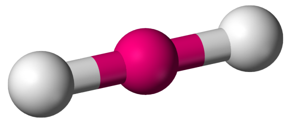
1

Electronic structure of molecules

In nature molecules can 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

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

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.

`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 gain or lose 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: $\cdot\dot{\underset{\cdot}{\mathrm{P}}}\!:$. Another example, oxygen has six valence electrons and hence, the electron-dot structure would be $\cdot\ddot{\underset{\cdot}{\mathrm{O}}}\!:$ Similarly, the electron-dot structure of fluorine would be $:\ddot{\underset{\cdot}{\mathrm{F}}}\!:$. 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 $:\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\!:^{2-}$. 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 $\cdot\dot{\underset{\cdot}{\mathrm{N}}}\!:$ and this atom needs to gain three electrons to reach the noble gas configuration with eight electrons $:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}\!:^{3-}$ hence its valence is -3.

Sample Problem 2

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

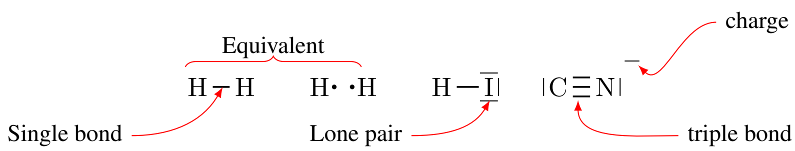
SOLUTION

N has five valence electrons, whereas C has four. Hence the electron-dot for both will be: $\cdot\ddot{\underset{\cdot}{\mathrm{N}}}\cdot$ and $\cdot\dot{\underset{\cdot}{\mathrm{C}}}\cdot$. Cl^- has eight valence electrons, that is seven plus one, and hence its electron-dot structure will be $:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\!:^-$.

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.

$$H \quad Cl$$

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

$$H{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:} \quad \text{or} \quad H-\underline{\overline{Cl}}|$$

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. $H:\ddot{\underset{\cdot\cdot}{O}}:H:$ 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

$$:N\equiv N: \text{ and } \dot{:}\dot{O}=\dot{O}\dot{:}$$

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

$$H-C-\ddot{\underset{\cdot\cdot}{N}}:$$

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

$$H-C\equiv N:$$

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.

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
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

Sample Problem 5

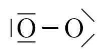
Construct the electron-dot structure of O_2.

SOLUTION

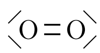
1 **Step one:** We first arrange the atoms in the molecule as

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 O − O (we have five extra pairs to distribute at this point), and we place the remaining pairs on top of the oxygen atoms



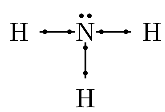
The right oxygen do not follow the octet rule. In order to enforce the octet rule we move lone pairs into the bond



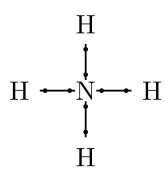
STUDY CHECK

Construct the electron-dot structure of CO_2.

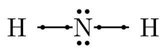
Atomic charges in a molecule In order to build up the electron-dot structures of a molecule you needs to count the overall number of valence electrons of the molecule given that each atom brings a different number of valence electrons. For example, 2 H atoms brings one electron each, whereas O brings two electrons that gives a total of six electrons for water. When you arrange the electron pairs in the molecule, each atoms should be surrounded by the number of electrons that they bring. For example, in the electron-dot structure below



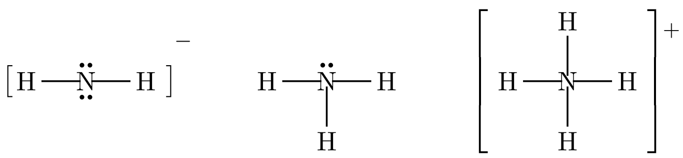
the central atom, nitrogen, has a five valence electrons. After counting the electrons surrounding nitrogen–remember in a bond each atom shared an electron and hence each line around an atom counts as one electron–we find that this atoms is surrounded by five electrons. As the number of valence electrons 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 atoms is neutral. In this 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 conclude that the atoms has 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. In this last example,

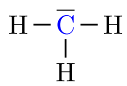


The number of electrons surrounding nitrogen is six electrons, more than the number of electrons originally brought to the molecule. We conclude that the atoms has negative charge, and the effective atomic charge of nitrogen is Q=-1. In all the molecules above, hydrogen remains neutral and hence the 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.



