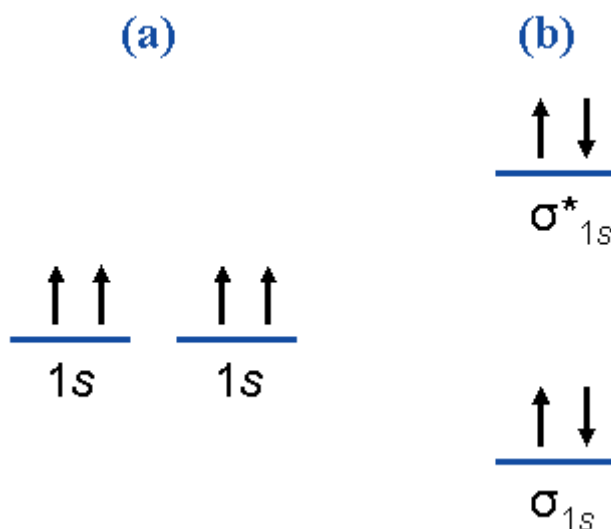


Example 2- E:*Molecular orbitals in a “helium molecule”*

A helium atom has both of its valence electrons in the 1s-orbital. When two helium atoms approach each other two molecular orbital can be formed which is sketched in Figure 2- 7.

**Figure 2- 7: Molecular orbitals in a “helium molecule”**

(a) The two atomic orbitals (1s) when the atoms appear in single. (b) The two atomic orbitals “melt” together and two new molecular orbitals are created. One of the molecular orbitals is a bond orbital (σ_{1s}) and one is an anti-bond orbital (σ^*_{1s}) but no chemical bond is created since the bond order is zero.

Since only two electrons can be hosted in each orbital, the total number of four valence electrons has to be distributed into two electrons in the bond orbital and two electrons into the anti-bond orbital. The bond order is then calculated by use of equation (2- 1) from page 55:

$$\text{Bond order} = \frac{2 - 2}{2} = 0$$

This situation gives a bond order of zero according to equation (2- 1) and thus it is not beneficial for two helium atoms to join and form a covalent bond. This is hence the answer to the question about why two hydrogen atoms form a molecule while two helium atoms do not.

When talking about molecular orbital theory you have to be aware of the following:

It is only the atomic orbitals of the valence electrons that are transformed into molecular orbitals.

The total number of valence electron atomic orbitals equals the number of molecular orbitals.

For two identical atoms: Molecular orbitals are denoted σ (bond orbital) and σ^* (anti-bond orbital)

respectively followed by the name of the former atomic orbitals (see for example Figure 2- 6 on page 54 and Figure 2- 7 on page 56)

It can be quite a difficult task to find out which molecular orbitals that are formed and which energy levels these orbital have when we are looking at other atoms than hydrogen and helium; especially when we are dealing with different atoms with different numbers of valence electrons in different types of atomic orbitals. In this book we are not going to go more into molecular orbital theory. This was just a brief introduction to a model which could explain why some atoms form molecules and why other atoms do not. It is all a matter of bond orders. If the bond order is zero there is no benefit in terms of energy of forming a molecule. If the bond order is larger than zero it is beneficial in terms of energy to form a molecule.

Molecular orbital theory can also be used to explain other phenomena such as diamagnetism and paramagnetism. According to Hund's rule (see section 1.2.2 *Electron configuration*) the electrons would rather prefer to stay unpaired in the atomic orbitals if this is possible. This is also the case in the molecular orbitals. If it is possible for the electrons to stay unpaired in the molecular orbitals they will do so and the molecules will appear paramagnetic. This is for example the case with the oxygen molecule (O_2) which has two unpaired electrons in two of the anti-bond orbitals.

