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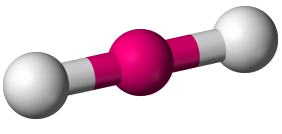
Electronic structure of molecules



IN nature molecules can be found in a myriad of different shapes. Some like carbon dioxide are one-dimensional or linear, others like methane have a shape that expands in the three directions of the space–they have a three-dimensional shape. The shape of molecules results from the chemical bonds connecting atoms in a molecule and from the existence of lone pairs of electrons. This chapter covers the analysis of the molecular shape and gains insight into advanced models of the chemical bond. After studying the ideas in this chapter you will be able to draw the connections between the atoms of a molecule and to draft Lewis structures used as graphical representations of the molecular bonds. At the end of the chapter, we will address the idea of molecular polarity, which results from the distribution of charge in a molecule. Polarity will understand the reasons why you use soap to get rid of oil while doing dished.

GOALS

1. Compute atomic charges from Lewis structures
2. Construct electron-dot structures
3. Identify bond hybridizations
4. Predict the magnetic character
5. Identify molecular geometries
6. Identify the polar character of a molecule

1.1 Electron-dot structures of atoms & molecules

Protons, neutrons, and electrons make the atoms. Electrons–in particular valence electrons–are responsible for the main chemical properties of an atom. These electrons are loosely bound and can be exchanged easily with other atoms, in contrast to the strongly-tied core electrons. The electron-dot structure of an atom or a molecule–also called Lewis structures–is a visual representation of the electronic arrangement of the valence electrons. Atoms in a molecule will tend to be surrounded by eight electrons so that its electron configuration resembles a noble gas. This arrangement is known as the octet rule. This rule is responsible for the common negative charge of F, and the positive charge of Na: F ($[He]2s^22p^5$) can easily receive an extra electron producing ionic F^- ($[He]2s^22p^6$=[Ne]), and atomic Na ($[Ne]3s^1$) can lose an electron producing ionic Na^+ ($[He]2s^22p^6 = [Ne]$). There are a few exceptions. A remarkable one is the case of the hydrogen atom that follows the duet rule.

`Discussion:` oil spills on your shirt during a dinner. List three chemicals than can remove the stain

`Valence electrons of atoms, and molecules and pairs of electrons`

The electrons of an atom are divided into core electrons and valence electrons. The valence electrons of an atom are involved in chemical bonds as they are less bonded to the nucleus. *The number of valence electrons of an atom* corresponds to the group number. For example, hydrogen H belongs to the group IA, and hence it has one valence electron. Similarly, oxygen O belongs to the group VIA, having six valence electrons. Similarly, we can count the *number of valence electrons of a molecule* by adding the valence electrons of the atoms that make the molecule. For example, water (H_2O) has eight valence electrons as each oxygen has one valence electron and oxygen has six. The number of *pairs of electrons* is just the overall number of valence electrons

divided by two. For example, water has eight valence electrons that correspond to 4 pairs of electrons.

Sample Problem 1

Indicate the number of valence electrons for the following atoms: N, O, C and S, and the number of pairs of electrons of the following molecules: NH_3, and CO_2.

SOLUTION

Nitrogen is in group VA and hence it has five valence electrons ($5e^-$). Oxygen belongs to the group VIA and C belong to IVA, hence they have wiz and four valence electrons, respectively. For the molecules, we have that ammonia has 8 electrons (nitrogen has five valence electrons and each hydrogen has one electron) that correspond to four pairs, whereas carbon dioxide has 16 electrons (carbon has four electrons and each oxygen has six) and eight pairs.

STUDY CHECK

Indicate the number of valence electrons for the following atoms: Cl and B.

The octet rule Atoms exchange electrons when they combine to form molecules. This electron exchange is the driving force that drives the formation of molecules from single atoms. The octet rule states that each atom in a stable molecule should be surrounded by eight (octet) electrons achieving noble gas electron configurations. There are two important exceptions to this rule as H is surrounded only by two electrons (this is called the duet rule), and B by six. This rule comes from the experimental observation of numerous molecules.

Electron-dot structure of an atom The electron-dot structure of an atom is a visual representation of the arrangement of the valence electrons of the atom. To write the electron-dot structure of an atom, you just need to write down the symbol of the atom surrounded by the valence electrons located in the four directions of the space: top, bottom, right, and left. To place the electrons, you start in any of the directions and fill one electron at a time. For example, for the case of three electrons we would have: $\cdot\dot{\mathrm{B}}\cdot$. After all four directions have been filled, you need to start pairing the electrons. For example, for the case of five electrons, we would have: $\cdot\dot{\mathrm{P}}\colon$. Another example, oxygen has six valence electrons and hence, the electron-dot structure would be $\cdot\ddot{\mathrm{O}}\colon$ Similarly, the electron-dot structure of fluorine would be $\colon\ddot{\mathrm{F}}\colon$. For ions, you need to add (if its an anion) or subtract (if its a cation) valence electrons, and for example the electron-dot structure of the oxide anion O^{2-} is $\colon\ddot{\mathrm{O}}\colon^{2-}$. The electron-dot structure of atoms is useful to predict–or make sense–of the atomic valence. Mind that the number of valence electrons of an atom is not the same as the valence of the atom. The valence of an atom is a number used to combine with other atoms forming compounds. For example, the electron-dot structure of nitrogen is $\cdot\dot{\mathrm{N}}\colon$ and this atom needs to gain three electrons to reach the noble gas configuration with eight electrons $\colon\ddot{\mathrm{N}}\colon^{3-}$ hence its valence is -3.

Sample Problem 2

Write down the electron-dot structure for the following atoms: N, C and Cl^-.

SOLUTION

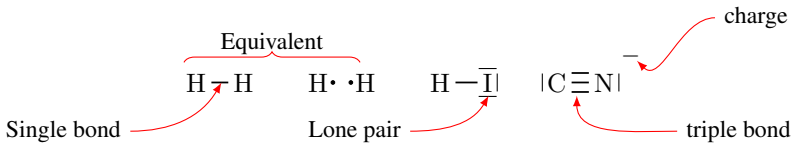
N has five valence electrons, whereas C has four. Hence the electron-dot for

both will be: ·N̈· and ·C̈·. Cl^- has eight valence electrons, that is seven plus one, and hence its electron-dot structure will be :C̈l:⁻.

STUDY CHECK

Write down the electron-dot structure for N^{3-}

An introduction to electron-dot structures Bellow, you will find some examples of electron-dot structures. Mind that the lines represent pairs of electrons hence below there are two equivalent representations for the hydrogen molecule. In these structures, you will find two different types of lines. Some pairs of electrons connect atoms. We call these types of pairs bonds. Other pairs lay on atoms. We call these lone pairs. Each atom can have a different number of lone pairs. For example, in the Lewis structures below carbon has one lone pair whereas iodide has three pairs. Bonds can be simple or multiple, double or triple. Finally, some molecules are charged and the charge is normally indicated on the top right side of the representation.



Electron-dot structure of diatomic molecules Electron-dot structures–or Lewis structures–of diatomic molecules are the most simple electron-dot structures of molecules that you will see. To obtain these structures, you need to follow the next steps. The first step is (1) to set up the atoms in the molecule in the form of a line. After that, (2) you need to count the total number of valence electrons in the molecule by adding the valence electrons of each atom (remember the number of valence electrons corresponds to the group number in the A notation). Then (3) compute the pairs of electrons represented by lines–the total number of valence electrons divided by two. Finally, (4) you need to start distributing the electron pairs in the molecule in a very specific way, first connecting the atoms among themselves, and then placing the remaining pairs surrounding the atoms. Following the octet rule, each atom except for H and B should be surrounded by four pairs, counting as pair both the bonds and lone pairs.

