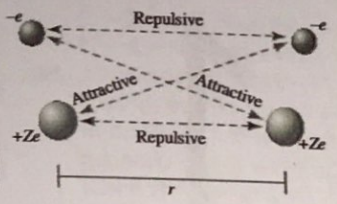


▲ FIGURE 11-1
Type of interactions between two hydrogen atoms
The types of interactions that occur as two hydrogen atoms, infinitely separated, approach each other. The dashed lines represent the types of interactions (red for attractive interactions and blue and black for repulsive interactions). The solid black line represents the internuclear distance, *r*, between the two hydrogen atoms.

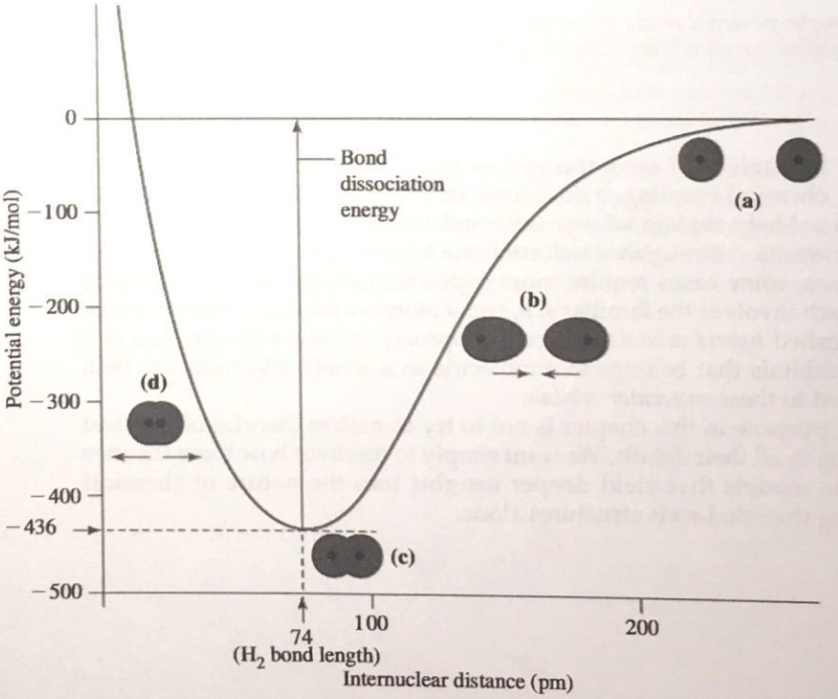
11-1 What a Bonding Theory Should Do

The hydrogen molecule is a simple model for discussing bonding theories. Imagine bringing together two H atoms that are initially very far apart. When the H atoms are infinitely far apart, the two H atoms do not interact with each other, and by convention the net energy of interaction between the H atoms is zero. As the two H atoms approach each other, three types of interactions occur: (1) each electron is attracted to the other nucleus (illustrated by a red dashed line in Fig. 11-1); (2) the electrons repel each other (illustrated by a blue dashed line in Fig. 11-1); and (3) the two nuclei repel each other (illustrated by a black dashed line in Fig. 11-1).

We can plot potential energy—the net energy of interaction of the atoms—as a function of the distance between the atomic nuclei.

Figure 11-2 shows the net energy of interaction of two H atoms. This starts at zero when the atoms are very far apart (condition a). At intermediate distances (condition b), attractive forces predominate and the potential energy is negative. At very small internuclear distances (condition d), repulsive forces exceed attractive forces and the potential energy is positive. At one particular internuclear distance (74 pm, condition c) the potential energy reaches its lowest value (−436 kJ/mol). This is the condition in which the two H atoms combine into a H_2 molecule through a covalent bond. The nuclei continuously move back and forth; that is, the molecule vibrates, but the average internuclear distance remains constant. This internuclear distance corresponds to the *bond length*. The potential energy corresponds to the negative of the *bond-dissociation energy*. A theory of covalent bonding should help us understand why a given molecule has its particular set of observed properties—bond-dissociation energies, bond lengths, bond angles, and so on.

