

Chemical Bonding: Molecular Geometry If we have a Lewis structure we're ready to go from 2D to 3D. The 3D shape of a molecule has a lot to do with how the molecule behaves.

The point group symmetry of a molecule can be described by 5 types of symmetry element. This is also called an n-fold rotational axis and abbreviated C_n . Examples are the C_2 axis in water and the C_3 axis in ammonia. A molecule can have more than one symmetry axis; the one with the highest n is called the principal axis, and by convention is aligned with the z-axis in a Cartesian coordinate system. A third type of symmetry plane exists: A symmetry plane can also be identified by its Cartesian orientation, e. Center of symmetry or inversion center, abbreviated i. A molecule has a center of symmetry when, for any atom in the molecule, an identical atom exists diametrically opposite this center an equal distance from it. In other words, a molecule has a center of symmetry when the points x,y,z and $-x,-y,-z$ correspond to identical objects. For example, if there is an oxygen atom in some point x,y,z , then there is an oxygen atom in the point $-x,-y,-z$. There may or may not be an atom at the inversion center itself. Examples are xenon tetrafluoride where the inversion center is at the Xe atom, and benzene C_6H_6 where the inversion center is at the center of the ring. Also called an n-fold improper rotation axis, it is abbreviated S_n . Examples are present in tetrahedral silicon tetrafluoride, with three S_4 axes, and the staggered conformation of ethane with one S_6 axis. While this element seems physically trivial, it must be included in the list of symmetry elements so that they form a mathematical group, whose definition requires inclusion of the identity element. It is so called because it is analogous to multiplying by one unity. In other words, E is a property that any object needs to have regardless of its symmetry properties. These five axes plus the mirror plane perpendicular to the C_4 axis define the D_{4h} symmetry group of the molecule. The five symmetry elements have associated with them five types of symmetry operation, which leave the molecule in a state indistinguishable from the starting state. They are sometimes distinguished from symmetry elements by a caret or circumflex. A symmetry element can have more than one symmetry operation associated with it. In a symmetry group, the group elements are the symmetry operations not the symmetry elements, and the binary combination consists of applying first one symmetry operation and then the other. By convention the order of operations is from right to left. A symmetry group obeys the defining properties of any group. This means that the group is closed so that combining two elements produces no new elements. Symmetry operations have this property because a sequence of two operations will produce a third state indistinguishable from the second and therefore from the first, so that the net effect on the molecule is still a symmetry operation. There must be an element say e in G such that product any element of G with e make no change to the element. For each element x in G, there must be an element y in G such that product of x and y is the identity element e. For groups of small orders, the group properties can be easily verified by considering its composition table, a table whose rows and columns correspond to elements of the group and whose entries correspond to their products. Point groups and permutation-inversion groups[edit] Chart for determining Point Group The successive application or composition of one or more symmetry operations of a molecule has an effect equivalent to that of some single symmetry operation of the molecule. This group is called the point group of that molecule, because the set of symmetry operations leave at least one point fixed though for some symmetries an entire axis or an entire plane remains fixed. In other words, a point group is a group that summarizes all symmetry operations that all molecules in that category have. One can determine the symmetry operations of the point group for a particular molecule by considering the geometrical symmetry of its molecular model. However, when one USES a point group, the operations in it are not to be interpreted in the same way. They are "symmetry operations" for that vibronic Hamiltonian. The point group is used to classify by symmetry the vibronic eigenstates. The symmetry classification of the rotational levels, the eigenstates of the full rovibronic nuclear spin Hamiltonian, requires the use of the appropriate permutation-inversion group as introduced by Longuet-Higgins [9]. The relation between point groups and permutation-inversion groups is explained in this pdf file Link. Examples of point groups[edit] Assigning each molecule a point group classifies molecules

into categories with similar symmetry properties. The description of structure includes common shapes of molecules, which can be explained by the VSEPR model. Point group Simple description of typical geometry Example 1.

Chapter 2 : Molecular Geometry - Chemistry LibreTexts

The Shape of Molecules. The three dimensional shape or configuration of a molecule is an important characteristic. This shape is dependent on the preferred spatial orientation of covalent bonds to atoms having two or more bonding partners.

