10.1: Hybrid Orbitals Account for Molecular Shape

> **◗ Learning Objectives**
>
> - Introduce hybrid orbital to explain non-linear molecular structure

Valence bond (VB) theory is one of two basic theories, along with molecular orbital (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory, which will be discussed elsewhere, predict wavefunctions that cover the entire molecule.

Review of Diatomics

Let us consider H_2. Recall that the Lewis structure for a single H atom is $H\cdot$ and for H_2, it is $H:H$. Thus, each hydrogen brings one unpaired electron to the bond. Let the two protons be denoted A and B and the two electrons 1 and 2. Now, consider the potential energy

$$V = V_{ee} + V_{en} + V_{nn} \tag{10.1.1}$$

$$= \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R_{AB}}\right] \tag{10.1.2}$$

But as $R_{AB} \to \infty$, the $1/r_{12}$, $1/r_{1B}$, $1/r_{2A}$, and $1/R_{AB}$ terms vanish and the potential energy becomes simply that of two noninteracting hydrogen atoms

$$V \to -\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{1A}} + \frac{1}{r_{2B}}\right]$$

Since the potential energy becomes a simple sum of separate energies for electrons 1 and 2, the wavefunction should simply be a product $\psi_{1s}(r_1 - r_A)\psi_{1s}(r_2 - r_B)$. But as we let $R_{AB} \to R_e$, where R_e is the equilibrium bond length, the electrons mix, and we can no longer tell if electron 1 belongs to atom A or atom B and the same for electron 2. Thus, we need to construct a combination of products that is consistent with the Pauli exclusion principle. If we just consider the coordinates r_1 and r_2 of the electrons, then the only wavefunction we can construct from a product of 1s orbitals is

$$\psi_u(r_1, r_2) = C_u[\psi_{1s}^A(r_1)\psi_{1s}^B(r_2) - \psi_{1s}^A(r_2)\psi_{1s}^B(r_1)]$$

where the u designator indicates that this is an odd function. The constant C_u is the overall noramlization constant. Unfortunately, like in the LCAO method, such a wavefunction is antibonding and is not a good representation of the ground state. If, however, we construct the wavefunction

$$\psi_g(r_1, r_2) = C_g[\psi_{1s}^A(r_1)\psi_{1s}^B(r_2) + \psi_{1s}^A(r_2)\psi_{1s}^B(r_1)]$$

(where g designates that this is an even function), we violate the Pauli exclusion principle, even though such a wavefunction leads to a stable chemical bond.

What is missing here is the fact that we have not considered the spins of the electrons. Since the electrons are identical, if we exchange coordinates *and* spins, then the wavefunction should change sign. Thus, we can make both wavefunctions above consistent with the Pauli exclusion principle by multiplying by an appropriate spin wavefunction. We obtain

$$\psi_u(r_1, r_2, s_1, s_2) = \psi_u(x_1, x_2) = C_u[\psi_{1s}^A(r_1)\psi_{1s}^B(r_2) - \psi_{1s}^A(r_2)\psi_{1s}^B(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.3}$$

$$\psi_g(r_1, r_2, s_1, s_2) = \psi_g(x_1, x_2) = C_g[\psi_{1s}^A(r_1)\psi_{1s}B(r_2) + \psi_{1s}^A(r_2)\psi_{1s}^B(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.4}$$

where s_1 and s_2 are the z-components of spin for electrons 1 and 2, respectively. We can now use ψ_g as an approximate 2-electron wavefunction that leads to a stable chemical bond in H_2.