Sample Problem 3

Construct the electron-dot structure of HCl.

SOLUTION

We first arrange the atoms in the molecule as indicated below and then we count the number of valence electrons: H(1) and Cl(7) that gives a total of eight electrons. We have four pairs of electrons.

H Cl

Now we distribute the pair on each atoms knowing that each atom has to have four pairs with the exception of hydrogen that can only be surrounded by one pair. We can use lines instead of pairs

H:C̈l: or H − C̄l|

STUDY CHECK

Construct the electron-dot structure of HF.

Electron-dot structure of general molecules Now we will address how to build up electron-dot structures of more complex molecules given that one of the atoms is the central atom and the others are connected to this central atom. The first step is (1) to arrange the atoms in the molecule, in the form of a central atom and the remaining atoms around it; the central atom is the one with a lower index in the molecule (e.g. in H_2O is O or in NH_3 is N). After that, (2) you need to count the total number of valence electrons in the molecule, dividing this number by two to obtain the number of pairs of electrons represented by lines. In the following (3) you need to connect the surrounding atoms to the central atom with electron pairs, and then (4) place electron pairs on top of the surrounding atoms, always placing a maximum of four atoms. Finally (5) place the remaining pairs in the central atom. Overall, each atom should be surrounded by four pairs (this is the octet rule) with the exception of H and B which should be surrounded by one and three pairs respectively. When drawing Lewis structures it is not important the atom arrangement (if the molecule looks like a line, a triangle or so) as long as the connectivity (which atom goes in the center and in the surroundings) is correct.

Sample Problem 4

Construct the electron-dot structure of H_2O indicating the number of bonds and lone pairs.

SOLUTION

1. **Step one:** we first arrange the atoms in the molecule as H O H. The central atom is O as oxygen has the lower index in the H_2O molecule–the index for O is one and the index for H is two.
2. **Step two:** now we count the total number of valence electrons, including all atoms: 2xH(1) and O(6) that gives a total of eight electrons.
3. **Step three:** let us count the pairs of electrons; we have eight electrons and that is four pairs.
4. **Step four:** now we distribute the pair on each atoms knowing that each atom has to have four pairs with the exception of hydrogen that can only be surrounded by one pair. H:$\ddot{\underline{O}}$:H: and using lines instead of pairs (this is not necessary but makes the electron-dot structure look better) we obtain $H-\overline{\underline{O}}-H$. The molecule has two bonds, each one connecting and H to the oxygen atom and two lone pairs located on the oxygen atom.

STUDY CHECK

Construct the electron-dot structure of NH_3 indicating the number of bonds and lone pairs.

Multiple bonds Often times you are going to encounter electron-dot structures like the ones below

:N≡N: and $\ddot{O}=\ddot{O}$

in which the atoms are connected by means of multiple bonds, double or triple bond. Multiple bonds are formed while constructing electron-dot structures in order to impose the octet rule. Look for example the lewis structure for the HCN molecule below

$H-C-\ddot{\underline{N}}:$

On this structure, carbon do not follow the octet rule. We can enforce the octet rule by moving lone pairs from the atoms into the bond forming the structure below

$$\mathrm{H-C\equiv N:}$$

In this structure both carbon and nitrogen follow the octet rule. Hence, we need to add one more step to the Lewis structure construction scheme: convert lone pairs of electrons into bonds in order to enforce the octet rule.

Sample Problem 5

Construct the electron-dot structure of O_2.

SOLUTION

1 **Step one:** We first arrange the atoms in the molecule as

$$\mathrm{O\ O}$$

Now we count the total number of valence electrons, including all atoms: 2xO(6) that gives a total of twelve electrons. Let us count the pairs of electrons; we have twelve electrons and that is six pairs. Then we distribute the pairs, fist connecting the atoms $\mathrm{O-O}$ (we have five extra pairs to distribute at this point), and we place the remaining pairs on top of the oxygen atoms

$$\mathrm{|\overline{\underline{O}}-O\rangle}$$

The right oxygen do not follow the octet rule. In order to enforce the octet rule we move lone pairs into the bond

$$\mathrm{\langle O=O\rangle}$$

STUDY CHECK

Construct the electron-dot structure of CO_2.

Atomic charges in a molecule The electron-dot structure of a molecule results from counting the overall number of valence electrons of the molecule given that each atom brings a different number of valence electrons (n_e^{free}). For example, two H atoms bring one electron each, whereas O brings two electrons, giving a total of six valence electrons. When arranging the electron pairs in the molecule, the number of electrons surrounding an atom is called the valence of this atom in the molecule (n_e^{bonded}). We calculate the number of valence electrons of an atom in a molecule by accounting for the number of lone pairs on this atom and half the number of bonds:

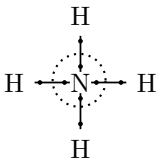
$$\mathrm{n}_e^{bonded} = \text{number of lone pairs} + 1/2\text{number of bonds}$$

It is important to note that the valence of a free atom and the valence of this atom in a molecule is not necessarily the same. Indeed the difference between the valence electron of a free atom and the same atom in a molecule is the effective charge of that atom in the molecule, Q:

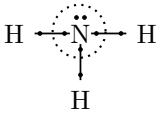
$$Q_{eff} = \mathrm{n}_e^{free} - \mathrm{n}_e^{bonded}$$

When the valence of an atom in a molecule is larger than the valence of the free atoms we have negative effective charges. In the example below

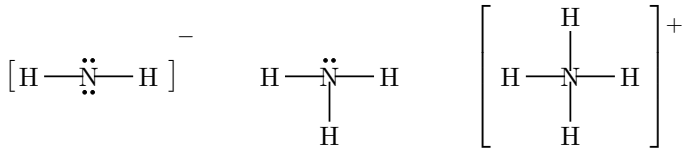
the number of electrons surrounding nitrogen is six electrons, more than the number of electrons originally brought to the molecule (five). We conclude that the atoms has negative charge, and the effective atomic charge of nitrogen is Q=-1. In the next example,



the central atom, nitrogen, still has a five valence electrons. After counting the electrons surrounding nitrogen, this time we find that this atoms is surrounded by four electrons, less than the number of electrons originally brought to the molecule. We can conclude that nitrogen has a positive charge. In particular, the effective atomic charge of nitrogen in this molecule is the number of valence electrons menus the number of surrounding electrons. In this case, the atomic charge is Q=+1. When the valence of an atom in a molecule is the same as the valence of the free atoms we have zero effective charges. In this last example



the central atom, nitrogen, has a five valence electrons. After counting the electrons surrounding nitrogen–remember in a bond each atom shared an electron and hence each line around an atom counts as one electron–we find that this atom is surrounded by five electrons. As the number of valence electrons brought to the molecule is the same as the number of electrons surrounding the atom, we say the atomic charge of this atom is zero (Q=0). Hence, the atom is neutral. In all the molecules above, hydrogen remains neutral and hence the atomic charge of nitrogen corresponds to the molecular charge of the molecule. We can hence summarize the three scenarios indicated, as we have a neutral molecule on the center, a positive molecule on the right and a negative molecule on the left.

