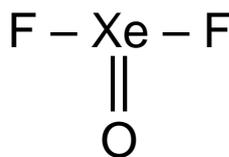
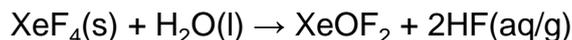
XeOF₄ (xenon(VI) oxyfluoride or xenon oxytetrafluoride) is a colourless liquid and is produced by hydrolysis of XeF₆:



At low temperature Xe reacts with OF₂:



XeOF₂ (xenon(IV) oxyfluoride or xenon oxydifluoride) is also formed by hydrolysis of XeF₄ at low temperatures:



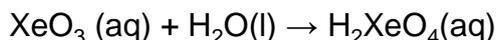
At –20°C:



XeO₂F₂ decomposes at room temperature: $\text{XeO}_2\text{F}_2 \rightarrow \text{XeF}_2 + \text{O}_2$

Xenates

Dissolving XeO_3 in water forms xenic acid:



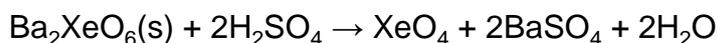
the salts of which are xenates, e.g. Ba_3XeO_6 .

in neutral or alkaline solution xenates disproportionate (simultaneously oxidise and reduce) to give perxenates (xenon(VIII)), e.g. Ba_2XeO_6 .

Reaction of XeF_6 with alkali gives sodium xenate:

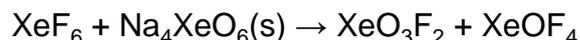


Reaction of xenate with a stronger acid (displacement of a weaker acid from its salt):



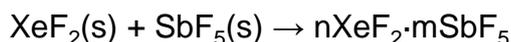
(in the cold, as XeO_4 decomposes explosively above $-36^\circ\text{C} \rightarrow \text{Xe} + \text{O}_2$).

reaction of sodium xenate with xenon hexafluoride yields volatile xenon(VIII) oxyfluoride or xenon trioxydifluoride, XeO_3F_2 :



Mixed Fluorides

Xenon fluorides react with other fluorides to form mixed fluorides, in which the xenon fluoride dissolves to form a solid solution:



(in BrF_5 solution)

where $n:m = \{ 1:1, 1:2, 2:1, 1:1.5, 1:6 \}$

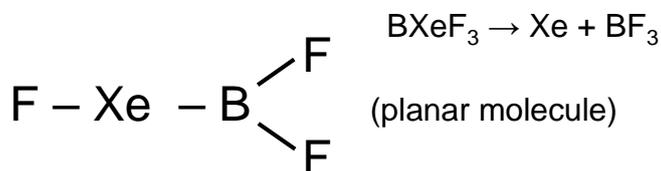
similarly, also known are the following: $\text{XeF}_4 \cdot \text{SbF}_5$, $\text{XeF}_4 \cdot 2\text{SbF}_5$, $\text{XeOF}_4 \cdot \text{SbF}_5$, $\text{XeOF}_4 \cdot 2\text{SbF}_5$, $\text{XeOF}_2 \cdot 2\text{SbF}_5$, also solutions with SbF_5 as solvent. With AuF_5 as solvent, $\text{XeF}_6 \cdot \text{AuF}_5$ and $2\text{XeF}_6 \cdot \text{AuF}_5$ are known.

Other Compounds

At -100°C :



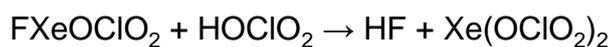
which decomposes at -30°C and above:



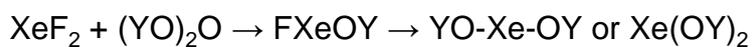
In very strong acids (acids stronger than sulphuric or nitric acid), such as perchloric acid (HOClO_2), HSeF_5 , or HOSO_2F , and others (general formula HOY) the fluorines of xenon difluoride are sequentially replaced:



e.g.



and with the anhydrides, $(\text{YO})_2\text{O}$, of these acids:



e.g. with $(\text{SeF}_5\text{O})_2\text{O}$, $\text{Y} = \text{SeF}_5$, the anhydride of HSeF_5 acid:



The Helium Atom

The helium atom is the next simplest stable atom after hydrogen. Whereas hydrogen consists of one proton and one electron (and sometimes one or two neutrons), helium consists of two electrons, two protons and two neutrons (${}^4\text{He}$) or one neutron (the rarer ${}^3\text{He}$ isotope). The position of two electrons, two identical particles, deserves special attention since this reveals some interesting physics.

Recall that electrons are spin- $\frac{1}{2}$ particles, meaning they have a spin of either $+\frac{1}{2}$ (designated spin up or \uparrow) or $-\frac{1}{2}$ (spin down or \downarrow). This spin is the quantum mechanical equivalent of angular momentum due to the rotation of the particle, in units of \hbar ($\hbar = h/2\pi$ and $h = \text{Planck's constant}$ is approximately 6.626×10^{-34} Js (Js = Joule second)). We can picture the electron as a ball rotating either clockwise (spin-up) or anticlockwise (spin-down), although this simple picture is not strictly correct, since electrons are not objects of definite extent that follow defined trajectories (they are more like wave-packets) and such a picture is useful if we do not take it too seriously.

We have already seen how the a general particle state, such as the hydrogen atom, is described by a wave-function, which is a solution of Schrodinger's wave equation. This results in the hydrogen-atom orbitals, such as s, p and d-orbitals. However, Schrodinger's equation ignores electron spin and the total state of an electron, or pair of electrons, is described by the usual spatial wave-function (orbital) multiplied by the spin-state function. (Spin is treated more exactly by Dirac's relativistic wave equation).

Designating the spin-up state by the symbol α and the spin-down state by β , these are spin-functions, there are four possible simple combinations of spins for two electrons in a single atom:

$$\alpha(1)\cdot\alpha(2) \text{ or } \uparrow\uparrow$$

$$\alpha(1)\cdot\beta(2) \text{ or } \uparrow\downarrow$$

$$\alpha(2)\cdot\beta(1) \text{ or } \downarrow\uparrow$$

$$\beta(1)\cdot\beta(2) \text{ or } \downarrow\downarrow$$

Where we have labeled the first electron 1 and the second electron 2 and the combined state is the product of the individual electron states. A two-particle state is described as **antisymmetric** if on interchanging the labels 1 and 2 (swapping the states of the two electrons) the sign of the combined state function changes and **symmetric** if the sign stays the same. Of the four spin-states above, the first and fourth states are clearly symmetric, since changing the labels can have no effect on the sign, since both spin states are the same. With the second and third states it is not obvious whether interchanging the labels will change the sign or not, since α and β may be described by functions such as the sin function, as is the case with certain spatial wave functions, in which case whether or not the sign changes depends upon the exact values of the arguments – these states are neither symmetric nor antisymmetric.

