

[Molecular Geometry](#) is the general 3D shape of a molecule.

It is determined by the relative positions of the atomic nuclei.

Valence Shell Electron Pair Repulsion (VSEPR) Model

- VSEPR predicts shapes of molecules and ions by assuming that the valence-shell e^{-1} pairs are arranged so that they are as [far apart](#) as possible, which minimizes repulsive forces.
- [Figure 7.16](#) shows the pair arrangements, including bond angles and names.
- Electron pair arrangement about central atom includes both bonding pairs (covalent bonds) and nonbonding pairs (not connected to another atom).
- [Figure 7.19](#) shows both arrangement pair arrangement and molecular geometry.
- Molecular geometry is different from the electron pair arrangement if lone pairs are involved.

Steps for VSEPR

1. Write e^{-1} dot structure from molecular formula.
2. Count the total number of e^{-1} pairs around the central atom.
3. Determine the e^{-1} pair arrangement. (Refer to Figure 7.16)
4. Determine the geometry. (Refer to Figure 7.19)

Ex 10.01 Using AXE formulas: A = central atom X = bonding pairs E = nonbonding pairs

- a. $\begin{array}{c} \ddot{\text{Cl}} \\ \vdots \\ \text{:Cl:} \\ \vdots \\ \ddot{\text{Cl}} \end{array} \text{: Be :} \begin{array}{c} \ddot{\text{Cl}} \\ \vdots \\ \text{:Cl:} \\ \vdots \\ \ddot{\text{Cl}} \end{array} \text{:}$ Two bonding pairs only around Be, which is linear (AX_2E_0).
- b. $\begin{array}{c} \ddot{\text{N}} \\ \vdots \\ \text{:O:} \\ \vdots \\ \ddot{\text{O}} \end{array} \text{:} \text{---} \text{:O:} \text{:}$ Double bond only counts as one pair, so the total is three pairs.
Pair arrangement is triangular planar.
But, one pair is nonbonding, so geometry is bent (AX_2E_1).
- c. $\begin{array}{c} \ddot{\text{Cl}} \\ \vdots \\ \text{:Cl:} \\ \vdots \\ \ddot{\text{Cl}} \end{array} \text{: Si :} \begin{array}{c} \ddot{\text{Cl}} \\ \vdots \\ \text{:Cl:} \\ \vdots \\ \ddot{\text{Cl}} \end{array} \text{:}$ Four bonding pairs, no nonbonding pairs.
Geometry is tetrahedral (AX_4E_0).

Bond Angles

- For symmetrical tetrahedral e^{-1} pairs, like in SiCl_4 , the bond angle is 109.5° .
- For triangular planar, like BF_3 and SO_3 , the bond angle is 120° (which is $360^\circ/3$).
- The e^{-1} 's in [lone pairs](#) and [double bonds](#) require more space. In tetrahedral molecules, the angles between these e^{-1} 's and the bonds to outer atoms are slightly greater than 109.5° . The atoms, as a result, are pushed closer together, and are less than 109.5° from each other.
- Lone pairs on O (water) and N (ammonia) push the H's closer together, and their tetrahedral bond angles are less than 109.5° .
- Double bonds between C's and O's (formaldehyde) also push H's closer together.

Exceptions to Octet Rule (more than 8 e⁻¹'s around central atom)

- Five pairs of e⁻¹'s is the [trigonal bipyramidal](#) pair arrangement.
This arrangement has two kinds of e⁻¹ pairs.
The three pairs in one plane are equatorial, and are 120° apart.
The two pairs perpendicular to the other 3 are axial, and are 90° away from equatorial.
- Six pairs of e⁻¹'s is the [octahedral](#) pair arrangement.
Equatorial and axial are indistinguishable.
All bond angles are 90°.

Ex 10.02 Molecular Geometry for an Exception to the Octet Rule (TeCl₄)

- Te has six valence e⁻¹, and with one more from each Cl, the total is ten e⁻¹'s, or five pairs.
- One pair is nonbonding, so the molecule is AX₄E₁ and has see-saw geometry.
- Two of the Cl's are equatorial (middle), and the other two are axial (top and bottom).