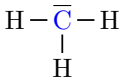


The atomic charge of an isolated atom can be well defined. However, the atomic charge of an atom in a molecule is arbitrarily defined, and more than one definition exists. Formal charges are one of the possible definitions of atomic charges in a molecule, whereas redox numbers are an alternative definition of atomic charges in molecules. None of these definitions is exactly correct. For example, redox numbers tend to overestimate the atomic charges, as they assume that all shared electrons in a bond belong to the most electronegative atom. Normally, negative formal charges tend to reside on electronegative atoms and not on electropositive atoms. At the same time, the sum of all effective charges needs to give the overall charge of the species. Furthermore, atoms in molecules tend to achieve formal charges as close to zero as possible. One can use formal charges to assess the validity of a Lewis structure. When comparing a series of equivalent Lewis structures for a molecule, the structures that best describe

the bonding in the molecule tend to be those with small effective charges located on electronegative atoms.

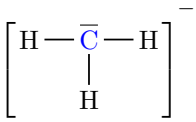
Sample Problem 6

Indicate the atomic charges of the blue highlighted atom



SOLUTION

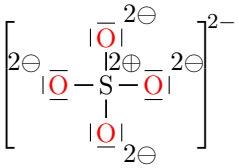
The carbon atoms brings four electrons and in the molecule it is surrounded by eight electrons, five of which belongs to it. Hence the charge of C is -1; this means that carbon has one extra electron. Each hydrogen brings one electron and in the molecule each hydrogen has one electron (they share two electrons with C, one for C and one for H). The final lewis structure with the local charge of carbon can be indicated as:



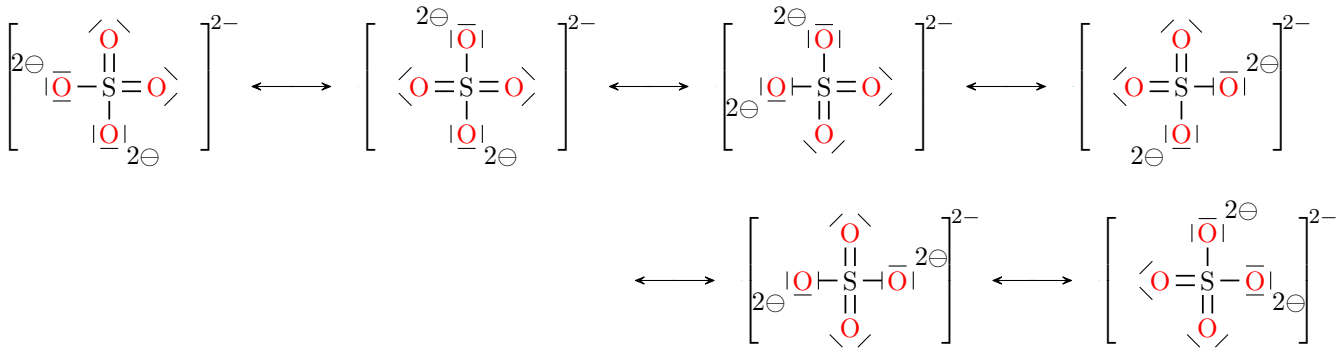
STUDY CHECK

Indicate the atomic charges of all atoms in the Lewis structure below

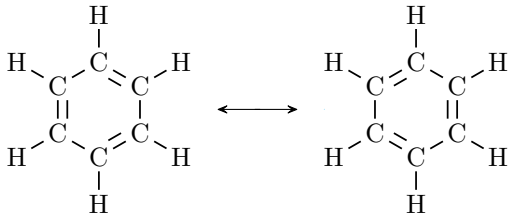
Resonant structures Let us analyze the Lewis structure of the sulfate ion, $SO_4{}^{-2}$. The goal is to analyze the Lewis structure in order to gain insight into the bonding state of the molecule, with an emphasis on the S – O bond length. The total number of electrons in the ion is 32, which corresponds to 16 pairs. We will first set up the atomic structure of the ion, using sulfur as a central atom and connect the central atom to the surrounding oxygens using four pairs of electrons. Still we have pairs of electrons that will be localized as lone pairs on the oxygen atoms given the structure below:



The structure above is a valid Lewis structure. However, it does not accurately represent the bonding of the sulfate ion, as the formal charges are very high: the formal charge of S is $+2$ and the formal charge of each O is -1, giving the overall ionic charge of -2. All oxygen atoms and sulfur follow the octet rule. Still, the charge on sulfur can be minimized by moving two lone pairs into a bond. There are several ways to do this movement. Indeed there is no reason to choose a particular oxygen atom to generate a double bond. In particular, one can think of six equivalent but yet different Lewis structures listed below:



Often there are several equivalent lewis structures for the same molecule. These structures do not differ on the atomic connections but the electron distribution. For these situations, we say there is resonance between the different structures. Resonance exists on the sulfate ion, hence the bonds are neither single nor double, all S-O bonds are equivalent, with equivalent length. The arrows above indicate that all structures are equivalent, and it does not represent any type of equilibrium. The concept of resonance is in contrast with the assumption of the Lewis structures which are based on a localized bond model: molecules contain localized bonds and lone pairs. However, this model is less than perfect and goes against the quantum nature of the electron in which electrons exist in a delocalized state. The existence of resonance has other strong consequences. Molecules with numerous resonant structures are stabilized by resonance. This means they are more stable than equivalent molecules without resonance. For example, benzene–a molecule with 15 pairs of electrons–is a very stable molecule with two resonant structures which stabilize its structure.



Exceptions to the octet rule The octet rule assumes that all atoms are surrounded by eight pairs of electrons (either lone pairs or bonds) as atoms tend to achieve a stable noble gas configuration. However, not all atoms follow the octet rule. Is fair to say that most of the second-period atoms, C, N, O, and F follow the octet rule. Hydrogen does not follow the octet rule. It follows the duet rule being surrounded by a single pair of electrons. Similarly, Boron does not follow the octet rule and tends to form a maximum of three bonds. The Lewis structure of a boron compound is presented below:

Boron and hydrogen have a reduced octet, with less than eight electrons. At the same time, atoms belonging to the third period (e.g. S, P) do not tend to follow the octet rule. They tend to have an expanded octet, being surrounded by more than eight electrons. This is because the model behind the octet rule, the localized electron model, assumes that all atoms use their s and p orbitals to create bonds. However, atoms in the third period can also use the d orbitals with can fit extra pairs of electrons. The Lewis

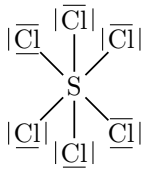
structure of a phosphorous compound is presented above. When dealing with expanded octets it is safe to assume that the central atom locates the expanded octet and hence the extra pairs of electrons.

Sample Problem 7

Obtain the Lewis structure of SCl_6.

SOLUTION

We have that in the sulfur hexachloride molecule, sulfur is connected to six chlorine atoms. Hence, in this molecule, sulfur has an expanded octet. Let us first count the number of electrons and pairs of electrons. The valence of sulfur is six and the valence of chlorine is seven. Overall we have 48 electrons and 24 pairs. The Lewis structure of this molecule will be:



STUDY CHECK

Obtain the Lewis structure of I_3^-

Molecules with odd number of electrons Lewis structures are based on the localized electron models that assume that molecules are made of atoms connected by means of pairs of electrons. Some molecules have an odd number of molecules and for those, the localized electron model does not work. An example is nitrogen monoxide NO that has eleven electrons. Nitrogen monoxide forms as a result of the combustion of gasoline in car engines. The localized electron model does not handle well molecules with odd number of electrons and more advanced models would be required to describe the bonding state of these molecules.

