Assigning Hybridization: A Tutorial

Goal: In this tutorial you'll learn how to assign hybridization (sp³, sp², sp, or nonhybridized) for atoms in organic molecules.

Vocabulary to Review

Here are some vocabulary words you'll need to understand this tutorial. Check the Illustrated Glossary of Organic Chemistry on the course web site if your understanding of any term is weak.

(a) Atomic orbital  (g) p orbital  (m) Sigma bond (σ bond)
(b) Bond angle  (h) Pi bond (π bond)  (n) sp orbital
(c) Covalent bond  (i) px orbital  (o) sp² orbital
(d) Hybrid orbital  (j) py orbital  (p) sp³ orbital
(e) Orbital  (k) pz orbital  (q) Valence shell
(f) Orbital lobe  (l) s orbital

Why Use Hybrid Orbitals?

A covalent bond is formed by the overlap of two orbitals, one orbital from each atom involved in the bond. In order for the molecule's bonds to have the correct geometry, the orbitals involved must point in the correct direction. For example, methane is tetrahedral; the four hydrogen atoms point to the corners of a pyramid made of four equilateral triangles. The H–C–H bond angles are 109.5°.

Molecular geometry of methane. Bond angles in methane.

To construct methane's C–H bonds we might start with overlap of a hydrogen 1s orbital and one of carbon's valence shell atomic orbitals (2s, 2px, 2py, or 2pz). The 2p orbitals are perpendicular to each other, so the resultant C–H bonds are also perpendicular.

Carbon's 2px (blue), 2py (not colored), and 2pz (yellow) orbitals are perpendicular.
Two C–H bonds formed from carbon's $2p_x$ and $2p_z$ orbitals are perpendicular.

Methane's actual H–C–H bond angle is 109.5° and not 90°, so using carbon's $2p$ orbitals does not give the correct bond angles.

The solution (as suggested by Linus Pauling) is to mathematically combine carbon's $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals to create a new set of orbitals, pointing to the corners of a tetrahedron, and having the necessary 109.5° bond angles. These mathematically combined orbitals are called hybrid orbitals. Overlap of carbon's hybrid orbitals with hydrogen $s$ orbitals gives C–H bonds with the correct bond angles.

Verify the bond angles by using your model kit (as shown below) and a protractor. (If you haven't mastered your molecular model kit, now is a good time to start. Check out the model kit tutorials posted at the course web site.)

The hybrid orbitals for tetrahedral geometry are separated by 109.5°.

With only rare exceptions, every carbon, nitrogen, oxygen, and halogen atom you'll encounter in organic chemistry uses hybrid orbitals for covalent bonding. Hydrogen is never hybridized; it always uses only $1s$ orbitals.

**Constructing Hybrid Orbitals: Basic Rules**

Hybrid orbitals are constructed by mathematical combination of $s$, $p_x$, $p_y$, and $p_z$ valence shell orbitals. Hybridization can also involve $d$ orbitals, but these are rarely
important in introductory organic chemistry. To learn how to construct hybrid orbitals, we first need to know two rules (from quantum mechanics) that govern the hybridization process:

- When hybridizing, the number of orbitals is conserved. If we need four hybrid orbitals (perhaps to accommodate the four C–H bonds of methane), then we must mix four nonhybridized orbitals (s, px, py, and pz) to make these hybrid orbitals.

- When selecting which orbitals to mix, we must start with s and then add as many p orbitals as necessary to produce the correct number of hybrid orbitals.

Constructing Hybrid Orbitals: Tetrahedral Geometry

Let's construct the hybrid orbitals for methane. We need four hybrid orbitals for the four tetrahedral C–H bonds. So we mix carbon's 2s, 2px, 2py, and 2pz orbitals. The four hybrid orbitals thus created are each called sp³ orbitals because these orbitals are composed of one part s and three parts p. We say the carbon atom is now sp³ hybridized.

\[
2s + 2px + 2py + 2pz \rightarrow sp^3 + sp^3 + sp^3 + sp^3
\]

Mix four nonhybridized orbitals to produce four new hybrid orbitals.

Note that this sp³ hybridization scheme uses all of the starting orbitals, so there is no leftover, nonhybridized p orbital. (We'll see below that sp² hybridization leaves one nonhybridized p orbital, and that sp hybridization leaves two nonhybridized p orbitals.)

To make the four C–H bonds, each of the four carbon sp³ orbitals overlaps with a hydrogen s orbital to make one C–H bond.

Four carbon sp³ orbitals plus four hydrogen atoms produce the four C–H bonds of methane.

The same process applies to other tetrahedral (or nearly tetrahedral) atoms, such as the nitrogen atom of ammonia (NH₃) or the oxygen atom of water (H₂O).