Dipole Moment

- The dipole moment is the net charge separation in a polar molecule.
- It is the product of the charge times the distance between the two charge centers.
The units are either in Coulomb-meters (C-m) or in Debyes (1 Debye = 3.34 × 10⁻³⁰ C-m).
- The dipole moment is caused by differences in e/n between two bonded atoms (bond polarities).
- Individual bond polarities may be either reinforced or cancelled by molecular geometry.
[Table 2](#) shows which molecular geometries can have nonzero dipole moments.
- O=C=O is linear, so the two polarities cancel completely, and the molecule is nonpolar.
- H₂O is bent and polar because both H's are approximately on the same side of the O.

Ex 10.03 Dipole Moment as a Function of Molecular Geometry

- SO₂ is AX₂E₁, which is bent, not linear. S has a lone pair.
The oxygen atoms do not cancel each other. The molecule is asymmetrical and polar.
- NF₃ is AX₃E₁, which is trigonal pyramidal. N has a lone pair.
The three F's do not cancel each other. The molecule is asymmetrical and polar.
- BF₃ is AX₃E₀, which is triangular planar. B does not have a lone pair.
The three F's do cancel each other. This molecule is symmetrical and nonpolar.

Intermolecular Forces

- Polar molecules orient themselves in liquid and solid phases.
As a result, they have higher intermolecular forces than nonpolar molecules.
That is, the molecules are held together more strongly.
- Polar liquids generally have higher boiling points than nonpolar liquids.
For example, there are two related cis and trans isomers of [1,2-dichloroethene](#).
The cis (Z) molecule is polar, and the trans (E) molecule is nonpolar.
The polar cis molecule has the higher boiling point.

Valence Bond Theory (explains covalent bonding with quantum mechanics)

1. An orbital from one atom occupies the same space as an orbital from an adjoining atom.
This is called overlap.
2. The total number of e^{-1} 's for both orbitals combined is no more than two.
That is, the two orbitals share the two e^{-1} 's.

Hybrid Orbitals

- Hybrid orbitals are combinations of atomic orbitals from more than one subshell.
- Hybridization of different types of orbitals creates a set of composite orbitals which all have the same shape, size, and energy.
- The hybrid orbitals' shape, size, and energy are essentially averages of all of those properties from the component orbitals.
- The total number of orbitals does not change.
- Hund's rule predicts that an orbital with two e^{-1} 's will donate one e^{-1} to an empty orbital which has the same energy.
- As a result, hybridization maximizes the number of half-filled orbitals which are available to form covalent bonds
- The name of the hybrid orbital type uses the letters of the component subshells, along with superscripts denoting the number of orbitals from that subshell.
For instance, one s orbital and three p orbitals will form four identical (averaged) sp^3 orbitals.
- Carbon has four valence orbitals in two subshells.
They contain four valence e^{-1} 's, and their unhybridized configuration is $2s^22p^2$.
This configuration has only two unpaired e^{-1} 's, which could only form two normal covalent bonds. But, carbon can actually form four.
- The s orbital can hybridize with up to three p orbitals.
The s orbital, along with three p orbitals, will form four sp^3 orbitals.
Each hybridized sp^3 orbital will have one unpaired e^{-1} and can make a covalent bond.
- The sp^3 configuration forms four identical normal covalent bonds in compounds such as CH_4 .
These bonds are also equally spaced apart, so that the geometry is tetrahedral (109.5°).
- [Figure 8.21](#) lists common types of hybrid orbitals, along with their pair arrangements.
If the pair arrangement is determined from dot structure using the VSEPR method, the hybridization can then be predicted from the table.
- The number of hybrid orbitals = $X + E = s + p + d$ (s = 1 and $p \leq 3$)

Ex 10.04 Valence Bond Theory for H_2O

- The O in H_2O is AX_2E_2 , which has a bent geometry and a tetrahedral pair arrangement.
- The number of hybrid orbitals = $X + E = 2 + 2 = 4$, so $s = 1$ and $p = 3$.
- Figure 8.21 shows that this geometry is sp^3 hybridization also.
- O has six valence e^{-1} 's. Four of those e^{-1} 's are in two filled sp^3 orbitals that are nonbonding.
There is one e^{-1} in each of two other sp^3 orbitals. Those form the two covalent bonds with H's.

