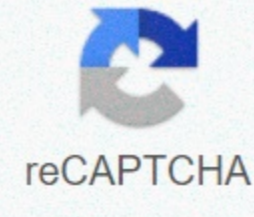




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Hybridization of central atom

Learning goals Explain the concept of atomic orbital hybridity determine the hybrid pathways associated with different molecular geometries thinking in terms of overlapping atomic pathways is one way for us to explain how chemical connections form in diatomic molecules. However, to understand how molecules with more than two atoms form stable connections, we require a more detailed model. As an example, let's consider the water molecule, where we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of two 2p orbitals). The Valence bond theory would have predicted that the two O-H bonds form from the overlap of these two 2p orbitals with 1s orbitals of hydrogen atoms. If this were the case, the angle of the bond would be 90° , as shown in the letter (a), because the p-orbitals are perpendicular to each other. Experimental evidence shows that the angle of the bond is 104.5° , not 90° . The prediction of a valence bond theory model does not match the real-world observations of a water molecule; Another model is needed. (b) The hypothetical overlap of two 2p orbitals on an oxygen atom (red) with 1s orbitals of two hydrogen atoms (blue) will produce a 90° contact angle. This is inconsistent with experimental evidence. 1 Quantum-mechanical calculations indicate that the contact angles observed in H₂O differ from those predicted by the 1s orbital of the hydrogen atoms with the oxygen atom's 2p orbitals. The mathematical expression known as the wave function, ψ , contains information about each orbital and the wave-like properties of electrons in an isolated atom. When atoms are related to a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining wave functions into atomic orbitals is called hybrid and mathematical concept by the linear combination of atomic orbitals, LCAO, (a technique you will encounter again later). The resulting new orbitals are called hybrid orbitals. The Valence orbitals in an isolated oxygen atom are 2s and three 2p orbitals. They consist of four parallel hybrid orbitals that point roughly towards the corners of a tetrahedron (Figure (c)). As a result, the overlap of the O and H orbitals should cause a tetrahedral contact angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence's hybridization theory must include a hybrid component to give accurate predictions. (d) A water molecule has four areas of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (e) Two of the hybrid pathways on oxygen contain individual pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O-H bonds in H₂O. This description is consistent with the experimental structure. The following ideas are important for understanding hybridization: hybrid pathways do not exist in isolated atoms. They're only made in atoms that are bonded. Hybrid orbitals have very different shapes and directions than those of the atomic orbitals in isolated atoms. A group of hybrid orbitals is formed by combining atomic orbitals. The number of hybrid orbitals in the set equals the number of atomic orbitals incorporated to produce the set. All orbitals in a set of hybrid orbitals are equal in shape and energy. The type of hybrid orbitals created in a central atom depends on the geometry of the electron pairs as predicted by the VSEPR theory. Hybrid orbitals overlap to create a bond. Not all orbitals overlap to make contact. In the following sections, we will discuss the common types of hybrid orbitals. A beryllium atom in the BeCl₂ gaseous molecule is an example of a central atom without individual pairs of electrons in a linear arrangement of three atoms. There are two areas of electron density and value in the BeCl₂ molecule that correspond to the two covalent Be-Cl bonds. To accommodate these two electron regions, two of the atom's four valence orbitals will mix to yield two hybrid orbitals. This hybrid process involves mixing the valence orbitals with one of the p valence orbitals to yield two parallel hybrid sp orbitals that are guided in linear geometry (Figure (f)). In this figure, the set of sp orbitals looks similar in shape to the original p-orbital, but there is an important difference. The number of combined atomic orbitals is always equal to the number of hybrid orbitals created. A p-orbital is one orbital that can contain up to two electrons. The sp set is two parallel orbitals that are 180° from each other. The two electrons that were originally in the p-orbital are now distributed to the two sp orbitals, which are half full. In the gas BeCl₂, these half-full hybrid orbitals will fit into orbitals from the chlorine atoms to form two bonds. (g) A hybrid of the s (blue) and p (red) orbitals of the same atom produces two hybrid sp orbitals (yellow). Each hybrid orbital is guided primarily in one direction only. Note that each sp orbital contains one electron, which is consistent with the geometry for two bonds. We illustrate the electronic differences in an isolated Be atom and a Be atom that is connected by an energy-level diagram in orbit with the letter (h). These diagrams represent each path by a horizontal line (indicating its energy) and each electron using an arrow. The energy rises towards the top of the diagram. We use one upward arrow to indicate one electron in orbit and two arrows (up and down) to indicate two electrons of opposite