Constructing Hybrid Orbitals: Trigonal Planar Geometry

Now let's try borane (BH₃). The Lewis structure shows that boron has three bonds and no lone pairs. (If you don't see this, perhaps this would be a good time to review the
formal charge tutorial.) Whenever we have a central atom surrounded by three attachments, the geometry that places these attachments as far apart as possible (to minimize electron repulsion) is trigonal planar. The H–B–H bond angles are 120°. (Build trigonal planar BH₃ with your model kit, and verify the bond angles with a protractor.)

Molecular model of BH₃, showing 120° H–B–H bond angles.

What orbitals are involved? Boron and carbon are both in the second row of the periodic table, so they have the same nonhybridized valence shell atomic orbitals: 2s, 2px, 2py, and 2pz. Combining these nonhybridized boron orbitals with hydrogen s orbitals to form B–H bonds does not give the required 120° bond angles. So we need to construct a set of three hybrid orbitals (three hybrid orbitals because the boron has three attachments) to get the correct bond angles. We combine boron’s s orbital and two boron p orbitals (is does not matter which two) to construct three new orbitals, called sp² orbitals. Note that the unused p_z orbital is still present after hybridization.

\[
[2s + 2p_x + 2p_y] + 2p_z \rightarrow sp^2 + sp^2 + sp^2 + 2p_z
\]

Mix three nonhybridized orbitals to produce three new hybrid orbitals.
The orbitals that are combined are enclosed in brackets.

The new sp² orbitals lie in the x-y plane because they were constructed from 2px and 2py. The leftover, nonhybridized 2pz orbital (shown below in green) is perpendicular to the sp² orbital plane, because 2pz is perpendicular to 2px and 2py. Visualize the geometry of these orbitals by using your model kit (as shown below). In BH₃, each boron sp² orbital overlaps a hydrogen 1s orbital to make a B–H bond.

The three sp² orbitals (shown in blue) of trigonal planar boron each combine with a hydrogen s orbital to form three B–H bonds. The 2pz orbital (shown in green) is left over.

In general, an atom with three attachments uses sp² hybridization to achieve a trigonal planar geometry. This leaves a 2p orbital, which is perpendicular to the plane of the three sp² orbitals. When two or more sp² atoms are adjacent, their parallel 2p orbitals can form a pi bond. A pi bond is a result of hybridization (due to overlap of leftover 2p orbitals), not a cause of hybridization.
Constructing Hybrid Orbitals: Linear Geometry

To demonstrate the process for linear geometry, let's explore the hybrid orbitals in acetylene, H–C≡C–H. Each carbon has just two attachments (a hydrogen atom and another carbon atom), so the preferred bond angle is 180°. We could accommodate this without hybridization by using both lobes of one 2p orbital (such as 2px) to form both bonds, but other rules (which we won't go into here) prevent this. So we need a set of hybrid orbitals to make two new bonds with 180° H–C–C bond angles. Two hybrid orbitals (called sp orbitals) are constructed from two nonhybridized orbitals:

\[ [2s + 2p_x] + 2p_y + 2p_z \rightarrow sp + sp + 2p_y + 2p_z \]

Mix two nonhybridized orbitals to produce two new hybrid orbitals. The orbitals that are combined are enclosed in brackets.

As before, it does not matter which 2p orbital we mix. In this case we used 2px, so the unused 2py and 2pz orbitals lie in the y-z plane, perpendicular to the axis of our sp orbitals. (If we mixed 2s with 2pz, the unused 2px and 2py orbitals lie in the x-y plane.) The C–H σ bond comes from overlap of a carbon sp orbital with a hydrogen 1s orbital. The σ bond portion of the carbon-carbon triple bond comes from overlap of a pair of sp orbitals, one from each carbon. The two π bonds of the triple bond are formed by overlap of a pair of 2py orbitals (one on each carbon) to form one π bond, and a pair of 2pz orbitals (also one on each carbon) to form the second π bond (which is perpendicular to the first).

\[ \text{2} \times \text{sp} + \text{2} \times \text{hydrogen 1s} \rightarrow \text{C–H σ bond (pink)} \]

A carbon sp orbital (shown in blue) overlaps with a hydrogen 1s orbital to form a C–H σ bond (pink). The carbon-carbon σ bond (yellow) is formed by overlap of one sp orbital on each carbon atom. The 2py orbitals (green) overlap to form one π bond (green tape; perpendicular to the plane of your computer screen), and the 2pz orbitals (green) overlap to form another π bond (orange tape; parallel to the plane of your computer screen), perpendicular to the first.

