The Hybridization Model of Atoms in Molecules

An important question facing chemists about 80 years ago, was, “How does one go from recently invented atomic orbitals to rationalizing the three common shapes continually found in organic chemistry and biochemistry (tetrahedral, trigonal planar and linear)?” Linus Pauling, a two time Nobel prize winner (for chemistry and peace), was the chemist who figured out how to make the mathematics of quantum mechanics into qualitative pictures that organic chemists could understand in the 1930s. His approach was so simple and so good that we are still using it today, even though there are more modern alternative ways of explaining organic shapes. Thank you Linus!

The following molecules provide examples of all three basic shapes found in organic chemistry. In these drawings a simple line indicates a bond in the plane of the paper, a wedged line indicates a bond coming out in front of the page and a dashed line indicates a bond projecting behind the page. You will have to become at least a mediocre artist to survive in organic chemistry.

- **Ethane**: Tetrahedral carbon atoms
  - HCH bond angles $\approx 109^\circ$
  - HCC bond angles $\approx 109^\circ$

- **Ethene**: Trigonal planar carbon atoms
  - HCH bond angles $\approx 120^\circ$ ($116^\circ$)
  - CCH bond angles $\approx 120^\circ$ ($122^\circ$)

- **Ethyne**: Linear carbon atoms
  - HCC bond angles $= 180^\circ$

- **Allene**: Trigonal planar carbon atoms at the ends and a linear carbon atom in the middle
  - HCC$_a$H bond angles $\approx 120^\circ$
  - HCC$_b$ bond angles $\approx 120^\circ$
  - C$_a$C$_b$C$_a$ bond angles $= 180^\circ$

Our current task is to understand hybridization. Even though you probably already studied hybridization, this topic is way too important to assume you know it from a previous course. Hybrids are new creations, resulting from mixtures of more than one thing. Our mixtures will be simple combinations of the valence electrons in the 2s and 2p orbitals on a single carbon atom. Though not exactly applicable in the same way for nitrogen, oxygen and the halogens, this model will work fine for our purposes in beginning organic chemistry. We will mix these orbitals three ways to generate the three common shapes of organic chemistry: linear (2s+2p), trigonal planar (2s+2p+2p) and tetrahedral (2s+2p+2p+2p).

We will first show how the three shapes can be generated from the atomic orbitals, and then we will survey a number of organic structures, using both two-dimensional and three dimensional drawings to give you abundant practice in using these shapes. You should be able to easily manipulate these shapes, using only your imagination and, perhaps, pencil and paper, if a structure is a little more complicated. If you have molecular models, now is a good time to get them out and assemble them whenever you are having a problem visualizing or drawing a structure. Your hands and your eyes will train your mind to see and draw what you are trying to understand and explain.

Organic chemistry and biochemistry are three dimensional subjects. Just like you don’t look at every letter in a word while you are reading, you can’t afford to struggle with the shape of every atom while examining a structure. If you are struggling to comprehend “shapes”, you will never be able to understand more complicated concepts such as conformations, stereochemistry or resonance as stand alone topics, or as tools for understanding reaction mechanisms. You have to practice (correct your errors), practice (correct your errors), practice (correct your errors) until this skill is second nature, and the pictures and terminology are instantly comprehended when you see a structure…and you have to do it.
quickly, because there’s a lot more material still to be covered. However, anyone reading these words can do this – and that includes you!

**Carbon as our first example of hybridization**

1. **sp hybridization** – carbon and other atoms of organic chemistry

Our first example of hybridization is the easiest and merely mixes a 2s and a 2p atomic orbital to form two sp hybrid orbitals. Remember that when we mix atomic orbitals together, we create the same number of new “mixture” orbitals. This is true for molecular orbitals on multiple atoms, as shown just above (σ, σ*, π and π*), and for hybrid orbitals on a single atom, as shown below (sp, sp² and sp³). We might expect that our newly created hybrid orbitals will have features of the orbitals from which they are created…and that’s true. The 2s orbital has no spatially distinct features, other than it fills up all three dimensions in a spherical way. A 2p orbital, on the other hand, is very directional. Its two oppositely phased lobes lie along a single axis, in a linear manner. Newly created sp hybrid orbitals will also lay along a straight line in a linear fashion, with oppositely phased lobes, because of the 2p orbital’s contribution. The two new sp hybrid orbitals point in opposite directions, having 180° bond angles about the sp hybridized atom.

The scheme below shows a hypothetical process to change an isolated “atomic” carbon atom into an sp hybridized carbon atom having four unpaired electrons, ready for bonding. The vertical scale in the diagram indicates potential energy changes as electrons move farther from the nucleus. Unpairing the 2s electrons allows carbon to make two additional bonds and acquire the neon Noble gas configuration by sharing with four other electrons. There is an energy cost to promote one of the 2s electrons to a 2p orbital, but this is partially compensated by decreased electron/electron repulsion when one of the paired electrons moves to an empty orbital. The really big advantage, however, is that two additional highly directional sigma bonds can form, each lowering the energy of the carbon atom by a considerable amount (lower potential energy is more stable). The combination of all the energy changes is quite favorable for carbon atoms, whether sp, sp² or sp³ hybridized. It’s important that you understand the qualitative ideas presented here with two orbitals (2s + 2p), because we are going to do it all over again with three orbitals (2s + 2p + 2p = three sp² hybrid orbitals) and four orbitals (2s + 2p + 2p + 2p = four sp³ hybrid orbitals).

2p's

2s

isolated carbon atom (not typical in our world)

promote a 2s electron to a 2p orbital

mix (2s and 2p), two ways (2s + 2p) and (2s - 2p) to create two sp hybrid orbitals

Overall, this would be a favorable trade.

- cost = promotion energy ≈ 100 kcal/mole
- gain = electron/electron repulsion in s orbital is removed ≈ 20-40 kcal/mole
- gain = two additional bonds are possible ≈ 150-200 kcal/mole
- gain = more directional orbitals form, that have better overlap of electron density between the bonding atoms, thus forming stronger bonds
The energy diagram shows that 2s electrons are held more tightly than 2p electrons (because they are closer to the nucleus, on average). Because sp electrons have 50% s orbital contribution, they are also held more tightly than 2p electrons [2s (100% s) > sp (50% s) > \( \text{sp}^2 \) (33% s) > \( \text{sp}^3 \) (25% s) > 2p (0% s)]. The greater the percent 2s contribution in a hybrid orbital, the more tightly the electrons are held by the atom. In a sense, this is a property similar to electronegativity, except that changes occur within the same kind of atom, based on hybridization, instead of in different types of atoms based on \( Z_{\text{effective}} \) or distance from the nucleus. This idea will be developed more fully in our acid/base topic.

Creating the hybrid orbitals

We can show the orbital mixing to create sp hybrid orbitals pictorially by using images of 2s and 2p orbitals. We simplistically represent the mathematics of the mixing by showing addition of the two orbitals and subtraction of the two orbitals. This is close to what happens, but not exactly correct. It does serve our purpose of symbolically changing the phase of the 2p orbital in the subtraction, generating the second sp hybrid orbital pointing 180° in the opposite direction from the first sp hybrid orbital. Phase is important here and adds constructively when it is the same (bonding) and destructively when it is opposite (antibonding). This will produce a larger lobe on the bonding side of the sp hybrid orbital (more electron density to hold the atoms together) and a smaller lobe on the antibonding side of the sp orbital (less electron density). Greater electron density between the bonded atoms will produce a stronger bond.