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2.2.3 Lewis structure

In section 2.2.2 *Molecular orbital theory* we saw among other things that bond orders can be explained from molecular orbital theory. In this section we are going to look at another theory that can explain bond orders as well as helping us to determine the position of the atoms inside molecule relative to each other. We are going to spend some time on the Lewis theory which is named after the American scientist G. N. Lewis. According to Lewis' theory the atoms have one goal when they join and form molecules:

The goal of the atoms during the formation of molecules is to get the valence electron orbital filled up with electron (Lewis' theory)

For a while let us forget all about molecular orbital theory and think in terms of atomic orbitals. When atoms join and form molecules they will seek to get their valence electron orbitals filled with electrons according to the theory of G.N. Lewis. This implies the following:

Hydrogen pursues to be surrounded by 2 electrons so that the valence electron atomic orbital $1s$ will be filled up with electrons.

Elements in the 2nd period pursue to be surrounded by 8 electrons so that the valence electron atomic orbitals ($2s$ and $3 \times 2p$) will be filled up with electrons. This is referred to as the *octet rule* since “octa” means “eight”.

The atoms can obtain this by sharing electrons. The elements in the 3rd period and downwards have the ability of being surrounded by more than eight electrons since their empty 3d-atomic orbitals can assist in hosting the shared electron pairs. When you want to determine the bond order in a molecule, the molecule with all its atoms can be written in so-called *dot form*. This is done by writing the letter symbol of the atom surrounded by a number of dots corresponding to the number of valence electrons for that particular atom. The atoms in dot forms can then be combined into *Lewis structures* for different molecules. First we are going to write different atoms in “dot form” in the following example.

Example 2- F:

Atoms in “dot notation”

In Figure 2- 8 different atoms are given in *electron dot form*. First the number of valence electrons is determined from the position in the periodic table. Then a number of dots are placed around the letter symbol for the atom corresponding to the number of valence electrons. We have to notice that it is *only* the valence electrons that are represented by dots.



Figure 2- 8: Atoms in “dot notation”

The hydrogen atom has one valence electron, the helium atom has two valence electrons, the silicon atom has four valence electrons and the argon atom has eight valence electrons (the octet rule is fulfilled for argon).

The number of dots corresponds to the number of valence electrons in the particular atom. When the atom is surrounded by eight electrons the octet rule is satisfied. The electrons are often placed in pairs. Such an electron pair is called a *lone pair*.

By use of Lewis' theory and atoms in “electron dot forms” we are prepared to look at how atoms are arranged inside the molecules relative to each other. When the so-called *Lewis structure* of a molecule or composite ion is to be written down, the following guidelines have to be followed:

Determine the total number of valence electrons for the molecule/composite ion. This is done by summing up the number of valence electrons for the individual atoms (plus the eventual “extra ionic charge” if we are dealing with a composite ion). Thus the number of “dots” of the individual atoms has to be counted. (2- 2)

Connect all atoms by using one electron pair.

Arrange the remaining valence electrons such that hydrogen atoms are surrounded by 2 atoms and that the octet rule is satisfied for the elements from the 2nd period. It can be necessary to let more than one electron pair be a part of chemical bond (creation of double or triple bonds).

In the following examples we are going to write down the Lewis structures for different molecules and composite ions by using these three steps given in (2- 2).

Example 2- G:

The ammonia molecule in Lewis structure

An ammonia molecule consists of three hydrogen atoms and one nitrogen atom. How are these atoms placed relative to each other? In order to answer this question we will write down the Lewis structure according to the guidelines given in (2- 2) on page 59.

Number of valence electrons = 5 (from nitrogen) + 3 × 1 (from hydrogen) = 8

Use one electron pair to connect each N-H atom pair

The last $8 - 3 \times 2 = 2$ electrons are arranged so that the octet rule is satisfied

These three steps are sketched in Figure 2- 9.

