Topic 2.7: VSEPR and Hybridization

Revision Notes · AP Chemistry

UNIT 2 · COMPOUND STRUCTURE AND PROPERTIES

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From a Lewis Diagram to a Three Dimensional Structure

A Lewis diagram is flat, but a molecule is not. VSEPR theory turns the diagram into a three dimensional prediction by treating every region of electron density around a central atom as an electron domain. Domains repel through Coulombic repulsion and arrange themselves as far apart as possible.

An electron domain is one single bond, one double bond, one triple bond, or one lone pair. Bond order does not change the count: a C=O double bond occupies one direction from carbon, so it is one domain, although its greater density repels more strongly than a single bond.

Work in a fixed order: draw the Lewis diagram, count bonding domains and lone pairs, name the electron domain geometry, then ignore the lone pairs to name the molecular geometry. Angles, hybridization and polarity follow.

The Domain Count Sets the Electron Geometry

Two domains: linear, 180°. Carbon in CO_2 has two double bond domains and no lone pair, so its electron and molecular geometries are both linear.

Three domains: trigonal planar, 120°. Boron in BF_3 has three bonding domains and no lone pair, so both geometries are trigonal planar. With one lone pair, as in SO_2 or O_3, the molecular geometry is bent at a little below 120°.

Four domains: tetrahedral, 109.5°. CH_4 has four bonding domains and no lone pair, so both geometries are tetrahedral. NH_3 has three bonds and one lone pair: tetrahedral electron geometry, trigonal pyramidal molecular geometry. H_2O has two bonds and two lone pairs: tetrahedral electron geometry, bent geometry.

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Five domains: trigonal bipyramidal, 90°, 120° and 180°. Three domains occupy equatorial positions in a plane; two occupy axial positions. Lone pairs choose equatorial positions, where they have fewer close 90° interactions. That gives seesaw, T-shaped and linear molecular geometries for one, two and three lone pairs; I_3^- is linear, with three equatorial lone pairs on central iodine.

Six domains: octahedral, 90° and 180°. SF_6 has six bonding domains and no lone pair, so it is octahedral in both senses. XeF_4 has four bonds and two lone pairs: its electron geometry is octahedral, the lone pairs sit opposite each other, and its molecular geometry is square planar.

Lone Pairs Change the Name and Squeeze the Angles

Electron geometry counts every domain; molecular geometry counts only atom positions. NH_3 and H_2O therefore share tetrahedral electron geometry but differ in molecular geometry and bond angle.

Lone pairs are held by one nucleus only, so their density sits closer to the central atom and spreads through more angular space than a bonding pair. Repulsion follows lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair.

The four domain family shows the effect cleanly. CH_4, with no lone pair, keeps 109.5°. NH_3, with one lone pair, is compressed to about 107°. H_2O, with two lone pairs, reaches about 104.5°. Each additional lone pair pushed the bonding pairs closer together.

Hybridization Names the Domain Arrangement

Hybridization is the orbital language for the same domain count. Atomic s and p orbitals combine into equivalent hybrid orbitals pointing toward the domains. In the AP Chemistry CED: two domains use sp, three use sp^2, and four use sp^3.

An sp atom has two hybrid orbitals, a linear arrangement and an ideal angle of 180°, as at carbon in CO_2 or HCN. An sp^2 atom has three hybrid orbitals, a trigonal planar arrangement and 120°, as at boron in BF_3 or either carbon in ethene. An sp^3 atom has four hybrid orbitals, a tetrahedral electron arrangement and 109.5°, as at carbon in CH_4 or CCl_4.

Hybridization follows total domains, not molecular geometry. Nitrogen in NH_3 is sp^3 because it has four domains, although its molecular geometry is trigonal pyramidal. Oxygen in H_2O is also sp^3: two bonds and two lone pairs make four domains, although its molecular geometry is bent.

The CED sequence stops at sp, sp^2 and sp^3. Five and six domain species still have VSEPR geometries, justified by repulsion and lone pair placement, not d orbital hybrid labels.

