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Chapter 9: Molecular Geometry and Hybridization of Atomic Orbitals

Section 9.1: Molecular Geometry and the VSEPR Model

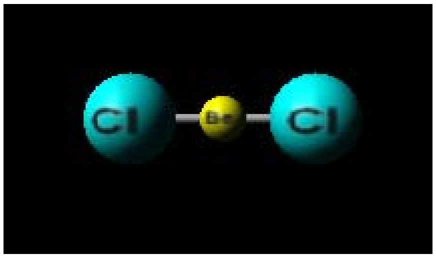
Molecular geometry is the three-dimensional arrangement of atoms in a molecule. The arrangement of atoms in a molecule affects the physical and chemical properties of a molecule. The question is how to predict the three-dimensional arrangement of atoms in a molecule? The answer involves an assumption that the electron pairs in the valence energy level (i.e. the outermost energy level) repel one another. The valence energy level is called the valence shell. The valence shell holds electrons that are involved in bonding. In a polyatomic molecule, there are two or more bonds between the central atom and the surrounding atoms.

Molecular geometry is the three-dimensional arrangement of atoms in a molecule. The geometry that the polyatomic molecule assumes minimizes the valence shell electron repulsions. This study of molecular geometry is called the **valence shell electron-pair repulsion model**.

This is abbreviated as **VSEPR Model**.

Section 9.2: The VSEPR Model for Molecules with Two Charge Clouds

Consider $BeCl_2$: The total number of valence electrons is 2 + 14 = 16. The Lewis dot structure with all atoms having a formal charge of zero is:



Look at the central atom.

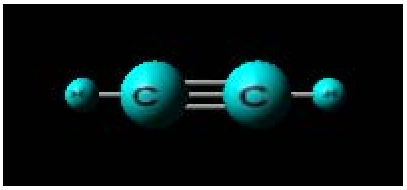
(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge clouds.

Hence, in $BeCl_2$ there are two charge clouds.

Rule: When there are two charge clouds around the central atom, the geometry of the molecule is "Linear."

In a linear geometry the bond angle from the central atom is 180°. In general, for a molecule AB_2, where A is the central atom, the geometry is "Linear".

Consider C_2H_2: The total number of valence electrons is 8 + 2 = 10. The Lewis dot structure satisfying both the octet rule and duet rules, and both C-atoms having a formal charge of 0 is:

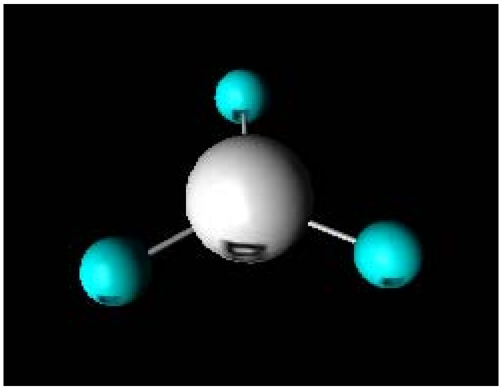


Look at the C-atom on the left-hand side. It has a single bond with the H-atom and a triple bond with the other C-atom. *Always consider a multiple bond as a single charge cloud*. Hence, this C-atom only has two charge clouds. The same argument holds true for the right-hand side C-atom. Thus, the molecular geometry of C_2H_2 is linear with a bond angle of 180°.

Other molecules having this geometry are CO_2, HCN, etc…

Section 9.3: The VSEPR Model for Molecules with Three Charge Clouds

Consider BF_3: The total number of valence electrons is 3 + 21 = 24. The Lewis dot structure with all atoms having a formal charge of zero is:



Look at the central atom.

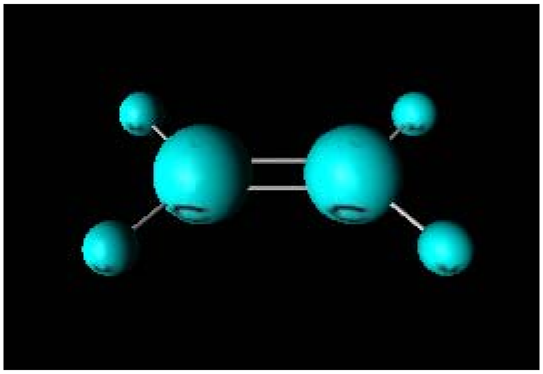
(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

Hence, in BF_3 there are <u>three</u> charge clouds.

Rule: In a molecule where there are <u>three</u> charge clouds around the central atom, the arrangement of the electron pairs is "Trigonal Planar".

In a trigonal planar structure, the bond angles from the central atom are 120^o. In general, for a molecule AB_3, where A is the central atom, the structure is "Trigonal Planar".

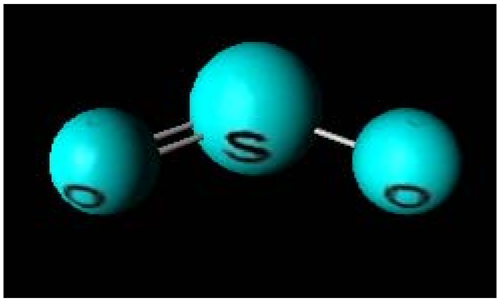
Consider C_2H_4: The total number of valence electrons is 8 + 4 = 12. The Lewis dot structure satisfying both the octet and duet rules, and both C-atoms having a formal charge of 0 is:



Look at the C-atom on the left-hand side. It has two single bonds with two H-atoms and a double bond with the other C-atom. *Always consider a multiple bond as a single charge cloud.* Hence, this C-atom has only <u>three</u> charge clouds. The same argument holds true for the right-hand side C-atom. Thus, the molecular geometry of C_2H_4 is Trigonal Planar with bond angles of 120^o.

Another molecule having this geometry is SO_3.

Consider SO_2: The total number of valence electrons is 6 + 12 = 18. The Lewis dot structure satisfying the octet rule, and having the smallest formal charges on atoms is:



Note: This is a resonance structure.

Look at the central atom.

(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as a charge cloud.

Always consider a multiple bond as a single charge cloud. Thus, the S-atom has three charge clouds. The general formula for a molecule of this type would be AB_2E. E represents the lone pair of electrons on the central atom A.