Skills to Develop Make sure you thoroughly understand the following essential ideas: Describe the manner in which repulsion between electron-pairs affects the orientation of the regions that contain them. Define coordination geometry, and describe the particular geometry associated with electron-pair repulsion between two, three, four, five, or six identical bonding regions. Explain the distinction between coordination geometry and molecular geometry, and provide an illustration based on the structure of water or ammonia. Draw a diagram of a tetrahedral or octahedral molecule. The Lewis electron-dot structures you have learned to draw have no geometrical significance other than depicting the order in which the various atoms are connected to one another. Nevertheless, a slight extension of the simple shared-electron pair concept is capable of rationalizing and predicting the geometry of the bonds around a given atom in a wide variety of situations. Like all electrons, these occupy regions of space which we can visualize as electron clouds "regions of negative electric charge, also known as orbitals" whose precise character can be left to more detailed theories. The covalent model of chemical bonding assumes that the electron pairs responsible for bonding are concentrated into the region of space between the bonded atoms. The fundamental idea of VSEPR theory is that these regions of negative electric charge will repel each other, causing them and thus the chemical bonds that they form to stay as far apart as possible. We therefore expect the two chemical bonds to extend in opposite directions, producing a linear molecule. The orbitals containing the various bonding and nonbonding pairs in the valence shell will extend out from the central atom in directions that minimize their mutual repulsions. If you write out the electron dot formula for carbon dioxide, you will see that the C-O bonds are double bonds. Tetrahedral coordination Methane, CH₄, contains a carbon atom bonded to four hydrogens. What bond angle would lead to the greatest possible separation between the electron clouds associated with these bonds? The latter calculation would be correct if all the atoms were constrained to be in the same plane we will see cases where this happens later, but here there is no such restriction. The angle between any two bonds will be This is called tetrahedral coordination. This is the most important coordination geometry in Chemistry: It is interesting to note that the tetrahedral coordination of carbon in most of its organic compounds was worked out in the nineteenth century on purely geometrical grounds and chemical evidence, long before direct methods of determining molecular shapes were developed. For example, it was noted that there is only one dichloromethane, CH₂Cl₂. If the coordination around the carbon were square, then there would have to be two isomers of CH₂Cl₂, as shown in the pair of structures here. The distances between the two chlorine atoms would be different, giving rise to differences in physical properties would allow the two isomers to be distinguished and separated. If you study the tetrahedral figure closely, you may be able to convince yourself that it represents the connectivity shown on both of the "square" structures at the top. A three-dimensional ball-and-stick mechanical model would illustrate this very clearly. Tetrahedrally-coordinated carbon chains Carbon atoms are well known for their tendency to link together to form the millions of organic molecules that are known. We can work out the simpler hydrocarbon chains by looking at each central atom separately. Notice that these "straight chain hydrocarbons" as they are often known have a carbon "backbone" structure that is not really straight, as is illustrated by the zig-zag figure that is frequently used to denote hydrocarbon structures. Coordination geometry and molecular geometry Coordination number refers to the number of electron pairs that surround a given atom; we often refer to this atom as the central atom even if this atom is not really located at the geometrical center of the molecule. If all of the electron pairs surrounding the central atom are shared with neighboring atoms, then the coordination geometry is the same as the molecular geometry. The application of VSEPR theory then reduces to the simple problem of naming and visualizing the geometric shapes associated with various numbers of points surrounding a central point the central atom at the greatest possible angles. Both classes of geometry are

named after the shapes of the imaginary geometric figures mostly regular solid polygons that would be centered on the central atom and would have an electron pair at each vertex. If one or more of the electron pairs surrounding the central atom is not shared with a neighboring atom that is, if it is a lone pair, then the molecular geometry is simpler than the coordination geometry, and it can be worked out by inspecting a sketch of the coordination geometry figure. Tetrahedral coordination with lone pairs In the examples we have discussed so far, the shape of the molecule is defined by the coordination geometry; thus the carbon in methane is tetrahedrally coordinated, and there is a hydrogen at each corner of the tetrahedron, so the molecular shape is also tetrahedral. This convention is known as the "AXE Method. The reason is that the nonbonding electrons are also in orbitals that occupy space and repel the other orbitals. This means that in figuring the coordination number around the central atom, we must count both the bonded atoms and the nonbonding pairs. The oxygen atom will therefore be tetrahedrally coordinated, meaning that it sits at the center of the tetrahedron as shown below. Two of the coordination positions are occupied by the shared electron-pairs that constitute the O-H bonds, and the other two by the non-bonding pairs. Thus although the oxygen atom is tetrahedrally coordinated, the bonding geometry shape of the H₂O molecule is described as bent. There is an important difference between bonding and non-bonding electron orbitals. Because a nonbonding orbital has no atomic nucleus at its far end to draw the electron cloud toward it, the charge in such an orbital will be concentrated closer to the central atom. As a consequence, nonbonding orbitals exert more repulsion on other orbitals than do bonding orbitals. Thus in H₂O, the two nonbonding orbitals push the bonding orbitals closer together, making the H-O-H angle This image was produced by a computer simulation based on the more complete molecular orbital model that we describe in the next lesson. This charge unbalance gives rise to many of the so-called anomalous properties of water. This means that there are three bonded atoms and one lone pair, for a coordination number of four around the nitrogen, the same as occurs in H₂O. We can therefore predict that the three hydrogen atom will lie at the corners of a tetrahedron centered on the nitrogen atom. The lone pair orbital will point toward the fourth corner of the tetrahedron, but since that position will be vacant, the NH₃ molecule itself cannot be tetrahedral. Instead, it assumes a pyramidal shape. More precisely, the shape is that of a trigonal pyramid i. In what directions can five electron pairs arrange themselves in space so as to minimize their mutual repulsions? In the cases of coordination numbers 2, 3, 4, and 6, we could imagine that the electron pairs distributed themselves as far apart as possible on the surface of a sphere; for the two higher numbers, the resulting shapes correspond to the regular polyhedron having the same number of sides. The problem with coordination number 5 is that there is no such thing as a regular polyhedron with five vertices. Besides the five regular solids, there can be 15 semi-regular isogonal solids in which the faces have different shapes, but the vertex angles are all the same. These geometrical principles are quite important in modern structural chemistry. This consists simply of two triangular-base pyramids joined base-to-base. Equatorial and axial atoms have different geometrical relationships to their neighbors, and thus differ slightly in their chemical behavior. Octahedral coordination Just as four electron pairs experience the minimum repulsion when they are directed toward the corners of a tetrahedron, six electron pairs will try to point toward the corners of an octahedron. An octahedron is not as complex a shape as its name might imply; it is simply two square-based pyramids joined base to base. You should be able to sketch this shape as well as that of the tetrahedron. It turns out, however, that this is one of the most commonly encountered coordination numbers in inorganic chemistry. There are two main reasons for this: Many transition metal ions form coordinate covalent bonds with lone-pair electron donor atoms such as N in NH₃ and O in H₂O. Since transition elements can have an outer configuration of d¹⁰s², up to six electron pairs can be accommodated around the central atom. Although the central atom of most molecules is bonded to fewer than six other atoms, there is often a sufficient number of lone pair electrons to bring the total number of electron pairs to six. Octahedral coordination with lone pairs There are well known examples of 6-coordinate central atoms with 1, 2, and 3 lone pairs. Thus all three of the molecules whose shapes are depicted below possess octahedral coordination around the central atom. Note also that the orientation of the shaded planes shown in the two rightmost images are arbitrary; since all six vertices of an octahedron are identical, the planes could just as well be drawn in any of the three possible vertical orientations. Its