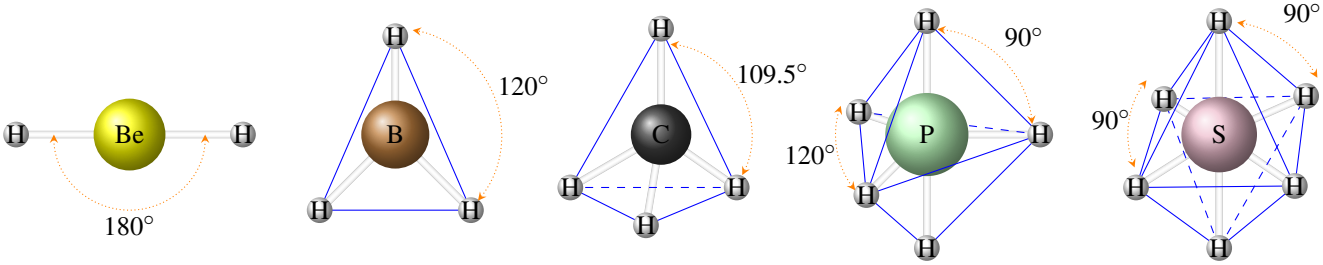
Steps to obtain Lewis structures The following steps can be used to obtain the Lewis structure of a general molecule:

1. **Step one:** Arrange the atoms in the molecule, in the form of a central atom and the surrounding atoms
2. **Step two:** Obtain the number of pairs of valence electrons by dividing the total number of valence electrons of the molecule by two
3. **Step three:** Connect the surrounding atoms to the central atom with electron pairs
4. **Step four:** Place electron pairs on top of the surrounding atoms, always placing a maximum of four atoms
5. **Step five:** Place the remaining pairs in the central atom.
6. **Step six:** Convert lone pairs of electrons into bonds in order to enforce the octet rule
7. **Step seven:** For extended octets place the extra electrons on the central atom
8. **Step seight:** When numerous equivalent Lewis structures exist, the best structures would have low formal charges, with negative charges located on electronegative atoms

1.2 Molecular shape

Molecules consist of arrangements of atoms presented in different forms. Let us use as an example the H_2O molecule, which contains two hydrogen atoms and one oxygen. Knowing that both hydrogens are connected to oxygen by means of a covalent bond, one can envision several molecular geometries such as a linear geometry or maybe a v-shaped geometry with oxygen at the point. The geometry of a molecule determines its properties, and small geometrical changes can have severe consequences on the functioning of molecules. For example, at high temperatures, when proteins in the body denaturalize loosing their unique structure they also loose their functionality. The goal of this section is to identify the approximate shape of a given molecule.

The VSEP model The VSEPR model, also known as the valence shell electron-pair repulsion model, is a model that predicts the geometries of molecules made of nonmetals. This model predicts the atomic arrangement of the molecules with an emphasis on the shape of the arrangement. However, it is not a very accurate model to predict geometries and there are better methods to obtain molecular geometries. The model predicts, for example, that water molecules have a v-shaped geometry and not a linear geometry while giving an estimate of the angle between the two O-H bonds. Still, VSEPR is not accurate enough to predict the O-H bond length and more advanced methods should be used for this purpose. The VSEPS model is based on the premise that the structure around a given atom results from minimizing the electron-pair repulsion. This way, the bonding and nonbonding pairs of electrons around a central atom are differently accounted for. Let us analyze a few cases in which the central atom only has bonding pairs of electrons. For example, the BeH_2 molecule has two bonding pairs around Be and the arrangement that maximizes the distance between both pairs hence minimizing repulsion is a linear arrangement. Hence, the BeH_2 molecule is linear with a 180° angle between both Be-H bonds. Another example would be the BH_3 molecules, a molecule with three bonding pairs. The geometry that maximizes the distance between the three pairs hence minimizing repulsion is a trigonal planar structure in which the three bonding pairs are in the same plane with an angle of 120° between the three bonds. A final example would be the methane molecule (CH_4), a molecule with fours bonding pairs. A tetrahedral arrangement with 109.5° between the C-H bonds is the most stable arrangement for this case.

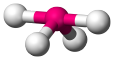
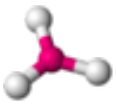
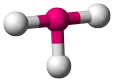
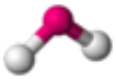
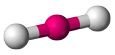
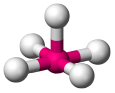
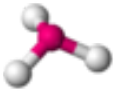
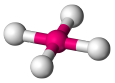
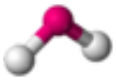


Linear | Planar trigonal | Tetrahedral | Trigonal bipyramidal | Octahedral

For the case of five bonds, the geometrical arrangement that minimizes the electron-pair interaction is a trigonal bipyramidal arrangement consisting in two pyramidal arrangements sharing a common base. The PH_5 molecule presents this arrangement. In this arrangement, there are two different bond angles: 90° between the vertical and in-plane and and 120° for the in-plane bonds. Finally, the octahedral structure

minimizes the pair repulsion in the case of six bonds and for example the SH_6 molecule has an octahedral arrangement. In this arrangement, all bonds have a 90° angle. All atomic arrangements discussed above are presented in the diagram below.

Table 1.1 Molecular geometries

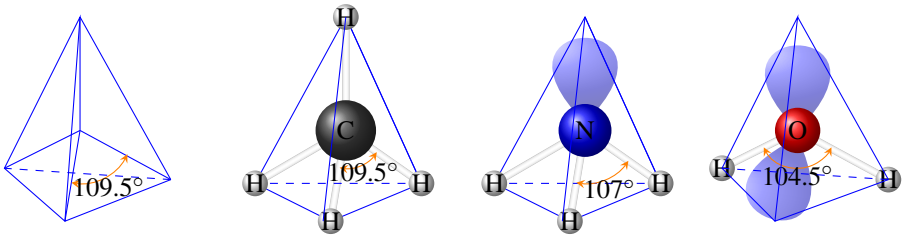
ABE Code	Molecular shape	Bond Angle	3D model	ABE Code	Molecular shape	Bond Angle	3D model
AB_2	Linear	180°		AB_4E	see-saw	180°,120°, 90°	
AB_3	Trigonal Planar	120°		AB_3E_2	T-shaped	90°, 180°	
AB_2E	Bent	120°		AB_2E_3	Linear	180°	
AB_4	Tetrahedral	109°		AB_5E	square pyramidal	90°	
AB_3E	Trigonal pyramidal	109°		AB_4E_2	square planar	90°, 180°	
AB_2E_2	Bent	109°					
AB_5	trigonal bipyramidal	90°, 120°,180°					
AB_6	octahedral	90°, 180°,180°					

ABE Molecular code We will use the ABE code to identify the molecular geometry of more complex molecules, with bonds and lone pairs. This code is based on the Lewis structure of the molecule, with B referring to the number of atoms connected to the central atom in the molecule, and E is the number of lone pairs on the central atom. The Table 1.1 gives the corresponding geometry for different ABE codes. For example, an AB_2 molecule will be linear, whereas an AB_2E_2 is bent. The electron-dot structure of water and ammonia are:

$$\mathrm{H-\underline{\overline{O}}-H} \quad \text{and} \quad \mathrm{H-\underset{\underset{\displaystyle H}{|}}{\overline{N}}-H}$$

