Orbital hybridisation

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Jump to: navigation, search

Four $sp^3$ orbitals.

Three $sp^2$ orbitals.

In chemistry, hybridisation (or hybridization) is the concept of mixing atomic orbitals to form new hybrid orbitals suitable for the qualitative description of atomic bonding properties. Hybridised orbitals are very useful in the explanation of the shape of molecular orbitals for molecules. It is an integral part of valence bond theory. Although sometimes taught together with the valence shell electron-pair repulsion (VSEPR) theory, valence bond and hybridization are in fact not related to the VSEPR model.[1]

The hybrids are named based on the atomic orbitals that are involved in the hybridization, and the geometries of the hybrids are also reflective of those of the atomic-orbital contributors. For example, in methane (CH₄) a set of $sp^3$ orbitals are formed by mixing one s and three p orbitals on the carbon atom, and are directed towards the four hydrogen atoms which are located at the vertices of a regular tetrahedron.

Contents

[hide]

- 1 Historical development
- 2 Types of hybridisation
  - 2.1 $sp^3$ hybrids
  - 2.2 $sp^2$ hybrids
  - 2.3 $sp$ hybrids
Chemist Linus Pauling first developed the hybridisation theory in order to explain the structure of molecules such as methane (CH₄). This concept was developed for such simple chemical systems, but the approach was later applied more widely, and today it is considered an effective heuristic for rationalizing the structures of organic compounds.

For quantitative calculations of electronic structure and molecular properties, hybridisation theory is not as practical as molecular orbital theory. Problems with hybridisation are especially notable when the d orbitals are involved in bonding, as in coordination chemistry and organometallic chemistry. Although hybridisation schemes in transition metal chemistry can be used, they are not generally as accurate.

Orbitals are a model representation of the behaviour of electrons within molecules. In the case of simple hybridisation, this approximation is based on atomic orbitals, similar to those obtained for the hydrogen atom, the only atom for which an exact analytic solution to its Schrödinger equation is known. In heavier atoms, like carbon, nitrogen, and oxygen, the atomic orbitals used are the 2s and 2p orbitals, similar to excited state orbitals for hydrogen. Hybridised orbitals are assumed to be mixtures of these atomic orbitals, superimposed on each other in various proportions. The theory of hybridisation is most applicable under these assumptions. It gives a simple orbital picture equivalent to Lewis structures. Hybridisation is not required to describe molecules, but for molecules made up from carbon, nitrogen and oxygen (and to a lesser extent, sulfur and phosphorus) the hybridisation theory/model makes the description much easier.

The hybridisation theory finds its use mainly in organic chemistry. Its explanation starts with the way bonding is organized in methane.
Hybridisation describes the bonding atoms from an atom's point of view. That is, for a tetrahedrally coordinated carbon (e.g., methane, CH₄), the carbon should have 4 orbitals with the correct symmetry to bond to the 4 hydrogen atoms. The problem with the existence of methane is now this: carbon's ground state configuration is $1s^2 \ 2s^2 \ 2p_x^1 \ 2p_y^1$ or more easily read:

$$\begin{array}{c}
1s \\
2s \\
2p_x \\
2p_y \\
2p_z
\end{array}$$

The valence bond theory would predict, based on the existence of two half-filled $p$-type orbitals (the designations $p_x \ p_y$ or $p_z$ are meaningless at this point, as they do not fill in any particular order), that C forms two covalent bonds, i.e., CH₂ (methylene). However, methylene is a very reactive molecule (see also: carbene) and cannot exist outside of a molecular system. Therefore, this theory alone cannot explain the existence of CH₄.

Furthermore, ground state orbitals cannot be used for bonding in CH₄. While exciting a 2s electron into a 2p orbital would, in theory, allow for four bonds according to the valence bond theory, (which has been proved experimentally correct for systems like O₂) this would imply that the various bonds of CH₄ would have differing energies due to differing levels of orbital overlap. Once again, this has been experimentally disproved: any hydrogen can be removed from a carbon with equal ease.

To summarise, to explain the existence of CH₄ (and many other molecules) a method by which as many as 12 bonds (for transition metals) of equal strength (and therefore equal length) may be explained was required.

The first step in hybridisation is the excitation of one (or more) electrons (we consider the carbon atom in methane, for simplicity of the discussion):

$$\begin{array}{c}
1s \\
2s \\
2p_x \\
2p_y \\
2p_z
\end{array}$$

The proton that forms the nucleus of a hydrogen atom attracts one of the lower-energy valence electrons on carbon. This causes an excitation, moving a 2s electron into a 2p orbital. This, however, increases the influence of the carbon nucleus on the valence electrons by increasing the effective core potential (the amount of charge the nucleus exerts on a given electron = Charge of Core − Charge of all electrons closer to the nucleus). The effective core potential is also known as the effective nuclear charge, or $Z_{\text{eff}}$.

The solution to the Schrödinger equation for this configuration is a linear combination of the s and p wave functions, or orbitals, known as a hybridized orbital. In the case of carbon attempting to bond with four hydrogens, four valence-shell orbitals are required. (Core orbitals are almost never involved in bonding.) Therefore, the 2s orbital "mixes"
with the three 2p orbitals to form four sp³ hybrids (read as s-p-three). See graphical summary below.

\[
C^+ \\
\begin{array}{c}
1s \\
\text{sp}^3 \\
\text{sp}^3 \\
\text{sp}^3 \\
\text{sp}^3
\end{array}
\]

becomes

In CH₄, four sp³ hybridised orbitals are overlapped by hydrogen's 1s orbital, yielding four \( \sigma \) (sigma) bonds (that is, four single covalent bonds). The four bonds are of the same length and strength. This theory fits our requirements.

An alternative view is: View the carbon as the C⁴⁻ anion. In this case all the orbitals on the carbon are filled:

\[
C^{4-} \\
\begin{array}{c}
1s \\
2s \\
2p_z \\
2p_y \\
2p_x
\end{array}
\]

If we now recombine these orbitals with the empty s-orbitals of 4 hydrogens (4 protons, H⁺) and then allow maximum separation between the 4 hydrogens (i.e., tetrahedral surrounding of the carbon), we see that at any orientation of the p-orbitals, a single hydrogen has an overlap of 25% with the s-orbital of the C, and a total of 75% of overlap with the 3 p-orbitals (see that the relative percentages are the same as the character of the respective orbital in an sp³-hybridisation model, 25% s- and 75% p-character).

According to the orbital hybridisation theory, the valence electrons in methane should be equal in energy but its photoelectron spectrum shows two bands, one at 12.7 eV (one electron pair) and one at 23 eV (three electron pairs). This apparent inconsistency can be explained when one considers additional orbital mixing taking place when the sp³ orbitals mix with the 4 hydrogen orbitals.

[edit] sp² hybrids