There are several approaches to understanding bonding. The approach used depends on the situation because different methods have different strengths and weaknesses. The strength of the Lewis theory is in the ease with which it can be applied; a Lewis structure can be written rather quickly. VSEPR theory makes it possible to propose molecular shapes that are generally in good agreement with



▶ FIGURE 11-2
Energy of interaction of two hydrogen atoms plotted for internuclear separations from zero to infinity
(a) The potential energy is defined as zero when the two H atoms are infinitely separated. **(b)** Where the curve slopes downward from right to left, the net interaction is attractive. When the interaction is attractive, the potential energy decreases as the internuclear distance, *r*, decreases. **(c)** Where the curve is flat, at the bottom of the potential energy well, there is no tendency either to attract or to repel. The molecule is most stable at this internuclear distance (74 pm). **(d)** Where the curve slopes upward from right to left, the interaction is repulsive. When the interaction is repulsive, the potential energy increases as the internuclear distance, *r*, decreases.

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experimental results. However, neither method yields quantitative information about bond energies and bond lengths, and the Lewis theory has problems with odd-electron species and situations in which it is not possible to represent a molecule through a single structure (resonance).

11-2 Introduction to the Valence-Bond Method

Recall the region of high electron probability in a H atom that we described in Chapter 8 through the mathematical function called a 1*s* orbital (page 328). As the two H atoms pictured in Figure 11-2 approach each other, these regions begin to interpenetrate. We say that the two orbitals overlap. Furthermore, we can say that a bond is produced between the two atoms because of the high electron density probability found in the region between the atomic nuclei where the 1*s* orbitals overlap. The increased electron density, with its negative charge, attracts the two positively charged nuclei. In this way, a covalent bond is formed between the two H atoms in the H_2 molecule.

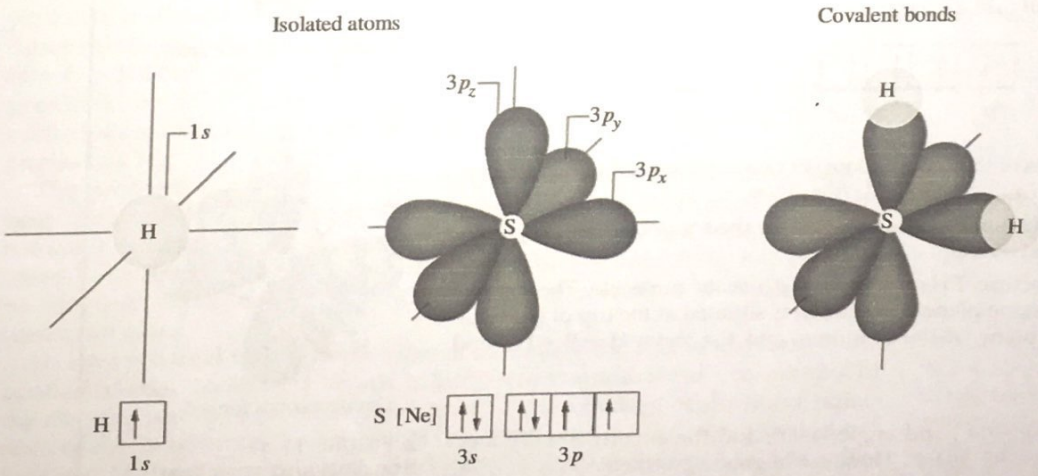
A description of covalent bond formation in terms of atomic orbital overlap is called the **valence-bond method**. The creation of a covalent bond in the valence-bond method is normally based on the overlap of half-filled orbitals, but sometimes such an overlap involves a filled orbital on one atom and an empty orbital on another. The valence-bond method gives a *localized* electron model of bonding: Core electrons and lone-pair valence electrons retain the same orbital locations as in the separated atoms, and the charge density of the bonding electrons is concentrated in the region of orbital overlap.