The fact that ψ_u is antibonding can be easily determined by looking for a nodal plane between the two atoms, in this case, in the plane that exactly bisects the line joining the two atoms, midway between them. That this is, indeed, a nodal plane can be seen by considering two points r_1 and r_2 for the two electrons that are taken to lie in this plane. By symmetry, the functions $\psi_{1s}^A(r_1)$ and $\psi_{1s}^B(r_1)$ have the same value for r_1 in this plane, and the same for $\psi_{1s}^B(r_2)$ and $\psi_{1s}^A(r_2)$. Let us assign the following values:

$$\psi_{1s}^A(r_1) = \psi_{1s}^B(r_1) = A \tag{10.1.5}$$

$$\psi_{1s}^B(r_2) = \psi_{1s}^A(r_2) = A' \tag{10.1.6}$$

Substituting these into $\psi_u(x_1, x_2)$, we obtain

$$\psi_u(x_1, x_2) = C_u[AA' - A'A][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] = 0$$

Since the wavefunction has a node midway between the two atoms, it is clearly antibonding and should have a *higher energy* than the corresponding bonding wavefunction ψ_g.

A similar argument can be used for the molecule F_2. Each F has an electronic configuration

$$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$$

and the Lewis structure of F_2 is

$$: \ddot{\text{F}} : \ddot{\text{F}} :$$

Figure 10.1.1 : Lewis structure of F_2.

Most of the electrons are in lone pairs, but the $2p_z$ electrons, which are unpaired in each F come together to form the bond. Thus, the bonding wavefunction should be a 2-electron wavefunction constructed from $2p_z$ orbitals. The bonding wavefunction takes the "gerade" form as in H_2:

$$\psi_g(r_1, r_2, s_1, s_2) = C_g[\psi_{2p_z}^A(r_1)\psi_{2p_z}^B(r_2) + \psi_{2p_z}^A(r_2)\psi_{2p_z}^B(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]$$

For HF, the $2p_z$ orbital on F and $1s$ orbital on H come together to form the bonding wavefunction. To be consistent with the Pauli principle, we need a wavefunction of the form

$$\psi(r_1, r_2, s_1, s_2) = [\psi_{1s}^H(1)\psi_{2p_z}^F(2) + \psi_{1s}^H(2)\psi_{2p_z}^F(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]) \tag{10.1.7}$$

Looking at the HF example, it becomes clear how much valence bond theory attempts to appear as a "quantum version" of the Lewis dot structure model. Valence bond theory attempts to construct very approximate wavefunctions for the bonding electrons in a Lewis structure, leaving the orbitals unused in the construction of the valence bond wavefunctions for the lone pair electrons. In the case of HF, we use the $2p_z$ orbitals of F, which leaves the $2s$, $2p_x$ and $2p_y$ orbitals unused. Since there are three lone pairs, these three orbitals are sufficient to hold each of the lone pairs as spin-up/spin-down couples.

Hybridization

For polyatomic molecules, the valence bond theory becomes a very poor approximation because the directionalities of the $2s$ and $2p$ orbitals is too restrictive to describe molecules with steric numbers ranging between 2 and 4. The example considered above of H_2O illustrates this rather dramatically! Let us consider an even simpler molecule, BeH_2, which has a steric number of 2 and is linear. Let the atoms lie entirely along the z-axis in the arrangement $H - Be - H$.

Although Be has a ground-state electronic configuration of $1s^2 2s^2$, but if we "promote" one of the $2s$ electrons to a state with higher energy and allow its electronic structure to be $1s^2 2s 2p_z$, then the unpaired electrons in the $2s$ and $2p_z$ orbitals can combine with the unpaired electrons in each of the hydrogen atoms to form bonds. The energy needed to excite the electron in Be would be ``repaid'' by the energy gained in the formation of stable bonds. The two valence-bond wavefunctions we would construct would be

$$\psi_1(1, 2) = C_1\left[\psi_{1s}^{H_1}(1)\psi_{2s}^{Be}(2) + \psi_{1s}^{H_1}(2)\psi_{2s}^{Be}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.8}$$

$$\psi_2(1, 2) = C_2\left[\psi_{1s}^{H_2}(1)\psi_{2p_z}^{Be}(2) + \psi_{1s}^{H_2}(2)\psi_{2p_z}^{Be}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.9}$$

Unfortunately, even this simple scheme does not work entirely because the two $Be - H$ bonds would be different due to their construction from different combinations of orbitals. By symmetry, however, we can see that the two BeH bonds should be equivalent. A solution to this problem was proposed by Linus Pauling in the 30s in the form of *orbital hybridization*, a scheme that we still use today.