Empirical observation tells us that the total state function (the product of the spatial wave function and the spin-state function) is antisymmetric for particles called fermions and symmetric for bosons. All particles are either fermions or bosons. electrons are fermions. this means that for a full description we need states that are definitely symmetric and also states that are definitely antisymmetric. Recall, that the solutions of a linear wave equation, like Schrodingers equation, can be linearly combined to form a new state that is also a solution of the wave equation. By linear combination we mean adding or subtracting simple multiples of two or more states together to form a new state. Keeping the two symmetric states we have obtained so far, we can add the two remaining mixed states to form a symmetric state, or subtract them to form an antisymmetric state (and multiply each by $1/\sqrt{2}$ to ensure that when we square the wave function to obtain the probability density function describing the states that the total probability = 1 as it should). This gives the following four states, three symmetric and one antisymmetric:

Symmetric triplet states (parallel spins $\uparrow\uparrow$):

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$\alpha(1)\alpha(2)$$

$$\beta(1)\beta(2)$$

Antisymmetric singlet state (antiparallel spins $\uparrow\downarrow$):

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

For illustration think of electron 1 as being in a spin-up state, $\alpha(1) = +\frac{1}{2}$, $\beta(1) = 0$; whilst electron 2 is in a spin-down state with $\alpha(2) = 0$ and $\beta(2) = -\frac{1}{2}$. In the symmetric state we now have $1/\sqrt{2}[(+\frac{1}{2} \times -\frac{1}{2}) + (0 \times 0)] = 1/\sqrt{2}[-\frac{1}{4}]$ and swapping the labels 1 and 2 (swapping the states of each electron) so that $\alpha(1) = 0$, $\beta(1) = -\frac{1}{2}$ and $\alpha(2) = +\frac{1}{2}$, $\beta(2) = 0$, results in the same value: $1/\sqrt{2}[(0 \times 0) + (+\frac{1}{2} \times -\frac{1}{2})] = 1/\sqrt{2}[-\frac{1}{4}]$.

In the antisymmetric case we initially have $1/\sqrt{2}[(+\frac{1}{2} \times -\frac{1}{2}) - (0 \times 0)] = 1/\sqrt{2}[-\frac{1}{4}]$ and on interchanging 1 and 2, we have $1/\sqrt{2}[(0 \times 0) - (+\frac{1}{2} \times -\frac{1}{2})] = 1/\sqrt{2}[\frac{1}{4}]$, so the sign of the value has changed. This is why this combination of base states is antisymmetric! In reality, states may be mixed states and this introduces sin and cosine terms into α and β , but the principles governing sign changes remain the same.

Multiplicity. The symmetric state is described as a **triplet state**, since it is a group of three sub-states and the antisymmetric state is a **singlet**.

Consider a helium atom, He, in which 2 electrons now orbit the nucleus. If the electrons were like billiard balls, then we could label one as ball A and the other as ball B and track the balls so that we know at all times which is which - the balls are distinguishable since they are two separate objects. In quantum mechanics (QM) particles like electrons can not follow definite trajectories (the Heisenberg Uncertainty Principle forbids it) since their positions and momenta cannot be both precisely known - there are no trajectories in QM (assuming there are no 'hidden variables') as particles are not really like billiard balls, they are more like wave-packets. Now we have an interesting effect indeed: the two electrons in a He atom are so close together that their wavefunctions (or the uncertainties in their positions) overlap and it is impossible in principle to distinguish one electron from the other. The electrons behave and indeed become a single entity or state. They lose their identities! **The two electrons are fundamentally indistinguishable.** This is not just a practical problem, the electrons really are merged into a single entity.

What we require is:

$$\psi_A(x_1) \cdot \psi_B(x_2) \equiv \psi_B(x_2) \cdot \psi_A(x_1)$$

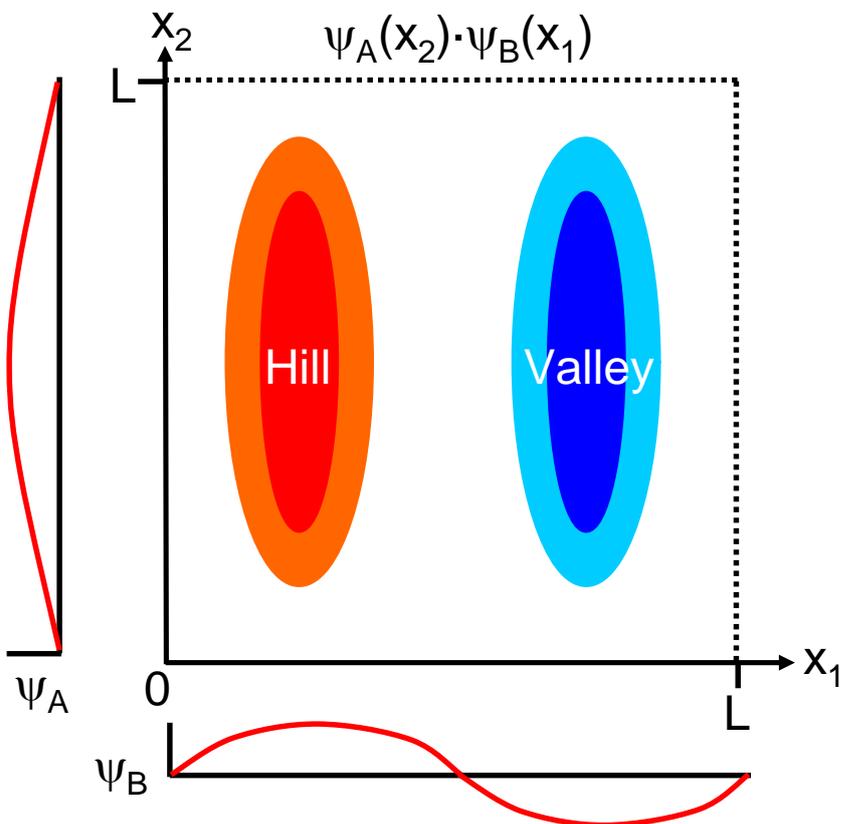
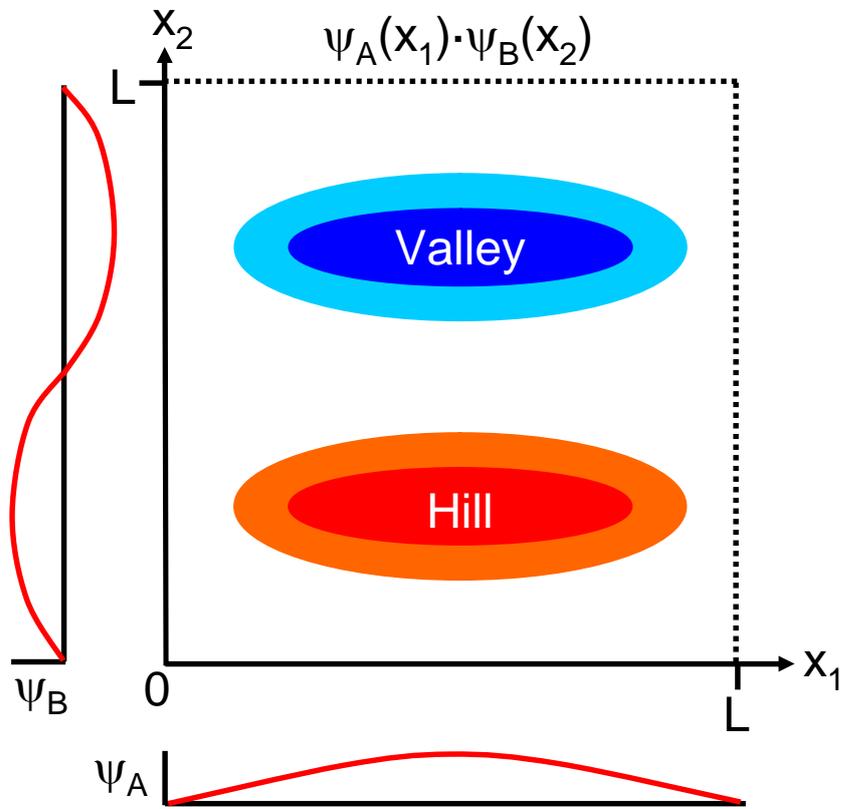
Where ψ_A is the wavefunction of electron A