Figure 11-3 shows the imagined overlap of atomic orbitals in the formation of hydrogen-to-sulfur bonds in hydrogen sulfide. Note especially that maximum overlap between the 1*s* orbital of a H atom and a 3*p* orbital of a S atom occurs along a line joining the centers of the H and S atoms. The two half-filled sulfur

◀ What we are calling "overlap" is actually an interpenetration of two orbitals.

KEEP IN MIND

the actual orbital shapes are pointed out on page 331. The orbitals here, as well as those throughout the rest of the book, are schematic representations.



▲ FIGURE 11-3
Bonding in H_2S represented by atomic orbital overlap
For S, only 3*p* orbitals are shown. The phases of the lobes of the sulfur 3*p* orbitals are shown in red and blue for positive and negative. However, we do not know which lobe is positive or negative; all we know is that they are opposite. Although the angular part of the *p* orbital is circular, when multiplied by the radial part of the wave function, each lobe is more pear shaped, similar to the probability distribution shown in Figure 8-27(c). Bond formation occurs between orbitals that are in phase (same color), although the hydrogen 1*s* orbital is colored yellow for clarity.

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3*p* orbitals that overlap in H_2S are perpendicular to each other, and the valence-bond method suggests a H—S—H bond angle of 90°. This is in good agreement with the observed angle of 92°.

11-1 ARE YOU WOND

Why the overlap of orbitals

The origin of this extra stability comes f
which the two atomic wave functions are
ference of the wave functions between
electron density between the two nuclei.
negative charge, attracts the two positivel
that is lower than that of the two separat
charge density between the nuclei produc
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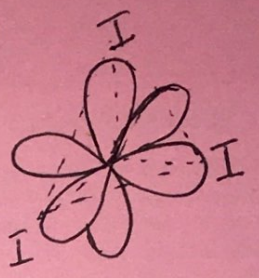
PE A)



~~trigonal~~
trigonal-pyramidal

EXAMPLE 11-1 Using the Valence-Bond Method to Describe a Molecular Structure

Describe the phosphine molecule, PH_3, by the valence-bond method.

Analyze

We use four steps when applying the valence-bond method. First, we identify the valence orbitals of the central atom. Second, we sketch the valence orbitals. Third, we bring in the atoms to be bonded to the central atom and sketch the orbital overlap. Finally, we describe the resulting structure. These steps are illustrated in Figure 11-4.

Solve

Step 1. Draw valence-shell orbital diagrams for the separate atoms.

P [Ne] ⇅ | ↑ | ↑ | ↑ H ↑

3*s* 3*p* 1*s*

Step 2. Sketch the orbitals of the central atom (P) that are involved in the overlap. These are the half-filled 3*p* orbitals (Fig. 11-4).

Step 3. Complete the structure by bringing together the bonded atoms and representing the orbital overlap.

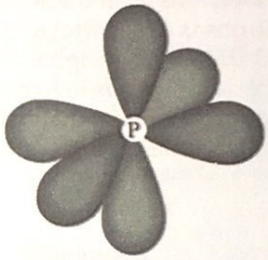
Step 4. Describe the structure. PH_3 is a *trigonal-pyramidal* molecule. The three H atoms lie in the same plane. The P atom is situated at the top of the pyramid above the plane of the H atoms, and the three H—P—H bond angles are 90°.

Assess

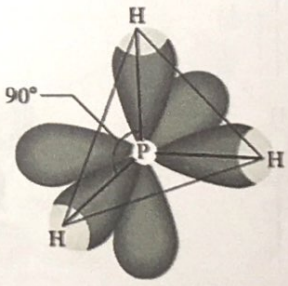
The predicted H—P—H bond angle is 90°, and the experimentally measured bond angles are 93° to 94°. These are in good agreement.

PRACTICE EXAMPLE A: Use the valence-bond method to describe bonding and the expected molecular geometry in nitrogen triiodide, NI_3.

PRACTICE EXAMPLE B: Describe the molecular geometry of NH_3, first using the VSEPR method and then using the valence-bond method described above. How do your answers differ? Which method seems to be more appropriate in this case? Explain.