The 2s and 2p orbitals are artificially separated in the first part of the scheme for easier viewing. Even though the orbitals are drawn separately, remember that the center of the carbon atom is at the middle of the 2s orbital and at the node of all of the hybrid and p orbitals.

The Complete Picture of an sp Hybridized Carbon Atom
An isolated sp hybridized carbon atom for viewing. A bonded carbon atom would need orbital overlap for each orbital present, sp<sub>a</sub>, sp<sub>b</sub>, 2p<sub>z</sub> and 2p<sub>x</sub>.

This represents the sp<sub>b</sub> hybrid orbital. The small, opposite phase lobe on the backside has been left off to simplify the picture.

This represents the sp<sub>a</sub> hybrid orbital. The small, opposite phase lobe on the backside has been left off to simplify the picture.

Carbon has one electron available for each orbital to share with bonding partners.

There remain two 2p orbitals which are perpendicular to the two sp hybrid orbitals and to each other. Each 2p orbital extends along its entire axis with opposite phase in each lobe.

Two sp carbon atoms bonded in a molecule of ethyne (…its common name is acetylene)

The simplest possible way to place our sp hybridized carbon into a neutral molecule is to bring another sp hybridized carbon up to bond with three of its atomic orbitals: one sp hybrid sigma bond, along the bonding axis of the two carbon atoms and two pi bonds. One of the pi bonds will lie above and below the sigma bonded carbon atoms in the plain of the page. The other pi bond will lie in front and in back of the carbon atoms, perpendicular to the plane of the page. On the other side of each carbon atom, 180º away from the other carbon atom, we can attach a simple hydrogen atom, using its 1s atomic orbital to overlap in a sigma bond along the bonding axis (a first bond is always sigma bond).

Ethyne has five total bonds: three sigma bonds and two pi bonds.

The shape of each sp carbon atom is linear and allows the electrons in the σ bonds and the atoms they are bonded to, to be as far apart in space as possible, minimizing the electron/electron repulsion. The small backside lobe of each sp orbital has been omitted for clarity, since the bond on the side of the large lobe has the bulk of the electron density and determines where the bonded atom will be.

In organic chemistry sigma bonds (σ) are always the first bond between two atoms, resulting from overlap along the bonding axis (of hybrid orbitals), while pi bonds (π) are second and third bonds resulting from the overlap of p orbitals, above and below (or in front and back of) the bonding axis. (I’m repeating myself on purpose.)
Our molecule of ethyne now looks as shown, including all of the lobes of the orbitals (except for the small backside lobes of the hybrid orbitals). However, it looks a little too congested with details to see everything clearly, and it’s way too much work to draw routinely. If we tried to add other non-hydrogen atoms, it would get too messy as well.

We rarely draw our 3D structures like this, preferring simpler ways of representing the details. In my early years of teaching, my preference was to draw single lines for the sigma bonds (simple lines in the plain of the paper, wedged lines in front of the paper and dashed lines in back of the paper), and to include the lobes of the p orbitals with a line connecting the lobes on both sides to show the nature of the pi bonding. However, over the years the students have convinced me that it is easier for them to see the details if the p orbitals are also drawn as straight lines (same 3D conventions: simple, wedged and dashed lines). Connecting lines are still drawn on both sides between overlapping 2p orbitals to show the pi bonding (these two lines represent only one bond). I will draw p orbitals as straight lines, on both sides of an atom, because the students are right; it is easier to visualize the three dimensional shapes this way (the third drawing below). Of course, you should draw 3D structures the way your instructor wants them drawn.

I explicitly include two dots for the pi electrons, because I want you to think of those electrons the way you think of lone pair electrons (remember pushing curved arrows to move electrons in the acid/base reactions?). Much of the chemistry of pi bond compounds (alkenes, alkynes and aromatics) begins with these pi electrons. Most of our arrow pushing mechanisms, for these classes of compounds, will begin with a curved arrow moving from the pi electrons, just as we begin much of the chemistry of heteroatoms (nitrogen, oxygen and halogens) with an arrow moving from their lone pair electrons.
Alternative ways of drawing 3D structures that are simpler than the above drawing at showing the 3D details.

3D ethyne drawn with p orbitals as lobes (p orbitals with phase shown in the left structure and without phase in the right structure.

3D ethyne drawn with p orbitals as lines and pi electrons explicitly drawn in, in a manner similar to showing lone pair electrons. In this book I will usually draw pi bonds this way in 3D structures.

We will practice drawing many 3D structures to train our minds to imagine in three dimensions and to help us understand a topic under discussion, such as parallel p orbitals in resonance, or understanding a mechanism we are learning for the first time. However, even our simplified 3D structures are too complicated for drawing structures in typical discussions of organic molecules. Most of the time our organic structures will be condensed to very simple representations that are quick to draw and easy to see at a glance. Sometimes we will include letters to symbolically represent the atoms and sometimes we will merely have lines on the page, almost to the point where the structures become a foreign language writing system. Some additional ways of drawing ethyne are shown below. Each subsequent representation puts a greater burden on you to interpret its meaning. Your advantage is that every non-hydrogen atom you view (carbon, nitrogen, oxygen and halogens) has to be one of the three shapes we are developing in this topic, so your choices are pretty limited (sp, sp² or sp³).
Each line represents a bond. While the three simple lines of the triple bond appear equivalent, we know that the first bond formed is a sigma bond of overlapping sp hybrid orbitals. The second and third bonds are overlapping 2p orbitals, above and below and in front and in back. Since the C-H bonds are single bonds, we know that they are sigma bonds too, using hybrid orbitals. This is how you will determine the hybridization of any atom in a structure. Knowing how many pi bonds are present will tell you how many 2p orbitals are being used in those pi bonds. The remaining s and 2p orbitals must be mixed together in hybrid orbitals (in this example, only an s and a 2p remain to form two sp hybrid orbitals).

The connections of the atoms are implied by the linear way the formula is drawn. You have to fill in the details about the number of bonds and where they are from your understanding of each atom's bonding patterns. A C-H bond can only be a single bond so there must be three bonds between the carbon atoms to total carbon's normal number of four bonds. This means, of course, that the second and third bonds are pi bonds, using 2p orbitals, leaving an s and p orbitals to mix, forming two sp hybrid orbitals.

A bond line formula only shows lines connecting the carbon atoms and leaves off the hydrogen atoms. Every end of a line is a carbon (two in this drawing) and every bend in a line is a carbon (none in this drawing). You have to figure out how many hydrogen atoms are present by subtracting the number of lines shown (bonds to non-hydrogen atoms) from four, the total number of bonds of a neutral carbon (4 - 3 = 1H in this drawing). The shape of the carbon atoms must be linear, because we know the hybridization is sp.