application to predicting molecular structures can be summarized as follows: Electron pairs surrounding a central atom repel each other; this repulsion will be minimized if the orbitals containing these electron pairs point as far away from each other as possible. The coordination geometry around the central atom corresponds to the polyhedron whose number of vertices is equal to the number of surrounding electron pairs coordination number. Except for the special case of 5, and the trivial cases of 2 and 3, the shape will be one of the regular polyhedra. If some of the electron pairs are nonbonding, the shape of the molecule will be simpler than that of the coordination polyhedron. Orbitals that contain nonbonding electrons are more concentrated near the central atom, and therefore offer more repulsion than bonding pairs to other orbitals. While VSEPR theory is quite good at predicting the general shapes of most molecules, it cannot yield exact details. For example, it does not explain why the bond angle in H₂O is This is not surprising, considering that the emphasis is on electronic repulsions, without regard to the detailed nature of the orbitals containing the electrons, and thus of the bonds themselves. Although it post-dates the more complete quantum mechanical models, it is easy to grasp and within a decade had become a staple of every first-year college chemistry course.

Chapter 3 : Symmetry in chemical bonding and structure (Book,) [racedaydvl.com]

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Using the valence bond approximation this can be understood by the type of bonds between the atoms that make up the molecule. When atoms interact to form a chemical bond, the atomic orbitals of each atom are said to combine in a process called orbital hybridisation. The two most common types of bonds are sigma bonds usually formed by hybrid orbitals and pi bonds formed by unhybridized p orbitals for atoms of main group elements. The geometry can also be understood by molecular orbital theory where the electrons are delocalised. An understanding of the wavelike behavior of electrons in atoms and molecules is the subject of quantum chemistry.

Isomers[edit] Isomers are types of molecules that share a chemical formula but have different geometries, resulting in different properties: A pure substance is composed of only one type of isomer of a molecule all have the same geometrical structure. Structural isomers have the same chemical formula but different physical arrangements, often forming alternate molecular geometries with very different properties. The atoms are not bonded connected together in the same orders. Functional isomers are special kinds of structural isomers, where certain groups of atoms exhibit a special kind of behavior, such as an ether or an alcohol. Stereoisomers may have many similar physicochemical properties melting point, boiling point and at the same time very different biochemical activities. This is because they exhibit a handedness that is commonly found in living systems. One manifestation of this chirality or handedness is that they have the ability to rotate polarized light in different directions. Protein folding concerns the complex geometries and different isomers that proteins can take.