Bonding orbitals of P atom



Covalent bonds formed

▲ FIGURE 11-4
Bonding and structure of the PH_3 molecule—Example 11-1 illustrated
Only bonding orbitals are shown. The 1s orbitals (yellow) of three H atoms overlap with the three 3*p* orbitals of the P atom.

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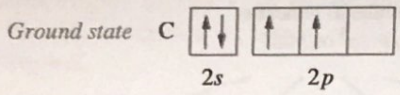
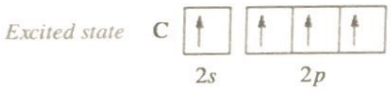
11-3 Hybridization of Atomic Orbitals

If we try to extend the unmodified valence-bond method of Section 11-2 to a greater number of molecules, we are quickly disappointed. In most cases, our descriptions of molecular geometry based on the simple overlap of unmodified atomic orbitals do not conform to observed measurements. For example, based on the *ground-state* electron configuration of the valence shell of carbon

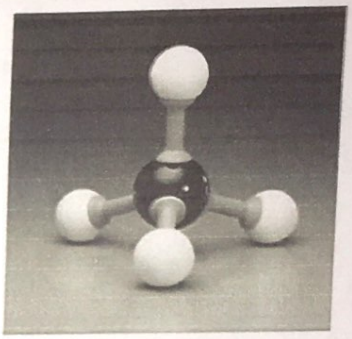


and employing only half-filled orbitals, we expect the existence of a molecule with the formula CH_2 and a bond angle of 90°. The CH_2 molecule is a highly reactive molecule observed only under specially designed circumstances.

The simplest hydrocarbon observed under normal laboratory conditions is methane, CH_4. This is a stable, unreactive molecule with a molecular formula consistent with the octet rule of the Lewis theory. To obtain this molecular formula by the valence-bond method, we need an orbital diagram for carbon in which there are four unpaired electrons so that orbital overlap leads to four C—H bonds. To get such a diagram, imagine that one of the 2*s* electrons in a ground-state C atom absorbs energy and is promoted to the empty 2*p* orbital. The resulting electron configuration is that of an *excited state*.



The electron configuration of this excited state suggests a molecule with three mutually perpendicular C—H bonds based on the 2*p* orbitals of the C atom (90° bond angles). The fourth bond would be directed to whatever position in the molecule could accommodate the fourth H atom. This description, however, does not agree with the experimentally determined H—C—H bond angles, all four of which are found to be 109.5°, the same as predicted by VSEPR theory (Fig. 11-5). A bonding scheme based on the excited-state electron configuration does a poor job of explaining the bond angles in CH_4.



▲ FIGURE 11-5
Ball-and-stick model of methane, CH_4
The molecule has a tetrahedral structure, and the H—C—H bond angles are 109.5°.

The problem is not with the theory but with the way the situation has been defined. We have been describing *bonded* atoms as though they have the same kinds of orbitals (that is, *s*, *p*, and so on) as isolated, *nonbonded* atoms. This assumption worked rather well for H_2S and PH_3, but we have no reason to expect these unmodified pure atomic orbitals to work equally well in all cases.

One way to deal with this problem is to modify the atomic orbitals of the bonded atoms. Recall that atomic orbitals are mathematical expressions of the electron waves in an atom. An algebraic combination of the wave equations of the 2*s* and three 2*p* orbitals of the carbon atom produces a new set of four identical orbitals. These new orbitals, which are directed in a tetrahedral fashion, have energies that are intermediate between those of the 2*s* and 2*p* orbitals. This mathematical process of replacing pure atomic orbitals with reformulated atomic orbitals for bonded atoms is called **hybridization**, and the new orbitals are called **hybrid orbitals**. Figure 11-6 pictures the hybridization of one *s* and three *p* orbitals into a new set of four sp^3 **hybrid orbitals**. Each sp^3 hybrid orbital has 25% *s* character and 75% *p* character.