This is the ultimate in condensing a structure. Merely writing the atoms that are present and how many of them there are provides no details about the connectivity of the atoms. It only works for extremely simple molecules that have only one way that they can be drawn. Ethyne is an example of such molecule. Other formulas may have several, hundreds, thousands, millions, or more ways for drawing structures. Formulas written in this manner are usually not very helpful.

<table>
<thead>
<tr>
<th>carbon atom shape</th>
<th>linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybridization</td>
<td>sp</td>
</tr>
<tr>
<td>bond angles about sp carbon</td>
<td>180°</td>
</tr>
<tr>
<td>number of sigma bonds</td>
<td>2</td>
</tr>
<tr>
<td>number of pi bonds</td>
<td>2</td>
</tr>
</tbody>
</table>

All of the details in this group go together. If you have any one of them, you should be able to fill in the remaining details.
Molecular Orbitals of Ethyne

We made two very simple molecular orbitals using hydrogen atoms (σ and σ*) and p orbitals (π and π*) above. The process works pretty much the same when we are making bonds using carbon and hydrogen atoms (…and nitrogen, oxygen and halogen atoms)? Let’s quickly develop the molecular orbitals for ethyne. First we need to form the sigma and sigma-star MOs between the two carbon atoms using their sp hybrid orbitals (σ_{cc} and σ^{*}_{cc}). The vertical scale represents relative potential energy among the various orbitals. Lower is more stable.

\[ \sigma_{cc} = sp_{a} + sp_{b} = bonding \text{ MO} \]
\[ \sigma_{cc}^{*} = sp_{a} - sp_{b} = antibonding \text{ MO} \]

Next we need to form sigma and sigma-star MOs between each carbon atom and a hydrogen atom using each carbon atom’s other sp hybrid orbital and a hydrogen atom’s 1s atomic orbital (σ_{CH} and σ^{*}_{CH}).

\[ \sigma_{CH} = sp + 1s = \text{ bonding MO} \]
\[ \sigma_{CH}^{*} = sp - 1s = \text{ antibonding MO} \]

Two C-H sigma/sigma-star MOs form. This scheme shows one of them. The other would look just like it.

Finally we need to form two pi and pi-star MOs between the carbon atoms using carbon 2p orbitals (π_{cc} and π^{*}_{cc}). We’ll just show one MO diagram and you can imagine doing it a second time. This is going to look almost exactly like our example of a pi bond presented earlier.
If we put all of the molecular orbitals of ethyne together, in a single energy diagram, it would look as follows. The π MOs determine the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). The 2p orbital overlap is the least bonding and the least antibonding. The HOMO electrons are the easiest place to donate electrons from (least tightly held) and the LUMO orbital is the best place to accept electrons, if accepted into the molecular orbitals (lowest potential energy empty orbital = most stable of the empty orbitals). The π molecular orbitals determine much of the chemistry of alkynes.

This represents 1/3 of the bonding pictures you need to understand. I hope it wasn’t too painful. We need to extend this approach two more times for sp² and sp³ hybridized atoms.
2. **sp\(^2\)** hybridization

Our second hybridization example mixes the 2s orbital with two 2p atomic orbitals, creating three new sp\(^2\) hybrid orbitals. One 2p orbital remains unchanged, and it will help form a pi bond. The relative energy scheme showing electron promotion and orbital mixing is almost identical to the sp hybrid example above. The major difference is the mixing of a second 2p orbital, which alters our hybrid creations from linear to planar. As above, promoting a 2s electron allows for four bonds to form and allows the carbon atom to acquire the neon Noble gas configuration. As mentioned in the example of sp hybridization, electrons in sp\(^2\) orbitals are held more tightly than electrons in 2p orbitals, but less tightly than electrons in 2s orbitals. Among atoms of the same type, an atom’s relative electronegativity is dependent on the amount of 2s character [2s (100% s) > sp (50% s) > sp\(^2\) (33% s) > sp\(^3\) (25% s) > p (0% s)].

**Diagram:**
- Initial 2s orbital
- Promotion of 2s electron to a 2p orbital
- Mixing of 2s and 2p orbitals
- Formation of three sp\(^2\) hybrid orbitals
- One p orbital remains for a pi bond

**Cost:**
- Promotion energy \(\approx 100\) kcal/mole

**Gain:**
- Electron/electron repulsion in s orbital is removed \(\approx 20-40\) kcal/mole
- Two additional bonds are possible \(\approx 150-200\) kcal/mole
- More directional orbitals form, with better overlap of electron density between bonding atoms, thus forming stronger bonds

Creating the sp\(^2\) hybrid orbitals

Because two 2p orbitals lie in a plane, the three sp\(^2\) hybrid creations will also lie in a plane. The picture below shows one possible example of orbital mixing. Two additional combinations are necessary (not shown). Dividing a plane (same as a circle = 360°) into three equal divisions forms 120° bond angles between the orbitals, where the sigma bonds will be. This allows the electrons in the sigma bonds to be as far apart in space as possible and minimizes the electron/electron repulsion. The descriptive term for this shape is trigonal planar. The hybrid orbitals will form sigma bonds and the p orbital will usually form a pi bond.
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**Sp² Hybridization**

Mathematically, mix three ways

One example of mixing 2s+2p+2p

Similar phase mixes constructively in the right front quadrant

The "mixing" process symbolized here is repeated two additional ways, creating three sp² hybrid orbitals.

All three sp² hybrid orbitals lie in a plane and divide a circle into three equal pie wedges of 120°. The descriptive term for the shape is trigonal planar.

This picture shows the sp² hybrid orbitals without their small backside lobes and no p orbital is shown. These hybrid orbitals will form sigma bonds.

**The Complete Picture of an sp² Hybridized Carbon Atom**

An isolated sp² hybridized carbon atom for viewing. A bonded carbon atom would need orbital overlap for each orbital present, sp²a, sp²b, sp²c and 2pz.

These represent sp²a hybrid orbitals. The small, opposite phase lobe on the backside has been left off to simplify the picture.

There remains one 2p orbital perpendicular to the three sp² hybrid orbitals. The 2p orbital extends along the entire axis with opposite phase in each lobe.

There are more convenient alternative methods of drawing a three dimensional sp² carbon atom, using simple lines, dashed lines and wedged lines. The first drawing below shows the lobes of the 2p orbital with its relative phases. The second drawing shows the lobes, but not the phases. The third drawing uses only simple lines instead of lobes for the p orbitals. It is quicker to draw, obscures less
background, yet still shows the directionality of the 2p orbitals, which is an important feature of resonance.

Two \( sp^2 \) carbon atoms bonded in a molecule of ethene (…its common name is ethylene)

As in our sp example, the simplest possible way to place our \( sp^2 \) carbon atom into a neutral molecule is to bring another \( sp^2 \) carbon atom up to overlap with two of its atomic orbitals: a sigma bond using an \( sp^2 \) hybrid orbital, along the bonding axis of the atoms and a pi bond, using the 2p orbital. The pi bond lies above and below the carbon-carbon sigma bond, in the plane of the paper, the way we have drawn it. Four additional sigma bonds can form around the outside of the two carbons using the remaining \( sp^2 \) hybrid orbitals. The easiest bonding arrangement is to bond four hydrogen atoms, using their 1s atomic orbitals. As with ethyne, this way of drawing a three dimensional structure is too cumbersome for routine use.