Pauling used the fact that in the first and second periods, the $2s$ and $2p$ orbitals have similar energies. Indeed, for H, the energies are exactly the same. Given that these energies are not that different, we can combine s and p orbitals and still have a valid solution

of the Schrödinger equation. That is, a general orbital

$$\chi(r) = C_1 \psi_{2s}(r) + C_2 \psi_{2p_x}(r) + C_3 \psi_{2p_y}(r) + C_4 \psi_{2p_z}(r)$$

is also a solution of the Schrödinger equation with the same energy as a $2s$ or $2p$ orbitals individually (this is exactly true for H). In the case of BeH_2, the external potential on the electrons in Be by the two hydrogens changes the energy levels and creates a near degeneracy between the $2s$ and $2p_z$ orbitals, hence, we are now free to combine the into linear combinations that are more suitable to the construction both of valence bond wavefunctions *and* MOs via the LCAO procedure.

sp Hybrid Orbitals

For Be, we now allow the s and p orbitals to mix and create two *hybrid* orbitals known as sp orbitals. The two new hybrid wavefunctions as linear combination of the functions for 2s and 2p$_z$ (using Dirac Notation):

$$|\chi_i\rangle = a_1 |2s\rangle + b_1 |2p_z\rangle \tag{10.1.10}$$

$$|\chi_j\rangle = a_2 |2s\rangle + b_2 |2p_z\rangle \tag{10.1.11}$$

These two wavefunctions must be orthogonal.

$$\langle \chi_i | \chi_j \rangle = \delta_{ij}$$

Which can be separated into the following relationships:

$$\langle \chi_i | \chi_i \rangle = 1 \tag{10.1.12}$$

and

$$\langle \chi_j | \chi_j \rangle = 1 \tag{10.1.13}$$

and

$$\langle \chi_i | \chi_j \rangle = \langle \chi_j | \chi_i \rangle = 0 \tag{10.1.14}$$

Equations 10.1.12 and 10.1.13 are the normality requirement and Equation 10.1.14 is the orthogonality requirement for the new hybrid wavefunctions. Substituting 10.1.10 into 10.1.12 results in

$$\langle \chi_i | \chi_i \rangle = a_1^2 \underbrace{\langle 2s | 2s \rangle}_{1} + a_1 b_1 \underbrace{\langle 2s | 2p_z \rangle}_{0} + a_1 b_1 \underbrace{\langle 2p_z | 2s \rangle}_{0} + b_1^2 \underbrace{\langle 2p_z | 2p_z \rangle}_{1} = 1$$

and similarly for $\langle \chi_j | \chi_j \rangle$

$$\langle \chi_j | \chi_j \rangle = a_2^2 \underbrace{\langle 2s | 2s \rangle}_{1} + a_2 b_2 \underbrace{\langle 2s | 2p_z \rangle}_{0} + a_2 b_2 \underbrace{\langle 2p_z | 2s \rangle}_{0} + b_2^2 \underbrace{\langle 2p_z | 2p_z \rangle}_{1} = 1$$

results in the following relationships

$$\langle \chi_i | \chi_i \rangle = a_1^2 + b_1^2 = 1 \tag{10.1.15}$$

$$\langle \chi_j | \chi_j \rangle = a_2^2 + b_2^2 = 1 \tag{10.1.16}$$

and

$$\langle \chi_i | \chi_j \rangle = a_1 a_2 + b_1 b_2 = 0 \tag{10.1.17}$$

These are four unknowns and three equations. The fourth "constraint" is that we assume contribution of $|s\rangle$ is the same for both hybrid orbitals.