Types of molecular structure[edit] A bond angle is the geometric angle between two adjacent bonds. Some common shapes of simple molecules include: In a linear model, atoms are connected in a straight line. For example, carbon dioxide and nitric oxide have a linear molecular shape. Molecules with the trigonal planar shape are somewhat triangular and in one plane flat. For example, boron trifluoride. Angular molecules also called bent or V-shaped have a non-linear shape. A water molecule has two pairs of bonded electrons and two unshared lone pairs. Tetra- signifies four, and -hedral relates to a face of a solid, so " tetrahedral " literally means "having four faces". This shape is found when there are four bonds all on one central atom, with no extra unshared electron pairs. For example, methane CH₄ is a tetrahedral molecule. Octa- signifies eight, and -hedral relates to a face of a solid, so " octahedral " means "having eight faces". The bond angle is 90 degrees. For example, sulfur hexafluoride SF₆ is an octahedral molecule. A trigonal pyramidal molecule has a pyramid-like shape with a triangular base. Unlike the linear and trigonal planar shapes but similar to the tetrahedral orientation, pyramidal shapes require three dimensions in order to fully separate the electrons. Here, there are only three pairs of bonded electrons, leaving one unshared lone pair. Lone pair -> bond pair repulsions change the bond angle from the tetrahedral angle to a slightly lower value. For many cases, such as trigonal pyramidal and bent, the actual angle for the example differs from the ideal angle, and examples differ by different amounts.

Chapter 7 Chemical Bonding and Molecular Geometry Figure Nicknamed "buckyballs," buckminsterfullerene molecules (C60) contain only carbon racedaydvl.com they are shown in a ball-and-stick model (left).

Save Lewis Structure of HO indicating bond angle and bond length Water HO is a simple triatomic bent molecule with C_{2v} molecular symmetry and bond angle of 104.5° . Despite being one of the simplest triatomic molecules, its chemical bonding scheme is nonetheless complex as many of its bonding properties such as bond angle, ionization energy, and electronic state energy cannot be explained by one unified bonding model. Valence bond theory suggests that HO is sp^3 hybridized in which the $2s$ atomic orbital and the three $2p$ orbitals of oxygen are hybridized to form four new hybridized orbitals which then participate in bonding by overlapping with the hydrogen $1s$ orbitals. As such, the predicted shape and bond angle of sp^3 hybridization is tetrahedral and this is in open agreement with the true bond angle of 104.5° . The difference between the predicted bond angle and the measured bond angle is traditionally explained by the electron repulsion of the two lone pairs occupying two sp^3 hybridized orbitals. While valence bond theory is suitable for predicting the geometry and bond angle of HO, its prediction of electronic states does not agree with the experimentally measured reality. In the valence bond model, the two sigma bonds are of identical energy and so are the two lone pairs since they both reside in the same bonding and nonbonding orbitals, thus corresponding to two energy levels in the photoelectron spectrum. In other words, if water was formed from two identical O-H bonds and two identical sp^3 lone pairs on the oxygen atom as predicted by valence bond theory, then its photoelectron spectrum PES would have two degenerate peaks and energy, one for the two O-H bonds and the other for the two sp^3 lone pairs. However, the photoelectron spectrum of HO reveals four different energy levels that correspond to the ionization energies of the two bonding and two nonbonding pairs of electrons at Molecular orbital treatment of HO Simple Molecular Orbital MO diagram of HO Simple MO of HO In contrast to localizing electrons within their atomic orbitals in valence bond theory, the molecular orbital approach considers electrons to be delocalized across the entire molecule. The simple MO diagram of HO is shown on the right. Orbitals of same symmetry and similar energy levels can then be mixed to form a new set of molecular orbitals with bonding, nonbonding, and antibonding characteristics. In the simple MO diagram of HO, the $2s$ orbital of oxygen is mixed with the premixed hydrogen orbitals, forming a new bonding $2a_1$ and antibonding orbital $4a_1$. Similarly, the $2p$ orbital b_1 and the other premixed hydrogen $1s$ orbitals b_1 are mixed to make bonding orbital $1b_1$ and antibonding orbital $2b_1$. The two remaining $2p$ orbitals are unmixed. While this simple MO diagram does not provide four different energy levels as experimentally determined from PES, the two bonding orbitals are nonetheless distinctly different thus providing differentiation on the bonding electron energy levels. Hybridized Molecular Orbital MO diagram of HO To further distinguish the electron energy differences between the two non-bonding orbitals, orbital mixing can be further performed between the $2p$ $3a_1$ orbital on oxygen and the antibonding $4a_1$ orbital since they are of the same symmetry and close in energy level. Mixing these two orbitals affords two new sets of orbitals as shown in the right boxed in red. Significant mixing of these two orbitals results in both energy changes and changes in the shape of the molecular orbital. Consequently, the two nonbonding orbitals are now at different energies,[5] providing the four distinct energy levels consistent with the PES. Alternatively, instead of mixing the $3a_1$ nonbonding orbital with the $4a_1$ antibonding orbital, one can also mix the $3a_1$ nonbonding orbital with the $2a_1$ bonding orbital to produce a similar MO diagram of HO. This alternative HO MO diagram can also be derived by performing the Walsh diagram treatment via adjusting bonding geometry from linear to bent shape. In addition, these MO diagrams can be generated from bottom up by first hybridizing the oxygen $2s$ and $2p$ orbitals assume sp^2 hybridization and then mixing orbitals of same symmetry. For simple molecules, pictorially generating their MO diagram can be achieved without extensive knowledge of point group theory and using reducible and irreducible representations. Hybridized MO of HO Note that the size of the atomic orbitals in the final molecular orbital are different from the size of the original atomic orbitals, this is due to different mixing proportions between the oxygen and hydrogen orbitals since their initial atomic orbital energies are different.