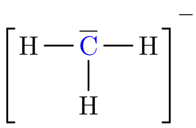
Sample Problem 6

Indicate the atomic charges of the blue highlighted atom



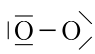
SOLUTION

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:

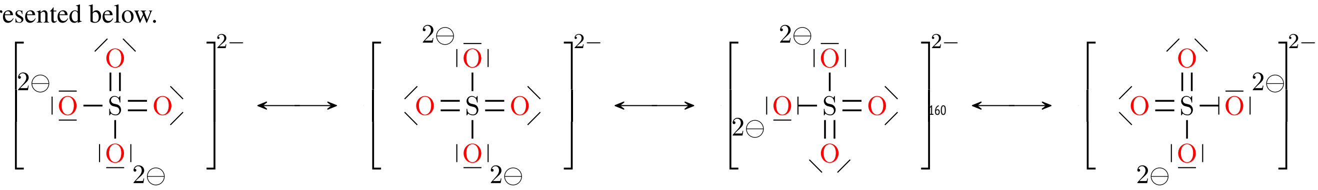


STUDY CHECK

Indicate the atomic charges of the blue highlighted atom



Resonant structures Often there are several equivalent lewis structures for the same molecule. These structures do not depend on the atomic connection but the electron distribution. For these situations, we say there is resonance between the different structures. Resonance exists on the sulfate ion, which resonant structures are presented below.



1.2 Molecular shape

Molecules are arrangements of atoms, and these arrangements can be presented in different form. 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 $H-\overline{\underline{O}}-H$ or maybe $H\diagup\overline{\underline{O}}\diagdown H$. The goal of this section is to identify the geometry of a given molecule. In order to do this, the electron-dot structure of the molecule are the key.

`ABE Molecular code` If the molecule contains two atoms, there is only a possible geometry these two atoms can exhibit, and this is a linear arrangement. For the case of more complex molecules, in order to identify the geometry you need to figure out the ABE code of the molecule. In this code B refers to the number of atoms connected to the central atom in a molecule, and E is the number of lone pairs on the central atom. For example, the electron-dot $H-\overline{\underline{O}}-H$ structure has two bonds with the central atom B_2 and two lone pairs on top of the central atom E_2 and hence the ABE code of the molecule would be AB_2E_2. Another example the ABE code for ammonia $H-\overline{N}(-H)-H$ would be AB_3E, as the molecule has three atoms connected to the central nitrogen and and N has a single lone pair. You can find a list of the equivalence between ABE codes and the molecular geometry in Table **??**. In order to predict the geometry of a molecule, once you have the ABE code, Table **??** will give you the geometry. For example, an AB_2 molecule will be linear, whereas an AB_2E_2 is bent. The bond angles are also indicated in the table, and for example a CO_2 molecule, which will be linear will have a $180°$ angle. This means both C-O bonds will form a line.

Sample Problem 7

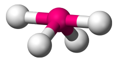
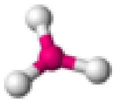
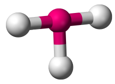
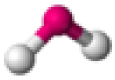
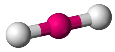
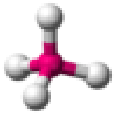
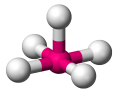
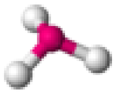
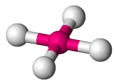
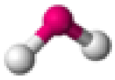
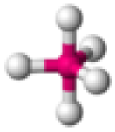
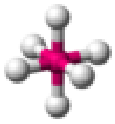
Identify the geometry of the following molecules: BF_3 and SO_2.