spin. (i) The orbital energy-level diagram shows the hybrid sp orbitals on Be in a BeCl₂ linear molecule. Each of the two hybrid sp orbitals holds one electron and is therefore half fully available for bonding through overlap with the 3p orbitals. When the atomic orbitals from beryllium and chlorine overlap, the resulting hybrid orbitals overlap to form two Be-Cl bonds. Each central atom is surrounded by only two areas of electron density and value in the molecule will demonstrate a hybrid sp. Other examples include the mercury atom in the linear molecule HgCl₂, the zinc atom in Zn(CH₃)₂, which contains a linear C-Zn-C arrangement, and the carbon atoms in H₂C=CH₂ and CO₂. The Valence orbitals of a central atom surrounded by three areas of electron density consist of a set of three hybrid sp² orbitals and one unhybridized p-orbital. This arrangement stems from sp² hybridization, mixing of one orbital and two p-orbitals to produce three hybrid orbitals that are the same in the direction of trigonal planar geometry (Figure (j)). (k) A hybrid of a track (blue) and two p (red) orbitals produces three parallel (yellow) hybrid sp² orbitals in a 120° direction relative to each other. The remaining non-hybrid p-orbital is not shown here, but is located along the z-axis. Although quantum mechanics yields the spindly plump lobes as described in figure (l), sometimes for clarity these orbitals are shown as thin rods, such as figure (m), to avoid obscuring other features of a given illustration. We will use these thin representations whenever the real landscape is too dense to easily imagine. (n) This alternative way of drawing the trigonal planar sp² hybrid orbitals is sometimes used in denser characters. The observed structure of the B₃ molecule, BH₃, offers sp² hybrid orbitals for boron in this compound. The molecule is a trigonal planar, and the boron atom is involved in three connections to hydrogen atoms (Figure (o)). BH₃ is an electron deficient molecule with a trigonal planar structure. We can illustrate the comparison of orbitals and distribution of electrons in an isolated boron atom and the atom associated with BH₃ as described in the orbital energy level diagram in Figure (p). Redistribute the three valence electrons of boron atom in three hybrid sp² orbitals, and each boron electron pairs with hydrogen electron when the B-H bond forms. (q) In an isolated B atom, there are three s-orbitals and three 2p-orbitals. The three semi-complete hybrid orbitals each overlap with a hydrogen orbital to form carbon-hydrogen bonds. The structure and overall outlines of the resulting orbitals are shown in Figure (r). The direction of the two CH₃ groups is not fixed relative to each other. Experimental evidence shows that rotation around the C-C bond occurs easily. (s) In the molecule ethane, C₂H₆, each carbon has four sp³ hybrid orbitals. (t) These four orbitals overlap to form seven C-H bonds. A sp³ hybrid orbital can also contain a single pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three pairs of bonding and a single pair of electrons directed to the four corners of the tetrahedron. The nitrogen atom is a hybrid sp³ with one hybrid orbital occupied by the lone pair. The molecular structure of the water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. So we say that the oxygen atom is a hybrid sp³, with two hybrid orbitals occupied by individual couples and two by bonding pairs. Because individual couples take up more space than bonding pairs, structures containing lone pairs have slightly distorted angles of connection than the ideal. The perfect tetrahedron has angles of 109.5° , but the angles observed in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp³ hybridization include CCl₄, PCl₃, and NCl₃. With octahedral arrangement of six hybrid orbitals, we need to use six atomic orbitals (the s-orbital, the three p-orbitals, and two d-orbitals in its valence shell), providing six hybrid sp^{3d²} orbitals. This hybrid is only possible for atoms that have d-orbitals in their valence shells (that is, not those in the first or second period). (u) The three compounds in the image are shown in the sp^{3d} hybrid in the central atom and a trigonal bipyramidal form. SF₄ and ClF₃ have one lone pair of electrons on the central atom, and ClF₃ has two lone pairs giving it the T-shape shown. In the molecule of pentachloride phosphorus, PCl₅, there are five lone pairs of valence electrons around the phosphorus atom are aimed at corners of the trigonal bipyramid. We use track 3s, three 3p orbitals, and one of the 3d orbitals to create the set of five hybrid sp^{3d} orbitals (Figure (v)) involved in the P-Cl bond. Other atoms that display sp^{3d} hybrids include the sulfur atom in SF₄ and the chlorine atoms in ClF₃ and in ClF₄⁺. (The electrons on fluorine atoms are omitted for brightness.) (w) The five areas of electron density around phosphorus in PCl₅ require five hybrid sp^{3d} orbitals. (x) These tracks combine to form a trigonal two-legged structure, with each large lobe of the hybrid orbital pointing to a vertex. As in the past, there are also small lobes pointed in the opposite direction for each track (not shown for brightness). The sulfur atom in the hexafluoride sulfur, SF₆, presents a sp^{3d²} hybrid. A molecule of sulfuric hexafluoride has six bonding pairs of electrons that connect six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To