

WHAT ARE HYBRID ORBITALS?

About orbitals: a review

First, recall that the electron, being a quantum particle, cannot have a distinct location; the most we can do is define the region of space around the nucleus in which the probability of finding the electron exceeds some arbitrary value, such as 90% or 99%. This region of space is the **orbital**. Because of the wavelike character of matter, the orbital corresponds to a standing wave pattern in 3-dimensional space which we can often represent more clearly in 2-dimensional cross section. The quantity that is varying (“waving”) is a **number** denoted by ψ (psi) whose value varies from point to point according to the wave function for that particular orbital.

Orbitals of all types are simply mathematical functions that describe particular standing-wave patterns that can be plotted on a graph but have no physical reality of their own. Because of their wavelike nature, two or more orbitals (i.e., two or more functions ψ) can be combined both in-phase and out-of-phase to yield a pair of resultant orbitals which, to be useful, must have squares that describe actual electron distributions in the atom or molecule.

The s, p, d and f orbitals that you are familiar with are the most convenient ones for describing the electron distribution in isolated atoms because assignment of electrons to them according to the usual rules always yields an overall function Ψ^2 that predicts a spherically symmetric electron distribution, consistent with all physical evidence that atoms are in fact spherical. For atoms having more than one electron, however, the s, p, d, f basis set is only one of many possible ways of arriving at the same observed electron distribution. We use it not because it is unique, but because it is the simplest.

In the case of a molecule such as BeH_2 , we know from experimental evidence that the molecule is linear and therefore the electron density surrounding the central atom is no longer spherical, but must be concentrated along two directions 180° apart, and we need to construct a function Ψ^2 having these geometrical properties. There are any number of ways of doing this, but it is convenient is to use a particular set of functions ψ (which we call hybrid orbitals) that are constructed by combining the atomic s, p, d, and f functions that are already familiar to us.

You should understand that hybridization is not a physical phenomenon; it is merely a mathematical operation that combines the atomic orbitals we are familiar with in such a way that the new (hybrid) orbitals possess the geometric and other properties that are reasonably consistent with what we observe in a wide range

(but certainly not in all) molecules. In other words, hybrid orbitals are abstractions that describe reality fairly well in certain classes of molecules (and fortunately, in much of the very large class of organic substances) and are therefore a useful means of organizing a large body of chemical knowledge... but they are far from infallible.

This approach, which assumes that the orbitals remain more or less localized on one central atom, is the basis of the theory which was developed in the early 1930s, mainly by Linus Pauling.

Although the hybrid orbital approach has proven very powerful (especially in organic chemistry), it does have its limitations. For example, it predicts that both H₂O and H₂S will be tetrahedrally coordinated bent molecules with bond angles slightly smaller than the tetrahedral angle of 109.5° owing to greater repulsion by the nonbonding pair. This description fits water (104.5°) quite well, but the bond angle in hydrogen sulfide is only 92°, suggesting that atomic p orbitals (which are 90° apart) provide a better description of the electron distribution about the sulfur atom than do sp³ hybrid orbitals.

The hybrid orbital model is fairly simple to apply and understand, but it is best regarded as one special way of looking at a molecule that can often be misleading. Another viewpoint, called the molecular orbital theory, offers us

a complementary perspective that it is important to have if we wish to develop a really thorough understanding of chemical bonding in a wider range of molecules.

Source: <http://www.chem1.com/acad/webtext/chembond/cb06.html>