and ψ_B is the wavefunction of electron B;

x_1 is the spatial position of electron A and x_2 of electron B.

This is stating that interchanging the electron labels should leave the total wave-function for both electrons (each of which consists of a spatial wave-function and a spin-state) must remain the same – interchanging the electrons must have no observable effect! Note that the composite state of the two particles (e.g. electrons in He) is obtained by multiplying together their individual wavefunctions. This expression tells us that the state is unchanged if we interchange the two electrons A and B. This is what must hold as the two electrons are indistinguishable.

However, if we consider a standard QM system such as infinite square well of width L (in which particles are trapped in a potential well of infinite depth, that is a force-field of infinite strength, which is square-shaped) and we ignore spin for the moment and focus on the spatial wave-functions only, then interchanging the two particles does not result in an unchanged state! (An infinite square well is a mathematical simplification to demonstrate the solution of wave equations in a relatively simple system, however, it is an approximation that can be rarely applied in real-life; for our purposes the shape of the well does not matter, we are simply illustrating a general point). This is illustrated diagrammatically below, in which one particle is in the lowest energy-state, with no nodes (points at which the wave-function passes zero, ignoring the points at the ends) and the other particle in the next lowest available energy-state (with one node). Note that the way in which the wave-functions combine to create a reinforced peak (hill) and a reinforced trough (valley) ensures that swapping the state of the two particles produces a different combined wave-function:



These graphs show the wave-functions of the two particles, which are occupying the two lowest energy states (the lowest has no nodes or points where it crosses the x-axis, the second lowest has one node, the third lowest would have 2 nodes, etc, so that the frequency of the wave increases as its energy increases). The only change we have made is to swap the positions (x_1 and x_2) of the two particles, however, the two states are clearly different, so particle exchange symmetry has been violated.

The way around this is to actually describe the particle states using linear combinations of the two wavefunctions, which is possible since we are dealing with (linear) waves and it is possible to add waves together to get a new wave, both the original waves and the new composite waves will satisfy our wave equation and so both are permissible. The simplest combination that works is:

Symmetric combination :

$$\psi_S(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_A(x_1) \cdot \psi_B(x_2) + \psi_A(x_2) \cdot \psi_B(x_1)]$$

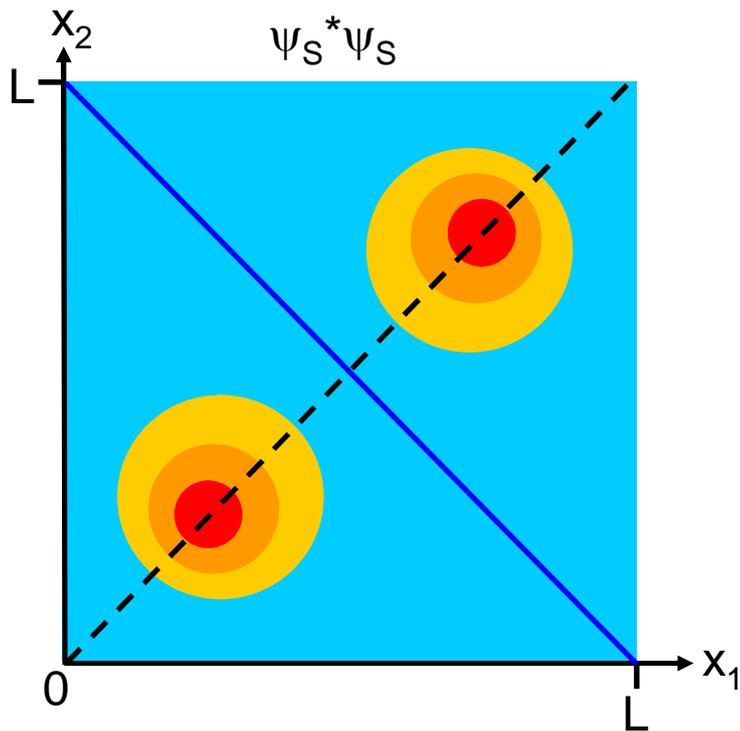
Antisymmetric combination :

$$\psi_a(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_A(x_1) \cdot \psi_B(x_2) - \psi_A(x_2) \cdot \psi_B(x_1)]$$

This is similar to the antisymmetric and symmetric spin states we have already looked at, but these are spatial states that do not include spin, which we are currently ignoring.