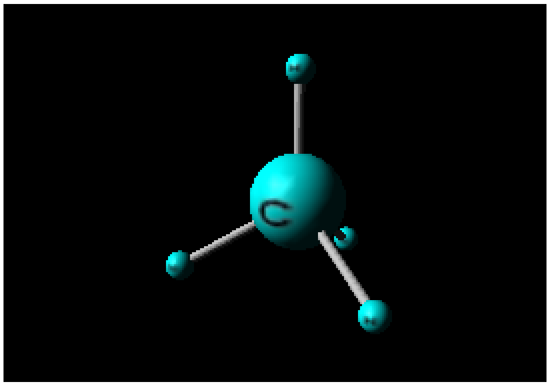
Rule: In a molecule when there are three charge clouds around the central atom, the arrangement of electron pairs is "Trigonal Planar."

However, when there are two bonds and one lone pair in three charge clouds, the geometry is "Bent or V-shaped." In a bent or V-shaped geometry, the bond angle is a little less than 120^{o}.

Other molecules having this geometry are O_3, $PbCl_2$, $SnBr_2$, etc…

Section 9.4: The VSEPR Model for Molecules with Four Charge Clouds

Consider CH_4: The total number of valence electrons is 4 + 4 = 8. The Lewis dot structure satisfying both the duet and octet rules, and the C-atom having a formal charge of zero is:



Look at the central atom.

(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

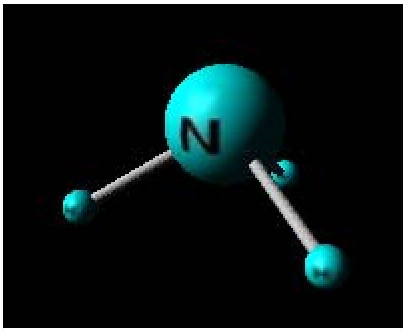
Hence, in CH_4 there are <u>four</u> charge clouds.

Rule: In a molecule where there are <u>four</u> charge clouds around the central atom, the arrangement of the electron pairs is "Tetrahedral."

In a tetrahedral geometry, the bond angles from the central atom are 109.5°. In general, for a molecule AB_4, where A is the central atom, the molecular geometry is "Tetrahedral".

Another molecule having this geometry is $SiCl_4$.

Consider NH_3: The total number of valence electrons is 5 + 3 = 8. The Lewis dot structure satisfying both the octet and duet rules and the N-atom having a formal charge of zero is:



Look at the central atom.

(a) All bonds from the central atom are called charge clouds.

(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

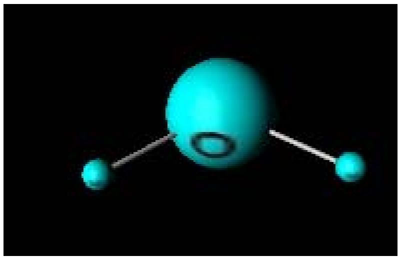
Thus, the N-atom has four charge clouds.

The general formula for a molecule of this type would be AB_3E. E represents a lone pair of electrons on the central atom A.

Rule: In a molecule where there are four charge clouds around the central atom, the arrangement of electron pairs is "Tetrahedral."

However, when there are three bonds and one lone pair in four charge clouds, the molecular geometry is "Trigonal Pyramidal." In a trigonal pyramidal geometry the bond angles from the central atom are a little less than 109.5^o. Other molecules having this geometry are PF_3, ClO_3, etc.

Consider H_2O: The total number of valence electrons is 2 + 6 = 8. The Lewis dot structure satisfying both the octet and duet rules, and the O-atom having a formal charge of zero is:



Look at the central atom.

(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

Thus, the O-atom has four charge clouds.

The general formula for a molecule of this type would be AB_2E_2. E represents a lone pair of electrons on the central atom A.

Rule: In a molecule where there are four charge clouds around the central atom, the arrangement of electron pairs is "Tetrahedral."

However, when there are two bonds and two lone pairs in four charge clouds, the molecular geometry is "Bent or V-shaped." In a bent or V-shaped geometry the bond angles from the central atom are less than 109.5^o.

Other molecules having this geometry are OF_2, SCl_2, etc…

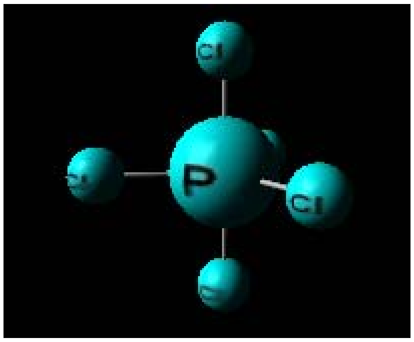
Summary

Molecule	Total # of Charge Clouds	# of Bonds	# of Lone Pairs	Arrangement of Charge Clouds	Geometry	Bond Angle
AB_4	4	4	0	Tetrahedral	Tetrahedral	109.5
AB_3E	4	3	1	Tetrahedral	Trigonal Pyramidal	<109.5
AB_2E_2	4	2	2	Tetrahedral	Bent or V-shaped	<109.5

All these concepts can be applied in predicting the geometry of polyatomic ions.

Section 9.5: The VSEPR Model for Molecules with Five Charge Clouds

Consider PCl_5: The total number of valence electrons is: 5 + 35 = 40. The Lewis dot structure in which P and Cl atoms have a formal charge of zero is:



Look at the central atom.

(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

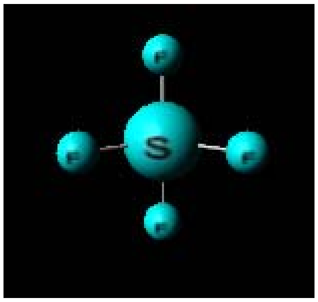
Hence, in PCl_5 there are five charge clouds.

Rule: In a molecule where there are five charge clouds around the central atom, the arrangement of electron pairs is "Trigonal Bipyramidal."

In a trigonal bipyramidal geometry, the bond angles from the central atom are 90^o, 120^o and 180^o. In general, for a molecule AB_5, where A is the central atom, the molecular geometry is "Trigonal Bipyramidal".

Other molecules having this geometry are PF_5, AsF_5, SOF_4, etc…

Consider SF_4: The total number of valence electrons is 6 + 28 = 34. The Lewis dot structure in which S and F atoms have a formal charge of zero is:



Look at the central atom.