$$a_1 = a_2$$

Equations 10.1.15 to 10.1.17 revert to

$$a_1^2 + b_1^2 = 1 \tag{10.1.18}$$

$$a_1^2 + b_2^2 = 1 \tag{10.1.19}$$

$$b_1^2 = b_2^2 \tag{10.1.20}$$

Therefore

$$b_1 = -b_2$$

and

$$a_1 = b_1 \qquad\qquad (10.1.21)$$

Insert Equation 10.1.21 into 10.1.20 to get

$$a_1 = \frac{1}{\sqrt{2}}$$

and the two hybrid orbitals are

$$\chi_1(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) + \psi_{2p_z}(r)] \qquad\qquad (10.1.22)$$

$$\chi_2(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) - \psi_{2p_z}(r)] \qquad\qquad (10.1.23)$$

Note that these orbitals are both normalized and orthogonal:

$$\int |\chi_1(r)|^2 dV = 1 \ ; \ \int |\chi_2(r)|^2 dV = 1 \ ; \ \int \chi_1^*(r)\chi_2(r)dV = 0$$

These orbitals appear as shown in Figure 10.1.3
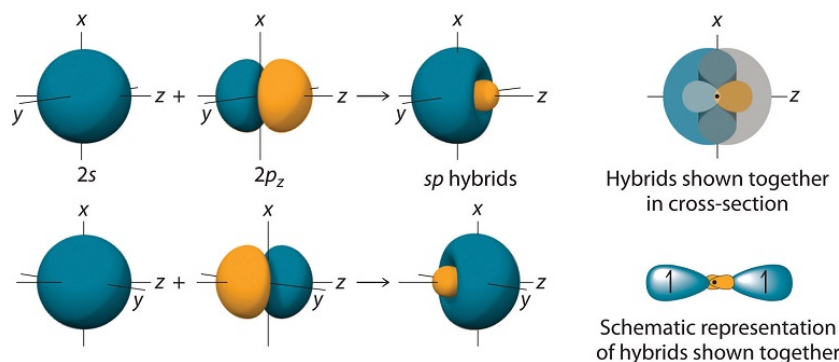
Figure 10.1.3 : The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

Given that the two *sp* hybrid orbitals are mirror images of each other, they can overlap with the $1s$ orbital of H (shown in the figure) and create two equal bonds, as needed for BeH_2. Using the valence bond formulation, now, one of the BeH bonds will be described by a wavefunction of the form:

$$\psi_1(1,2) = C_1[\psi_{1s}^{H_1}(1)\chi_1^{Be}(2) + \psi_{1s}^{H_1}(2)\chi_1^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \qquad (10.1.24)$$

$$\psi_2(1,2) = C_2[\psi_{1s}^{H_2}(1)\chi_2^{Be}(2) + \psi_{1s}^{H_2}(2)\chi_2^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \qquad (10.1.25)$$

In the above wavefunctions, it is clear that H_1 is on the right and H_2 is on the left, based on the directionalities of χ_1 and χ_2.

sp^2 Hybrid Orbitals

For trigonal planar molecules such as BH_3, we start with the electronic configuration of B, which is $1s^2 2s^2 2p_x$, and we promote one of the $2s$ electrons to a $2p_y$ orbital, so that we have $1s^2 2s 2p_x 2p_y$. Suppose the geometry of BH_3 is such that one of the hydrogens lies along the positive x axis. The remaining hydrogens would be in the 3rd and 4th quadrants, respectively, as shown in Figure 10.1.4 .
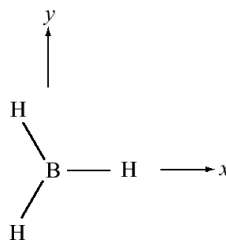
Figure 10.1.4 : Geometry of BH_3.

If we simply combine the $2s$ with the $2p_x$ and $2p_y$ orbitals of boron, the resulting hybrid orbitals will not point in the correct direction. For this reason, we will create rotated versions of the p_x and p_y orbitals, which, as we will see are tantamount to taking new combinations of $2p_x$ and $2p_y$ orbitals to combine with the $2s$. Since the rotation occurs in the xy plane, the coordinate that controls this is the azimuthal angle ϕ. For the p_x and p_y orbitals, the ϕ dependence is

$$\psi_{2p_x} \sim \cos\phi \; ; \; \psi_{2p_y} \sim \sin\phi$$

If we rotate $2p_y$ by -30 degrees (Figure 10.1.5 ; blue is positive and red is negative), the ϕ dependence becomes
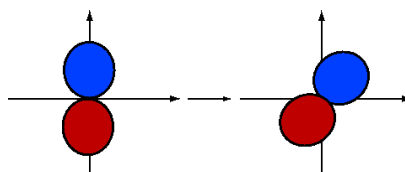
$$\psi_{2p_y}^{(rot)} \sim \sin(\phi + 30)$$

Figure 10.1.5 : Rotation of a $2p_y$ orbital by -30 degrees.