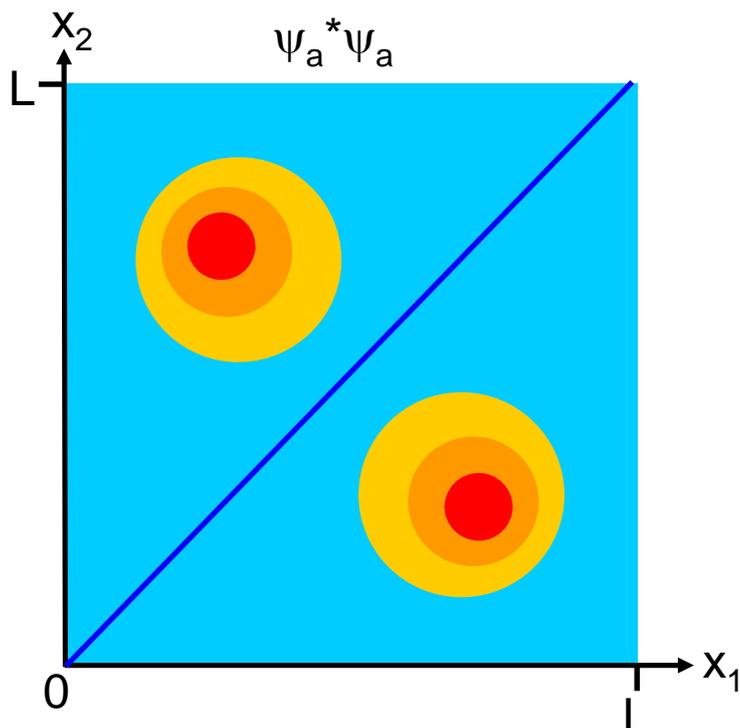
One combination is symmetric, since it results in no change to the wave-function, whereas the antisymmetric combination results in a change of sign of the wave-function (i.e. if it is positive then exchanging particles makes it negative, if negative then exchange makes it positive). However, since that we observe is the probability density, obtained by squaring the wave-function (taking the square of the modulus) the sign of the wave-function makes no difference (consider $-2 \times -2 = 2 \times 2 = 4$). Thus, both combinations are acceptable solutions. The $1/\text{square-root of } 2$ multiplying factor ensures that when we square the wave-functions the total probability adds to 1, as it must (the probability of finding the particles somewhere has to be zero) and is called a **normalisation factor**.

Plotting the probability distributions for a pair of identical particles, at positions x_1 and x_2 in our infinite square well, in the symmetric state gives the following, where red indicates higher probability, blue lower probability of finding the particles:



The dark-blue diagonal line shows us where the probability of finding either particle is zero. If both particles occupy the same position in space, then $x_1 = x_2$ and the particles are somewhere on the dashed diagonal-line, which passes through the red areas where the particles are very likely to be found - that is the particles are more likely to be found close together. In other words, **when two particles are in a symmetric state, they tend to 'huddle together'**.

The equivalent plot for two particles in the antisymmetric state gives the following:



This time when the particles are together, with $x_1 = x_2$, they lie along the dark-blue line which is impossible, since this is a region of zero probability! **In the antisymmetric state, the two particles tend to avoid one-another.**

A mysterious quantum-mechanical force has appeared, causing the particles to move closer together if they are symmetric, or to repel if they are antisymmetric. This is the **exchange force** and results purely from the fact that the two particles are indistinguishable.

Whether or not particles are symmetric or antisymmetric is a fundamental property of the particle type. Electrons, neutrons and protons, and composite particles containing an odd-number of these particles, e.g. a He-3 atom (two electrons, two protons and one neutron) are antisymmetric and these are called **fermions**. Particles like photons and composite particles containing an even-number of fermions, e.g. the He-4 atom (two electrons, two protons and two neutrons) are symmetric and are called **bosons**.

Fermions, like electrons, are antisymmetric and tend to avoid one-another and must occupy different quantum states.

Bosons, like photons, are symmetric and tend to huddle together and can occupy the same quantum state.

The ability of bosons to huddle together can give rise to some very strange effects. When liquid He-4 is cooled to near absolute zero, the wave-functions of the atoms extend and overlap so that the whole body of liquid behaves as a single quantum state. It becomes a **superfluid**, flowing with zero friction, flowing uphill as easily as downhill. Furthermore, if a ladle of such liquid is withdrawn from a vessel, then the liquid in the ladle flows up over the sides and back into the vessel, so that the whole liquid remains in the same state as a single entity (or as near as possible)! (Check out videos of this on Youtube).

Now we must incorporate spin! The total wavefunction for an electron is the product of its spatial wavefunction and its spin-state function. It is **the total wavefunction that must be antisymmetric!** Multiplying two antisymmetric functions together gives a symmetric function (interchanging particle labels or states changes the sign twice and so it is left overall unchanged as in the symmetric case). An antisymmetric multiplied by a symmetric function gives an antisymmetric total function. Multiplying together two symmetric functions gives a symmetric total function. In other words:

Symmetric total wave - function :

$$\psi_s \chi_s \text{ or } \psi_a \chi_a$$

Antisymmetric total wave - function :

$$\psi_s \chi_a \text{ or } \psi_a \chi_s$$

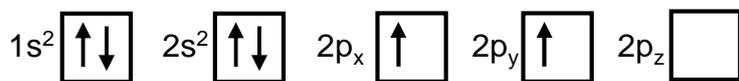
Where ψ is the spatial wave - function,

χ the spin wave - function,

and s donates symmetric, a antisymmetric.

The two electrons can be in a symmetric spatial state, huddled together in the same orbital, such as an s or p_x orbital, but then their spin-state must be antisymmetric and thus their spins must be antiparallel, $\uparrow\downarrow$. This is how electrons pair when they occupy the same orbital, e.g. $1s^2$ in a H^- (hydride) ion. If the electrons are apart and occupying different orbitals, e.g. one electron in p_x the other in p_y , then their spatial wavefunction is antisymmetric and so their spin-state must be symmetric, so as to make the total wavefunction antisymmetric and their spins are parallel: $\uparrow\uparrow$.

One more factor must be included. Electrons are negatively charged particles and so they repel one-another by a **repulsive Coulomb force**. This means that when paired together, $\uparrow\downarrow$, the repulsion raises their energy. This means that the unpaired triplet state, $\uparrow\uparrow$, has a slightly lower energy than the paired singlet state, $\uparrow\downarrow$. Thus, if two or more orbitals are degenerate, that is they have the same energy (or so long as their energies are very similar the following applies) then the electrons prefer to spread out and adopt a triplet state. this is why we write the (ground or lowest energy state) electron configuration of an atom like carbon as:



In which the two 2p electrons spread-out to fill two of the three degenerate p-orbitals. This is the basis of **Hund's rule** (of maximum multiplicity) which states that the state of highest multiplicity (e.g. triplet state) is usually the more stable state and therefore preferred (it is the ground or lowest energy state).