In other words, when two orbitals mix, the amount the orbitals mix is inversely proportional to the initial difference in energy of the orbitals. Therefore, orbitals which are initially close in energy mix i. When two orbitals of different energy mix i. When two orbitals can interact and they are of the same initial energy, then the two resultant combination orbitals are derived equally from the two initial orbitals. Second order perturbation theory. In short, s character is accumulated in lone pair orbitals because s character is energy lowering relative to p character, and lone pair electrons are closely held with unshared electron density. In contrast, bonding pairs are localized further away and electron density is shared with another atom, so additional s character does not lower energy quite as effectively. Hence, comparatively more p character is distributed into the bonding orbitals. For molecules with lone pairs, the bonding orbitals are isovalent hybrids since different fractions of s and p orbitals are mixed to achieve optimal bonding. For molecules containing lone pairs, the true hybridization of these molecules depends on the amount of s and p characters of the central atom which is related to its electronegativity. By the above discussion, this will decrease the bond angle. This increased p character in those orbitals decreases the bond angle between them to less than the tetrahedral. Despite continued heated debate on which model more accurately depict the true bonding scheme of molecules, scientists now view MO and VB theories as complimentary and teammates. With the development of modern high speed computers and advanced molecular modeling programs, both MO and VB theories are used widely today, though for generally different purposes. In general, MO theory can accurately predict the ground state energy of the system, the different electronic states energies of bonding and nonbonding orbitals, and magnetic and ionization properties in a straight forward manner. On the other hand, VB theory is traditionally useful for predicting bond angle and mechanism drawing. Modern valence bond theory can provide the same electronic information obtained by MO theory, though the process is more complicated. In addition, modern VB theory can also predict excited states energies in which MO theory cannot easily achieve. The truth is, both theories are equally important in understanding chemical bonding that while neither theory is completely comprehensive, the two together nonetheless provides a in-depth model for chemical bonds. In the words of Roald Hoffmann: Insistence on a journey Discarding any one of the two theories undermines the intellectual heritage of chemistry. When treating electrons in localized orbitals VB theory , one can fairly accurately predict and measure its shape, geometry and position, but cannot accurate predict its energy and momentum. When treating electrons in delocalized orbitals MO theory , one gains more measurements on its energy and momentum, but loses accuracy on its position. In other words, MO and VB theory should be used appropriately depending on what one wishes to measure.

Chapter 5 : Molecular symmetry - Wikipedia

CHAPTER CHEMICAL BONDING II (c) The Lewis structure of SiH_4 is shown below. Like part (b), it is a tetrahedral AB_4 molecule. (d) The Lewis structure of TeCl_4 is shown below.

Molecular shapes and VSEPR theory There is a sharp distinction between ionic and covalent bonds when the geometric arrangements of atoms in compounds are considered. In essence, ionic bonding is nondirectional, whereas covalent bonding is directional. That is, in ionic compounds there is no intrinsically preferred direction in which a neighbour should lie for the strength of bonding to be maximized. In contrast, in a covalently bonded compound, the atoms adopt specific locations relative to one another, as in the tetrahedral arrangement of hydrogen atoms around the central carbon atom in methane, CH_4 , or the angular arrangement of atoms in H_2O . The lack of directionality of ionic bonds stems from the isotropy spherical symmetry of the electrostatic forces between ions. As has already been pointed out, the result of this isotropy is that ions stack together in the locations necessary to achieve the lowest energy and in this way give rise to the common packing patterns characteristic of many ionic solids. When deviations from stacking schemes are observed that seem to indicate that the ions are being held in certain orientations relative to their neighbours, it is a sign that covalent bonding is beginning to influence the structure of the solid and that the bonding is not purely ionic. This is the case, for example, in the compound nickel arsenide NiAs , which has a structure that suggests that a degree of covalent bonding is present Figure 6. It is fully apparent in the structure of diamond Figure 7, in which each carbon atom is in a tetrahedral position relative to its neighbour and in which the bonding is essentially purely covalent. The crystal structure of nickel arsenide. This type of structure departs strongly from that expected for ionic bonding and shows the importance of covalence. There is also some direct nickel-nickel bonding that tends to draw the nickel atoms together. The crystal structure of diamond. Each carbon atom is bonded covalently to four neighbours arranged tetrahedrally around the central atom. The structure is highly rigid. The rationalization of the structures adopted by purely ionic solids is essentially a straightforward exercise in the analysis of electrostatic interactions between ions. The problem of the structures of covalent compounds, both individual molecules, such as methane, and covalently bonded solids, such as diamond, is much more subtle, for it involves delving into the characteristics of the electron arrangements in individual atoms. Thus, if the formation of a covalent bond is regarded as corresponding to the accumulation of electrons in a particular region of an atom, then, to form a second bond, electrons can be accumulated into only certain parts of the atom relative to that first region of enhanced electron density. As a result, the bonds will lie in a geometric array that is characteristic of the atom. The remainder of this section focuses on this problem, but a detailed quantum mechanical analysis is required for a full understanding of the matter. It stems from the work of the British chemists H. Powell and Nevil V. Sidgwick in the s and was extensively developed by R. Gillespie in Canada and Ronald S. Nyholm in London during the s. As such, it postdates quantum mechanical theories of bonding and shape but should be seen as is so common a motivation in chemistry as an attempt to identify the essential features of a problem and to formulate them into a simple qualitative procedure for rationalization and prediction. A Lewis structure, as shown above, is a topological portrayal of bonding in a molecule. It ascribes bonding influences to electron pairs that lie between atoms and acknowledges the existence of lone pairs of electrons that do not participate directly in the bonding. The VSEPR theory supposes that all electron pairs, both bonding pairs and lone pairs, repel each other particularly if they are close and that the molecular shape is such as to minimize these repulsions. The approach is commonly applied to species in which there is an identifiable central atom the oxygen atom in H_2O , for instance, but it is straightforward to extend it to discussions of the local shape at any given atom in a polyatomic species. The Lewis structure of this molecule ascribes four bonding electron pairs to the carbon atom Figure 8. These pairs repel one another, and their separation is maximized if they adopt a tetrahedral disposition around the central carbon atom. A hydrogen atom is attached by each bonding pair, so it can be predicted that CH_4 is likely to be a tetrahedral species, which is in fact the case. The structure of methane, CH_4 . This regular tetrahedral structure is explained in the VSEPR theory of molecular shape by supposing