◀ The algebraic combination of wave functions is, in fact, a linear combination of atomic orbitals; that is, they are simply added or subtracted. The resultant linear combinations are solutions to the Schrödinger equation of the molecule.

In a hybridization scheme, *the number of hybrid orbitals equals the total number of atomic orbitals that are combined.* The symbols identify the numbers and kinds of orbitals involved. Thus, sp^3 signifies that *one* *s* and *three* *p* orbitals are

◀ **Hybridization** occurs only when the bonds are being formed.

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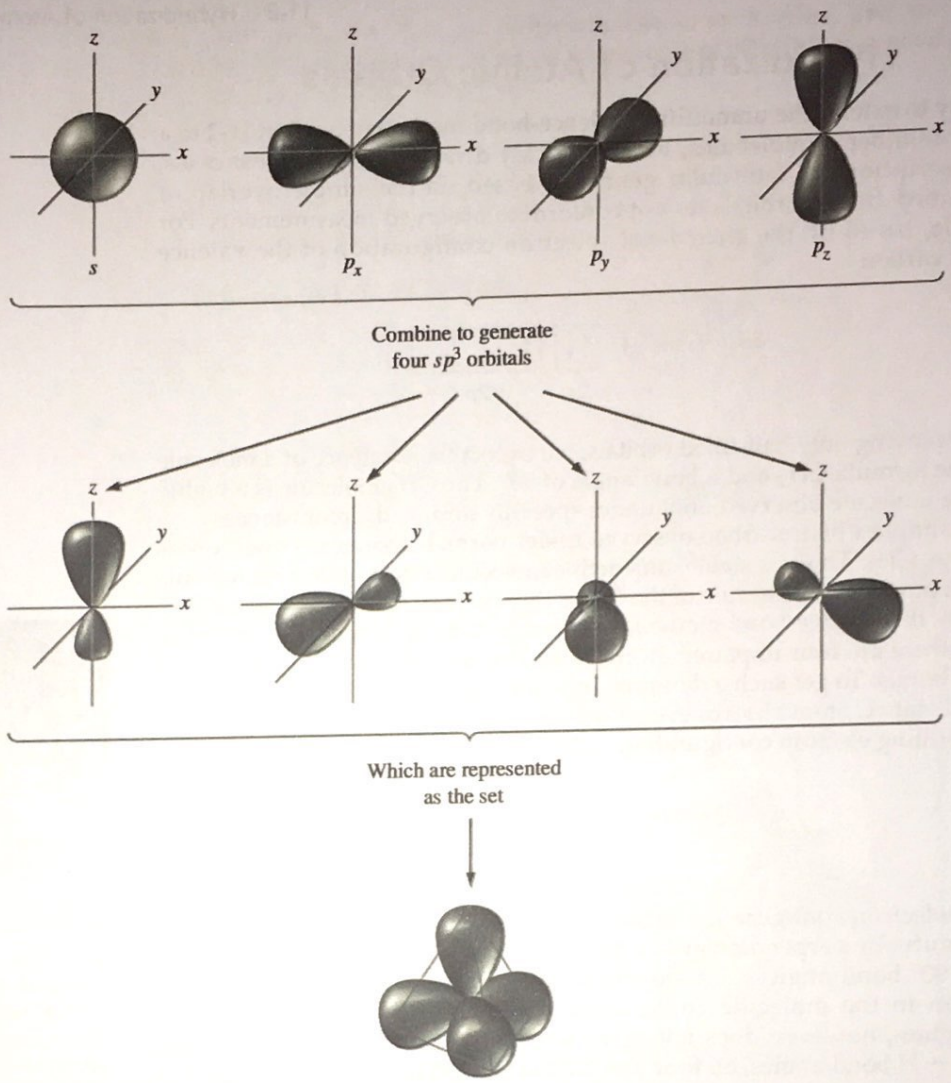
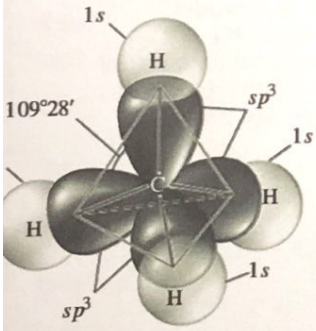
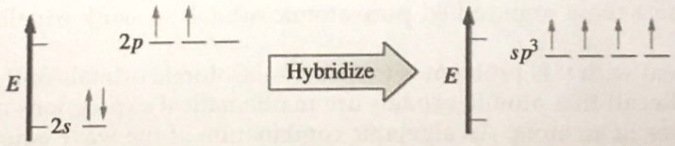