Models of the Helium Atom

1. No electron interactions

If we first assume that there are no interactions between the electrons (having spent so long talking about such interactions) then the time-independent Schrodinger wave equation (TISWE) can be separated into two single electron wave equations of the form:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\underline{r}) - \frac{2e^2}{4\pi\epsilon_0 r} \psi(\underline{r}) = E \psi(\underline{r})$$

Which is essentially the wave equation for a one-electron He^+ ion modeled as a H-like ion with twice the H-atom nuclear charge $2e$ as we are considering each electron separately.

The energy of the n th electron-level (eigenvalues) obtained by solving the TISWE is given by:

$$E_n = -\frac{me^4}{8\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^2} = -\frac{4E_R}{n^2}$$

(for each electron), $n = 1, 2, 3, \dots$

where

$E_R \approx 13.6eV$, is the Rydberg energy (ionisation energy of H atom)

The combined atomic energy of both electrons is given by:

$$E_{n_1, n_2} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

for $n_1, n_2 = 1, 2, 3, \dots$

(no electron interaction)

For the ground state ($n_1 = n_2 = 1$), $E_{1,1} = -8E_R = -108.8$ eV, or -54.4 eV per electron. This compares to the actual measured value of -78.9 eV per electron. Clearly electron interactions are important!

2. A Bohr Model of the Helium Atom

We can model the helium atom much as is done in Bohr's model of the hydrogen (H) atom. We can picture the electrons in circular orbits around the central nucleus. There are some differences with the H atom model, whereas the nuclear charge of the H atom is one unit of charge (e), that is the atomic number $Z = 1$, for He, $Z = 2$. The nuclear pull on the electrons in the helium atom is twice that in the hydrogen atom and so the electrons are closer. For the H atom the radius of the innermost electron orbit (the lowest energy ground state, $n = 1$) is the Bohr radius, $a_0 = 0.53$ Å. For the He atom it is half this value, $\frac{1}{2}a_0 = 0.265$ Å. (Note that $E_R = e^2/8\pi\epsilon_0 a_0 = 13.6$ eV).

Comparing the orbits of the H and He atoms according to the Bohr models:

	H atom	He atom
Radius	$n^2 a_0 / Z$ ($Z = 1$) $\rightarrow n^2 a_0$	$n^2 a_0 / Z$ ($Z = 2$) $\rightarrow n^2 a_0 / 2$
Energy	$-Z^2 E_R / n^2$ ($Z = 1$) $\rightarrow -E_R / n^2$	$-Z^2 E_R / n^2$ ($Z = 2$) $\rightarrow -4E_R / n^2$

For example, for the ground state innermost orbit, $n = 1$, for the H atom,

$$E_1 = -E_R \approx -13.6 \text{ eV}$$

and for the He atom,

$$E_1 = -4E_R \approx -54.4 \text{ eV}.$$

This value agrees with that of our QM model (model 1).

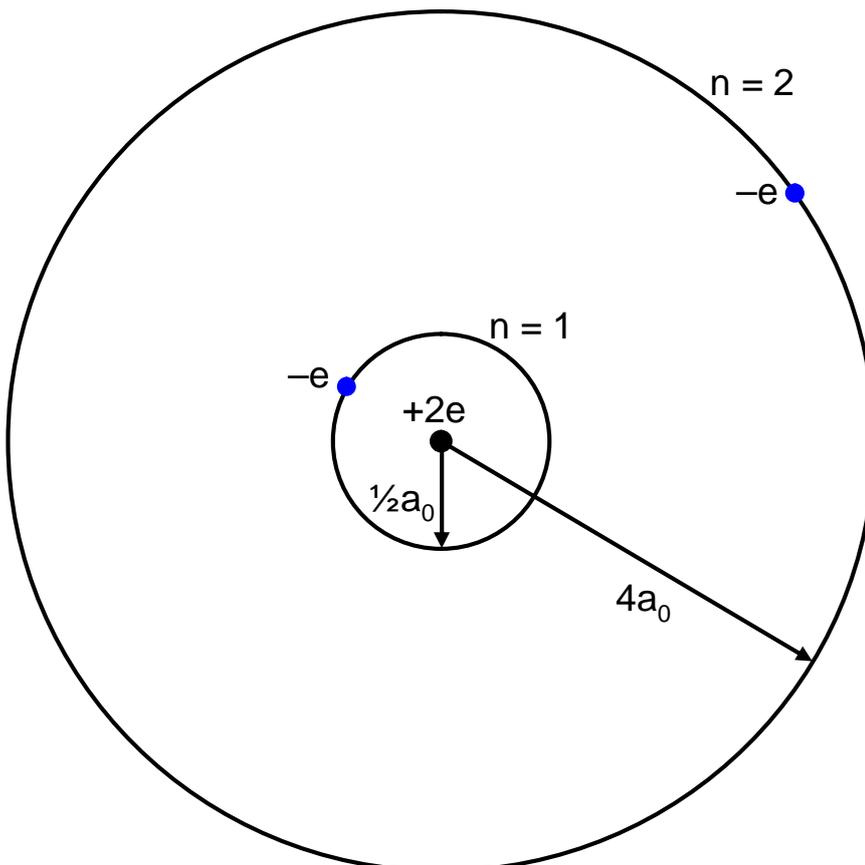
3. The Helium Atom with Coulomb Repulsion

If the electrons occupy the innermost $n = 1$ orbit in the ground state and repel one-another, we may expect them to occupy opposite ends of an orbital diameter (radius = $\frac{1}{2}a_0$, diameter = a_0). According to the Coulomb force, the energy of electrostatic repulsion between the two electrons (each of charge e) is:

$$e^2/4\pi\epsilon_0 a_0 = 2E_R = 27.2 \text{ eV}$$

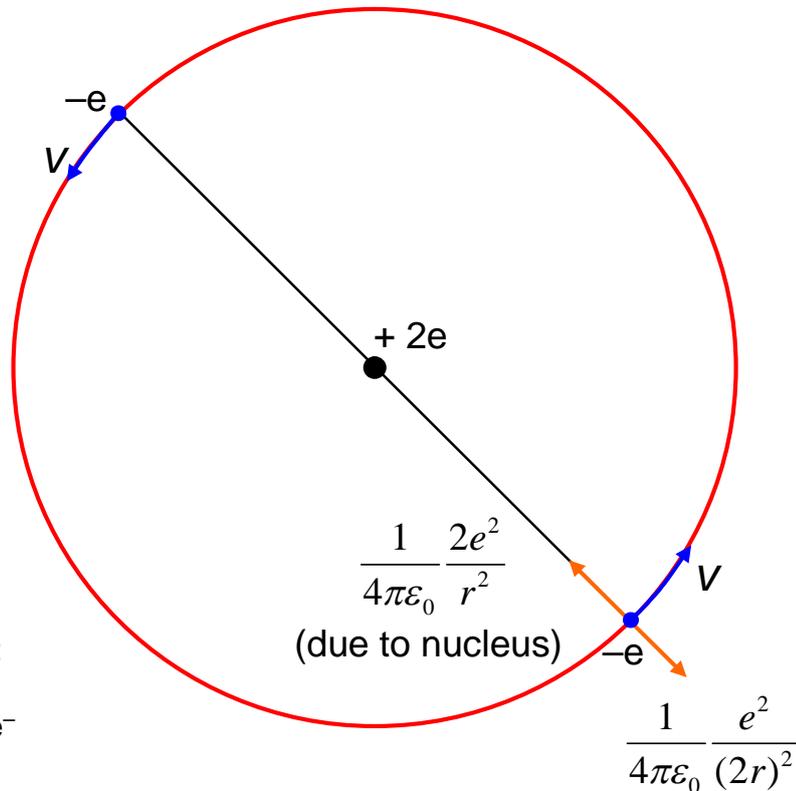
Adding this to the total energy obtained from model 1, which assumed no electron interaction, the energy of our model atom is now $(-108.8 + 27.2) \text{ eV} = -81.6 \text{ eV}$, which is closer to the actual value of -78.9 eV .

The ground state of the helium atom, in this model, is illustrated below (page 20). In this state, the two electrons occupy the same $n = 1$ orbit, but when electron repulsion is considered, the electrons stay as far apart from one-another as possible, sitting at opposite ends of the orbit diameter. In the first excited state, one electron remains in the $n = 1$ orbit (with radius $a_0/2$), whilst the excited electron enters the $n = 2$ orbit (with radius $4a_0$ since the inner electron partially screens out the nuclear charge, so the second electron sees a nuclear charge of only $+e$).



The first excited state of helium in the Bohr model (with no Coulomb repulsion)

Bohr Model of the He atom with Coulomb Repulsion



Ground state: both electrons occupy the innermost $n = 1$ orbit. Their repulsion means that they orbit opposite one-another. Blue curved arrows: electron velocity, orange arrows: Coulomb forces on e^-

Coulomb force magnitude, $F = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2}$ (due to other electron)

For each electron :

$$F = \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r^2} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{(2r)^2}$$

The orbital angular momentum of each electron, $l = mvr = \hbar$,

speed of electron $v = \hbar/mr$

Newton's second law for a circular orbit:

$$F = mv^2/r = \hbar^2/mr^3$$

Therefore, for each electron :

$$F = \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r^2} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{(2r)^2} = \frac{1}{4\pi\epsilon_0} \frac{7e^2}{4r^2} = \frac{\hbar^2}{mr^3}$$

Gives :

$$r = 4\pi\epsilon_0 \frac{4\hbar^2}{7me^2} = \frac{4}{7} a_0$$

(as expected the orbit radius is slightly increased by the mutual electron repulsion)

The total energy (kinetic + electrostatic potential) of each electron at this radius can now be calculated:

$$E = \frac{1}{2}mv^2 - \frac{2e^2}{4\pi\epsilon_0 r}$$

with

$$r = 4\pi\epsilon_0 \frac{4\hbar^2}{7me^2}$$

and

$$v = \frac{\hbar}{mr} = \frac{7\hbar me^2}{4\pi\epsilon_0 \cdot 4\hbar^2 m} = \frac{7}{4} \frac{e^2}{4\pi\epsilon_0 \hbar}$$

$$E = \frac{1}{2}m \left(\frac{7}{4} \frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 - \frac{2e^2}{(4\pi\epsilon_0)^2} \frac{7me^2}{4\hbar^2}$$

gives

$$E = \left(\frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \left(\frac{49}{32}m - \frac{14}{4}m \right) = \frac{e^4}{(4\pi\epsilon_0)^2 \hbar^2} \left(\frac{49}{32} - \frac{112}{32} \right) m$$

gives

$$E = -\frac{63}{32} \frac{me^4}{(4\pi\epsilon_0)^2 \hbar^2}$$

with

$$E_R = \frac{e^2}{8\pi\epsilon_0 a_0}, \text{ and } a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

$$E_R = \frac{me^4}{2(4\pi\epsilon_0)^2 \hbar^2}$$

and so

$$E = -\frac{63}{16} E_R \approx -53.57 eV$$

and the total energy of both electrons (including repulsion) is :

$$\text{Total } E = 2 - \left(\frac{63}{16} E_R \right) + \frac{7}{4} E_R = -\frac{49}{8} E_R \approx -83.3 eV$$

This estimate is still quite far out from the measured value of -78.9 eV. If one electron is removed from the atom, then the remaining electron occupies the slighter smaller orbit of radius $\frac{1}{2}a_0$ (in the absence of repulsion as the other electron has gone) with an energy of -54.4 eV, as in model 1 and model 2 ($E = -4E_R = -54.4$ eV). The first ionisation energy is, therefore, $(78.9 - 54.4)$ eV = 24.5 eV (actual measured value = 24.59 eV).

4. Quantum Mechanical Model with Coulomb Repulsion

Clearly the Bohr model can only take us so far, we need to return to a QM model, like model 1, but one incorporating electron interactions.

We can modify model 1 by adding in the mutual electron Coulomb repulsion. This involves adding an interaction term to Schrodinger's TISWE:

$$\left[\left(-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} \right) + \left(-\frac{\hbar^2}{2m_2} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} \right) + \frac{e^2}{r_{1,2}} \right] \psi(\underline{r}) = E\psi(\underline{r})$$

where

$\frac{e^2}{r_{1,2}}$ is the Coulomb repulsion term and $r_{1,2}$ the separation between the electrons.

Now the equation can not be separated into a separate equation for each electron and its solution is difficult. It can be approximately solved using an approximation method such as (first-order) **perturbation theory** in which the Coulomb repulsion is treated as a perturbation. The result is that the excited states, such as the first excited state with $n_1 = 1$ and $n_2 = 2$, sees the second electron shell, $n = 2$, split into sub-shells of slightly different energies according to the angular momentum, that is the energy differs slightly according to whether, for $n = 2$, the orbital angular momentum (l) is 0 or 1 (units of \hbar). The degeneracy due to angular momentum is lifted – the angular momentum alters the energy slightly and orbitals with the same n but different l now have slightly different energies, as they actually do. (An analogous situation exists in the H atom in which the sub-shells, s, p and d, etc. differ slightly in energy within each shell (n value)). Recall that, as in the H atom, for $n = 1$ the orbital angular momentum $l = 0$ only. For $n = 2$, $l = \{0, 1\}$, for $n = 3$, $l = \{0, 1, 2\}$, etc. The Coulomb repulsion perturbation has split the energy levels (which hitherto only depended on n) according to l . We now have electron shells (n quantum number) and sub-shells (l quantum number). The mathematical details of the perturbation theory calculation are not included here.