Water has two bonds with the central atom and hence two Bs and two lone pairs on top of the central atom and hence two Es. The ABE code of water is AB_2E_2 and its geometry based on Table 1.1 is bent. The ABE code of ammonia is AB_3E, as the molecule has three atoms connected to the central nitrogen and and N has a single lone pair. Its geometry would be trigonal pyramidal. Table 1.1 also gives the angles between the different bonds. For example, the angle between the two H-O bonds of water would be 104.5°, whereas the angle between two of the N-H bonds of ammonia would be 107°. The overall number of bonding and lone pairs is referred to as the number of electron regions and the molecular geometry of the molecule is not necessarily the geometry of the electron regions. For example, the molecule methane has four bonds and a tetrahedral geometry. Ammonia has two bonds and two lone pairs. The geometry of the electron regions is also tetrahedral with three bonds pointing towards the lower

part of the tetrahedron and the lone pair pointing towards the upper part. At the same time the molecular geometry of ammonia is trigonal pyramidal. For the case of water, we have that again the geometry of the four electron regions is tetrahedral whereas the molecular geometry is bent. We can also conclude that lone pairs requiere more room than bonding pairs and this has an impact on the molecular angles. For example, the angle between two bonds in a tetrahedron is 109.5° being this value the same as the molecule angles of methane. Differently the molecular angles of ammonia–a molecule with one lone pair–are 107°, and the molecular angle of water–a molecule with two lone pairs–is 104.5°. These results indicate that as the number of lone pairs increases the bonding pairs are more squeezed together.



Sample Problem 8

Identify the geometry of the following molecules: BF_3 and SO_2.

SOLUTION

We need first the electron-dot structure of both molecules. For BF_3 $\begin{array}{c}|\overline{F}|\\ |\\ |\underline{\overline{F}}-B-\underline{\overline{F}}|\end{array}$ The code of this molecule is AB_3 and hence its geometry would be trigonal planar. The correct way to draw the molecule respecting its geometry would be: $\begin{array}{c}|\overline{F}|\\ \diagdown\\ B-\underline{\overline{F}}|\\ \diagup\\ |\underline{F}|\end{array}$. The electron-dot structure for sulfur dioxide–remember this is covalent molecule–is $|\underline{O}=\overline{S}=\underline{O}|$ and its class is AB_2E. Hence the molecular geometry is linear.

STUDY CHECK

Identify and draw the geometry of methane (CH_4).

Complex molecules and multiple bonds In order to identify the ABE code we need to identify first the central and peripheral atoms. For some more complex molecules, there might not seem to be a central atom. An example of this case can be found in acetic acid.

$$\begin{array}{ccccccc} & & H & & \diagup O \diagdown & & \\ & & | & & \| & & \\ H & - & C & - & C & - & \underline{\overline{O}} - H \\ & & | & & & & \\ & & H & & & & \end{array}$$

In the molecule we have a carbon atom connected to three hydrogens and to another carbon which at the same time is connected to two oxygens, one of these is also connected to a final hydrogen. For this cases we just need to identify different geometry centers, that is, atoms that are central to the other connections and which are connected to at least two atoms. For this molecule, we have three atoms that are central. For each central atom there will be a molecular arrangement. For example, the ABE code

for the left carbon is AB_4 whereas for the right carbon is AB_3. The geometry for the left center would be tetrahedral, whereas for the right center would be planar trigonal. The right oxygen is also a central atom connected to a carbon and a hydrogen. The ABE code for this center is AB_2E_2 and the geometry is bent. Furthermore, in the ABE code double bonds count as a single bonding pair. For example, the Lewis structure of carbon dioxide is: $\langle O=C=O \rangle$. The ABE code for carbon dioxide would be AB_2 and its geometry would be linear with an $180°$ angle between the two C=O bonds. In the case of resonance, with several Lewis structures contributing to the chemical bond, any structure would predict the VSEPR geometry. Finally, it is important to stress that the VSPER model is just a simple model and we should be careful when predicting quantitative information. For example, we have that both molecules ammonia and phosphine, NH_3 and PH_3, both with code AB_3E have a trigonal pyramidal geometry. However, whereas the experimental bond angle of ammonia is $107°$–close to the value predicted by the model–the bond angle for phosphine is $94°$–very different than the angle predicted by the VSEPR model. Still this model is good enough to predict general molecular structures.

Steps to use the VSEPR model The following steps can be used to obtain the molecular geometry using the VSEPR model:

1. **Step one:** Identify the central and the peripheral atoms.
2. **Step two:** Obtain the Lewis structure of the molecule
3. **Step three:**Obtain the ABE code with B being the number of peripheral atoms and E the number of lone pairs. A represents the central atom. Multiple bonds (double, triple) count as a single B.
4. **Step four:** Use Table 1.1 to obtain the molecular geometry

1.3 Polarity of molecules

This section deals with bond and molecule polarity. A chemical bond will be polar or nonpolar depending on the tendency of the atoms in a bond to attract the electrons the bond. Polar bonds results in the existence of a permanent dipole moment that makes a molecule polar. Polar molecules can interact with polar molecules and mix.

Bond polarity Let us compare two different molecules: H_2 and HCl. We say H_2 is a non-polar molecule. The reason for this is that each atom in the covalent H-H bond equally share the electrons. Differently, HCl is a polar molecule, as H is an electropositive atom and Cl is electronegative. That implies that in the H-Cl covalent bond each atoms shares the electrons in the bond differently. H will be less prone to attract the electrons and Cl would tend to attract the bond electrons more than H. The result would be that the electrons in the bond would belong more to Cl than to H. Another consequence is that the molecule would have a permanent dipole–a permanent charge distribution–result of a uneven charge distribution in the chemical bond. We represent excess of charge as on Cl as $Cl^{\delta-}$ and electron deficiency in H as $H^{\delta+}$. The polarity of the bond is represented as:

$$\overset{+}{H}-\overset{-}{Cl}$$
$$\longmapsto$$

Polarity of diatomic molecules Molecules can either be polar or non-polar. The polarity of diatomic molecules only depends on the nature of the atoms that forms the molecule. If the atoms in the molecule are the same (e.g. H_2 or O_2), then the molecule would be non-polar. If the atoms are different then the molecule would be polar. Examples are H_2 a nonpolar molecule and HCl or HBr, both polar molecules. You can apply the same concept to a bond inside a molecule. The C-O bond in a CO_2 molecule is a polar covalent bond, as C and O have different electronegativities.

Water (H_2O) is a polar molecule. The ABE type of water of AB_2E_2 and hence its geometry is bent. That means both H-O bonds, which are polar, do not compensate with each other. Hence, the molecule will have a dipole moment and hence will be polar. Methanol (CH_3OH) is a polar molecule as well. The central atom of the molecule (C) is connected to three hydrogens and a OH group. Hence this will be a polar molecule as one of the atoms attached to carbon is different. Both molecules, water and methanol, will mix as they have the same polarity. Methane (CH_4) is a nonpolar molecule, as the four polar C-H bonds compensate each other. Similarly, CCl_4, tetrachloro methene, is another nonpolar molecule, for the same reason. Both molecules, CH_4 and CCl_4 will mix together. As a general rule: molecules with the same polarity (polar-polar or nonpolar-nonpolar) will mix.