SOLUTION

We need first the electron-dot structure of both molecules. For BF_3 $|\overline{\underline{F}}-B(-|\overline{\underline{F}}|)-\overline{\underline{F}}|$ 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: $B(\diagup|\overline{\underline{F}}|)(\diagdown|\overline{\underline{F}}|)-\overline{\underline{F}}|$. 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).

ometries						
ar shape	Bond Angle	3D model	ABE Code	Molecular shape	Bond Angle	3D model
	180°		AB_4E	see-saw	180°,120°, 90°	
Planar	120°		AB_3E_2	T-shaped	90°, 180°	
	120°		AB_2E_3	Linear	180°	
lral	109°		AB_5E	square pyramidal	90°	
pyramidal	109°		AB_4E_2	square planar	90°, 180°	
	109°					
bipyramidal	90°, 120°,180°					
ral	90°, 180°,180°					

1.3 Polarity of molecules

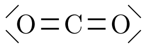
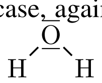
This section deals with bond and molecule polarity. A chemical bond will be polar or nonpolar depending on the tendency of the atoms in a bond to attract the electrons the bond. Polar bonds results in the existence of a permanent dipole moment that makes a molecule polar. Polar molecules can interact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

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

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.

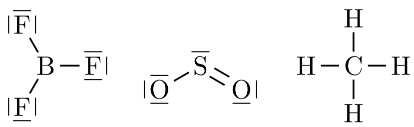
`Polarity of larger molecules` The polarity of larger molecules would depend on the molecular geometry. Let us analyze the case of CO_2. Each of the C-O bonds on the molecule are polar bonds. However, CO_2 is a linear molecule  and the polarity of each C-O bonds compensate so that at the end the molecule 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 8

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:



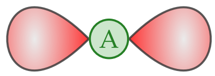
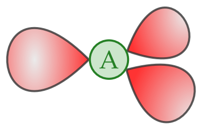
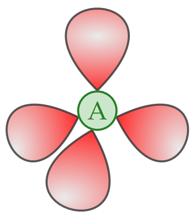
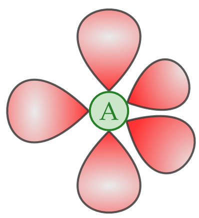
The bonds on SO_2 do not cancel out, as they do not point in opposite directions. Hence this molecule is polar. On the other hand, the bonds on methane and BF_3 cancel each other out and hence even when the C-H and B-F bonds is polar, these two molecules would be non-polar.

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.

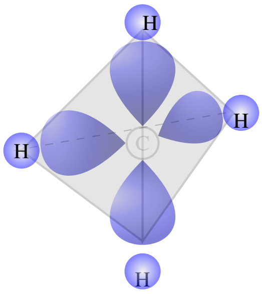
uivalency between the ABE code and the orbital hybridization

	Electron Regions	Hybrid	Shape	Bond Angle
	2	sp		180°
ABE_3	3	sp^2		120°
AB_2E_2,ABE_3	4	sp^3		109.5°
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

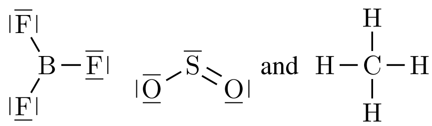


The molecular orbital theory is the most advanced bonding theory able to describe bond energies and bond lengths. Atomic orbitals are waves. When combining two waves one can obtain two possible results: a constructive combination and destructive combination. The molecular orbital theory assumes that 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 9

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



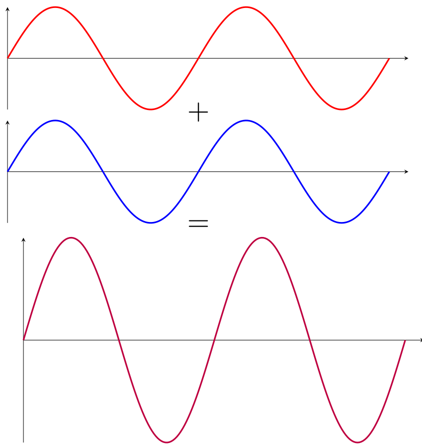
SOLUTION

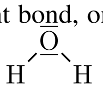
In order to identify the hybrid character of the central atom, we first need to obtain the ABE code. For BF_3 the class is AB_3, for SO_2 is AB_2E and finally for CH_4 is AB_4. The number of electron regions for BF_3 is three. Therefore we would need three hybrid orbitals: $sp2$. An empty p orbital will 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 are arrangements of atoms, and these arrangements can be presented in different form. 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 $\mathrm{H}-\overline{\underline{\mathrm{O}}}-\mathrm{H}$ or maybe  . The goal of this section is to identify the geometry of a given molecule. In order to do this, the electron-dot structure of the molecule are the key.