▲ FIGURE 11-6
The sp^3 hybridization scheme



▲ FIGURE 11-7
Bonding and structure of CH_4
The four carbon orbitals are sp^3 hybrid orbitals (blue). Those of the hydrogen atoms (yellow) are 1s. The structure is tetrahedral, with H—C—H bond angles of 109.5° (more precisely, 109.471). Remember that the hydrogen orbitals and the carbon hybrid orbitals have the same phase, but we have colored the hydrogen orbitals yellow for clarity.

combined. A useful representation of sp^3 hybridization of the valence-shell orbitals of carbon is



Note that the three p orbitals move down by $\frac{1}{4}$ of the energy difference between the s orbitals and the p orbitals and that the s orbital moves up by $\frac{3}{4}$ of that energy difference; that is, energy is conserved. Figure 11-7 shows sp^3 hybrid orbitals and bond formation in methane.

The objective of a hybridization scheme is an after-the-fact rationalization of the experimentally observed shape of a molecule. Hybridization is not an actual physical phenomenon. We cannot observe electron charge distributions changing from those of pure orbitals to those of hybrid orbitals. Moreover, for some covalent bonds no single hybridization scheme works well. Nevertheless,

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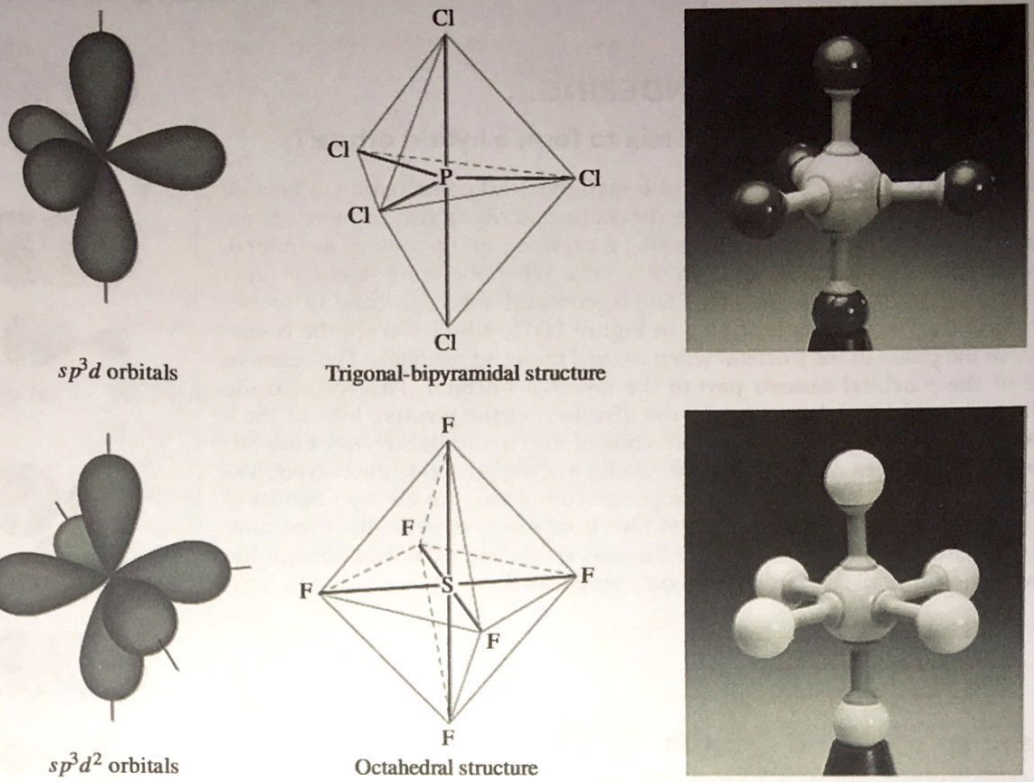