Using the fact that

$$\sin(\alpha \pm \beta) = \sin\alpha \cos\beta \pm cos\alpha sin\beta$$

this rotation gives

$$\psi_{2p_y}^{(rot,1)} \sim \sin\phi\cos 30 + \cos\phi\sin 30 \tag{10.1.26}$$

$$\sim \left[\frac{\sqrt{3}}{2}\sin\phi + \frac{1}{2}\cos\phi\right] \tag{10.1.27}$$

$$\sim \left[\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x}\right] \tag{10.1.28}$$

Similarly, consider rotating $-\psi_{2p_y}$ by $+30$ degrees (Figure 10.1.6). This gives

$$-\psi_{2p_y}^{(rot,2)} \sim -\sin(\phi - 30) \tag{10.1.29}$$

$$\sim -\left[\frac{\sqrt{3}}{2}\sin\phi - \frac{1}{2}\cos\phi\right] \tag{10.1.30}$$

$$\sim -\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x} \tag{10.1.31}$$
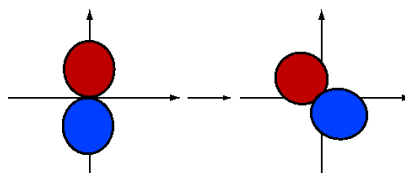

Figure 10.1.6 : Rotation of a $-2p_y$ orbital by 30 degrees.

So, we now take the hybrid orbitals to be of the form

$$\chi_1(r) = a\psi_{2s}(r) - b\psi_{2p_x} \tag{10.1.32}$$

$$\chi_2(r) = c\psi_{2s}(r) + d\psi_{2p_y}^{(rot,1)}(r) \tag{10.1.33}$$

$$\chi_3(r) = c\psi_{2s}(r) - d\psi_{2p_y}^{(rot,2)}(r) \tag{10.1.34}$$

The coefficients a, b, and c are determined by requiring that the orbitals are normalized and mutually orthogonal:

$$\int |\chi_1(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_2(r)dV = 0 \tag{10.1.35}$$

$$\int |\chi_2(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_3(r)dV = 0 \tag{10.1.36}$$

$$\int |\chi_3(r)|^2 dV = 1 \; ; \; \int \chi_2^*(r)\chi_3(r)dV = 0 \tag{10.1.37}$$

Carrying out the algebra, we obtain the following sp^2 hybrid orbitals:

$$\chi_1(r) = \frac{1}{\sqrt{3}}[\psi_{2s}(r) - \sqrt{2}\psi_{2p_x}(r)] \tag{10.1.38}$$

$$\chi_2(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) + \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.39}$$

$$\chi_3(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) - \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.40}$$

The sp^2 hybrids allow bonding at $120°$ degrees, and these orbitals appear as shown in Figure 10.1.7 :
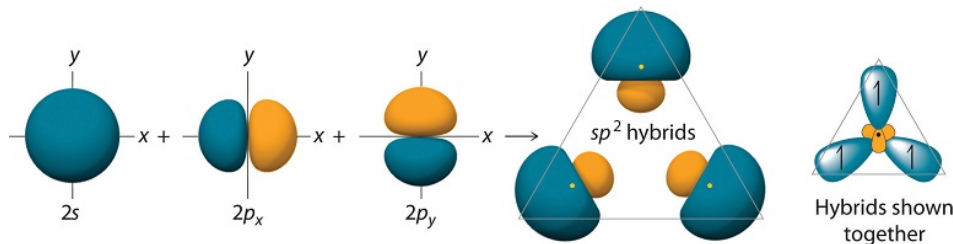