`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.

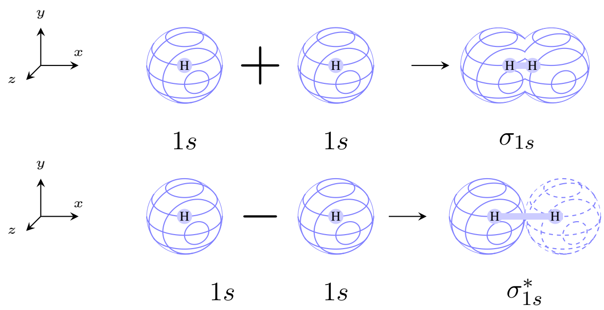
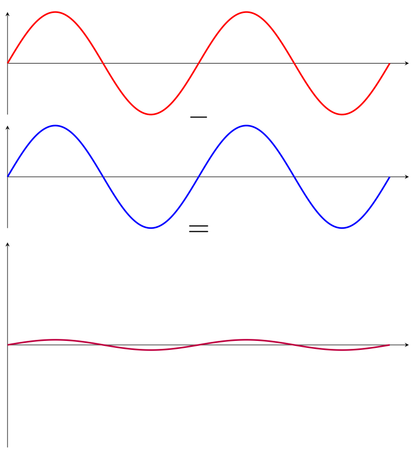


Figure ?? Bonding and antibonding σ orbitals resulting of combining two $1s$ atomic orbitals of Hydrogen.



`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.

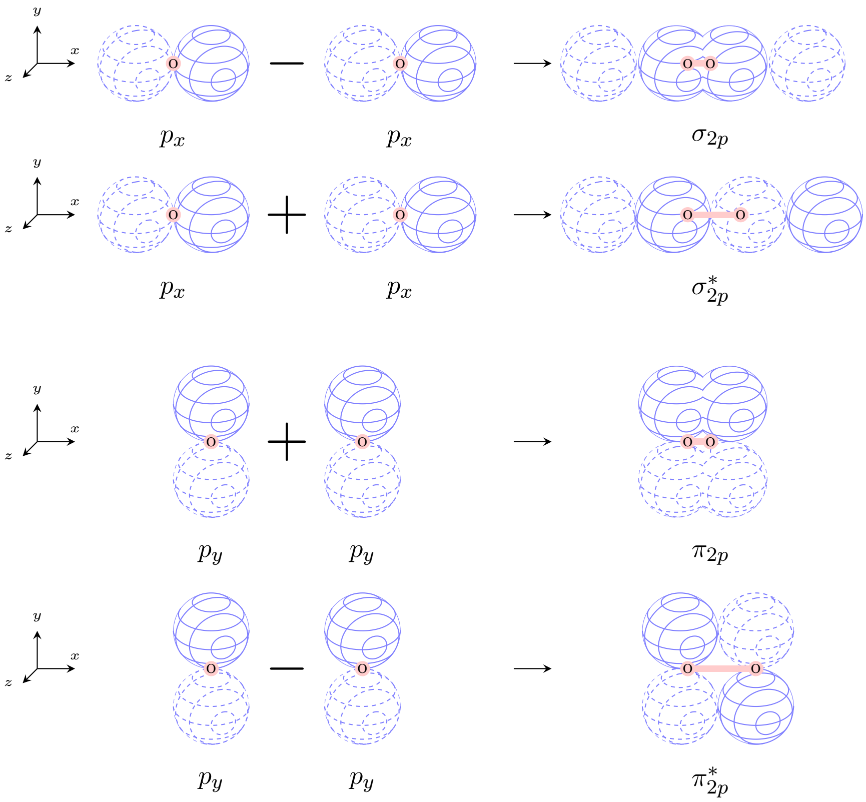
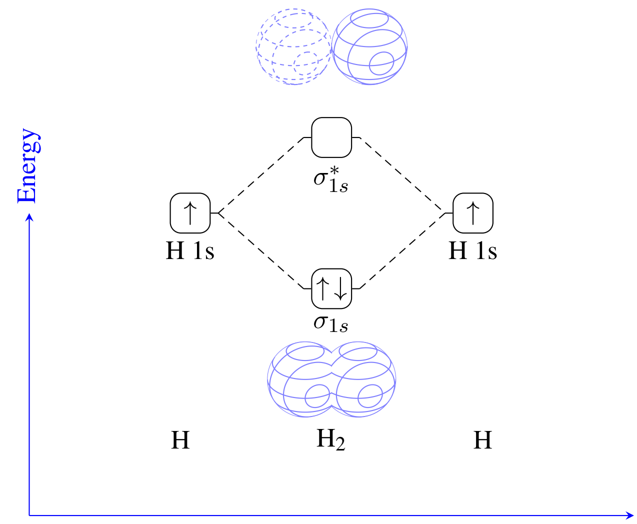
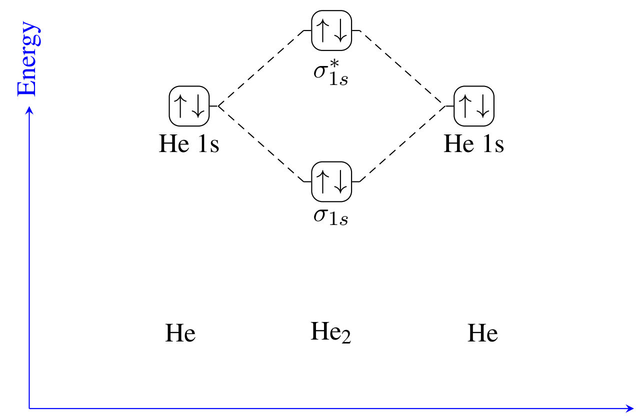