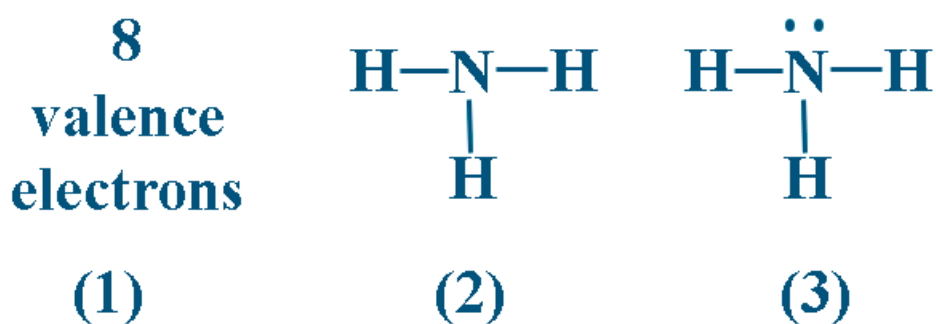


Figure 2- 9: Lewis structure for the ammonia molecule

The three steps in writing the Lewis structure. The octet rule has to be satisfied for all the atoms in the molecule. Thus the lone pair is placed on the nitrogen atom.

The only way in which the octet rule can be satisfied is by placing the atoms and electrons as sketched in the figure. Moreover it is seen that the three N-H bonds consist of single electron pairs which corresponds to single bonds. The Lewis structure has thus told us that in an ammonia molecule the nitrogen atom is placed in the centre connected to each of the three hydrogen atoms by single bonds. Further more a lone pair is “attached” to the nitrogen atom. We now know something about the internal arrangement of atoms and lone pairs inside the molecule but we do not know about the actual geometry of the molecule.

In an ammonia molecule all bonds are single bonds. Sometime in order to satisfy the octet rule when Lewis structures are to be written down for certain molecules it is necessary to let more than one electron pair go into a bond. This leads to a higher bond order than 1. We are going to look at such a case for a molecule of carbon dioxide.

Example 2- H:

The carbon dioxide molecule in Lewis structure

A molecule of carbon dioxide consists of a carbon atom and two oxygen atoms. We wish to write down the Lewis structure for this molecule in order to investigate the bond orders of the bonds inside the molecule. Thus we again follow the guidelines given in (2- 2) on page 59.

Number of valence electrons = 4 (from carbon) + 2 × 6 (from oxygen) = 16

Use one electron pair to connect each C-O bond

Arrange the last 16 - 2×2 = 12 electrons so that the octet rule is satisfied for all three atoms

The octet rule can only be satisfied if each C-O bond is made of two electron pairs which equals to four electrons. This corresponds to double bonds. The three steps are sketched in Figure 2- 10.

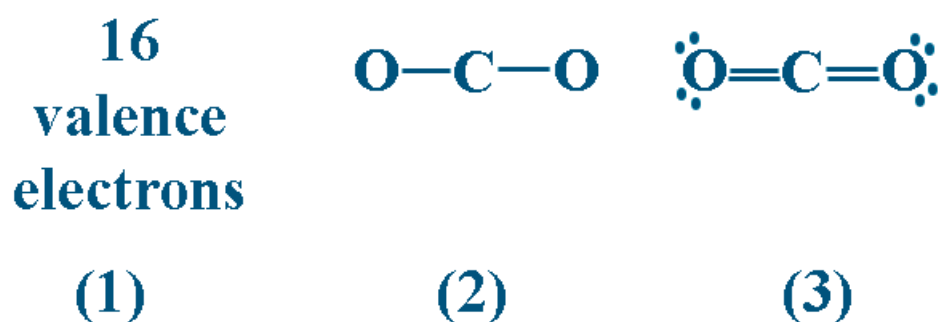


Figure 2- 10: Lewis structure for the carbon dioxide molecule

The three steps in writing the Lewis structure. The octet rule has to be satisfied for all the atoms in the molecule. Therefore it is necessary with double bonds between the carbon atom and the oxygen atoms.

That way the Lewis structure for carbon dioxide has now told us that in this molecule the carbon atom is placed in the centre. Each oxygen atom is double bonded to the carbon atom and two lone pairs are “attached” to each oxygen atom. But from the Lewis structure we know nothing about the actual molecular geometry.

We know that hydrogen (from the 1st period) pursues to be surrounded by *two* electrons and that elements from the 2nd period pursue satisfy the octet rule by being surrounded by *eight* electrons. The elements from the 3rd period and downwards can however be surrounded by more than eight atoms because their empty d-orbitals are able to assist in hosting more than the eight electrons. We are going to look more at such a case for a molecule of sulphur hexafluoride for which we are going to write the Lewis structure.