that the four pairs of bonding electrons represented by the gray clouds adopt positions that minimize their mutual repulsion. When applying VSEPR theory, attention is first focused on the electron pairs of the central atom, disregarding the distinction between bonding pairs and lone pairs. These pairs are then allowed to move around the central atom at a constant distance and to take up positions that maximize their mutual separations. As in the methane molecule, four pairs adopt a tetrahedral disposition. The arrangements adopted by two through six pairs are summarized in the table. At this stage, the atoms that are attached by the bonding pairs are introduced, and the shape of the molecule is reported on the basis of the arrangement of these atoms. The water molecule, H₂O, provides a simple example. The oxygen atom has four electron pairs, so these pairs adopt a tetrahedral arrangement. Two of the pairs are bonding, and hydrogen atoms are attached to them. Hence, the molecule is angular. Note that the shape of the molecule is determined by the disposition of the atoms, not the disposition of the electron pairs. The ammonia molecule, NH₃, has four electron pairs in a tetrahedral arrangement around the nitrogen atom; three of these pairs are used to bond hydrogen atoms, so the molecule is predicted to be trigonal pyramidal, with a lone pair in the apical position. Some of the names of the shapes of simple molecules are summarized in the table. The angle between electron pairs in a tetrahedral arrangement is 109.5° . In a sense, such close agreement is quite satisfactory for so simple an approach, but clearly there is more to explain. To account for variations in bond angle, it is supposed that electron pair repulsions are greatest between lone pairs, less between lone pairs and bonding pairs, and least between bonding pairs. The justification of this ordering has proved somewhat elusive; qualitatively it is presumed that lone pairs, being attached only to a single centre, spread over a greater volume than bonding pairs, which are pinned between two attracting centres. Whatever the reason may be, the order correlates quite well with observation. Thus, in H₂O the two lone pairs move apart a little, and the two bonding pairs move away from them by closing the angle between one another. Likewise, in NH₃ the three bonding pairs move back from the single lone pair to minimize their interaction with it. In each case, the predicted angle is less than the tetrahedral angle, as is observed experimentally. VSEPR theory is quite successful at predicting or at least rationalizing the overall shapes of molecules. Thus, the hypervalent species SF₆ sulfur hexafluoride, with six bonding pairs, is predicted and found to be a regular octahedron, and PCl₅ phosphorus pentachloride, with five bonding pairs, is predicted and found to be a trigonal bipyramid. The XeF₄ xenon tetrafluoride molecule is hypervalent with six electron pairs around the central xenon Xe atom. These pairs adopt an octahedral arrangement. Four of the pairs are bonding pairs, and two are lone pairs. According to VSEPR theory, the repulsion between the lone pairs is minimized if they lie on opposite sides of the xenon atom, leaving the four equatorial pairs as bonding pairs. This analysis suggests that XeF₄ should be a planar species, which is found to be the case. Molecules with multiple bonds There are further rules in VSEPR theory that simplify the discussion of species with multiple bonds and of species in which resonance must be considered. This rule can be justified by considering the geometric shapes that stem from two atoms sharing two or more pairs of electrons Figure 9. The geometric arrangement of atoms linked by two shared pairs of electrons in a double bond top can be simulated by treating the double bond as the result of the sharing of a single superpair of electrons bottom. All four pairs are bonding, so the ion is predicted to be a regular tetrahedron, which it indeed is. The same conclusion about the shape of the molecule would be drawn from another possible Lewis structure, in which each bond is single: The actual molecule is a resonance hybrid of these and related structures; but, as each one corresponds to the same geometry, no particular Lewis structure need be selected before one can make a prediction based on VSEPR theory. In other words, resonance does not affect the shapes of molecules.