Figure ?? (Top) Bonding and antibonding σ orbitals resulting of combining two $2p_x$ atomic orbitals of Oxygen. (Bottom) Bonding and antibonding π orbitals resulting of combining two $2p$ atomic orbitals of Oxygen.

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: $\mathrm{H}_2 = \sigma^2_{1s}$. 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.

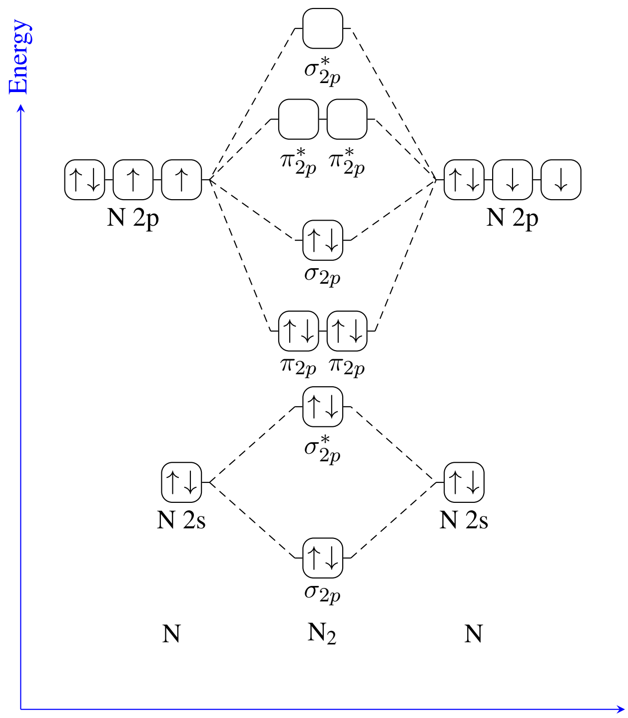


The case of molecular helium Let us analyze the case of the formation of the hypothetical Ne_2 molecule from two He atoms. Each He atom has one $1s$ orbital with two electrons. Therefore, according to the Molecular orbital theory, both orbitals will combine to produce two MO's with a total of four electrons. The resulting MOs will be as well: σ_{1s} and σ^*_{1s}. This time, MO configuration is: $\mathrm{He}_2 = \sigma^2_{1s}\sigma^{*2}_{1s}$. 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:

$$\mathrm{N}_2{=}\sigma^2_{2s}\sigma^{*2}_{2s}\pi^4_{2p}\sigma^2_{2p}$$



`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:

$$\boxed{BO = \frac{(n - n^*)}{2}}$$ 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 10

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 11

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.