Example 2- I:

The sulphur hexafluoride molecule in Lewis structure

A SF_6 molecule consists of one sulphur atom and six fluor atoms. We wish to write down the Lewis structure for this molecule in order to know something about the internal atomic arrangement and the positions of the lone pairs in this molecule. Thus the 3-step procedure given by (2- 2) on page 59 is used again:

Number of valence electrons = 6 (from sulphur) + 6×7 (from fluor) = 48

Use one electron pair pr. S-F bond. Since sulphur is from the 3rd period it can be surrounded by more than eight electrons.

The remaining $48 - 6 \times 2 = 36$ electrons are arranged so that the octet rule is satisfied for all fluor atoms.

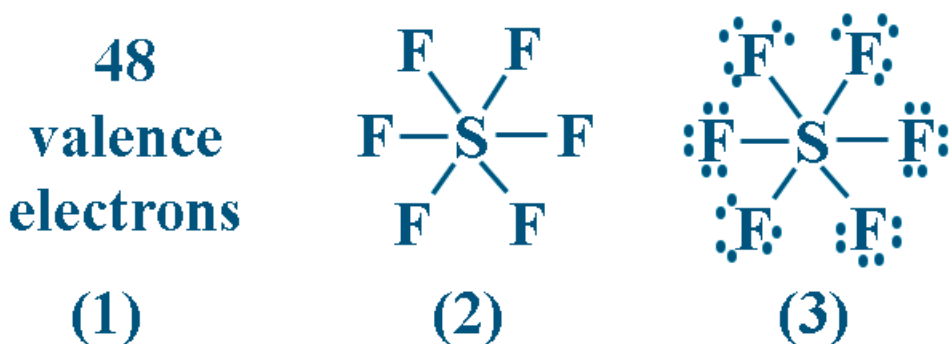


Figure 2- 11: Lewis structure for the sulphur hexafluoride molecule

The three steps in writing the Lewis structure. The octet rule has to be satisfied for all the atoms in the molecule. Sulphur from the 3rd period has the ability to be surrounded by more than eight electrons pairs by using its empty 3d-orbitals.

From the Lewis structure we now know that the sulphur atom is placed in the centre and is bonded to the six fluor atoms by single bonds. Furthermore we know that each fluor atom is surrounded by three lone pairs. But from the Lewis structure we know nothing about the actual geometry of the molecule.

The 3-step procedure given by (2- 2) on page 59 can also be applied for composite ions such as sulphate, nitrate, cyanide etc. We are going to look more into that in the following example where the Lewis structure for nitrate will be written down. During this procedure we will run into the concept of *resonance structures*.

Example 2- J:*Nitrat in Lewis structure*

Nitrate (NO_3^-) consists of a nitrogen atom, three oxygen atoms plus one negative charge. We wish to write down the Lewis structure for this composite ion. Thus we use the three steps given by (2- 2) on page 59.

Number of valence electrons = 5 (from nitrogen) + 3×6 (from oxygen) + 1 (one extra netagive charge) = 24

Use one electron pair pr. N-O bond.

The remaining $24 - 3 \times 2 = 18$ electrons are arranged so that the octet rule will be satisfied for all atoms.

Here it is necessary to let one of the N-O bonds be a double bond. Experiments have however proved that the bond energy for the three N-O bonds is equal which indicated that all three N-O bonds are similar.

Thus you consider the Lewis structure for nitrate to be a mixture of the three structures given in Figure 2- 12(3). These three possible Lewis structures given in Figure 2- 12(3) are called *resonance structures*.

Alternatively the bonds can be sketched by one full line and one dotted line to show the case of resonance.

