

6.4: The Quantum Mechanical Explanation of Valency

Helium atoms in their ground state do not form a stable diatomic molecule. In fact, helium does not combine with any neutral atom. Its valency, that is, its ability to form chemical bonds with other atoms, is zero. The electronic configuration of the helium atom is $1s^2(\uparrow\downarrow)$, a closed shell configuration. When two helium atoms are in contact, each electron on one atom encounters an electron on the other atom with a parallel spin. Because of the Pauli principle, neither electron on either atom can concentrate its density in the region they have in common, the region between the nuclei. Instead, the density is transferred to the antibinding regions behind each nucleus where the overlap of the two atomic density distributions is least. This is the same effect noted earlier for the approach of two hydrogen atoms with parallel spins.

Comparison of a series of density difference maps for the approach of two helium atoms (Figure [Math Processing Error]) with those given previously for H_2 (Fig. 6-10) reveals that one set is the opposite of the other. The regions of charge build-up and charge depletion are reversed in the two cases. The density difference diagrams are obtained by subtracting the distribution obtained by the overlap of the atomic charge densities from the molecular charge distribution. The former distribution, it will be recalled, does not place sufficient charge density in the binding region to balance the force of nuclear repulsion. Thus it is clear from Figure [Math Processing Error] that He_2 will be unstable because the molecular distribution places less charge density in the binding region than does the one obtained from the overlap of the atomic densities. The charge density in He_2 is transferred to the antibinding region where it exerts a force which, acting in the same direction as the nuclear force of repulsion, pulls the two nuclei apart. Repulsive forces will dominate in He_2 and no stable molecule is possible.

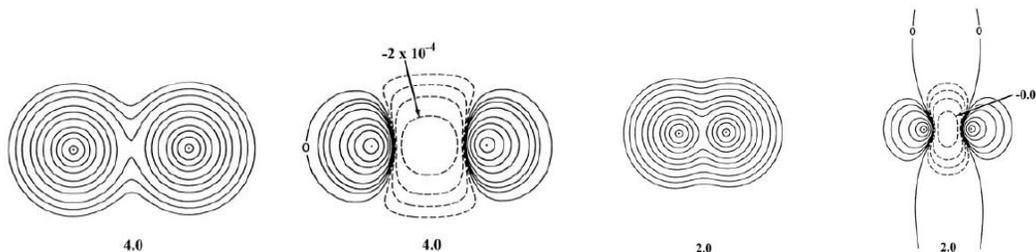


Figure [Math Processing Error]: Contour maps of the total molecular charge density and of the density difference for two He atoms at internuclear separations of 4.0 au and 2.0 au. The scale of contour values for the total density maps are the same as used in Fig 6-9 for H_2 . The outermost contour is 0.002 au and the innermost one is 2.0 au for $R = 4.0$ and $R = 2.0$ au. The scale used in the density difference plots is the same as that given in Fig. 6-10 beginning with $n = 5$ for $R = 4.0$ au and with $n = 3$ for $R = 2.0$ au. Note the increase in the amount of charge density transferred from the binding to the antibinding regions as the separation between the two atoms is decreased.

A comparison of the density difference profiles for He_2 (Figure [Math Processing Error]) and H_2 (Fig. 6-12) provides a striking contrast of the difference between the charge redistributions which result in the formation of unstable and stable molecules.

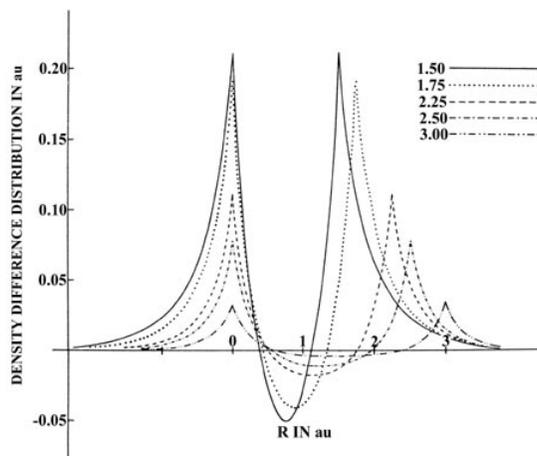


Figure [Math Processing Error]: Profiles of the density difference maps along the internuclear axis for the approach of two He atoms. One nucleus is held stationary. This figure should be contrasted with Fig. 6-12, the corresponding one for H_2 .

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The force on a helium nucleus in He_2 as a function of the internuclear separation is repulsive for the range of R values indicated in Figure [Math Processing Error].

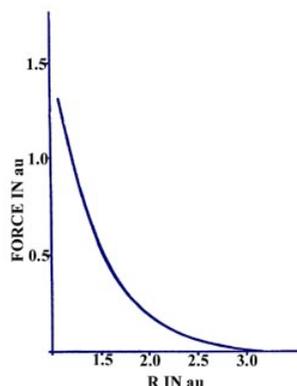


Figure [Math Processing Error]: Force on a [Math Processing Error] nucleus in [Math Processing Error] as a function of the internuclear separation. The general form of this curve is characteristic of an unstable molecular species.