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Sigma and Pi Bonds Complete the Picture

Every covalent bond contains one sigma bond, formed by overlap along the internuclear axis, directly between the two nuclei. Hybrid orbitals are used for sigma bonding and lone pairs. A pi bond forms by side to side overlap of unhybridized p orbitals on either side of that axis.

Bond composition follows bond order. A single bond is one sigma bond. A double bond is one sigma and one pi bond, as in C=O and C=C bonds. A triple bond is one sigma and two pi bonds, as in HCN and N_2.

Sigma overlap is more direct than pi overlap, so an individual sigma bond is stronger than an individual pi bond. A pi bond also locks the atoms against rotation about the bond axis: rotating one end would break the side to side overlap. For the same atom pair, increasing bond order means a shorter, stronger bond overall, although the bond still counts as one domain at each atom.

Symmetry Decides Whether Bond Dipoles Cancel

CO_2 has two polar C=O bonds, but its linear geometry points them in opposite directions, so the molecule is nonpolar. BF_3 has three polar B-F bonds in a trigonal planar arrangement; their vectors cancel. CH_4 is likewise nonpolar because its bonds are arranged symmetrically.

Remove the symmetry and the result changes. NF_3 is trigonal pyramidal, so its N-F dipoles do not cancel and the molecule is polar. H_2O is bent, so its O-H dipoles add. A lone pair therefore matters twice: it changes molecular geometry, and that geometry can leave a net dipole.

Traps That Cost Marks in Topic 2.7

Counting a double bond as two domains. Domains are directions of electron density, not bond lines. CO_2 has two domains at carbon, not four; ethene has three at each carbon. Counting bond order as domains destroys every answer that follows.

Giving NH_3 a tetrahedral molecular geometry. Four domains make its electron geometry tetrahedral, but molecular geometry names atoms only. Three hydrogens and one lone pair leave a trigonal pyramid. The same distinction makes H_2O bent.

Assigning hybridization from molecular shape alone. Bent H_2O is sp^3 at oxygen and bent SO_2 is sp^2 at sulfur, because the first has four domains and the second has three. Count bonds plus lone pairs first.

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Leaving angles at the ideal value when lone pairs are present. A lone pair also compresses the angles between the remaining bonds. NH_3 is about 107°, not 109.5°, and H_2O is about 104.5°.

Calling every molecule with polar bonds polar. CO_2 and BF_3 contain polar bonds but are nonpolar because their geometries make the dipoles cancel. Polarity belongs to the whole molecule, not one bond.

Key Relationships to Remember

- VSEPR (SAP-4.C): electron domains repel and maximize their separation; any bond counts as one domain, and each lone pair counts as one
- Domain count to electron geometry and ideal angle: 2 linear 180°, 3 trigonal planar 120°, 4 tetrahedral 109.5°, 5 trigonal bipyramidal 90°/120°/180°, 6 octahedral 90°/180°
- Molecular geometry names atoms only: NH_3 trigonal pyramidal, H_2O and SO_2 bent, I_3^- linear, XeF_4 square planar; their electron geometries are tetrahedral, trigonal planar, trigonal bipyramidal and octahedral in the order NH_3/H_2O, SO_2, I_3^-, XeF_4
- Lone pair compression: repulsion runs lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair: CH_4 109.5°, NH_3 about 107°, H_2O about 104.5°
- Hybridization (CED): 2 domains sp, 180°; 3 domains sp^2, 120°; 4 domains sp^3, 109.5°; five and six domain geometries use VSEPR without d hybrid labels
- Bond composition: single = 1 sigma, double = 1 sigma + 1 pi, triple = 1 sigma + 2 pi; sigma overlap is stronger than pi, pi restricts rotation, and higher bond order for the same atom pair means shorter and stronger
- Polarity: polar bonds plus unsymmetrical geometry give a polar molecule (H_2O, NH_3, NF_3); polar bonds in symmetrical geometry can cancel (CO_2, BF_3, CH_4)

Continue Revising

Topic 2.7 Quiz: VSEPR and Hybridization

Topic 2.7 Worksheet

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