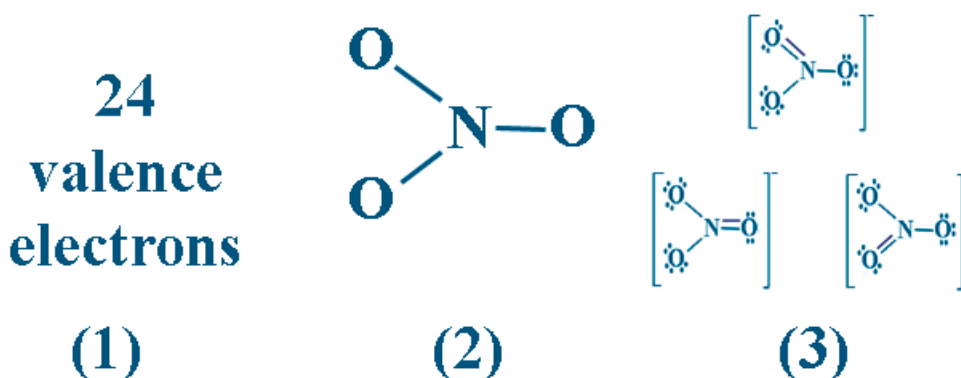


Figure 2- 12: Lewis structure for nitrate

The Lewis structure for nitrate is a combination of three resonance structures.

From the Lewis structure we now know that the structure of nitrate is given by three resonance structures. Furthermore we have information about the bond order (larger than 1 and less than 2) and placement of lone pairs. But we know nothing about the actual geometry of the composite ion.

In the examples we have been looking at till now in this section it has been pretty clear which atom would be the central atom. For some molecules or composite ions however it is not always so obvious which atom that is the central atom. In order to be able to write down the Lewis structure for such a molecule or composite ion, we have to introduce the concept of *formal charge*. The formal charge of an atom in a molecule or composite ion has the following definition:

$$\left. \begin{array}{l} \text{Formal charge} \\ \text{of an atom} \end{array} \right\} = (\text{number of surrounding electrons}) - (\text{number of valence electrons}) \quad (2-3)$$

The number of surrounding electrons is determined firstly by dividing the number of bond electrons equally between the two atoms among which the chemical bond is located. Secondly you count the number electrons surrounding the atom on the Lewis structure. The number of valence electrons for an element is known from its electron configuration and thus from its position in the periodic table. In the following example we are going to write down the Lewis structure for a dinitrogen oxide molecule and from the concept of formal charge we are going to evaluate which of more possible Lewis structures are the most realistic.

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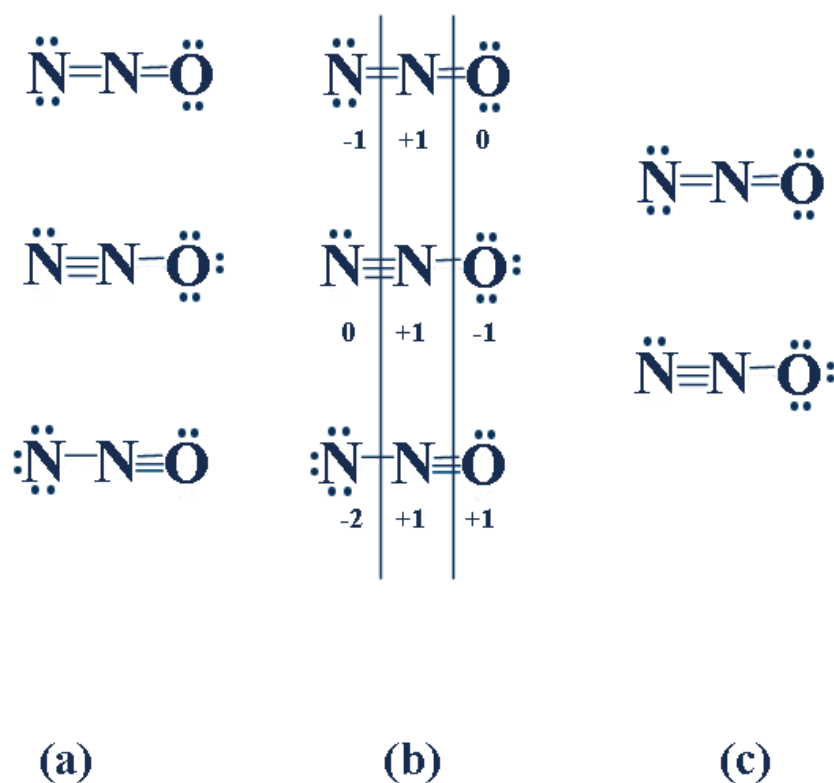