(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

Thus, the S-atom has five charge clouds.

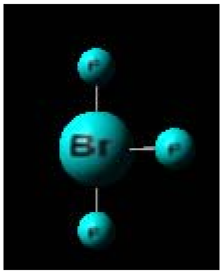
The general formula for a molecule of this type would be AB_4E. E represents a lone pair of electrons on the central atom A.

Rule: In a molecule where there are five charge clouds around the central atom, the arrangement of the electron pairs is "Trigonal Bipyramidal."

However, when there are four bonds and one lone pair in five charge clouds, the molecular geometry is "Seesaw." In seesaw geometry, the bond angles from the central atom are 90^o, 120^o and 180^o.

Another molecule having this geometry is XeO_2F_2.

Consider BrF_3: The total number of valence electrons is 7 + 21 = 28. The Lewis dot structure in which Br and F atoms have a formal charge of zero is:



Look at the central atom.

(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

Thus, the Br-atom has five charge clouds.

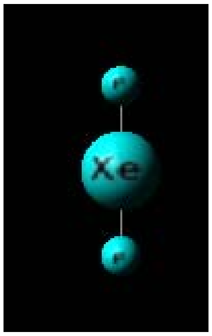
The general formula for a molecule of this type would be AB_3E_2. E represents the lone pair of electrons on the central atom A.

Rule: In a molecule where there are five charge clouds around the central atom, the arrangement of electron pairs is "Trigonal Bipyramidal."

However, when there are three bonds and two lone pairs in five charge clouds, the molecular geometry is "T-shaped." In a T-shaped geometry the bond angles from the central atom are 90^o and 180^o.

Another molecule having this geometry is ClF_3.

Consider XeF_2: The total number of valence electrons is 8 + 14 = 22. The Lewis dot structure in which Xe and F atoms have a formal charge of zero is:



Look at the central atom.

(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

Thus, the Xe-atom has five charge clouds.

The general formula for a molecule of this type would be AB_2E_3. E represents a lone pair of electrons on the central atom A.

Rule: In a molecule where there are five charge clouds around the central atom, the arrangement of electron pairs is "Trigonal Bipyramidal."

However, when there are two bonds and three lone pairs in five charge clouds, the molecular geometry is "Linear." In a Linear geometry, the bond angles are 180^o.

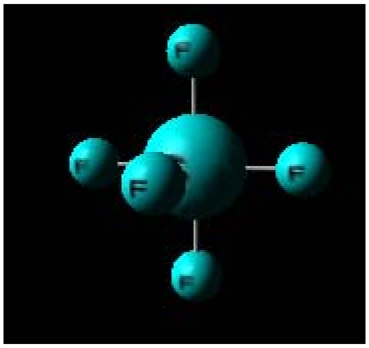
Summary:

Molecule	Total # of Charge Clouds	# of Bonds	# of Lone Pairs	Arrangement of Charge Clouds	Geometry	Bond Angle
AB_5	5	5	0	Trigonal Bipyramidal	Trigonal Bipyramidal	90^o 120^o 180^o
AB_4E	5	4	1	Trigonal Bipyramidal	See Saw	90^o 120^o 180^o
AB_3E_2	5	3	2	Trigonal Bipyramidal	T-shaped	90^o 180^o
AB_2E_3	5	2	3	Trigonal Bipyramidal	Linear	180^o

All these concepts can be applied in predicting the geometry of polyatomic ions.

Section 9.6: The VSEPR Model for Molecules with Six Charge Clouds

Consider SF_6: The total number of valence electrons is 6 + 42 = 48. The Lewis dot structure for S and F atoms have a formal charge of zero is:



Look at the central atom.

(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

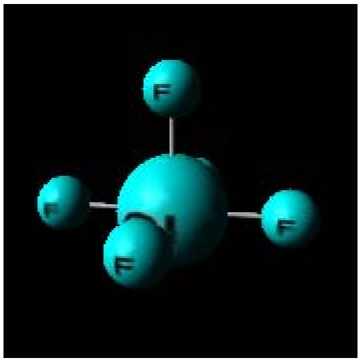
Hence, in SF_6 there are six charge clouds.

Rule: In a molecule where there are six charge clouds around the central atom, the arrangement of electron pairs is "Octahedral."

In an octahedral geometry the bond angles from the central atom are 90^o and 120^o. In general, for a molecule AB_6, where A is the central atom, the molecular geometry is "Octahedral".

Another molecule having this geometry is IOF_5.

Consider ClF_5: The total number of valence electrons is 7 + 35 = 42. The Lewis dot structure for Cl and F atoms having a formal charge of zero is:



Look at the central atom.

(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

Thus, Cl-atom has six charge clouds.

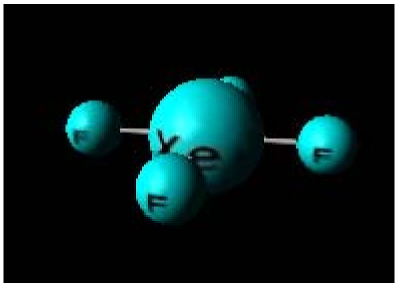
The general formula for a molecule of this type would be AB_5E. E represents a one pair of electrons on a central atom A.

Rule: In a molecule where there are six charge clouds around the central atom, the arrangement of electron pairs is "Octahedral."

However, when there are five bonds and one lone pair in six charge clouds, the molecular geometry is "Square Pyramidal." In Square Pyramidal geometry, the bond angles for the central atom are 90^o and 180^o.

Other molecules having this geometry are BrF_5, $XeOF_4$, etc…

Consider XeF_4: The total number of valence electrons is 8 + 28 = 36. The Lewis dot structure for Xe and F atoms have a formal charge of zero is:



Look at the central atom.

(a) All bonds from the central atom are called charge clouds.
(b) If there are any lone pairs of electrons on the central atom, then they are also considered as charge cloud.

Thus, the Xe-atom has six charge clouds.

The general formula for a molecule of this type would be AB_4E_2. E represents the lone pair of electrons on a central atom A.

Rule: In a molecule where there are six charge clouds around the central atom, the arrangement of electron pairs is "Octahedral."

However, when there are four bonds and two lone pairs in six charge clouds, the molecular geometry is "Square Planar." In Square Planar geometry, the bond angles are 90^o and 180^o.