Chapter 6 : Lewis Structures, Molecular Geometry, Bond Angle, and more. | Chemical Bonding

molecular geometry and chemical bonding theory Bonding to these orbitals is directional; that is, the bonding is in preferred directions. This explains why the bonding gives a particular molecular geometry.

The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

Answer Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. Lone Pairs on the Central Atom Predict the electron-pair geometry and molecular structure of a water molecule. Solution The Lewis structure of H₂O indicates that there are four regions of high electron density around the oxygen atom: Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than In fact, the bond angle is Predict the electron-pair geometry and molecular structure of this cation. Answer electron pair geometry: SF₄, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides i. Predict the electron-pair geometry and molecular structure of a SF₄ molecule. Solution The Lewis structure of SF₄ indicates five regions of electron density around the sulfur atom: We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. Answer The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear. XeF₄ Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF₄ molecule. Solution The Lewis structure of XeF₄ indicates six regions of high electron density around the xenon atom: The five atoms are all in the same plane and have a square planar molecular structure. What will the electron pair geometry and molecular structure be? The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached: Solution Consider each central atom independently. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached: Build the molecule HCN in the simulator based on the following Lewis structure: Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this? Solution The molecular structure is linear. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn. Answer Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. XeOF₄ is a molecule that adopts this structure. This separation of charge gives rise to a bond dipole moment. Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms. A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule or dipole ; otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure. For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br₂ and N₂ have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity. When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel vector sum equals zero , then the molecule is nonpolar. Each of the bonds is polar, but the molecule as a whole is nonpolar. The bond moments cancel because they are pointed in opposite directions. In this case, however, the molecular structure is bent

because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule dipole. The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. The OCS molecule has a structure similar to CO₂, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule: The C—O bond is considerably polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end. Chloromethane, CH₃Cl, is another example of a polar molecule. Although the polar C—Cl and C—H bonds are arranged in a tetrahedral geometry, the C—Cl bonds have a larger bond moment than the C—H bond, and the bond moments do not completely cancel each other. All of the dipoles have a upward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine: When we examine the highly symmetrical molecules BF₃ trigonal planar, CH₄ tetrahedral, PF₅ trigonal bipyramidal, and SF₆ octahedral, in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H₂S and NH₃. A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules: To summarize, to be polar, a molecule must: Contain at least one polar covalent bond. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel. We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if: A and C are very electronegative and B is in the middle of the range. A is very electronegative, and B and C are not. Solution Molecular dipole moment points immediately between A and C. Molecular dipole moment points along the A—B bond, toward A. Answer The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will. Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules those with an appreciable dipole moment interact with electric fields, whereas nonpolar molecules do not. Austin State University with contributing authors. Download for free at <http://>

Chapter 7 : Molecular Structure and Polarity - Chemistry LibreTexts

The ability to quantify the symmetry content of a given molecular system is important both for the quantitative prediction of its physical and chemical properties, as well as for the establishment of powerful theoretical concepts that can be derived solely from symmetry considerations.

The Lewis structure of H₂O describes the bonds as two sigma bonds between the central oxygen atom and the two peripheral hydrogen atoms with oxygen having two lone pairs of electrons. Valence bond theory suggests that H₂O is sp³ hybridized in which the 2s atomic orbital and the three 2p orbitals of oxygen are hybridized to form four new hybridized orbitals which then participate in bonding by overlapping with the hydrogen 1s orbitals. As such, the predicted shape and bond angle of sp³ hybridization is tetrahedral and This is in open agreement with the true bond angle of The difference between the predicted bond angle and the measured bond angle is traditionally explained by the electron repulsion of the two lone pairs occupying two sp³ hybridized orbitals. While valence bond theory is suitable for predicting the geometry and bond angle of H₂O, its prediction of electronic states does not agree with the experimentally measured reality. In the valence bond model, the two sigma bonds are of identical energy and so are the two lone pairs since they both resides in the same bonding and nonbonding orbitals, thus corresponding to two energy levels in the photoelectronic spectrum. In other words, if water was formed from two identical O-H bonds and two identical sp³ lone pairs on the oxygen atom as predicted by valence bond theory, then its photoelectron spectrum PES would have two degenerate peaks and energy, one for the two O-H bonds and the other for the two sp³ lone pairs. However, the photoelectronic spectrum of H₂O reveals four different energy levels that correspond to the ionization energies of the two bonding and two nonbonding pairs of electrons at Molecular orbital treatment of H₂O

Simple Molecular Orbital MO diagram of H₂O Simple MO of H₂O In contrast to localizing electrons within their atomic orbitals in valence bond theory, the molecular orbital approach considers electrons to be delocalized across the entire molecule. The simple MO diagram of H₂O is shown on the right. Orbitals of same symmetry and similar energy levels can then be mixed to form a new set of molecular orbitals with bonding, nonbonding, and antibonding characteristics. In the simple MO diagram of H₂O, the 2s orbital of oxygen is mixed with the premixed hydrogen orbitals, forming a new bonding 2a₁ and antibonding orbital 4a₁. Similarly, the 2p orbital b₁ and the other premixed hydrogen 1s orbitals b₁ are mixed to make bonding orbital 1b₁ and antibonding orbital 2b₁. The two remaining 2p orbitals are unmixed. While this simple MO diagram does not provide four different energy levels as experimentally determined from PES, the two bonding orbitals are nonetheless distinctly different thus providing differentiation on the bonding electron energy levels.