We will draw our 3D structures using more simplified representations. Each \( sp^2 \) carbon atom has trigonal planar geometry, with 120° bond angles. Our 3D representations include simple lines to indicate bonds in the plane of the page, wedges to indicate bonds extending in front of the page and dashed lines to indicate bonds extending behind the page. Possible 3D drawings are shown below.
2p orbitals drawn as lobes, with phase indicated

2p orbital drawn as lobes, without phase indicated

2p orbitals drawn as lines, no phase indicated. This will be our method of drawing 3D structures

| carbon atom shape = trigonal planar | All of the details in this group go together. If you have any one of them, you should be able to fill in the remaining details. |
| hybridization = sp² | |
| bond angles about sp carbon = 120° | |
| number of sigma bonds = 3 | |
| number of pi bonds = 1 | |

As with ethyne, some additional ways of drawing ethene are shown below. Each subsequent representation puts a greater burden on you to interpret its meaning. Your advantage is that every non-hydrogen atom you view (carbon, nitrogen, oxygen and halogens) has to be one of the three shapes we are developing in this topic, so your choices are pretty limited (sp, sp² or sp³).

Each line represents a bond. While the two simple lines of the double bond appear equivalent, we know that the first bond formed is a sigma bond of overlapping sp² hybrid orbitals. This means, of course, that the second bond is a pi bond, using a 2p orbital, leaving an s and two 2p orbitals to mix, forming three sp² hybrid orbitals.

H₂CCH₂

The connections of the atoms are implied by the linear way the formula is drawn. You have to fill in the details about the number of bonds and where they are from your understanding of each atom's bonding patterns. A CH₂ forms two single bonds, so there must be two bonds between the carbon atoms for carbon's normal number of four bonds. The second bond has overlapping 2p orbitals, above and below the bonding axis and means the carbon must be sp² hybridized.

H₂CCH₂ or CH₂CH₂

A bond line formula only shows lines connecting the carbon atoms and leaves off the hydrogen atoms. Every end of a line is a carbon (two in this drawing) and every bend in a line is a carbon (none in this drawing). You have to figure out how many hydrogens are present by subtracting the number of lines shown (bonds to non-hydrogen atoms) from four (the total number of bonds of a neutral carbon (4 - 2 = 2H in this drawing).

C₂H₄

This is the ultimate in condensing a structure. Merely writing the atoms that are present and how many of them there are provides no details about the connectivity of the atoms. It only works for extremely simple molecules that have only one way that they can be drawn. Ethene is an example of such molecule.

We won’t build all of the molecular orbitals for ethene from scratch since the process is essentially the same as that used for ethyne. However, we will provide a complete molecular orbital energy diagram, showing all of the sigma and sigma-star MOs and the pi and pi-star MOs. There are now five sigma bonds (four C-H and one C-C) and one pi bond (C=C). As is usually the case when a pi bond is present, the pi / pi-star orbitals form the important HOMO / LUMO molecular orbitals. The 2p orbital overlap is the least bonding (HOMO) and the least antibonding (LUMO). The HOMO electrons are the easiest
place to donate electrons from (it holds the highest potential energy electron pair = most reactive of the full orbitals), and the LUMO orbital is the best place to accept electrons into (it is the lowest potential energy empty orbital = least unstable of the empty orbitals). Most of the chemistry of alkenes uses these orbitals.

\[
\text{MO diagram for ethene}
\]

\[
\begin{align*}
\text{higher, less stable} & \quad \text{LUMOs} \\
\text{potential energy} & \quad \text{energy of orbitals on isolated atoms} \\
\text{lower, more stable} & \quad \text{HOMOs} \\
\end{align*}
\]

\[
\text{bond order between the carbon atoms} = \frac{(4) - (0)}{2} = 2 \text{ bonds}
\]

This completes the second of our three bonding pictures you need to understand. We need to extend this approach one more time with sp\(^3\) hybridized atoms.

### 3. sp\(^3\) hybridization

Our final example of hybridization mixes the 2s orbital with all three 2p atomic orbitals, creating four new, equivalent sp\(^3\) hybrid orbitals. The three 2p orbitals fill all three dimensions and the four sp\(^3\) hybrid orbitals created from them also fill all three dimensions. There are no \(\pi\) bonds, since no 2p orbitals remain to make them. All of the bonds are sigma bonds, because all of the bonding orbitals are hybrid orbitals. Your intuition about the bond angles probably fails you in this example (it fails me), so we’ll just accept that the bond angle between sp\(^3\) orbitals is approximately 109° (…and if you are really good at trigonometry, you can figure the exact bond angle out for yourself). We won’t worry about the exact bond angle (109° 28’ = 109.5°) since there is a considerable amount of variation about the 109° value in different molecules. The atomic shape of sp\(^3\) carbon atoms is described as tetrahedral, but not because of the shape about the carbon atom, as was the case in our previous two examples. The descriptive term for the shape of an sp\(^3\) atom is based on a geometric figure drawn by connecting the ends of the sigma bonds. A four sided figure of equilateral triangles is generated, called a tetrahedron. The energy scheme below is a hypothetical process to get sp\(^3\) hybridized carbon from atomic carbon.

As mentioned in the examples of sp and sp\(^2\) hybridization, electrons in sp\(^3\) orbitals are held more tightly than electrons in 2p orbitals, but less tightly than electrons in 2s orbitals. Among atoms of the same type, an atom’s relative electronegativity is dependent on the amount of s character \([2s (100\% s) > sp (50\% s) > sp^2 (33\% s) > sp^3 (25\% s) > 2p (0\% s)]\). The relative electronegativity of hybridized carbon increases with increasing percent 2s contribution: sp > sp\(^2\) > sp\(^3\).
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Creating the $sp^3$ hybrid orbitals

One example of a picture of orbital mixing is provided. Three additional combinations are used to create the other three $sp^3$ hybrid orbitals, but it is more difficult to show this with our simplistic representations than it was for $sp$ hybridization. The bottom line is that four atomic orbitals are mixed four ways to generate four equivalent $sp^3$ hybrid orbitals. An example of all four $sp^3$ orbitals is shown using our simple 3D conventions: a simple line indicates a bond in the plane of the page, a wedged line indicates a bond extending in front of the page and a dashed line indicates a bond behind the page. A tetrahedral figure is also drawn to show where the descriptive geometric term comes from.

Mathematically, mix four ways

2s, 2px, 2py, 2pz

One example is shown of mixing 2s+2p+2p+2p to form an $sp^3$ hybrid orbital.

Similar phases interact constructively in the front, right, upper octant where the large lobe will be located.