Summary

Molecule	Total # of Charge Clouds	# of Bonds	# of Lone Pairs	Arrangement of Charge Clouds	Geometry	Bond Angle
AB_6	6	6	0	Octahedral	Octahedral	90^o 180^o
AB_5E	6	5	1	Octahedral	Square Pyramidal	90^o 180^o
AB_4E_2	6	4	2	Octahedral	Square Planar	90^o 180^o

All these concepts can be applied in predicting the geometry of polyatomic ions.

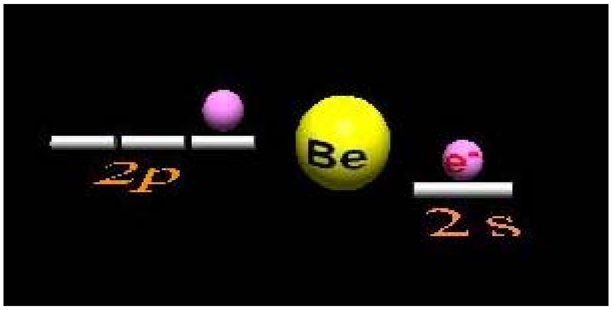
Section 9.7: Hybridization of Atomic Orbitals

A covalent bond forms when orbitals of two atoms overlap. This overlap is occupied by a pair of electrons having high probability of being located between the nuclei of two atoms. Linus Pauling proposed that the valence atomic orbitals in a molecule are different from those in the isolated atoms. These valence atomic orbitals lead to more stable bonds, and are consistent with the observed molecular shapes. The process of orbital mixing is called **hybridization**. The new atomic orbitals are called **hybrid orbitals**. There are five common types of hybridization. The spatial orientation of each type corresponds with the arrangement of electrons as predicted by the VSEPR Model.

sp Hybridization

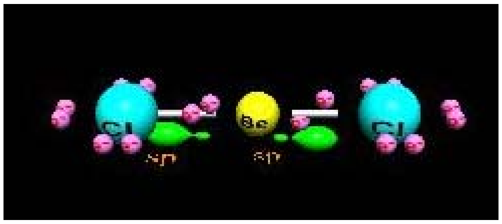
When there are two charge clouds around the central atom in a molecule, the geometry of the molecule is "Linear."

For example: In $BeCl_2$ the orbital diagram for the valence electrons in the Be-atom shows that in the ground state, the electrons are paired. Hence, the Be-atom will not form a bond with the Cl-atoms. However, as the Cl-atoms come closer to the Be-atom, one of the 2s electrons is promoted to the 2p orbital.



Now, there are two orbitals in the Be-atom available for bonding. One Cl-atom would share the 2s orbital, and the other Cl-atom would share the 2p orbital. This will result in two non-equivalent Be-Cl bonds. However, experiments suggest that the two Be-Cl bonds are equivalent in every respect.

Thus, the 2s and the 2p orbitals in the Be-atom must be hybridized to form two equivalent **sp hybrid orbitals**. The two hybrid orbitals lie on the same axis so that the angle between them is 180°.



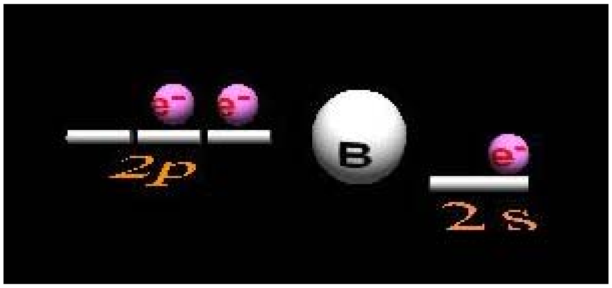
Thus, each Be-Cl bond is formed by the overlap of a Be-sp hybrid orbital and a Cl-3p orbital.

In general, central atoms of molecules having two charge clouds have **sp hybridization**.

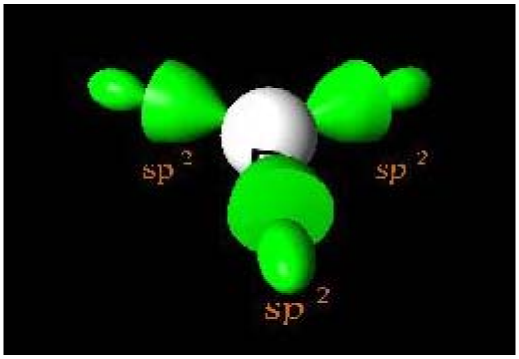
Section 9.8: sp^2 Hybridization

When there are three charge clouds around the central atom in a molecule, the geometry of the molecule is "Trigonal Planar."

For example: In BF_3 the orbital diagram for the valence electrons in the B-atom shows that in its ground state, there are 3 valence electrons: one pair in the 2s orbital and one unpaired in the 2p orbital. As the F-atoms come closer to the B-atom, one of the 2s electrons is promoted to the 2p orbital.



Now, there are three orbitals in the B-atom available for bonding. The 2s and 2p orbitals in the B-atom hybridize to form three equivalent **sp^2 hybrid orbitals**. The three hybrid orbitals lie in the same plane so that the angle between any two F-atoms is 120°. Thus, each B-F bond is formed by the overlap of a B-sp^2 hybrid orbital and a F-2p orbital.

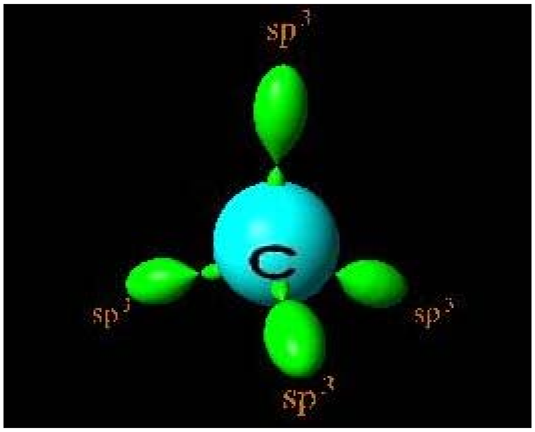


In general, central atoms of molecules having three charge clouds have **sp^2 hybridization**.

Section 9.9: sp^3 Hybridization

When there are four charge clouds around the central atom in a molecule, the geometry of the molecule is "Tetrahedral."