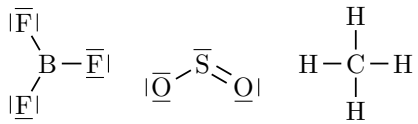
Polarity of larger molecules The polarity of larger molecules would depend on the molecular geometry. Let us analyze the case of CO_2. Each of the C-O bonds on the molecule are polar bonds. However, CO_2 is a linear molecule $\langle O{=}C{=}O \rangle$ and the polarity of each C-O bonds compensate so that at the end the molecule is polar. For the H_2O case, again, the H-O bond is polar. However, the molecule is bent and looks just like . Both H-O bonds do not compensate as they point in different direction and the directions do not cancel out what makes the water molecule to be a polar molecule.

Sample Problem 9

Identify the polar character (polar/nonpolar) of the following molecules: BF_3, SO_2 and CH_4.

SOLUTION

Let us analyze the geometries of the three molecules:



The bonds on SO_2 do not cancel out, as they do not point in opposite directions. Hence this molecule is polar. On the other hand, the bonds on methane and BF_3 cancel each other out and hence even when the C-H and B-F bonds is polar, these two molecules would be non-polar.

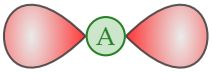
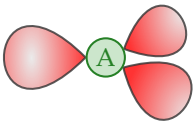
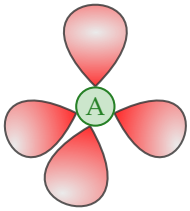
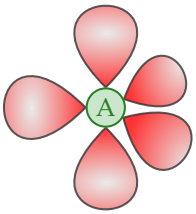
STUDY CHECK

Identify the polar character (polar/nonpolar) of the following molecules: O_2 and NH_3.

Polarity and mixing When you mix two different liquids or even gases, polarity is the key for the mixing process. If the molecules have the same polar character they will be able to mix, whereas they will not mix when the polar character is different.

This section will cover several examples of mixing an polarity.

Table 1.2 Equivalency between the ABE code and the orbital hybridization

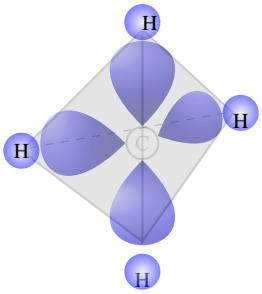
ABE Code	Electron Regions	Hybrid	Shape	Bond Angle
AB_2, ABE	2	sp		180°
AB_3, AB_2E,ABE_3	3	sp^2		120°
AB_4, AB_3E,AB_2E_2,ABE_3	4	sp^3		109.5°
AB_5, AB_4E,AB_3E_2,AB_2E_3	5	sp^3d		90° and 120°

Molecules with the same polarity Water (H_2O) is a polar molecule. The ABE type of water of AB_2E_2 and hence its geometry is bent. That means both H-O bonds, which are polar, do not compensate with each other. Hence, the molecule will have a dipole moment and hence will be polar. Methanol (CH_3OH) is a polar molecule as well. The central atom of the molecule (C) is connected to three hydrogens and a OH group. Hence this will be a polar molecule as one of the atoms attached to carbon is different. Both molecules, water and methanol, will mix as they have the same polarity. Methane (CH_4) is a nonpolar molecule, as the four polar C-H bonds compensate each other. Similarly, CCl_4, tetrachloro methene, is another nonpolar molecule, for the same reason. Both molecules, CH_4 and CCl_4 will mix together. As a general rule: molecules with the same polarity (polar-polar or nonpolar-nonpolar) will mix.

Molecules with different polarity CCl_4 is a nonpolar molecule, and H_2O is a polar molecule. As both have different polar character they will not mix together. If you mix water and CCl_4, tow phases will remain instead of a single mixed liquid phase. As a general rule: molecules with different polarity (polar-nonpolar) will not mix. Another example will be water and oil. Water is polar, and oil is a nonpolar molecule. As a consequence these two molecules will not mix together. Soap has a

polar and non-polar part. In order to remove oil from water, soap helps mixing both polar water and nonpolar oil.

1.4 Hybrid orbitals

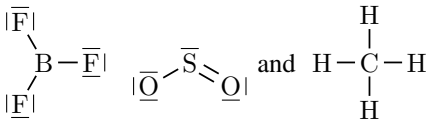


The molecular orbital theory is the most advanced bonding theory able to describe bond energies and bond lengths. Atomic orbitals are waves. When combining two waves one can obtain two possible results: a constructive combination and destructive combination. The molecular orbital theory assumes that atomic orbitals combine to form molecular orbitals. For every two atomic orbitals you can obtain two possible molecular orbitals: one is called bonding orbital, result from the constructive combination, and an other one called antibonding orbital, resulting from the destructive combination. In this section we will learn how to interpret molecular orbital diagrams.

From ABE code to hybridization In order to obtain the hybridization of an atomic center in a molecule we just need the ABE code and Table **??**. For example, if the code of a molecule is AB_4, the hybridization of the molecule will be sp^3. Similarly, if the class is AB_3 the hybridization will be sp^2 and in this case an empty p orbital will remain in the bond–mind there are three different p orbitals: p_x, p_y and p_z. Another example, would be a molecule with class AB. In this case, the hybridization will be sp and two empty p orbital will remain in the bond. A final example would be a molecule with class AB_4E. This time, the hybridization would be sp^3d^2. Mind that in general the number of hybrid orbitals correspond to adding the E and B from the class. For example, AB_4E_2, we have two E and four B with a total of six orbitals, hence we will need a s , three p's and two d's.

Sample Problem 10

Given the following Lewis structures, identify the hybridization of the central atom:



SOLUTION

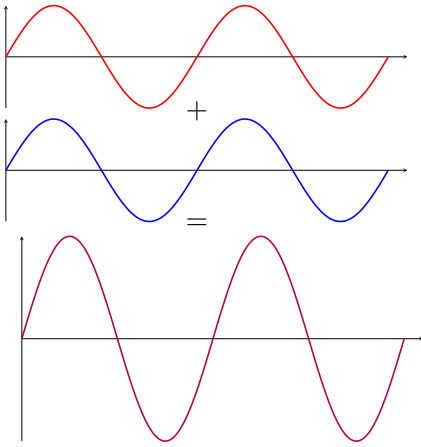
In order to identify the hybrid character of the central atom, we first need to obtain the ABE code. For BF_3 the class is AB_3, for SO_2 is AB_2E and finally for CH_4 is AB_4. The number of electron regions for BF_3 is three. Therefore we would need three hybrid orbitals: $sp2$. An empty p orbital will remain unused in the bond. For SO_2 we need three electron regions and hence the hybridization of the central atom will also be $sp2$. For the case of methane, the hybridization will be $sp3$, as the molecule has four electron regions.

STUDY CHECK

Identify the hybridization of the central atom for the following molecules: O_2 and NH_3.

1.5 Molecular orbital theory

Molecules consist of arrangements of atoms presented in different forms. Let us use as an example the H_2O molecule, which contains two hydrogen atoms and one oxygen. Knowing that both hydrogens are connected to oxygen by means of a covalent bond, one can envision several molecular geometries such as a linear geometry or maybe a v-shaped geometry with oxygen at the point. The geometry of a molecule determines its properties, and small geometrical changes can have severe consequences on the functioning of molecules. For example, at high temperatures, when proteins in the body denaturalize loosing their unique structure they also loose their functionality. The goal of this section is to identify the approximate shape of a given molecule.