team up with six fluorine atoms, a 3s orbital, three 3p orbitals, and two 3d orbitals form six equivalent sp^{3d²} hybrid orbitals, each aimed at a different corner of the octahedron. Other atoms showing sp^{3d²} hybridization include the phosphorus atom in SF₆, the iodine atom in the interhalogen IF₆⁺, IF₅, ClF₄⁺, and the xenon atom in XeF₄. (y) (A) The sulfur hexafluoride, SF₆, has an octahedral structure that requires sp^{3d²} hybridization. (B) The six sp^{3d²} orbitals form an octahedral structure around sulfur. Again, the small lobes of each track are not shown for clarity. A hybrid of an atom is determined based on the number of electron density areas surrounding it. The geometric renderings typical of the different groups of hybrid orbitals are displayed in the letter (z). These arrangements are the same as those of the geometries of electron pairs that predicted VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how these shapes are formed. To find a hybrid of a central atom, we can use the following guidelines: determine the Lewis structure of the molecule. Determine the number of areas of electron density around an atom using the VSEPR theory, in which individual connections, multiple connections, radicals and individual pairs are each considered as one area. Assign the hybrid orbital value from an illustration (aa) that corresponds to this geometry. (Figure (z)) The shapes of hybrid orbital sets are consistent with the geometries of electron pairs. For example, an atom surrounded by three areas of electron density is a hybrid sp², and the three sp² orbitals are trigonal. It is important to remember that hybridization was invented to rationalize molecular geometries observed experimentally, rather than the other way around. The model works well for molecules containing small central atoms, where the valence electron pairs are close together in space. However, for larger central atoms, the electron pairs of the valence shell are further away from the nucleus, and there is less repulsion. Their compounds present structures that are often inconsistent with the VSEPR theory, and hybrid pathways are not necessary to explain the observed data. For example, we discussed the H-O-H bond angle in H₂O, 104.5° , which is consistent with hybrid sp³ orbitals (109.5°) on the central atom than with 2p (90°) orbitals. Sulfur is in the same group as oxygen, and H₂S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates a much less hybrid on sulfur than oxygen. Further down the group, tellurium is even larger than sulfur and, for H₂Te, the observed bond angle (90°) is consistent with overlap of 5p orbitals, without triggering a hybrid. We operate a hybrid where necessary to explain the observed structures. Example (aa): Assigning ammonium sulfate hybridization is important as fertilizer. What is a hybrid of the sulfur atom in the sulfate ion, SO₄²⁻? Solving the Lewis structure of sulfur shows there are four areas of electron density. (Figure (aa)). Exercise (aa) What is a hybrid of the selenium atom in SeF₄? Answer the selenium atom is sp^{3d} hybrid. Example (ab): Hybrid orbital allocation, NH₂C(O)NH₂, is sometimes used as a nitrogen source in fertilizers. What is a hybrid of any nitrogen atom and carbon urea? Solving Urea's Lewis structure is Figure (aa). This is a hybrid of the nitrogen atoms coming from Urea. The carbon atom is surrounded by three areas of electron density, located in a trigonal planar arrangement. A hybrid in the trigonal geometry of lone electron pairs is sp² (Figure (aa)), which is a hybrid of the urea carbon atom. Exercise (ac) Acetic acid, H₃CC(O)OH, is the molecule that gives vinegar its sour smell and taste. What is a hybrid of the two carbon atoms in acetic acid? Answer H₃C, sp³; C(O)OH, sp² donors and acceptors we can use hybrid pathways, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the density of electrons around covalently bonded atoms. These hybrid pathways form sigma bonds available towards

other molecule atoms or contain individual pairs of electrons. We can determine the type of hybrid around a central atom from the geometry of the areas of Overcrowding on it. Two such areas imply hybrid sp; three, sp2 hybrid; four, sp3 hybrid; five, sp3d hybrid; And six, sp3d2 hybrid. Pi (β) bonds are formed from ungertered atomic orbits (p or d orbitals). Footnotes Note that orbits may sometimes be drawn in an elongated balloon shape rather than in a more realistic and plump way in order to make geometry easier to imagine. A hybrid orbital orbit created by combining atomic orbits on a centralized sealed hybrid model that describes the changes in atomic orbits of an atom when it creates one hybrid sp covalent compound of a group of two orbits with a linear arrangement resulting from a combination of one s and one p.p. orbital orbital sp2 one hybrid orbit of a group of three orbits with a trigonal design arrangement resulting from a combination of one and two p.p3 tracks. tetrahedral resulting from one s combination and three p sp3d tracks one hybrid orbit of a group of five orbits with trigonal bipyramidal arrangement resulting from one combination s, three p, and one d track sp3d2 tracks one hybrid route of a group of six orbits with an octhedral arrangement resulting from one track three people and two contributing to the attributions of donors and crammings,

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