Figure 10.1.7 : Formation of sp^2 Hybrid Orbitals. Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

The figure also shows the overlaps of these orbitals with the $1s$ orbitals of H.

sp^3 Hybrid Orbitals

Finally, we consider the case of methane CH_4. The electronic configuration of C is $1s^2 2s^2 2p_x 2p_y$. We now promote one of the $2s$ orbitals to the $2p_z$ orbital and write C as $1s^2 2s 2p_x 2p_y 2p_z$. We can now hybridize the $2s$ orbital with each of the $2p$ orbitals to create four hybrids:

$$\chi_1(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{10.1.41}$$

$$\chi_2(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{10.1.42}$$

$$\chi_3(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{10.1.43}$$

$$\chi_4(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{10.1.44}$$

The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 10.1.8). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.
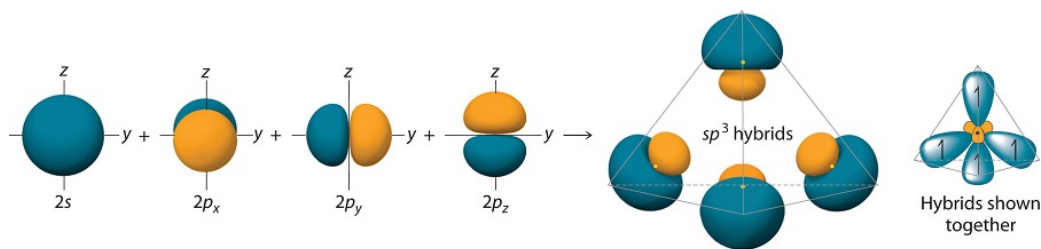
Figure 10.1.8 : Formation of sp^3 Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four *sp^3* hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

📌 Are hybrid orbitals Real?

Hybridization is an often misconceived concept. It only is a mathematical interpretation, which explains a certain bonding situation (in an intuitive fashion). In a molecule the equilibrium geometry will result from various factors, such as steric and electronic interactions, and further more interactions with the surroundings like a solvent or external field. The geometric arrangement will not be formed because a molecule is hybridized in a certain way, it is the other way around, i.e. a result of the geometry or more precise and interpretation of the wavefunction for the given molecular arrangement.

The justification we gave for invoking hybridization in molecules such as BeH_2, BF_3 and CH_4 was that the bonds in each are geometrically and chemically equivalent, whereas the atomic *s*- and *p*-orbitals on the central atoms are not. By combining these into new orbitals of *sp*, *sp^2* and *sp^3* types we obtain the required number of completely equivalent orbitals. This seemed easy enough to do on paper; we just drew little boxes and wrote "*sp^2*" or whatever below them. But what is really going on here?

The full answer is beyond the scope of this course, so we can only offer the following very general explanation. First, recall what we mean by "orbital": a mathematical function ψ having the character of a standing wave whose square ψ^2 is proportional to the probability of finding the electron at any particular location in space. The latter, the *electron density distribution*, can be observed (by X-ray scattering, for example), and in this sense is the only thing that is "real".

A given standing wave (ψ-function) can be synthesized by combining all kinds of fundamental wave patterns (that is, atomic orbitals) in much the same way that a color we observe can be reproduced by combining different sets of primary colors in various proportions. In neither case does it follow that these original orbitals (or colors) are actually present in the final product. So one could well argue that hybrid orbitals are not "real"; they simply turn out to be convenient for understanding the bonding of simple molecules at the elementary level, and this is why we use them.

Summary

The shape and bonding valecies of polyatomic molecules can be accounted for by hybrid orbitals. Molecular orbitals are formed from linear combinations of atomic orbitals which are similar in energy. These atomic orbitals could come from different atoms, or from the same atom. For example, the 2 sand 2patomic orbitals are very close energetically. When a linear combo of more than one atomic orbital from the **same atom** is formed, we have a hybrid orbital.