Example 10.05 Valence Bond Theory for Exceptions to the Octet Rule

- The Xe in XeF₄ has a total of six e⁻¹ pairs, as seen in example 9.10 (see chapter 9 notes).
- XeF₄ is AX₄E₂ and has square planar geometry.
- Six e⁻¹ pairs have an octahedral pair arrangement and can result from sp³d².
Two of the five orbitals in the 5d subshell are included in sp³d².
- Xe owns eight valence e⁻¹'s. So, there are two filled nonbonding sp³d² orbitals, and four sp³d² orbitals with one e⁻¹ each, which form four covalent bonds with F's.

Multiple Bonds

- More than one orbital from each atom has to overlap in a double or triple bond.
- No two covalent bonds can share exactly the same space, so only one bond in a double or triple bond can be with a hybridized orbital.
- The 2nd and 3rd e⁻¹ pairs of double and triple bonds use only unhybridized p orbitals.
- Only the p orbitals not involved with those bonds can hybridize with the s orbital. One of those hybridized orbitals is then used for the 1st e⁻¹ pair of the multiple bond. The remaining hybridized orbitals are used to bond with the remaining atoms.
- In C₂H₄, the 2nd e⁻¹ pair of the double bond uses unhybridized p orbitals from each C. The 2nd bond overlaps the two-lobed p orbitals to create a Π (pi) bond, as in [Figure 8.23](#).
- This leaves two 2p orbitals and one 2s orbital to hybridize as three sp² orbitals. The three sp² orbitals create three σ (sigma) bonds, one with the other C and two with the H's. These bonds have trigonal planar geometry, and are 120° apart, as in [Figure 8.24](#).
- In H:C:::C:H, the 2nd and 3rd e⁻¹ pairs of the triple bond use unhybridized p orbitals from each C. So, the 2nd and 3rd e⁻¹ pairs create two Π bonds, as in [Figure 8.25](#).
- This leaves one 2p orbital and one 2s orbital to hybridize as two sp orbitals. The two sp orbitals create two σ (sigma) bonds, one with the other C and one with the H. These two σ bonds have linear geometry and are 180° apart.

Ex 10.06 Valence Bond Theory for Multiple Bonds

- The N's in N₂F₂ share two e⁻¹ pairs in their double bond. Each N in N₂F₂ is AX₂E₁. So, each N in N₂F₂ has a trigonal planar pair arrangement and a bent geometry.
- Like with the C's in C₂H₄, the 2nd e⁻¹ pair creates a Π bond using unhybridized 2p orbitals, leaving three sp² orbitals that are formed from the remaining two 2p orbitals and one 2s orbital.
- Two of the three sp² orbitals on each N create a total of two σ bonds, one each to N and F. The third sp² orbital exists as a nonbonding (lone) pair.

Isomers

- Isomers are compounds with the same molecular formula, but different arrangements of the atoms.
- Isomers can be divided into two types: constitutional and geometric.
- Constitutional isomers have the same formula, but have different atomic bonding.
- For example, $\text{CH}_3\text{CH}_2\text{OH}$ (ethanol) and CH_3OCH_3 (dimethyl ether) both have the same overall formula $\text{C}_2\text{H}_6\text{O}$.
- Geometric isomers have the same atoms and atomic bonds, but have different spatial arrangements.
- Cis and trans [1,2-dichloroethene](#) are geometric isomers due to different spatial arrangements of atoms next to the double-bonded C's.
- Optical isomers are a type of geometric isomerism resulting from molecules with bonds which cause them to be mirror images of each other.
- For example, there are two [optical isomers](#) of lactic acid. The isomerism is due to one carbon atom that has four different bonds, which can be spatially arranged in two different ways.