Unlike the force curve for H_2 , there is no deep minimum in the curve which represents a range of (R) values for which the force is attractive. The force curve for [Math Processing Error] does cross the (R) axis at approximately 6 au (not indicated in Figure [Math Processing Error]) and becomes very slightly attractive for values of R greater than this value. This weak attractive force has its origin in the long-range mutual polarization of the atomic density distributions which was discussed in detail for the approach of two hydrogen atoms. For large internuclear separations, where there is no significant overlap of the atomic orbitals and hence no need to invoke the Pauli exclusion principle, the atomic charge distributions of two approaching helium atoms are polarized in the same way as are the charge distributions for two approaching hydrogen atoms, and the force is attractive. At smaller internuclear separations, however, where the overlap of the orbitals is significant and the Pauli exclusion principle is operative, the direction of the charge transfer in He_2 is reversed and the force is rapidly transformed into one of repulsion. Were it not for the weak long-range attractive forces - the van der Waals forces - gaseous helium could not be condensed into a liquid or a solid phase. As it is, the force of attraction between two helium atoms is so weak that at a temperature of only 4.2°K they have sufficient kinetic energy to overcome the forces of attraction between them and escape into the gas phase.

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If it was not necessary to satisfy the demands of the Pauli principle, electron density would accumulate in the binding region of He_2 , even for small values of R , as this region is of lower potential energy than is the antibinding region. However, when each electron detects another of like spin (when the orbitals overlap) they cannot concentrate their charge density in the region they have in common, the binding region. That it is indeed the Pauli principle which prevents the formation of He_2 is evident from the fact that He_2^+ , which possesses one less electron, **is stable!** When a helium atom approaches a helium ion, an orbital vacancy is present and the density from one pair of electrons (those with opposed spins) can be concentrated in the binding region.

All the rare gas atoms possess a closed shell structure and this accounts for their inertness in chemical reactions. No homonuclear diatomic molecules are found in this group of elements; all occur naturally in the atomic state. Compounds of Kr and Xe have been formed with fluorine, for the same reason that the formation of He_2^+ is possible. Fluorine has a very high electron affinity and a single vacancy in its outer quantum shell. Thus one of the electrons in the closed shell structure of Xe can be pulled into the orbital vacancy of the fluorine atom and density concentrated in the region between the nuclei.

Only an atom with a very high affinity for electrons will bond with a rare gas atom. The only species found with sufficient electron affinity to bind a helium atom (which holds its electrons the most tightly of all atoms) is a He^+ ion. If the helium atom has the highest ionization potential of all the elements, then the singly-charged He^+ ion must possess the highest electron affinity of all the neutral or singly-charged atoms.

Second Row Elements

Let us now attempt to explain the variation in the valency exhibited by the elements in the second row of the periodic table. The

File failed to load: <https://cdnjs.cloudflare.com/ajax/libs/mathjax/2.7.3/jax/output/HTML-CSS/jax.js> valency of the hydrogen atom is unity as it possesses

one unpaired electron and one orbital vacancy. It can form one electron pair bond. Therefore, the valencies exhibited in the above hydrides must be 1, 2, 3, 4, 3, 2, 1, as this is the number of hydrogens bound in each case. (By the way, while the BH_3 molecule is predicted to be stable with respect to the separated boron and hydrogen atoms it cannot be isolated as such, but only in the form of its dimer B_2H_6).

We will consider HF first.

Fluorine: The electron configuration of F is $1s^2 2s^2 2p^5$. Only one of the electrons in the $2p$ orbitals is unpaired. The $2p$ atomic orbital with the vacancy may overlap with the $1s$ atomic orbital of hydrogen, and if the spin of the electron on H is paired with the spin of the electron on F, all the requirements for the formation of a stable chemical bond will be met. The valency of F will be one as it possesses one unpaired electron and can form one electron pair bond.

Oxygen: The electronic configuration of oxygen is $1s^2 2s^2 2p^4$. Oxygen has two unpaired electrons, both of which may pair up with an electron on a hydrogen atom. The valency of oxygen should be two as is observed. It is obvious that all the requirements for a chemical bond can be met for every unpaired electron present in the outer or "valency" shell of an atom. ***Thus valency may be defined as being equal to the number of unpaired electrons present in the atom.***

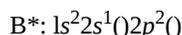
Nitrogen: The configuration of nitrogen is $1s^2 2s^2 2p^3$, and its hydride should be NH_3 as is indeed the case.

Carbon: Since the most stable electron configuration of carbon is $1s^2 2s^2 2p^2$ we predict its valency to be two. The molecule CH_2 (called methylene) is indeed known. However, CH_2 is very reactive and its products are not stable until four chemical bonds are formed to carbon as in the case of CH_4 . Four, not two, is the common valency for carbon. How can our theory account for this fact? The energy of a $2p$ orbital is not much greater than that of a $2s$ orbital. Because of this, relatively little energy is required to promote an electron from the $2s$ orbital on carbon to the vacant $2p$ orbital:



Carbon in the promoted state possesses four unpaired electrons and can now combine with four hydrogen atoms. Every bond to a hydrogen atom releases a large amount of energy. The energy required to unpair the $2s$ electrons and promote one of them to a $2p$ orbital is more than compensated for by the fact that **two** new C-H bonds are obtained.