The "mixing" process symbolized here is repeated three additional ways, creating four $sp^3$ hybrid orbitals.
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One sp³ carbon atom bonded in methane and two sp³ carbon atoms bonded in ethane

In both of our previous examples, we needed two carbons in order to form a pi bond, using the unhybridized 2p orbitals. Hydrogen atoms don’t have available p orbitals in the n = 1 shell and cannot form pi bonds. Since sp³ carbon atoms only make single bonds, this is our first example of hybridization where we can surround a carbon atom with only hydrogen atoms (four of them). This forms a molecule of methane, CH₄, one of the simplest organic molecules we will encounter. Notice there is only one type of bond now (σCH) and the HCH bond angles about the central carbon atom are 109° (plus a little bit that we ignore). This angle allows the electrons in the sigma bonds to be as far apart in space as possible, minimizing the electron/electron repulsion. The atomic shape is designated as tetrahedral. Since sp³ atoms fill all three dimensions, there is no choice but to use our 3D drawing conventions (simple lines, dashed lines and wedged lines).

All of the details in this group go together. If you have any one of them, you should be able to fill in the remaining details.

If we remove one of the hydrogen atoms of methane and replace it with the simplest possible carbon atom, CH₃, we would form molecular ethane. Ethane has two sp³ carbons connected by a single, sigma bond. The six hydrogen atoms in ethane occupy all three dimensions. The single bond between the two carbons allows rotation to occur and the three hydrogen atoms on one carbon atom can rotate past the three hydrogen atoms on the other carbon, like the spokes on a wheel. If you have models, why not build ethane and rotate the C-H bonds about the carbon-carbon axis to see how they move? The different shapes have slightly different potential energies, and this will be important to us in a later topic (conformational analysis).
As with ethyne and ethene, there are some additional ways of drawing ethane. Some of these are shown below. Each subsequent representation puts a greater burden on you to interpret its meaning. Your advantage is that every non-hydrogen atom you view (carbon, nitrogen, oxygen and halogens) has to be one of the three shapes we are developing in this topic, so your choices are pretty limited (sp, sp\(^2\) or sp\(^3\)).

Each line represents a bond. Since there are only single bonds, we know that they must be sigma bonds. There cannot be any pi bonds because there are no second or third bonds between the same two atoms. The 2s and all three 2p orbitals must all be mixed, meaning that the hybridization has to be sp\(^3\) and all of the terms that go along with sp\(^3\) hybridization.

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H\(_3\)CCH\(_3\)

or

CH\(_3\)CH\(_3\)

The connections of the atoms are implied by the linear way the formula is drawn. You have to fill in the details about the number of bonds and where they are located from your understanding of each atom's bonding patterns. A CH\(_3\) has three single bonds between carbon and hydrogen, so there can only be one additional bond between the carbon atoms to total carbon's normal number of four bonds. This means, of course, that there is no pi bond, using a 2p orbital, leaving the 2s and all three 2p orbitals to mix, forming four sp\(^3\) hybrid orbitals.

---

A bond line formula only shows lines connecting the carbon atoms and leaves off the hydrogen atoms. Every end of a line is a carbon (two in this drawing) and every bend in a line is a carbon (none in this drawing). You have to figure out how many hydrogens are present by subtracting the number of lines shown (bonds to non-hydrogen atoms) from four (the total number of bonds of a neutral carbon (4 - 1 = 3H on each carbon atom in this drawing).

---

C\(_2\)H\(_6\)

This is the ultimate in condensing a structure. Merely writing the atoms that are present and how many of them there are provides no details about the connectivity of the atoms. A structure can be generated only for extremely simple molecules that have only one way that they can be drawn. Ethane is an example of such a molecule.

---

As with ethene, we won’t build all of the molecular orbitals for ethane from scratch, but we will provide a qualitative molecular orbital energy diagram, showing all of the sigma and sigma-star MOs. There are no pi and pi-star MOs in ethane. There are now seven sigma bonds (six C-H and one C-C) and zero pi bonds. The important HOMO / LUMO orbitals have to be sigma and sigma-star MOs in this example (our designation of relative sigma energies is arbitrary). Because there are no pi / pi-star HOMO / LUMO molecular orbitals, ethane is much less reactive than ethyne and ethene.
Summary – Key features to determine hybridization of atoms in organic chemistry.

Use multiple bonds to determine the hybridization state of an atom. A second bond between two atoms is always made up of 2p orbitals, as part of a \( \pi \) bond, which leaves \( 2s + 2p + 2p \) to hybridize as \( sp^2 \). If a third bond is present between the same two atoms, or if a second \( \pi \) bond is present with a second atom, it also is made up of 2p orbitals, which leaves \( 2s + 2p \) to hybridize as \( sp \). If there are only single bonds, then all four atomic orbitals (\( 2s + 2p + 2p + 2p = sp^3 \)) must be mixed together. Essentially, the hybridization state is determined by subtracting any p orbitals of \( \pi \) bonds from the three 2p orbitals available for hybridization. Whatever is left over is mixed with the 2s to form hybrid orbitals. If you know the hybridization, then you know the bond angles, the shape and how many sigma and pi bonds are present. What you need now is lots of practice.
There is a second bond between the two carbon atoms. This must be a \( sp^2 \) bond and uses 2p orbitals. The hybridization must be \( sp^2 \) (\( 2s + 2p + 2p = sp^2 \)) and three atomic orbitals are mixed to form three \( sp^2 \) hybrid orbitals.

There is a second and a third bond between the same two atoms. There must be two pi bonds using two 2p orbitals. The hybridization must be \( sp \) (\( 2s + 2p = sp \)) and two atomic orbitals are mixed to form two \( sp \) hybrid orbitals.

There is a second bond with the atom on the left and again with the atom on the right. There must be two pi bonds using two 2p orbitals. The hybridization must be \( sp \) (\( 2s + 2p = sp \)) and two atomic orbitals are mixed to form two \( sp \) hybrid orbitals. The hybridization of the end carbons, is \( sp^2 \) (see the second example above). The planar shapes of the atoms of the two end carbons are twisted 90° relative to one another because the 2p orbitals on the middle carbon making the pi bonds with them are angled at 90° relative to one another.

We will be viewing and drawing many complicated structures in this book, as we work on problems and try to understand organic chemistry. To simplify this process, we will often use bond-line formulas. We have mentioned bond-line formulas, very briefly above, but now we will examine how they work using all of the features just discussed. The first structure drawn below shows all of the carbon atoms and hydrogen atoms. The second structure is a 2D Lewis structure. It takes some time to include such detail. Bond-line formulas allow us to more quickly draw such a structure without all of those atoms. The down side is that your organic knowledge has to be more sophisticated to interpret what they mean. Recall that every end of a line and every bend in a line is a carbon atom. We will also use the convention that a large “dot” in the structure is a carbon atom (see the structure below). Since hydrogen atoms are deliberately left out, for drawing convenience, you must determine the number of hydrogen atoms present in bond-line formulas by subtracting the number of bonds shown from four, the usual number of bonds on a neutral carbon atom.

Number of hydrogen atoms on a carbon = (4) – (number of bonds shown)
(you don’t see these)
See if your interpretation of the bond-line structure is the same as the more detailed structures provided. As an experiment, time yourself drawing this structure all three different ways, then multiply the difference in time by the number of structures you will draw during your organic career. I’m sure you’ll agree that it’s worth the effort to understand bond-line formulas.

Two structures showing all of the atoms. It's a lot of work to draw structures this way.