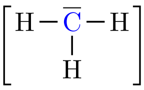
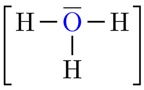
STUDY CHECK

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

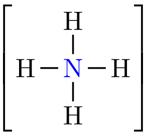
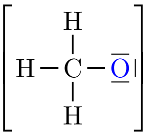
CHAPTER 1

Electron-Dot structures of molecules

1.1 Indicate the charge of the atom marked blue in the following electron-dot structure:

(a)  (b) 

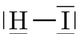
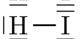
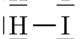
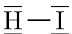
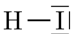
1.2 Indicate the charge of the atom marked blue in the following electron-dot structure:

(a)  (b) 

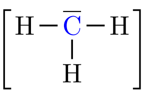
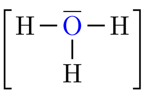
1.3 Draw the electron-dot structure of: (a) BH_3 (b) CH_4

1.4 Draw the electron-dot structure of: (a) NH_4^+ (b) H_3O^+

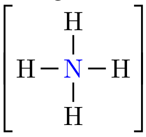
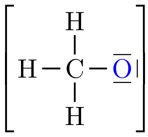
1.5 The electron-dot structure of HI is:

(a) 
(b) 
(c) 
(d) 
(e) 

1.6 Indicate the charge of the atom marked blue in the following electron-dot structure:

(a)  (b) 

1.7 Indicate the charge of the atom marked blue in the following electron-dot structure:

(a)  (b) 

Molecular shape

1.8 Identify the molecular shape of the molecules: NH_3 CH_4

1.9 Identify the molecular shape of the molecules: (a) H_2 (b) $BeCl_2$ BF_3

Polarity

1.10 Indicate the polarity or non-polarity for the following molecules: (a) H_2O (b) HCl (c) H_2

1.11 Indicate the polarity or non-polarity for the following molecules: (a) NH_3 (b) CO_2

Hybrid Orbitals

1.12 Indicate the hybridization of: (a) NH_3 (b) CH_4 (c) H_2O

1.13 Indicate the hybridization of: (a) NH_3 (b) CH_4 (c) H_2O

Molecular Orbital Theory

1.14 Using the MO order provided below

$$\sigma_{2s}\sigma^*_{2s}\pi_{2p}\sigma_{2p}\pi^*_{2p}\sigma^*_{2p}$$

obtain the MO configuration for: (a) B_2 (b) C_2

1.15 Using the MO order provided below

$$\sigma_{2s}\sigma^*_{2s}\pi_{2p}\sigma_{2p}\pi^*_{2p}\sigma^*_{2p}$$

obtain the MO configuration for: (a) O_2 (b) F_2^+

1.16 Indicate the magnetic (paramagnetic or diamagnegtic) configuration of the molecule with MO configuration: $\sigma^2_{2s}\sigma^{2*}_{2s}\sigma^2_{2p}\pi^4_{2p}\pi^{3*}_{2p}$

Answers **1.1** (a) -2 (b) +1 **1.3** (a) $\mathrm{H-\underset{\underset{H}{|}}{B}-H}$ (b) $\mathrm{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H}$ **1.5** $\mathrm{H-\overline{\underline{I}}|}$ **1.7** (a) +1 (b) -1 **1.9** (a) H_2 (Linear) (b) $BeCl_2$ (Linear) BF_3 (Trigonal planar) **1.11** (a) NH_3 (b) CO_2 **1.13** (a) NH_3 (sp^3) (b) CH_4 (sp^3) (c) H_2O (sp^3)