For example: In CH_4 the orbital diagram for the valence electrons in the C-atom shows in its ground state, there are 4 valence electrons. One pair in the 2s orbital and two unpaired in the 2p orbital. As the H-atoms come closer to the C-atom, one of the 2s electrons is promoted to the 2p orbital. Now, there are four orbitals in the C-atom available for bonding. The 2s and 2p orbitals in the C-atom hybridize to form four equivalent **sp^3 hybrid orbitals**. The four hybrid orbitals lie tetrahedrally, so that the angle between HCH-atoms is 109.5°.



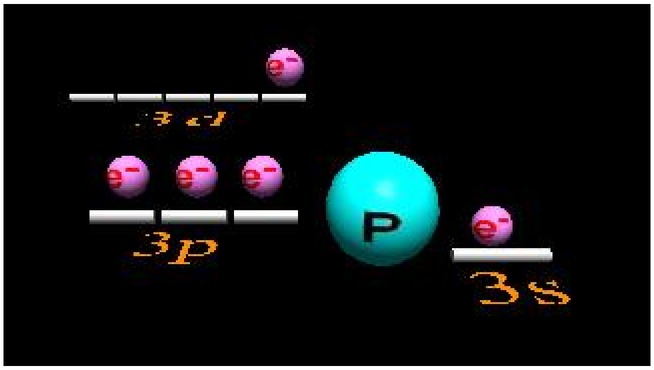
Thus, each C-H bond is formed by the overlap of a C-sp^3 hybrid orbital and a H-1s orbital.

In general, central atoms of molecules having four charge clouds have **sp^3 hybridization**.

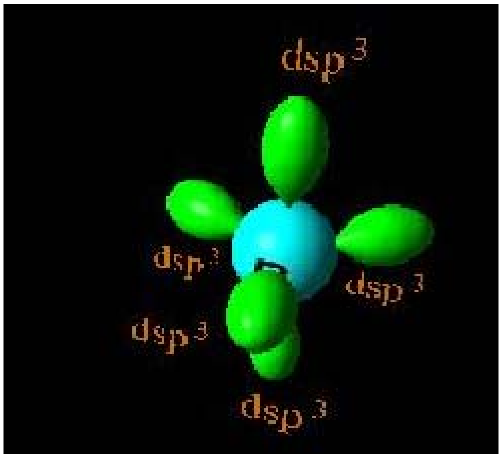
Section 9.10: sp^{3}d Hybridization

When there are <u>five</u> charge clouds around the central atom in a molecule, the geometry of the molecule is “Trigonal Bipyramidal.”

For example: In PBr_5 the orbital diagram for the valence electrons in the P-atom shows that in its ground state, there are 5 valence electrons: one pair in the 3s orbital and three unpaired in the 3p orbital. As the Br-atoms come closer to the P-atom, one of the 3s electrons is promoted to the 3d orbital.



Now, there are five orbitals in the P-atom available for bonding. The 3s, 3p, and 3d orbitals in the P-atom hybridize to form five equivalent **sp^{3}d hybrid orbitals**. The five hybrid orbitals are arranged in a trigonal bipyramidal geometry such that the bond angles are 90°, 120° and 180°.



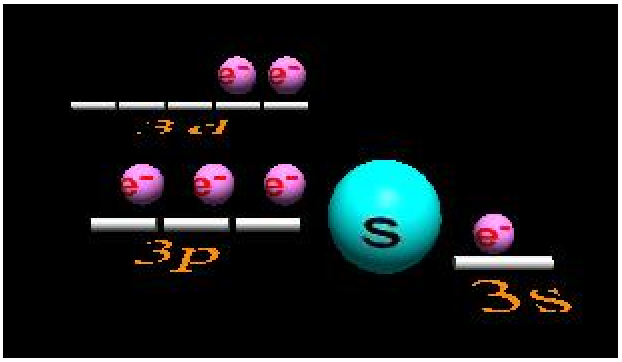
Thus, each P-Br bond is formed by the overlap of a P-sp^3d hybrid orbital and a Br-4p orbital.

In general, central atoms of molecules having five charge clouds have **sp^3d hybridization**.

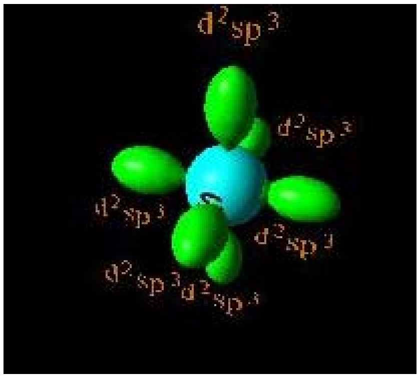
Section 9.11: sp^3d^2 Hybridization

When there are six charge clouds around the central atom in a molecule, the geometry of the molecule is "Octahedral."

For example: In SF_6 the orbital diagram for the valence electrons in the S-atom shows that in its ground state, there are 6 valence electrons: one pair in the 3s orbital, and one pair and two unpaired in the 3p orbital. As the F-atoms come closer to the S-atom, one of the 3s electrons and one of the paired 3p electrons are promoted to the two 3d orbitals.



Now, there are six orbitals in the S-atom available for bonding. The 3s, 3p, and 3d orbitals in the S-atom hybridize to form six equivalent **sp^3d^2 hybrid orbitals**. The six hybrid orbitals are arranged in an octahedral geometry such that the bond angles are 90° and 180°.



Thus, each S-F bond is formed by the overlap of a S-sp^3d^2 hybrid orbital and a F-2p orbital.

In general, central atoms of molecules having six charge clouds have **sp^3d^2 hybridization**.

Section 9.12: Summary of Hybridization

Molecule	Total # of Charge Clouds	Geometry	Hybridization
AB_2	2	Linear	sp
AB_3	3	Trigonal Planar	sp^2
AB_4	4	Tetrahedral	sp^3
AB_5	5	Trigonal Bipyramidal	sp^3d
AB_6	6	Octahedral	sp^3d^2

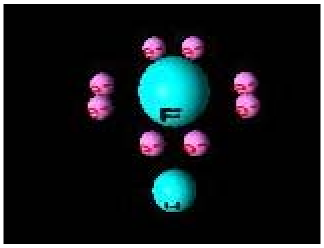
Note:

1. The concept of hybridization is a theoretical model used only to explain covalent bonding.
2. Hybridization is the mixing of at least two nonequivalent atomic orbitals.
3. A hybrid orbital has a very different shape than an atomic orbital.
4. The number of hybrid orbitals generated is equal to the number of atomic orbitals that participated in the hybridization.
5. Covalent bonds in polyatomic molecules and ions are formed by the overlap of hybrid orbitals.