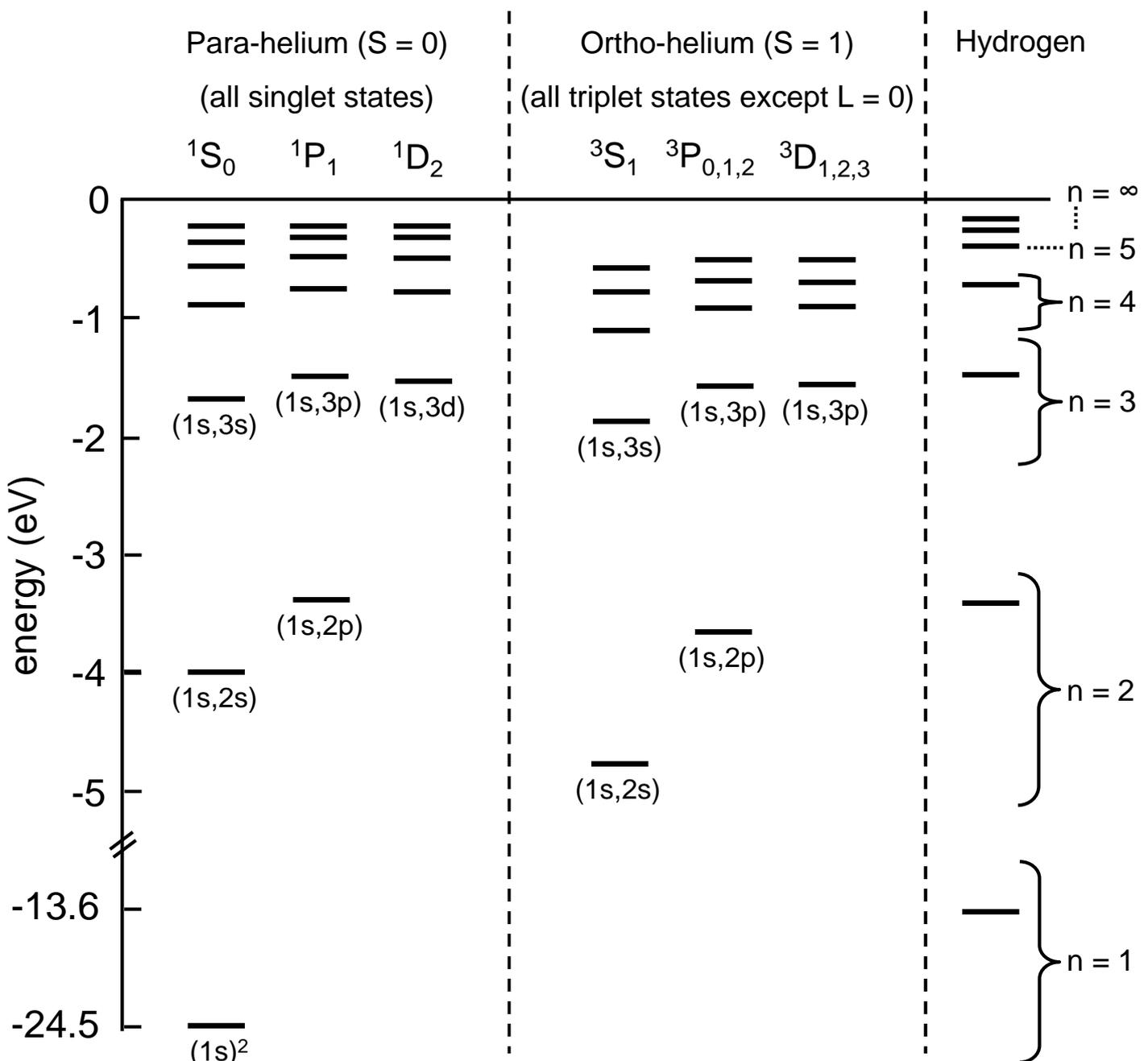
5. Quantum Mechanical model with Coulomb repulsion and Exchange Energy

Now we must factor in the quantum mechanical exchange energy, which we saw is due to the quantum indistinguishability of the two electrons. This can also be done as a perturbation, using perturbation theory. This involves adding an exchange term to the TISWE, which factors in the difference in energy between symmetric (triplet) and antisymmetric (singlet) states. The triplet symmetric state has a slightly lower energy than the antisymmetric singlet state. This finally gives a result which agrees well with measured values of experimental measurements of the energies (such as the ionisation energy and spectroscopic measurements).

Spectroscopic notation

When discussing the states of the H atom it is sufficient to use the single electron labels, 1s, 2s, 2p, 3d, etc. This uses s for a state in which the magnitude of the orbital angular momentum, $l = 0$, p for $l = 1$, d for $l = 2$, etc. With multielectron atoms we need a new notation. The magnitude of the total orbital angular momentum (L) of the atom's electrons is given a capital symbol: S (for $L = 0$), P ($L = 1$), D ($L = 2$), etc. To this is added a superscript designating the spin multiplicity (1 and 3 in this case, for the singlet and triplet states). A subscript indicates the total angular momentum magnitude, J ($J = L + S$).

Spectroscopy and Energy Levels of the Helium Atom



The magnitude of the total angular momentum J , can take three possible values for each value of L . This is because spin can be up or down (it is a vector) and so S can refer to a net up-spin, down-spin or zero net spin. E.g. for two electrons with spin-up, that is $s = +\frac{1}{2}$, $S = +\frac{1}{2} + +\frac{1}{2} = +1$, for one electron spin-up ($s = +\frac{1}{2}$) and the other spin-down ($s = -\frac{1}{2}$) $S = +\frac{1}{2} + -\frac{1}{2} = 0$, and for both electrons spin-down, $S = -1$. Thus J can then take three values for a given L : $L - 1, L, L + 1$. E.g. for $L = 1$, $J = \{0, 1, 2\}$, for $L = 2$ $J = \{1, 2, 3\}$. The exception is for $L = 0$: in this case one electron has to be spin-up and the other spin-down (they occupy the same orbital), so $S = 0$ and $J = 0$.