Same molecule using a bond-line structure showing only non-hydrogen bonds. A carbon atom is implied at every bend and every end of a line and every dot. This one is a lot easier and faster to draw.

<table>
<thead>
<tr>
<th>Carbon #</th>
<th>hybridization</th>
<th>bond angles</th>
<th>shape</th>
<th>number of hydrogen atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>sp</td>
<td>180°</td>
<td>linear</td>
<td>1</td>
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<tr>
<td>2</td>
<td>sp</td>
<td>180°</td>
<td>linear</td>
<td>0</td>
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<tr>
<td>3</td>
<td>sp^3</td>
<td>109°</td>
<td>tetrahedral</td>
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<td>sp^3</td>
<td>109°</td>
<td>tetrahedral</td>
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<td>5</td>
<td>sp^2</td>
<td>120°</td>
<td>trigonal planar</td>
<td>1</td>
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<tr>
<td>6</td>
<td>sp^2</td>
<td>120°</td>
<td>trigonal planar</td>
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<td>14</td>
<td>sp^3</td>
<td>109°</td>
<td>tetrahedral</td>
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</table>
Problem 12 - What is the hybridization of all carbon atoms in the structure below? What are the bond angles, shapes, number of sigma bonds, number of pi bonds and number's of attached hydrogen atoms? Bond line formulas are shorthand, symbolic representations of organic structures. Each bend represents a carbon, each end of a line represents a carbon and each dot represents a carbon. All carbon/carbon bonds are shown. The number of hydrogen atoms on a carbon is determined by the difference between four and the number of bonds shown.

<table>
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<tr>
<th>atom</th>
<th>hybridization</th>
<th>angles</th>
<th># H’s</th>
<th>shape</th>
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**Other Atoms in Organic Chemistry – nitrogen, oxygen and halogens**

Here is a perfect example of why you want to learn the logic and patterns of organic chemistry, and not use brute force memorization as a strategy. We still have a number of other elements to cover. How do these other atoms fit into the hybridization models developed above for carbon? Except for hydrogen, which only has 1s electrons and no hybrid orbitals, all of the other atoms are similar to carbon. There are a few minor differences mentioned earlier in this book. Nitrogen adds another proton for a $Z_{\text{eff}}$ of +5 and has five valence electrons. Oxygen also adds another proton for a $Z_{\text{eff}}$ of +6 and has six valence electrons (sulfur behaves similarly). Fluorine adds yet another proton for a $Z_{\text{eff}}$ of +7 and has seven valence electrons (Cl, Br, I are similar).

Fully bonded neutral atoms of carbon, nitrogen, oxygen and fluorine all have an octet of valence electrons. However, this is accomplished in different arrangements of bonds and lone pairs of electrons (nonbonded electron pairs). Carbon makes four bonds and has zero lone pairs, nitrogen makes three bonds and has one lone pair, oxygen makes two bonds and has two lone pairs and fluorine makes one bond and has three lone pairs. The increase in $Z_{\text{eff}}$ through this series makes each subsequent atom hold on more tightly to its valence electrons (higher electronegativity, F > O > N > C).

A lone pair of electrons can often be considered just like a sigma bond in determining the geometry about an atom. As such, it would occupy a hybrid orbital. However, when a lone pair is next to
a 2p orbital, either as part of a pi bond or an empty 2p orbital, the lone pair orbital changes its shape to that of a 2p orbital in order to spread out electron density and stabilize the structure by minimizing electron/electron repulsion and lowering its potential energy. As near as I can tell, this is one of the more difficult ideas to learn for beginning organic students.

In this book, resonance is a concept used to show how electron delocalization can occur. Resonance occurs in multiple parallel 2p orbitals, and it requires you to see and draw in two and three dimensions, so that you can recognize when parallel 2p orbitals are present. Parallel 2p orbitals allow delocalization of electron density through those parallel 2p orbitals. You also need to recognize formal charge (discussed below), and to use the concept of electronegativity to help evaluate the relative contributions of the various resonance structures. It is important that you are able to work with pi bonds and resonance structures, because they explain so much that happens in organic chemistry and biochemistry.

Even with all of these differences, nearly every single atomic shape that we study, will be one of the three hybridization states developed above for carbon. The following table shows almost every possibility of neutral atoms that you will see in organic chemistry. We will quickly add formal charge to our repertoire and find that all of the cation and anion possibilities also use one of our three different hybridizations. This is almost too good to be true – but it is!

### Valence Possibilities for Neutral Atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>sp&lt;sup&gt;3&lt;/sup&gt;</th>
<th>sp&lt;sup&gt;2&lt;/sup&gt;</th>
<th>sp</th>
<th># bonds</th>
<th># lone pairs</th>
<th>Z&lt;sub&gt;eff&lt;/sub&gt;</th>
<th>∆χ</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon</td>
<td>——C—-</td>
<td>——C=</td>
<td>——C≡</td>
<td>4</td>
<td>0</td>
<td>+4</td>
<td>2.5</td>
</tr>
<tr>
<td>nitrogen</td>
<td>——N:</td>
<td>——N=</td>
<td>: N≡</td>
<td>3</td>
<td>1</td>
<td>+5</td>
<td>3.0</td>
</tr>
<tr>
<td>oxygen</td>
<td>——O:</td>
<td>:O=</td>
<td>too many bonds</td>
<td>2</td>
<td>2</td>
<td>+6</td>
<td>3.5</td>
</tr>
<tr>
<td>fluorine</td>
<td>——F:</td>
<td>too many bonds</td>
<td>1</td>
<td>3</td>
<td>+7</td>
<td>4.0</td>
<td></td>
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<tr>
<td>hydrogen</td>
<td>——H (1s orbital)</td>
<td>too many bonds</td>
<td>1</td>
<td>0</td>
<td>+1</td>
<td>2.2</td>
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</table>

Problem 13 - What types of orbitals do the lone pair electrons occupy in each example above, according to our hybridization model? Hint: What is the hybridization of the atom? It has to use the same kind of hybrid orbital to hold the lone pair electrons…unless it is part of a resonant system.

Problem 14 – Can a nitrogen atom bond in the second sp pattern above for carbon (four bonds)? Can an oxygen atom bond in the first sp pattern above for carbon (three bonds)? How about the second sp pattern of carbon (four bonds)? Can a fluorine atom bond in the sp<sup>2</sup> pattern for carbon (two bonds)? Are any of these reasonable possibilities? Have you ever seen a structure with four bonds to a nitrogen atom or three bonds to an oxygen atom or two bonds to a fluorine atom? Would there be any necessary changes for the atoms in such arrangements? We’ll discuss the answers to these questions soon.
Our bond-line structures are changed, just a bit, when heteroatoms are present. A heteroatom is an atom different than carbon or hydrogen (for us heteroatoms will be nitrogen, oxygen, sulfur and the halogens). All heteroatoms are explicitly drawn in, as well as any hydrogen atoms attached to the heteroatoms.