Section 9.13: Bond and Molecular Polarity

Electronegativity is a property that helps distinguish bond polarity.

Consider the HF molecule:



The atoms in the molecule are covalently bonded. A F-atom is more electronegative than a H-atom. Hence, the H and F atoms do not share the bonding electrons equally. This unequal sharing of the bonding electron pair results in a relatively greater electron density near the F-atom, and a correspondingly lower electron density near the H-atom. The difference in the electronegativities of covalently bonded atoms results in a "**polar covalent bond**." The difference in the electronegativities of atoms in a covalently bonded molecule results in a molecule having a "**dipole moment**." A dipole moment is a vector (having both magnitude and direction). The magnitude of the dipole moment is equal to the product of the partial charge on either atom by the distance separating the atoms (that is the bond length).

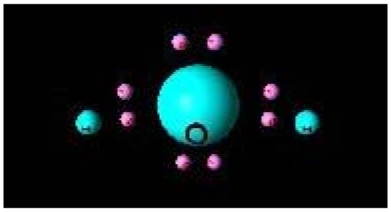
Since the electron density is greater towards F-atom, the dipole moment is indicated by an arrow pointing towards F-atom. The arrow has a positive (+) mark on the H-atom indicating that the H-atom is less electronegative that the F-atom.

Molecules having a dipole moment are called "**polar molecules**".

Thus, HF is a polar molecule. In considering the polarity of a molecule, one also has to consider the geometry of the molecule.

Consider H_2O:

From VSEPR theory, we know the arrangement of electrons around the central atom is tetrahedral.



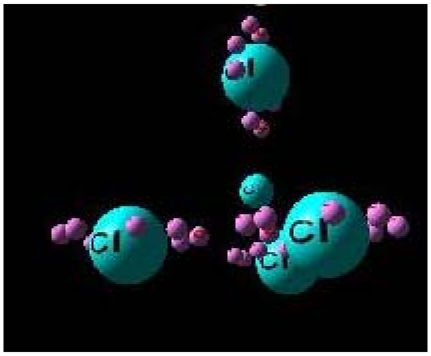
Because there are two bonds and two lone pairs on the central atom, the geometry of H_2O is "Bent or V-shaped." Since the O-atom is more electronegative than the H-atom, the bond polarity is represented as arrows pointing towards the O-atom. Thus, H_2O has a dipole moment and it is a polar molecule.

"Like Dissolves Like"

Thus, polar molecules dissolve in solvents made of other polar molecules.

Consider CCl_4:

From VSEPR theory, we know the arrangement of electrons around the central atom is Tetrahedral.



There are four bonds and no lone pairs around the central atom. Thus, the geometry of CCl_4 is tetrahedral. The Cl-atom is more electronegative than the C-atom. There are four Cl-atoms. As first glance, it may appear as though CCl_4 would be a polar molecule.

The polarity of each C-Cl bond points towards the Cl-atom. Because of the tetrahedral geometry of CCl_4, the dipole moments cancel out. Hence, CCl_4 has no dipole moment.

Molecules that have no dipole moment are called "**non-polar**" molecules.

"Like Dissolves Like"

Thus, non-polar molecules dissolve in solvents made of other non-polar molecules.

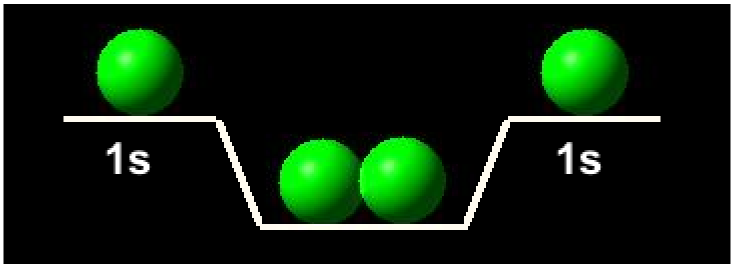
Section 9.14: Molecular Orbital Theory

The valence bond theory used in the understanding of hybrid orbitals does not adequately explain the magnetic properties of molecules. In order to understand the magnetic properties of molecules, the **Molecular Orbital (MO) theory** was developed. The MO theory is a quantum mechanical model for molecules. As atoms have atomic orbitals, molecules have molecular orbitals. The orbitals in a molecule have a given amount of energy. We know that the motion of an electron is complex, and approximations are required to solve the Schrödinger equation. Similar complications arise in the development of the MO theory. The principal approximation applied to the MO theory is that "the atomic orbitals of atoms combine to form molecular orbitals (MO)". Combine means atomic orbitals either add or subtract to form molecular orbitals.

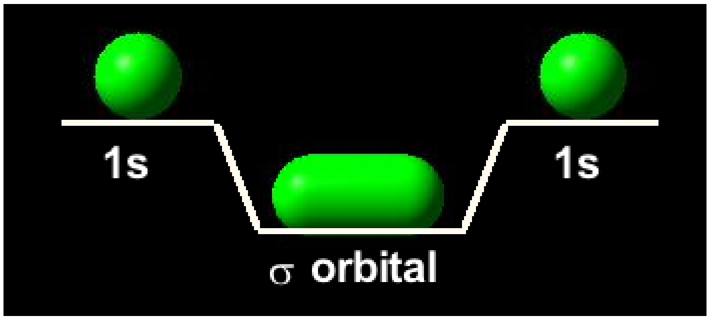
Consider the H_2 molecule:

The atomic orbitals of two H-atoms combine.

Adding the two orbitals. When two orbitals are added, the combination forms a "bonding MO."