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Example 2- K:*The dinitrogen oxid molecule in Lewis structure*

In the N_2O molecule it is not so obvious which of the atoms that should be the central atom and how the electrons shall be arranged in order to satisfy the octet rule for each atom. When the guidelines given in (2- 2) on page 59 are used you can reach the three Lewis structures given in Figure 2- 13a. In order to judge which of these three structures are the most realistic, the formal charge of each atom has to be determined according to (2- 3) on page 64. First the bond electrons are “shared” equally between the atoms as shown in Figure 2- 13b. The number of electrons surrounding each atom is counted. After that the number of valence electrons for that element is then drawn from the number of surrounding electrons and you then have the formal charge which is sketched in Figure 2- 13b. Since molecules normally seek to be as low in energy as possible, it is advantageous for them overall to be in as low formal charge as possible. Thus the most realistic of the Lewis structures given in Figure 2- 13a and b are the two upper ones. Thus the Lewis structure for the N_2O molecule can be considered as being a combination of the two structures given in Figure 2- 13c.

**Figure 2- 13 Lewis structure for the dinitrogen oxid molecule**

(a) Three possible Lewis structures. (b) The formal charge is determined for all three atoms in the molecule. (c) Lowest possible energy level is related with lowest possible formal charge for the single atoms. The first two structures are therefore more realistic than the last structure. The Lewis structure for the N_2O molecule is thus considered as a combination of the two upper structures.

It is seen in Figure 2- 13b that the formal charge is determined at the difference between number of surrounding electrons and valence electrons for a particular atom. A “half” single bond gives 1 surrounding electron pr. atom, a “half” double bond gives 2 surrounding electrons pr. atom and a “half” triple bond gives 3 surrounding electrons pr. atom. However from the Lewis structure we know nothing about the actual geometry of the molecule.

In the Lewis structure we now have a useful tool that can predict internal atomic arrangement and positions of lone pairs inside molecules and composite ions. Furthermore we can have valuable information about the bond orders (whether we are dealing with single, double or triple bonds) and we can get information about eventual resonance structures. The concept of formal charge could also be useful in judging which of more possible Lewis structures are the most realistic.

BUT the Lewis structures tell us nothing about the actual geometry of the molecules or composite ions.

Why is a carbon dioxide molecule linear?

Why is a water molecule V-shaped?

Why do ammonia molecules attain trigonal pyramid shape?

The answers to these questions can be found in the VSEPR theory which is the topic in the next section.

2.2.4 VSEPR theory

VSEPR stands for *valence shell electron pair repulsion*. VSEPR theory can be used to predict actual geometries of molecules and composite ions. To be more precise it is a matter of determining bond directions and angles from the central atom in a molecule or composite ion to the other atoms. VSEPR theory can very shortly be formulated as follows:

The electron groups surrounding the central atom in a molecule or composite ion will be located as far apart from each other as possible.

This statement or definition is based on an uncountable number of experimental studies of a numerous number of different molecules and composite ions during the times. A relevant question is now what an electron group really is? The answer to this is that an electron group can be the following:

- A single bond (one electron pair consisting of 2 electrons)
 - A double bond (two electron pairs consisting of 4 electrons)
 - A triple bond (three electron pairs consisting of 6 electrons)
 - A lone pair (one “free” electron pair consisting of 2 electrons)
 - A single electron (a radical)
- } different types of electron groups

When we are to determine how many electron groups that surround an atom, the Lewis structure can be of great help (see the previous section 2.2.3 *Lewis structure*). From the Lewis structure of a given molecule you can simply count how many bonds and lone pairs that surround an atom. That way you have the number of electron groups. The VSEPR theory tells us that these electron groups will be placed as far apart as possible. In the following example we will use the VSEPR theory to predict the molecular geometries of a water molecule and a carbon dioxide molecule. That way we will discover why a carbon dioxide molecule is linear and why a water molecule is V-shaped.

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