Hybridized Molecular Orbital MO diagram of H₂O To further distinguish the electron energy differences between the two non-bonding orbitals, orbital mixing can be further performed between the 2p 3a₁ orbital on oxygen and the antibonding 4a₁ orbital since they are of the same symmetry and close in energy level. Mixing these two orbitals affords two new sets of orbitals as shown in the right boxed in red. Significant mixing of these two orbitals results in both energy changes and changes in the shape of the molecular orbital. Consequently, the two nonbonding orbitals are now at different energies, [5] providing the four distinct energy levels consistent with the PES. Alternatively, instead of mixing the 3a₁ nonbonding orbital with the 4a₁ antibonding orbital, one can also mix the 3a₁ nonbinding orbital with the 2a₁ bonding orbital to produce a similar MO diagram of H₂O. This alternative H₂O MO diagram can also be derived by performing the Walsh diagram treatment via adjusting bonding geometry from linear to bent shape. In addition, these MO diagrams can be generated from bottom up by first hybridizing the oxygen 2s and 2p orbitals assume sp² hybridization and then mixing orbitals of same symmetry. For simple molecules, pictorially generating their MO diagram can be achieved without extensive knowledge of point group theory and using reducible and irreducible representations.

Hybridized MO of H₂O Note that the size of the atomic orbitals in the final molecular orbital are different from the size of the original atomic orbitals, this is due to different mixing proportions between the oxygen and hydrogen orbitals since their initial atomic orbital energies are different. In other words, when two orbitals mix, the amount the orbitals mix is inversely proportional to the initial

difference in energy of the orbitals. Therefore, orbitals which are initially close in energy mix. When two orbitals of different energy mix. When two orbitals can interact and they are of the same initial energy, then the two resultant combination orbitals are derived equally from the two initial orbitals. Second order perturbation theory. In short, s character is accumulated in lone pair orbitals because s character is energy lowering relative to p character, and lone pair electrons are closely held with unshared electron density. In contrast, bonding pairs are localized further away and electron density is shared with another atom, so additional s character does not lower energy quite as effectively. Hence, comparatively more p character is distributed into the bonding orbitals. For molecules with lone pairs, the bonding orbitals are isovalent hybrids since different fractions of s and p orbitals are mixed to achieve optimal bonding. For molecules containing lone pairs, the true hybridization of these molecules depends on the amount of s and p characters of the central atom which is related to its electronegativity. By the above discussion, this will decrease the bond angle. This increased p character in those orbitals decreases the bond angle between them to less than the tetrahedral. Despite continued heated debate on which model more accurately depict the true bonding scheme of molecules, scientists now view MO and VB theories as complimentary and teammates. With the development of modern high speed computers and advanced molecular modeling programs, both MO and VB theories are used widely today, though for generally different purposes. In general, MO theory can accurately predict the ground state energy of the system, the different electronic states energies of bonding and nonbonding orbitals, and magnetic and ionization properties in a straight forward manner. On the other hand, VB theory is traditionally useful for predicting bond angle and mechanism drawing. Modern valence bond theory can provide the same electronic information obtained by MO theory, though the process is more complicated. In addition, modern VB theory can also predict excited states energies in which MO theory cannot easily achieve. The truth is, both theories are equally important in understanding chemical bonding that while neither theory is completely comprehensive, the two together nonetheless provides a in-depth model for chemical bonds. In the words of Roald Hoffmann: Insistence on a journey Discarding any one of the two theories undermines the intellectual heritage of chemistry. When treating electrons in localized orbitals VB theory, one can fairly accurately predict and measure its shape, geometry and position, but cannot accurately predict its energy and momentum. When treating electrons in delocalized orbitals MO theory, one gains more measurements on its energy and momentum, but loses accuracy on its position. In other words, MO and VB theory should be used appropriately depending on what one wishes to measure.

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Molecular geometry is the three-dimensional arrangement of the atoms that constitute a molecule. It includes the general shape of the molecule as well as bond lengths, bond angles, torsional angles and any other geometrical parameters that determine the position of each atom.

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Define coordination geometry, and describe the particular geometry associated with electron-pair repulsion between two, three, four, five, or six identical bonding regions. Explain the distinction between coordination geometry and molecular geometry, and provide an illustration based on the structure of water or ammonia.