Boron: Boron has the electronic configuration $1s^2 2s^2 2p^1$. Its valency should be one and BH is known to exist. However, again through the mechanism of promotion, the valency of boron can be increased to three:



We might wonder why, with a $2p$ orbital still vacant, one of the $1s$ electrons is not promoted and thus give boron a valency of five. This does not happen because of the large difference in energy between the $1s$ and $2p$ orbitals as shown in the orbital energy level diagram (Fig. 5-3).

Beryllium: Beryllium has the configuration $1s^2 2s^2$ and should exhibit a valency of zero. The outer electron configuration of Be is similar to that of He, a closed shell of s electrons. Indeed, the molecule Be_2 exists only as a weakly bound van der Waals molecule. However, Be differs from He in that there are vacant orbitals available in its **valency** shell. The observed valency of two in the molecule BeH_2 can be explained by a promotion to the configuration $1s^2 2s^1 (2p^1)$.

Lithium. Lithium, with the configuration $1s^2 2s^1$, should exhibit only a valency of one.

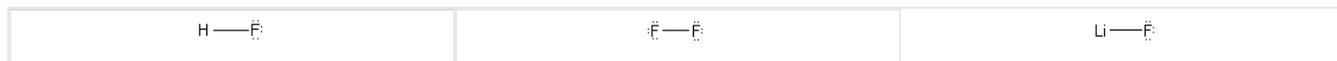
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Lewis Structures

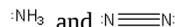
The concept of an electron pair bond is not restricted to bonds with hydrogen. The only requirements are an unpaired electron on each atom (which is another way of saying there is an orbital vacancy on each atom) with their spins opposed. Thus two fluorine atoms may combine to form the fluorine molecule F_2 through the overlap of the singly-occupied $2p$ orbital on one atom with a similar orbital on the other. This will result in F_2 being described as F-F where the single line denotes that one pair of electrons forms the bond between the two atoms. Similarly, the three singly-occupied $2p$ orbitals on one nitrogen atom may overlap with those on another to form the N_2 molecule. Since three pairs of electrons are shared between the nuclei in this case, we represent the molecule by the symbol N°N . The electrons in the valence shell of an atom which are not involved in the formation of a chemical bond (as they are already paired in an orbital on the atom) may also be indicated and the resulting symbols are called **Lewis**

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structures. Thus the three pairs of valency electrons on each F, ($2s^2 2p^4$), not involved in the bonding are often indicated by dots. For example,



(Lithium has only one outer electron and it is shared in the bond.) In compounds with nitrogen we may indicate the 2s pair of electrons:

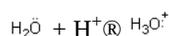


Recall that each line, since it denoted a bond in these diagrams, represents a pair of electrons shared between the two atoms joined by the line. If we add up the lines joined to each atom, multiply by two (to obtain the number of electrons) and add to this the number of dots which represents the remaining valence electrons, the number eight is obtained in many cases, particularly for the second-row elements ($n = 2$ valence orbitals). This so-called octet rule results from many elements having four outer orbitals ($nsnp_x np_y np_z$) which together may contain a total of eight electrons. Not all eight electrons belong to either atom in general as the electrons in a bond are shared (not necessarily equally as we shall see) between two atoms. Each bond contains two electrons with paired spins. Thus the orbital from one atom used to form the bond is, in a sense, filled as both spin possibilities are now accounted for.

The presence of an unshared pair of electrons in the valency shell of an atom can lead to the formation of another chemical bond. For example, the unshared pair of electrons in the 2s orbital on nitrogen in ammonia may attract and bind to the molecule another proton:

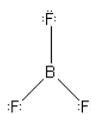


A similar reaction occurs for the water molecule which possesses two unshared pairs of electrons:



We must modify our previous rule regarding the requirements for the formation of an electron pair bond. Rather than both orbitals being half-filled, an orbital on one of the atoms may be filled if the orbital on the other atom is completely vacant. Molecules possessing an unshared pair of electrons, which may be used to bond another atom, are called **Lewis bases**. Only elements in groups V, VI and VII will exhibit this property. The elements in groups I to IV do not possess unshared pairs. Instead, the chemistry of the elements in groups II and III is largely characterized by the orbital vacancies which they possess in their valency shell.

The compound boron trifluoride represents the pairing of the three valence electrons of boron with the unpaired electrons on three F atoms. The boron is considered to be in the promoted configuration $1s^2 2s^1 (2p^2)$ and BF_3 is represented as



A 2p orbital on boron is vacant. It is not surprising to find that BF_3 may form another bond with a species which has an unshared pair of electrons, i.e., a Lewis base. For example,

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Since BF_3 accepts the electron pair it is termed a **Lewis acid**. Further examples from [Group 3](#) are

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and from [Group 2](#) (which have two orbital vacancies):

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