(a) sp^3d orbitals — Trigonal-bipyramidal structure

(b) sp^3d^2 orbitals — Octahedral structure

▲ FIGURE 11-12
sp^3d and sp^3d^2 hybrid orbitals

11-2 CONCEPT ASSESSMENT

Give the formula of a compound or ion composed of arsenic and fluorine in which the arsenic atom has a sp^3d^2 hybridization state.

Hybrid Orbitals and the Valence-Shell Electron-Pair Repulsion (VSEPR) Theory

In the previous section, we used either the experimental geometry or the geometry predicted by VSEPR theory to help us decide on the appropriate hybridization scheme for the central atom. The concept of hybridization arose before the formulation of the VSEPR theory as we used it in Chapter 10. In 1931, Linus Pauling introduced the concept of hybridization of orbitals to account for the known geometries of CH_4, H_2O, and NH_3. It was first suggested by Nevil Vincent Sidgwick and Herbert Marcus Powell in 1940 that molecular geometry was determined by the arrangement of electron pairs in the valence shell, and this suggestion was subsequently developed into the set of rules known as VSEPR by Ronald Gillespie and Ronald Nyholm in 1957. The advantage of VSEPR is that it has a predictive capability based on Lewis structures, whereas hybridization schemes, as described here, require a prior knowledge of the molecular geometry. So how should we proceed to describe the bonding in molecules? We can choose the likely hybridization scheme for a central atom in a structure in the valence-bond method by

- writing a plausible Lewis structure for the species of interest
- using VSEPR theory to predict the probable electron-group geometry of the central atom

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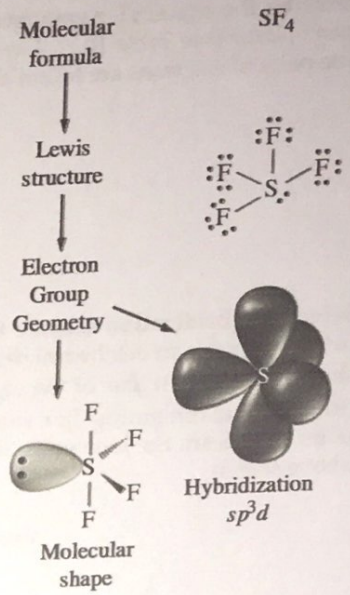
- selecting the hybridization scheme corresponding to the electron-group geometry

The procedure outlined above is illustrated in Figure 11-13 using the molecule SF_4 as an example.

As suggested by Table 11.1, the hybridization scheme adopted for a central atom should be the one producing the same number of hybrid orbitals as there are valence-shell electron groups, and in the same geometric orientation. Thus, an sp^3 hybridization scheme for the central atom predicts that four hybrid orbitals are distributed in a tetrahedral fashion. This results in molecular structures that are tetrahedral, trigonal-pyramidal, or angular, depending on how many hybrid orbitals are involved in orbital overlap and how many contain lone-pair electrons, corresponding to the VSEPR notations AX_4, AX_3E, and AX_2E_2 respectively.

The *s* and *p* orbital hybridization schemes are especially important in organic compounds, whose principal elements are C, O, and N, in addition to H. We will consider some important applications to organic chemistry in the next section.



▲ FIGURE 11-13
Using electron-group geometry to determine hybrid orbitals

TABLE 11.1 Some Hybrid Orbitals and Their Geometric Orientations

Hybrid Orbitals	Geometric Orientation	Example
sp	Linear	$BeCl_2$
sp^2	Trigonal-planar	BF_3
sp^3	Tetrahedral	CH_4
sp^3d	Trigonal-bipyramidal	PCl_5
sp^3d^2	Octahedral	SF_6

EXAMPLE 11-2 Proposing a Hybridization Scheme to Account for the Shape of a Molecule

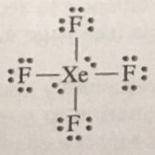
Predict the shape of the XeF_4 molecule and a hybridization scheme consistent with this prediction.