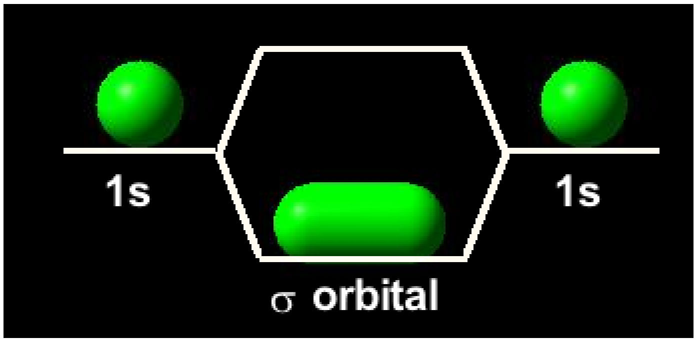


The bonding MO is lower in energy than the parent atomic orbitals.



The bonding MO is called the σ orbital. This overlap increases the probability that the electrons are between the nuclei.

Subtracting the two orbitals. When two orbitals are subtracted, the combination forms an "antibonding MO."

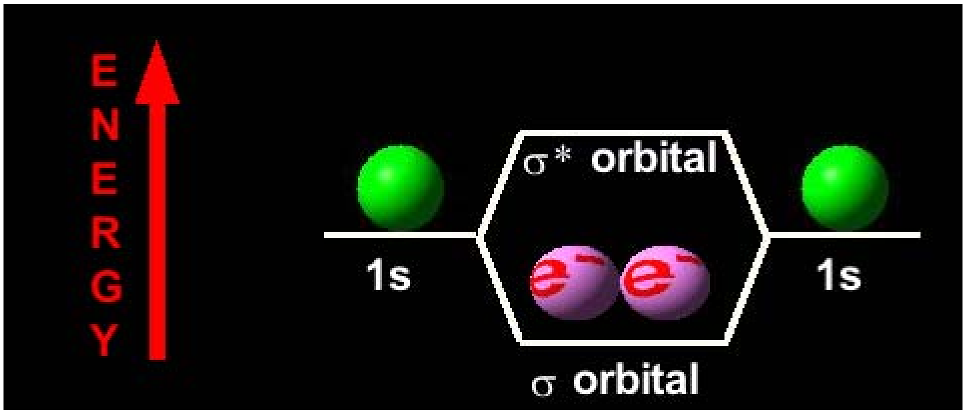


The antibonding MO is higher in energy than the parent atomic orbitals. The antibonding MO is called the σ* orbital. An antibonding MO has a "**node**" between the nuclei. "Node" means there is a region of zero electron density. This means that the probability to find electrons decreases to zero between the nuclei.

Rules for filling MO's with electrons

1. The MO's are filled in the order of increasing energy.
2. Each MO has a maximum capacity of two electrons with opposite spins.
3. If orbitals of equal energy are empty, the electrons prefer to remain unpaired, having parallel spins.

Based on these rules, the orbitals in H_2 molecules are filled as



Molecular Orbital (MO) bond order

The mathematical expression for the MO bond order is:

$$\text{Bond order} = \frac{1}{2}\left(\begin{matrix}\text{number of electrons} \\ \text{in bonding MO's}\end{matrix} - \begin{matrix}\text{number of electrons} \\ \text{in antibonding MO's}\end{matrix}\right)$$

Therefore, the bond order for the H_2 molecule is:

$$\text{Bond order} = \frac{1}{2}(2 - 0) = 1$$

A bond order:

1. Indicates the number of bonds in a molecule.
   In H_2, there is one bond (i.e. a single bond).

2. Indicates the strength of the bond.
   The higher the bond order, the stronger the bond.

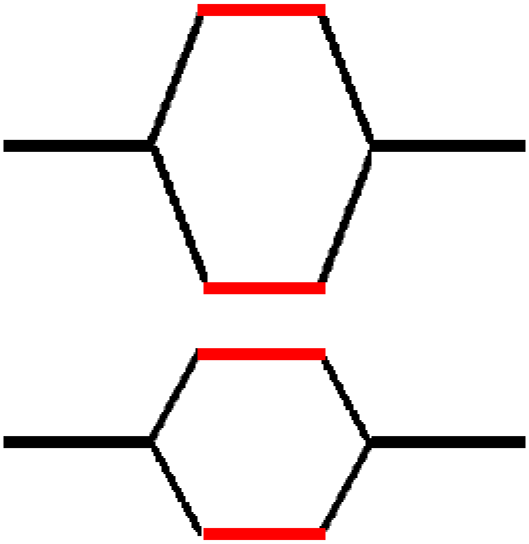
3. Can be a fraction.

4. Of zero means that the bond is not stable.

Section 9.15: MO Theory for Homonuclear Diatomic Molecules

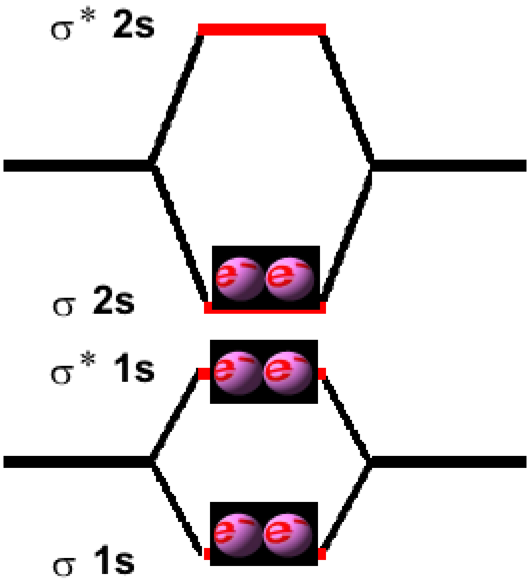
The MO diagrams of diatomic molecules containing atoms of the same element are discussed. For simplicity, only elements in period 2 are considered.

Consider the Lithium molecule, Li_2. Li_2 molecule has two Li atoms. Each Li atom has an electron configuration $1s^22s^1$. Thus, Li_2 has a total of 6 electrons. The MO energy level diagram is:



The overlap of two “s” orbitals results in the formation of a σ MO.