When the spectrum of helium was first measured, two distinct sets of lines were observed. These were thought to represent two distinct elements within the helium sample, and they were called para-helium and ortho-helium. It is now understood that these are not different elements, but two distinct states which helium atoms can occupy, depending on whether the electron spins were parallel (a triplet state, $S = 1$, as seen in ortho-helium) or anti-parallel (a singlet state, $S = 0$, as seen in para-helium). Note that when $L = 0$, there is only one orbital to accommodate the two electrons and so this must always be a singlet state (since no two electrons can have the same set of quantum numbers).

The reason that these spectra were seen as two distinct sets was because moving from a singlet to a triplet state, or vice versa, requires a spin-flip: one electron must change its direction of spin. These events do occur, but they are relatively rare (they are forbidden transitions). Thus, in any population of helium atoms there will be some ortho-helium and some para-helium, with each atom occasionally changing between the two. It then appears as if there are these two different types of helium atoms.

Summary of the helium atom models

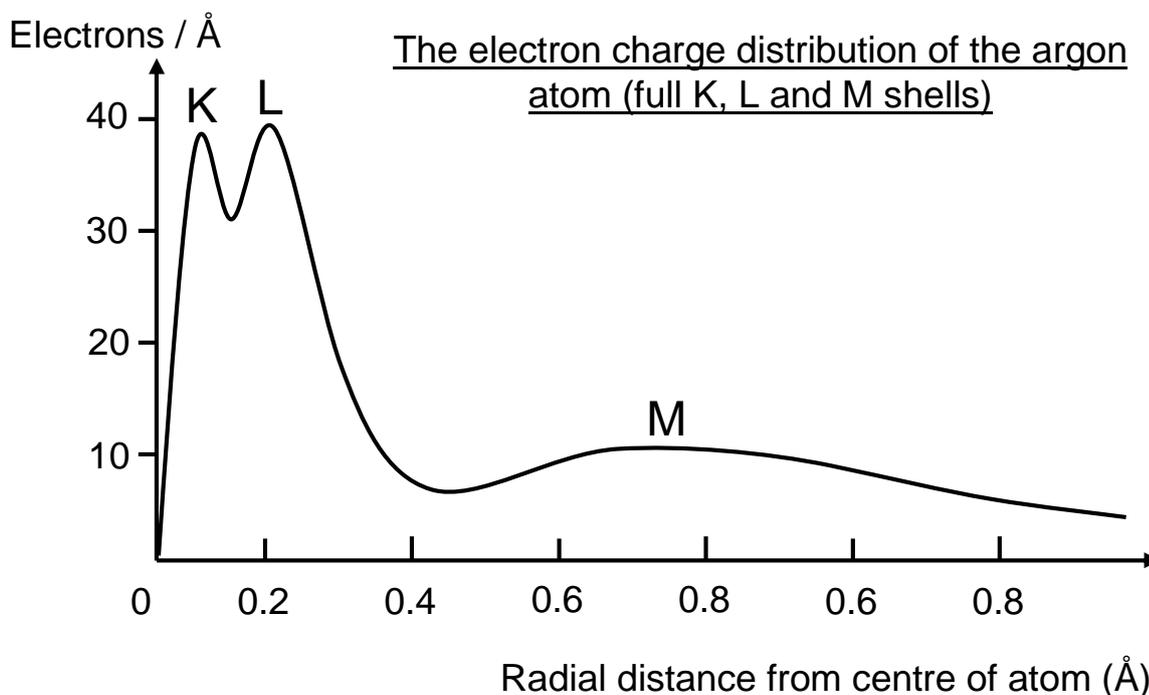
Although complicated, analysis of the helium atom has revealed some important concepts. First of all, electron repulsion appears responsible for the slight energy differences between states with the same principle quantum number, n , but different orbital angular momentum, L . The importance of the indistinguishability of the two electrons due to the significant overlap of their wavefunctions, a fundamental principle in quantum mechanics, accounts for the slight difference in energy between singlet and triplet states. There are often classical explanations given for these phenomena, but we have not mentioned these and although they can be aids to understanding, they are conceptually incorrect. Only the quantum mechanical model gives accurate and reliable predictions of the atomic spectrum of helium.

Many-Electron Atoms

The analysis of the helium atom with only two electrons was complex. When we have many electrons, the full analysis using the approach we have taken becomes prohibitively difficult. Computer modeling has enabled accurate calculations of the states and their energies in many-electron atoms. However, simpler conceptual approaches have provided reasonably good results. One of these is the **self-consistent field method**. The problem is that we may not know the exact distribution of charge that each electron sees resulting from the other electrons and the nucleus. The self-consistent field method takes an estimated charge distribution, that is an estimated potential, and then calculates the spatial probability distributions for the electron charge of all the electrons (by solving the TISWE for the potential we have chosen). This result is then used to obtain a predicted charge distribution. If the result matches our estimate, then the estimate is likely correct. If there is a discrepancy then we must adjust our estimate and **reiterate the process** until accuracy is obtained (until we obtain a self-consistent field).

Another, simpler but less accurate, approach is to use the **Aufbau principle**. With this principle we build up the atom one electron at a time. We begin with a naked nucleus and then add the first electron to the lowest available energy level. We then add successive electrons to the next available lowest energy level, taking into account screening of the nuclear charge by inner electrons (especially for full inner shells) and otherwise using one-electron energy levels.

For an atom like argon (18 electrons) what is predicted is in reasonable agreement with measurement: the electrons cluster into shells, the K shell ($n = 1$), the L shell ($n = 2$) and the M shell ($n = 3$). (Larger atoms will have additional higher shells).



Bibliography

The following constitute the main sources used (in no particular order):

- MacKay, K.M. and MacKay, R.A. 1981. Introduction to modern inorganic chemistry. 3rd ed. International textbook Company, London.
- Greenwood, N.N. and Earnshaw, A. 1997. Chemistry of the elements. 2nd ed. Elsevier.
- Cotton, F.A. and wilkinson, G. 1972. Advanced inorganic chemistry, a comprehensive text. 3rd ed. Interscience Publishers.
- French, A.P. and Taylor, E.F. 1998. An introduction to quantum physics. Stanley Thornes Ltd.
- Quantum mechanics, unit 15: Identical particles and atomic structure, 1998. The open University, SM355 Quantum Mechanics course text.
- Discovering physics, revolutions of modern physics. the Open University, 1994. S271 course text.
- Eisberg, R. and Resnick, R. 1985. Quantum physics of atoms, molecules, solids, nuclei and particles. 2nd ed, John Wiley & Sons.
- Wikipedia.