In general, an atom with just two attachments adopts linear geometry, and uses sp orbitals to form its sigma bonds. The two remaining, perpendicular p orbitals are available to form π bonds with other adjacent, parallel p orbitals.
Choosing Appropriate Hybridization: The Three Questions

It is a common misconception that only the number of attachments to that atom controls hybridization of an atom. Instead, hybridization is controlled by what gives the molecule the lowest energy. This lowest energy includes not only a minimization of electron repulsion, but also accommodates electron delocalization by resonance, conjugation, and aromaticity. Resonance, conjugation, and aromaticity all depend on overlap of adjacent $p$ orbitals. As it turns out, the hybridization requirements for resonance, conjugation, and aromaticity usually outweigh the hybridization requirements for electron repulsion.

Therefore when selecting the appropriate hybridization for an atom, first ask, "Does the molecular structure show the atom in question as part of pi bond?" (Recall that a pi bond is formed by overlap of $p$ orbitals on adjacent atoms.) If the answer is yes, then the atom in question must have a $p$ orbital, and therefore must have a hybridization that includes a $p$ orbital (either $sp^2$ or $sp$).

For example, each carbon atom of pyrrole (structure shown below) must have a $p$ orbital because each is part of a carbon-carbon double bond.

![Pyrrole molecule](image)

The alkyne carbons of propyne are each part of a carbon-carbon triple bond, so each of these carbons has a $p$ orbital. The methyl group carbon is not part of a pi bond, so we must ask other questions in order to correctly assign its hybridization.

If the atom in question is not part of a pi bond then next we ask, "would the molecule possibly gain more resonance, conjugation, or aromaticity if the atom in question had a $p$ orbital?" In other words, is there a $p$ orbital on at least one adjacent atom, allowing the formation of a pi bond, resonance, conjugation, or aromaticity? When the answer is yes, then assign a hybridization that has a $p$ orbital ($sp^2$, or less commonly, $sp$). When the answer is no, then you need only consider geometry when assigning hybridization. The following examples illustrate this concept.

![Hybridization examples](image)

Remember that a carbon or nitrogen atom with four covalent bonds (such as we find in $CH_4$ or $NH_4^+$) is $sp^3$ hybridized, and therefore lacks a $p$ orbital.

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In pyrrolidine, the carbons next to the nitrogen atom are \( sp^3 \) (they lack a \( p \) orbital). Even if the nitrogen had a \( p \) orbital there would be no resonance, conjugation, or aromaticity. The number of attachments is the only factor that dictates nitrogen's hybridization, which is \( sp^3 \).

In pyrrole, both carbons adjacent to the nitrogen atom are \( sp^2 \). We know this because these carbons have a pi bond. Therefore the nitrogen atom adopts a hybridization with a \( p \) orbital (it is \( sp^2 \)) so that nitrogen's \( p \) orbital can overlap with the adjacent carbon \( p \) orbitals. In this case the overlap allows for more resonance and conjugation than the molecule would have if the nitrogen did not have a \( p \) orbital. In addition, it completes the closed \( p \) orbital loop required for aromaticity.

To summarize: When accessing hybridization we ask three questions, in the following order:

1. Is the atom part of a pi bond?
2. Are there one or more adjacent \( p \) orbitals?
3. What geometry best accommodates the number of attachments?

**Student Exercises**

**Exercise #1:** What is the hybridization of the nitrogen atom in ammonia (\( \text{NH}_3 \))?

**Answer:** The atoms bonded to ammonia's nitrogen atom do not have \( p \) orbitals (they are hydrogen atoms), so the molecule would not gain increased resonance, conjugation, or aromaticity of the nitrogen atom has a \( p \) orbital. Therefore we assign nitrogen's hybridization based only on the number of attachments. The nitrogen has four attachments (three hydrogen atoms and one lone pair) so the nitrogen is \( sp^3 \).

**Exercise #2:** What is the hybrization of the nitrogen atom of an amide?

**Answer:** An amide nitrogen is adjacent to the carbonyl pi bond, so the molecule will gain increased resonance and conjugation when the nitrogen has a \( p \) orbital. Therefore we assign \( sp^2 \) hybridization to this nitrogen. The three nitrogen \( sp^2 \) orbitals are used for \( \sigma \) bonds, and the nonhybridized \( p \) orbital overlaps with the carbonyl pi bond.

**Summary**

In general, hybrid orbitals are used when nonhybridized atomic orbitals do not give the correct bond angles or when the presence of a \( p \) orbital provides additional
resonance, conjugation, or aromaticity. When an atom has tetrahedral geometry it uses $sp^3$ hybridization. For trigonal planar geometry $sp^2$ hybrid orbitals are used. When the geometry is linear, $sp$ hybrid orbitals are involved. When deciding hybridization, first we ask if the molecule in question would benefit (more resonance, conjugation, or aromaticity) if the atom in question has a $p$ orbital If the answer is yes, assign a hybridization that has a $p$ orbital ($sp^2$ or $sp$). If the answer is no, assign hybridization based only on the number of attachments to the atom in question. With only a very few, very rare exceptions, all carbons, oxygens, and nitrogens that you will encounter in organic chemistry use hybrid orbitals.