Bonding and antibonding orbitals Atomic orbitals (AOs) combine to produce molecular orbitals (MOs). The combination of two atomic orbitals results in two new molecular orbitals: a bonding orbital and a antibonding orbital. Bonding MOs are more stable than the corresponding atomic orbitals. Antibonding MOs are less stable–they have a higher more positive energy–than the corresponding AOs. Antibonding orbitals are normally labeled with a * sign. Let us analyze both combinations of a $1s$ orbital. We can add both $1s$ orbital and the result is a bonding orbital, or we can substract both $1s$ orbitals and the result is an antibonding orbital, as the electron density cancels.

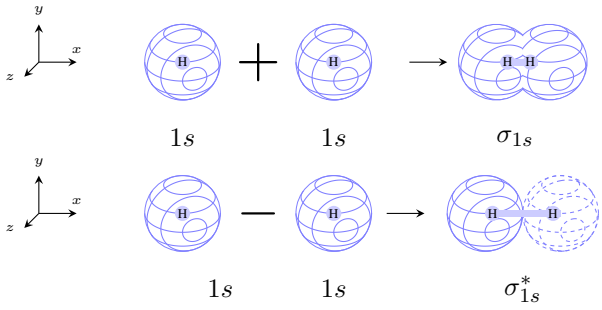
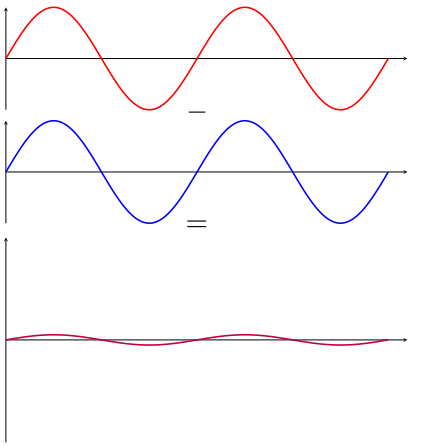


Figure 1.3 Bonding and antibonding σ orbitals resulting of combining two $1s$ atomic orbitals of Hydrogen.



Sigma and pi orbitals Let's analyze now the mixing of two $2p_x$ orbitals of two oxygen atoms in order to make an O_2 molecule. Mind that p orbitals look like dumbbells and each side of the dumbbell is called lobe. In the p_x orbital the positive lobe is in the right side and the negative love on the left side. When combining both $2p_x$ if we add both orbitals we obtain a bonding orbital and if we subtract them we obtain an antibonding orbital. Both of these orbitals are called σ orbitals, as the lobes of the orbitals mixing go though the axes of the molecule being formed–the molecule is located in the X axis. Differently, if we combine two $2p_y$ orbitals we will obtain two π orbitals, as the lobes of the molecular orbital is perpendicular the axes of the molecule being formed The first orbital is bonding as both lobes overlap constructively, whereas the second orbital is antibonding as both lobes cancel out.

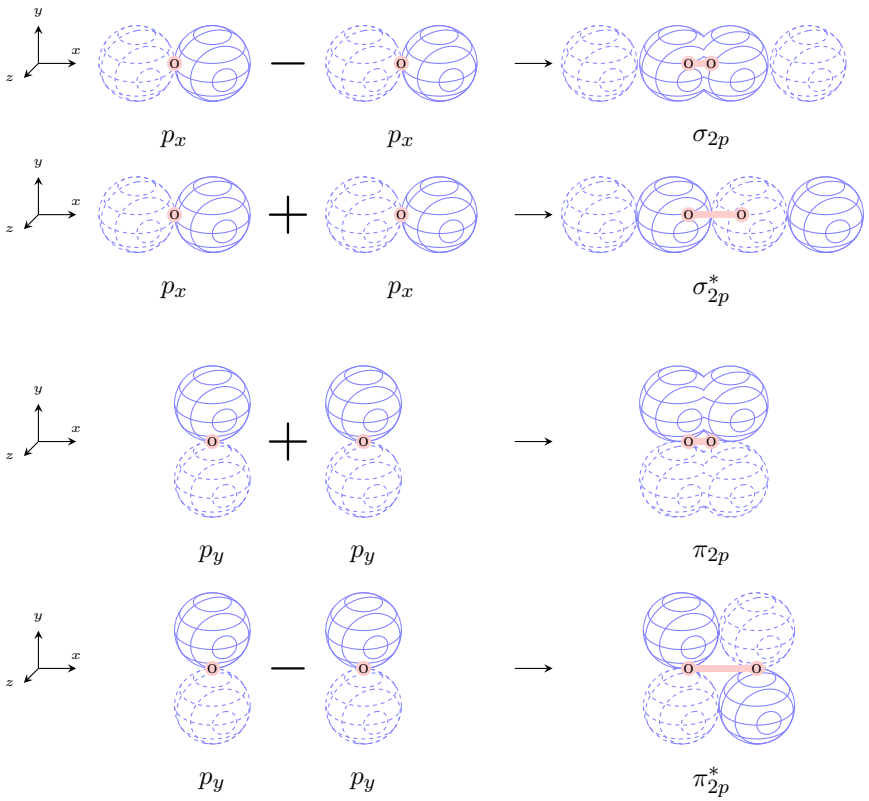
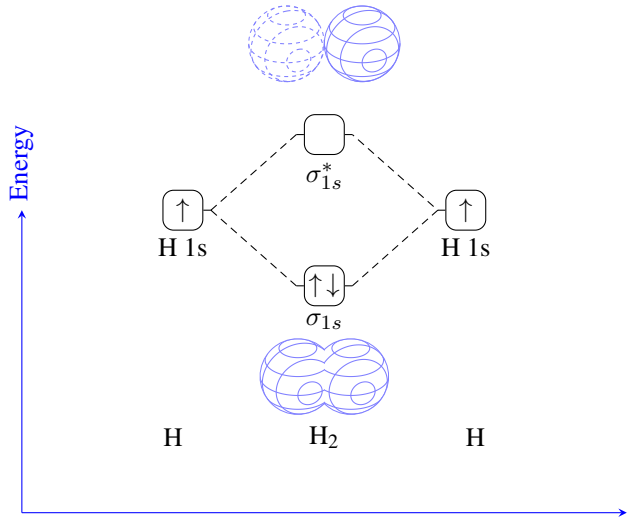
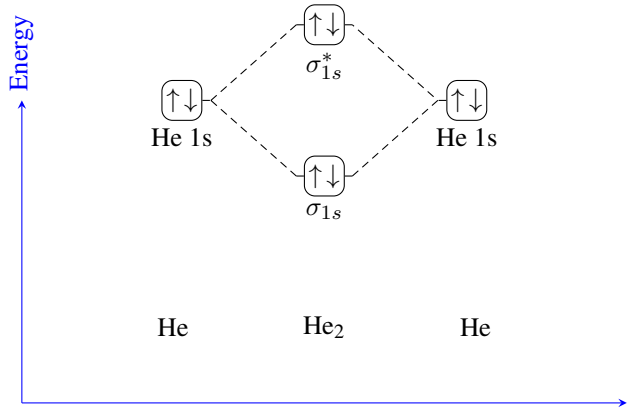


Figure 1.4 (Top) Bonding and antibonding σ orbitals resulting of combining two $2p_x$ atomic orbitals of Oxygen. (Bottom) Bonding and antibonding π orbitals resulting of combining two $2p$ atomic orbitals of Oxygen.