The arrangement of the electrons in the MO’s is:



$$\text{Bond order} = \frac{1}{2}(4 - 2) = 1$$

The electron configuration is $(\sigma\ 1s)^2\ (\sigma^*\ 1s)^2\ (\sigma\ 2s)^2$

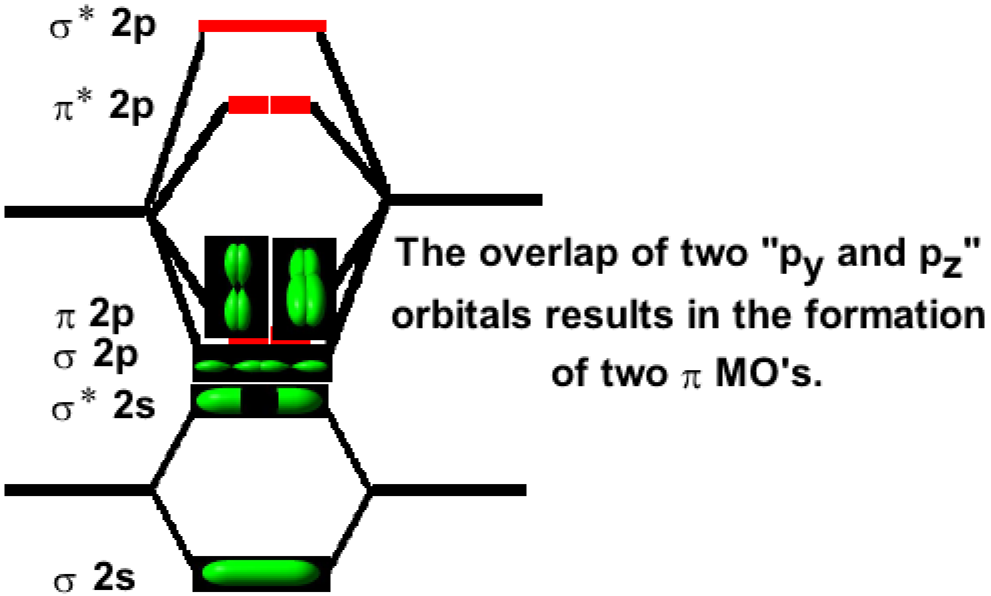
Since all electrons are paired, the molecule is “**diamagnetic**”. Diamagnetic means the molecules are not attracted by the opposite poles of a magnet.

The study of MO theory becomes more complex when the bonding involves the overlap of p-orbitals. Each atom has three p orbitals. They are p_x, p_y, and p_z, respectively.

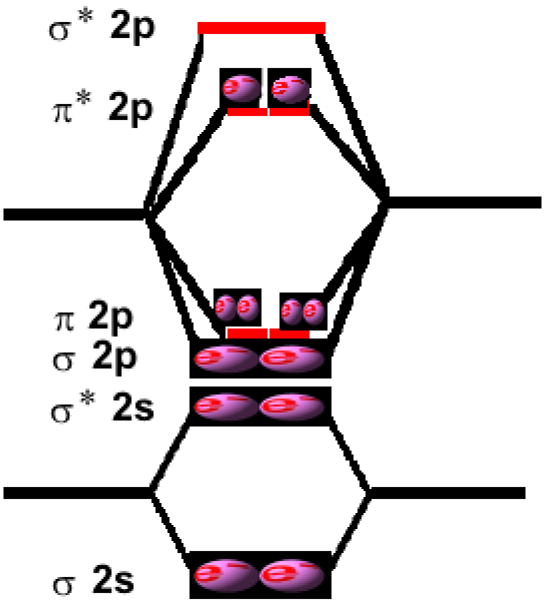
The overlap of two p_x orbitals results in the formation of a **σ (sigma) bond**. Since this is a good overlap, the σ bond is a strong bond.

The overlap of two p_y or two p_z orbitals results in the formation of a **π (pi) bond**. The overlap is not good. This weaker overlap results in a weaker π bond compared to the σ bond.

Consider the Oxygen molecule, O_2. O_2 molecule has two O atoms. Each O atom has an electron configuration $1s^2 2s^2 2p^4$. Thus, O_2 has a total of 16 electrons. The overlap of two “s” orbital results in the formation of a σ MO. For simplicity from here on, the MO energy level diagram will focus on only the valence electron atomic orbitals. Thus, each O atom has valence electron configuration $2s^2 2p^4$. Thus, O_2 has a total of 12 valence electrons.



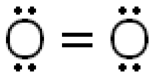
The overlap of two “p_x” orbitals results in the formation of a σ MO. The overlap of two “p_y and p_z” orbitals results in the formation of two π MO’s. The arrangement of the electrons in the MO’s is:



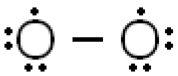
$$\text{Bond order} = \frac{1}{2}(8 - 4) = 2$$

The electron configuration is: $(\sigma\ 2s)^2$ $(\sigma^*\ 2s)^2$ $(\sigma\ 2p)^2$ $(\pi\ 2p)^4$ $(\pi^*\ 2p)^2$. Since this molecule has two unpaired electrons, it is "**paramagnetic**". Paramagnetic means the molecule is attracted to the opposite poles of a magnet.

Now, consider the Lewis dot structure of O_2



According to this structure all electrons are paired and therefore the molecule should be diamagnetic. However, the MO theory and the experimental observations show that O_2 is paramagnetic. Thus, the proposed Lewis dot structure for O_2 molecule in its <u>ground state</u> is:



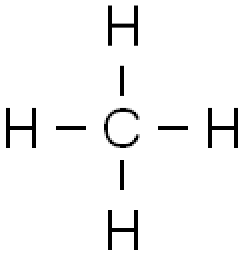
Now, the structure has a single bond with two unpaired electrons.

Section 9.16: Sigma and Pi Bonds

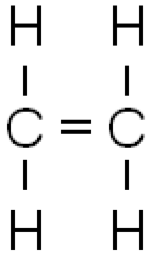
Consider three molecules:

CH_4 C_2H_4 C_2H_2

The Lewis dot structures of these three molecules satisfying both the octet and duet rules are:



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

$H-C\equiv C-H$

To count the number of σ (sigma) and π (pi) bonds in a molecule or ion remember:

1. Between any two bonded atoms in a molecule or ion there is always one σ bond.
2. All single bonds are σ bonds.
3. In a multiple bond between two atoms, there is always one σ bond and the others are π bonds.

Based on these three statements:

In CH_4 there are 4 σ bonds and 0 π bonds.

In C_2H_4 there are 5 σ bonds and 1 π bonds.

In C_2H_2 there are 3 σ bonds and 2 π bonds.

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