Problem 15 - What is the hybridization of all nonhydrogen atoms in the structures below? What are the bond angles, shapes, number of sigma bonds, number of pi bonds and number of hydrogens not shown? How many lone pairs are on each atom and in what kind of orbital are they located? As with carbon, use the number of pi bonds to determine how many 2p orbitals are not mixed in the hybrid orbitals. Mix the remaining orbitals to determine the hybridization, which then answers the remaining questions.

a.
b.

<table>
<thead>
<tr>
<th>atom</th>
<th>hybridization</th>
<th>angles</th>
<th># H's</th>
<th>shape</th>
<th># lone pairs</th>
<th>lone pair orbital</th>
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Formal Charge

Formal charge calculations help us track valence electron credit in chemical structures. This system of rules allows us to calculate if an atom in a molecule, ion or free radical has a normal, an excess or a deficient allotment of electron density. Calculations can be applied to resonance structures, showing how charge is spread out over the structure, which in turn, can provide clues about how stable a substance might be or how it might react in a chemical reaction. Formal charge calculations can also be applied to reactants and products in chemical reactions, providing insight into how those reactions proceed, by showing where new bonds have formed and where old bonds have broken.

Formal charge calculations assume that any valence electrons in bonds are shared evenly between the bonded atoms, even if it’s an oxygen atom bonded to a hydrogen atom or a carbon atom. This means if there is a single bond, each atom gets credit for one of the electrons, if there is a double bond each atom gets credit for two of the electrons, and if there is a triple bond each atom gets credit for three of the electrons. Formal charge calculations also assume that atoms having lone pair of electrons gets full credit for those electrons.

An atom’s total share of valence electrons (bonded and lone pairs) is compared with the opposing positive charge from the $Z_{\text{effective}}$ of that atom. The formal charge on an atom is assigned by using the following equation.

$$\text{Formal Charge} = \left( \text{protons in the nucleus balancing an atom’s normal contribution to the valence electrons} \right) - \left( \text{electrons in lone pairs} \right) - \left( \frac{1}{2} \right) \left( \text{electrons in covalent bonds} \right)$$

This number never changes for an atom and represents positive charge, $Z_{\text{eff}}$.

Total valence electrons - This number varies depending on the bonding arrangement. It is negative because electrons are negative.

The first term in the equation is a positive number and represents $Z_{\text{effective}}$, the portion of the positive charge in the nucleus that balances an atom’s usual number of valence electrons. $Z_{\text{eff}}$ is always the same for a particular type of atom and is equal to an atom’s group number in the periodic table (B = 3A, C = 4A, N = 5A, O = 6A and F = 7A). The second term credits all of an atom’s lone pair electrons to its formal charge calculation. The third term assumes that electrons in bonds are shared evenly between atoms, as stated above, and multiples the total number of bonded electrons by $\frac{1}{2}$. The second and third terms are negative because they indicate the number of valence electrons credited to an atom. If an atom’s $Z_{\text{eff}}$ is balanced equally by an atom’s share of valence electrons, there is zero formal charge. If an atom has more electron credit than $Z_{\text{eff}}$, it will have an extra negative formal charge for each extra electron. If an atom has less electron credit than its $Z_{\text{eff}}$, it will have a positive formal charge for each deficient electron. The equation is easier to use and remember, if you understand the logic contained within it.

Concise Rules of Formal Charge

1. When an atom’s total valence electron credit exactly matches its $Z_{\text{eff}}$, there is no formal charge.

2. Each deficiency of electron credit from an atom’s normal number of valence electrons produces an additional positive charge.
3. If the formal charge calculation shows excess electron credit over an atom’s normal number of valence electrons, a negative formal charge is added for each extra electron.

4. The total charge on a molecule, ion or free radical is the sum of all of the formal charges on the individual atoms.

**Rules of Formal Charge, with examples**

1. When an atom’s total valence electron credit exactly matches its $Z_{\text{eff}}$, (“unshielded protons in the nucleus”) there is no formal charge. The normal number of valence electrons can also be determined from the group number of the column in the periodic table.

2. Each deficiency of electron credit from an atom’s normal number of valence electrons produces an additional positive charge (cationic).

   This can happen in many different ways. Some of those ways are shown in several examples below, though other ways are possible (e.g. there are no one electron transfers shown). Chemical reactions can occur in a single step or in multiple steps. Most of the individual steps, even in multi-step reactions, involve a transfer of two electrons from an electron pair donor to a target atom (electron pair acceptor) that subsequently gives up two electrons to another atom, which then takes those electrons away. Typically, there are at least three atoms involved in this process. Each participant has a special name. The electron pair donor is a Lewis base, but in organic chemistry it also goes by the term “nucleophile”. The electron pair acceptor is a Lewis acid, and it also goes by the term “electrophile”. Finally, the atom or group that takes away the electrons is called a leaving group. You will see these terms countless times in your organic chemistry and biochemistry careers, so learn them well.

   - Lewis base = nucleophile = electron pair donor
   - Lewis acid = electrophile = electron pair acceptor
   - leaving group = takes away excess electron density from an electrophile

   Usually, bond formation (electron pair donation) and bond breakage (electron pair removal), step 1 and step 2 of the first reaction below, occur approximately simultaneously, but sometimes the steps are sequential. When step 1 and step 2 are sequential either bond formation can occur first or bond breakage can occur first. When bond formation occurs first, an atom’s valency must increase by two electrons. This is impossible for carbon, because that would violate the octet rule (but is possible at atoms that can expand their valency). We will never see reactions like this at carbon. However, there are reactions at carbon where bond breakage occurs first. We will study reactions where the first broken bond is a sigma bond and reactions where the first broken bond is pi a bond.

**Generic Examples of Organic Reaction Steps**

Four very general, and common, views of reaction steps in organic chemistry are shown below. Notice how formal charge changes as the reactions proceed in the generic examples below. Creation of positive charge indicates a loss of electron credit (e.g. $0 \rightarrow +1$), or becoming less negative (e.g. $-1 \rightarrow 0$), through loss of a lone pair or sigma electrons or pi electrons. Creation of negative charge (e.g. $0 \rightarrow -1$), or becoming less positive (e.g. $+1 \rightarrow 0$) indicates a gain of electron credit. Gained
electrons can show up as an additional lone pair of electrons or a gained sigma or pi bond at a particular atom. Pay special attention to how curved arrows are used to show electron movement in the reactions that follow. In the general examples 1-3 that follow, Y is often some form of carbon in organic chemistry, but there are plenty other atoms that can react in this manner. In example 4, carbon atoms are explicitly drawn and Y can be a variety of possibilities, including carbon.

In the reactions below, full headed, curved arrows indicate two electron movement in the reactants that shows how the products will form. The straight arrows in these examples are pointing to a related part of a structure that is being discussed in the narrative below the arrow.

Example 1 - Steps 1 and 2 are approximately simultaneous.

Example 2 - Steps 1 and 2 are approximately simultaneous.

Example 3 - Steps 1 and 2 are sequential. Such reactions at carbon require bond breaking before bond making (a sigma bond breaks in this example).
"Y" gives up electrons by breaking a polar sigma bond, allowing Y and "Z" to separate. "Z" takes electrons away because it is the more electronegative atom. "Z" is a leaving group, but there is no nucleophile or electrophile yet. Y\(^+\) will become an electrophile after Z leaves and will trap a nucleophile, X\(\text{:}\), in a subsequent step.