The case of molecular hydrogen Let us analyze the case of the formation of the H_2 molecule from two Hydrogen atoms. Each H atom has one $1s$ orbital. Therefore, according to the Molecular orbital theory, both orbitals will combine to produce two MO's. When you combine s atomic orbitals, the resulting MOs are always sigma. Sigma refers to the symmetry of the orbital. Therefore, the resulting MOs will be: σ_{1s} and σ^*_{1s}. Each AO contains one electron, hence the set of MO's will also contain two electrons that will occupy the most stable σ_{1s}. The resulting MO diagram is below. In this diagram, the atomic orbitals of H are on the left and right, whereas the MO's re in the center. We can also give the MO configuration as: $H_2 = \sigma^2_{1s}$. The hydrogen molecule is more stable than the separate hydrogen atoms. Why is that? the molecular orbitals of the molecule are lower in energy than the atomic orbitals of the hydrogen atoms. This means, the have more energy–as energy is negative that also means they are more stables. That is the reason why the hydrogen molecule is a stable existing molecule and takes energy to break down this molecule into atoms.

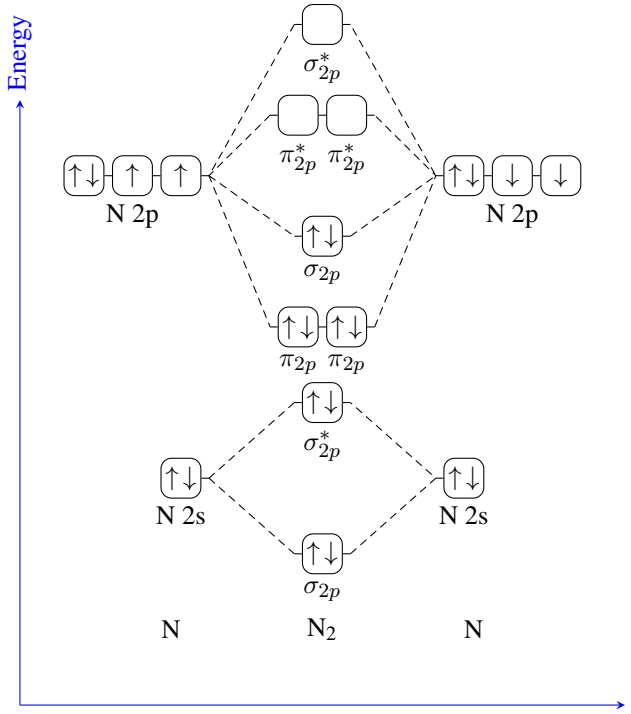


The case of molecular helium Let us analyze the case of the formation of the hypothetical Ne_2 molecule from two He atoms. Each He atom has one $1s$ orbital with two electrons. Therefore, according to the Molecular orbital theory, both orbitals will combine to produce two MO's with a total of four electrons. The resulting MOs will be as well: σ_{1s} and σ^*_{1s}. This time, MO configuration is: $He_2 = \sigma^2_{1s}\sigma^{*2}_{1s}$. In general antibonding orbitals are not stable. In the He molecule we stabilize the molecule by forming two σ^2_{1s} orbitals, but we also destabilize the molecule by forming σ^{*2}_{1s}. Hence the He_2 molecule will not be stable in compared to the atoms:



From MO diagram to MO configuration Obtaining a MO diagram is not obvious, and these diagrams can only be obtained after very complicated quantum mechanics simulations. However, after the MO diagram is given, one can obtain the MO configuration. From this configuration we can calculate two main properties: the bond order–related to the length of the molecule–and the magnetic character of the molecule. Let us use the case of N_2: In this diagram, the lower MO's are the most stables and should be filled first. The higher MO are less stable and they are listed in the right side of the MO configuration. For example, the MO configuration of N_2 would be:

$$N_2=\sigma^2_{2s}\sigma^{*2}_{2s}\pi^4_{2p}\sigma^2_{2p}$$



Bond order of a MO configuration Lets go back to the MO configuration for N_2. In this configuration we have some of the electrons occupying bonding MO and other occupying antibondoing MO's. The bond order is just the number of bonding electrons–the number of electrons occupying bonding MO's–minus the number of antibonding electrons–the number of electrons occupying antibonding MO's–divided by two. The formula is:

$$BO = \frac{(n - n^*)}{2} \quad \text{Bond Order}$$

where:

n is the number of electrons occupying bonding MO's

n^* is the number of electrons occupying antibonding MO's

The bond order is related to the stability of the molecule and to the length of its chemical bond. The larger the bond order the most stable is the molecule as more electrons occupy bonding orbitals. The larger the bond order the smaller the chemical bond, and the atoms are more loose.

Sample Problem 11

Given the following MO configurations: (a) $\sigma^2_{2s}\sigma^{*2}_{2s}\pi^4_{2p}\sigma^1_{2p}$ and (b) $\sigma^2_{2s}\sigma^{*2}_{2s}\pi^4_{2p}\sigma^2_{2p}\pi^{*3}_{2p}$. Calculate the bond order and compare the length of the chemical bond of both molecules.

SOLUTION

The bond order is the number of bonding electrons minus the number of antibonding electrons divided by two. For the first example, we have seven bonding electrons and tow antibonding. Hence the bond order will be 2.5. For the second example, we have eight bonding electrons and five antibonding. Hence the bond order will be 1.5. The larger the BO the smaller the bond, hence the second molecule has a smaller bond.

STUDY CHECK

Calculate the bond order for $\sigma_{2s}^2\sigma_{2s}^{*2}\pi_{2p}^4\sigma_{2p}^2$.

Paramagnetism and diamagnetism One of the uses of the MO configuration is to predict the magnetic character (magnetic or non-magnetic) of a molecule. By reading the MO configuration of a molecule, we can also predict its magnetic character and hence estimate its magnetic properties. Paramagnetic molecules (normally referred to as magnetic) are attracted by magnetic fields, whereas diamagnetic molecules (normally referred to as non-magnetic) are repelled by magnetic fields. The magnetic character results from the presence of unpaired electrons in the MO configuration. For example: $\sigma_{2s}^2\sigma_{2s}^{*1}$ is a paramagnetic (magnetic) molecule as we have one unpaired electron in the σ_{2s}^* orbital. In contrast, $\sigma_{2s}^2\sigma_{2s}^{*2}$ is a diamagnetic (non-magnetic) molecule, as it has no unpaired electrons.

Sample Problem 12

Given the following MO configurations, predict the magnetic character: (a) $\sigma_{2s}^2\sigma_{2s}^{*2}\pi_{2p}^4\sigma_{2p}^1$ and (b) $\sigma_{2s}^2\sigma_{2s}^{*2}\pi_{2p}^4\sigma_{2p}^2\pi_{2p}^{*3}$.

SOLUTION

The first example has an unpaired σ electron and hence it is paramagnetic. The second base also has a single unpaired electron, this time in the π_{2p}^* orbital. Mind π orbitals have capacity of four and hence can place two separate pairs of electrons.

STUDY CHECK

Given the following MO configurations, predict the magnetic character: (a) $\sigma_{2s}^2\sigma_{2s}^{*2}\pi_{2p}^4\sigma_{2p}^2$ and (b) $\sigma_{2s}^2\sigma_{2s}^{*2}\pi_{2p}^4\sigma_{2p}^2\pi_{2p}^{*2}$.