Analyze

Follow the procedure outlined in Figure 11-13.

Solve

1. **Write a plausible Lewis structure.** The Lewis structure we write must account for 36 valence electrons—*eight* from the Xe atom and *seven* each from the *four* F atoms. To place this many electrons in the Lewis structure, we must expand the valence shell of the Xe atom to accommodate 12 electrons. The Lewis structure is



2. **Use the VSEPR theory to establish the electron-group geometry of the central atom.** From the Lewis structure, we see that there are *six* electron groups around the Xe atom. Four electron groups are bond pairs and two are lone pairs. The electron-group geometry for *six* electron groups is *octahedral*.

(continued)

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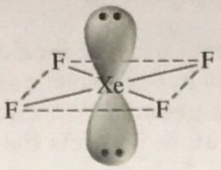
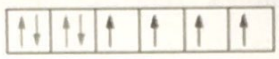
3. **Describe the molecular geometry.** The VSEPR notation for XeF_4 is AX_4E_2, and the molecular geometry is *square-planar* (see Table 10.1). The four pairs of bond electrons are directed to the corners of a square, and the lone pairs of electrons are found above and below the plane of the Xe and F atoms, as shown here.



4. **Select a hybridization scheme that corresponds to the VSEPR prediction.** The only hybridization scheme consistent with an octahedral distribution of *six* electron groups is sp^3d^2. The orbital diagram for this scheme shows clearly that *four* of the eight valence electrons of the central Xe atom singly occupy four of the sp^3d^2 orbitals. The remaining *four* valence electrons of the atom occupy the remaining two sp^3d^2 orbitals as lone pairs. These are the lone pairs of electrons situated above and below the plane of the Xe and F atoms in the above sketch.

Valence shell of Xe atom 

sp^3d^2

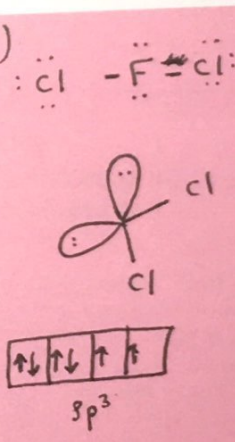
Assess

Note that the number of electron pairs in the electron-group geometry dictates how many orbitals are used in the hybridization scheme. We see that a combination of VSEPR and hybridization theory is an appealing way to describe the shape of and bonding in a molecule.

PRACTICE EXAMPLE A: Describe the molecular geometry and propose a plausible hybridization scheme for the central atom in the ion Cl_2F^+.

PRACTICE EXAMPLE B: Describe the molecular geometry and propose a plausible hybridization scheme for the central atom in the ion BrF_4^+.

PE A)



11-3 ARE YOU WO

Whether to use the VSE the valence-bond metho geometric shape of a m

There is no "correct" method for descr information is the experimental evide Once this experimental evidence is in this evidence by one method or ano which suggests a bond angle of 90°, observed 92° bond angle than does th H—S—H, VSEPR theory predicts a te in turn suggests a tetrahedral bond an ing this initial VSEPR prediction to ac pair–bond-pair repulsions (see page 4 109.5°.

VSEPR theory gives reasonably good results in the majority of cases. Unless you have specific information to suggest otherwise, describing a molecular shape with the VSEPR theory is a good bet. It is important to remember that both the VSEPR and valence-bond methods are simply models we use to rationalize the shapes and bonding of polyatomic molecules and as such, should be viewed with a critical eye, always keeping experimental results in sight.

KEEP IN MIND

that the VSEPR method uses empirical data to give an approximate molecular geometry, whereas the valence-bond method relates to the orbitals used in bonding based on a given geometry.

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