Example 4 - Steps 1 and 2 are sequential. Carbon-carbon pi bonds often react in this manner (alkenes, alkynes and aromatic compounds). From the point of view of Y-Z this reaction is not much different than example 1. However, from the point of view the electron pair donor (the pi bond), it is quite different. The donated electrons in this example are shared between two atoms, while in example 1, the lone pair electrons belonged to a single atom, X\(\text{:}\). In this example one of the carbon atoms will lose its shared pi electrons. This feature is more similar to the first step of example 3, where sigma electrons are lost by atom Y. Those electrons will have to be added back in a subsequent step of electron donation. In this example “R” represents any general organic possibility.
"Z" donates electrons to "Ca, making a new sigma bond. "Ca," is a carboxation and is an electrophile. There is no leaving group because Ca has an incomplete octet. By reacting with Z, Ca regains its octet of electrons. Nucleophilic Z is used here for convenience. Another electron pair donor could have supplied the necessary electrons to complete the valency of Ca. X: was used in the other examples 1-3.

Specific Examples of Organic Reaction Steps

The examples below are more specific to organic chemistry and biochemistry. One purpose of showing these reactions here is to feature an important aspect of formal charge. A second purpose is to get you thinking that many organic reactions have common themes in their reaction paths. Your organic quest is to discover these common themes and learn them.

Example 1 - An atom (oxygen, below) shares one of its lone pairs with another atom (a proton is a common target). You will see this happen many times in acid/base reactions. "X takes two electrons away, because it is usually pretty stable on its own as a leaving group.

1. A neutral alcohol molecule, ROH, reacts as a Lewis base and a nucleophile by donating an electron pair (this is a more "organic chemistry" way to think about the reaction) "R" indicates a generic carbon group.
2. H-X reacts as a Lewis acid and an electrophile by accepting an electron pair (the organic way of thinking).
3. The oxygen atom used one lone pair to form a new bond with a proton, so those electrons are now shared in a covalent sigma bond. Oxygen's electron credit went down by one electron. The positive charge shows that this oxygen is electron deficient (0 → +1).
4. Atom X, the leaving group, gained one lone pair (0 → -1). These electrons were formerly shared in a covalent sigma bond. X’s electron credit went up by one electron. The negative charge shows that X is now electron rich. Usually X is pretty stable on its own, as an anion or as a neutral molecule, if “H-X” had a positive charge (e.g. H₃O⁺).

Example 2 - Similar to a, except the oxygen atom is sp² hybridized in a carbonyl group (C=O).
1. A neutral oxygen atom from a carbonyl group (C=O) reacts as a Lewis base and a nucleophile by donating a lone pair (organic focuses on electron pairs). X must remove two electrons to maintain hydrogen’s Noble gas configuration.
2. H-X reacts as a Lewis acid and electrophile by accepting an electron pair.
3. The oxygen atom used one lone pair to form a new bond with a proton, so those electrons are now shared in a covalent bond. Oxygen's electron credit went down by one electron. The positive charge shows that this oxygen is electron deficient.
4. Atom X, the leaving group, gained one lone pair. These electrons were formerly shared in a covalent sigma bond. X’s electron credit went up by one electron. The negative charge shows that X is now electron rich.

Example 3 - The protonated carbonyl group (C=O⁻-H) from example 2 has a useful resonance structure that shows why the carbon atom carries a significant portion of the positive charge. This makes the electrophilic carbon a good target for attack by a nucleophilic lone pair of electrons (from the alcohol oxygen atom, here), just as hydrogen was attacked in the previous two examples. The bond broken in this reaction is the carbon-oxygen pi bond. The carbon and oxygen atoms do not separate because the sigma bond remains to hold them together. The sequence of events, however, is the similar to the previous two examples: 1. electron pair donation to a target atom to make a bond, 2. electrons are lost by the target atom and 3. an atom takes an electron pair away when the former bond is broken. Notice how the reactant alcohol oxygen atom has acquired a positive formal charge in the product. The protonated alcohol is now ready to undergo the same sort of reaction as H-X of example 1. (Lewis base attacks the proton and makes a sigma bond with the proton as the alcohol oxygen atom leaves with a pair of electrons.)
1. A neutral alcohol (ROH) oxygen atom reacts as a Lewis base and nucleophile by donating a lone pair of electrons (partially negative) to the partially positive carbon atom.

2. The carbon of the protonated carbonyl group reacts as a Lewis acid and electrophile by accepting an electron pair at carbon, forcing the pi electrons to the partially positive oxygen atom, which becomes neutral. This allows the carbon atom to maintain its Noble gas configuration and allows oxygen to regain its full credit of electron density. There is no leaving group in this step, only leaving electrons.

3. The alcohol oxygen atom that donated its lone pair formed a new bond with the carbon atom, so those electrons are now shared in a covalent bond. That oxygen atom's electron credit goes down by one electron. The positive charge shows that this oxygen has become electron deficient (0 \rightarrow +1). The carbonyl oxygen atom gained an extra electron pair, so its electron credit went up by one and its positive charge went down by one to neutral (+1 \rightarrow 0). Notice how the positive charge shifted from the carbonyl group to the alcohol oxygen atom.

Example 4 – The carbon of a neutral carbonyl group (C=O) can also be attacked by a lone pair of electrons, if the electron pair donor is strong enough. The carbanion shown here is one of the strongest electron pair donors known. We will study many examples of this type of reaction. Notice the similar sequence of events: 1. electron pair donation to a target atom to make a bond, 2. electrons are lost by the target atom and 3. an atom takes an electron pair away when the former bond is broken (a pi bond, here).

Example 5 - Carbon-carbon pi bonds occur in alkenes, alkynes and aromatic compounds. It is useful to think of pi electrons as Lewis bases and nucleophiles. They are closely analogous to lone pairs of
electrons, that we explicitly draw. If you recall, I did ask you to explicitly draw them in our 3D structures of pi bonds. If you reexamine example 1 above, you can see how similar these two examples are.

1. A neutral pi bond reacts as a Lewis base and nucleophile by donating an electron pair from its pi bond. There is some similarity to example 1. However, only one of the carbon atoms of the pi bond keeps the electrons. The other carbon atom loses those electrons, and becomes an electrophilic carbocation. This part is different from example 1.

2. HX is a Lewis acid and electrophile, and reacts by accepting an electron pair.

3. One carbon atom used the pi electrons to form a new sigma bond with a hydrogen atom, so these electrons are retained and now shared in a covalent sigma bond with that hydrogen atom. This carbon atom's electron credit stays the same and it is still neutral (0 → 0). The other carbon atom's electron credit goes down by one electron, since it lost its electron when the pi bond reacts (0 → +1). The positive charge shows that this carbon atom is electron deficient. A carbon atom like this is called a carbocation and is a strong Lewis acid and electrophile.

4. Atom X gained one lone pair; electrons which were shared in a covalent bond. Its electron credit went up by one electron (0 → -1). The negative charge shows that X is now electron rich. In many organic reactions of this type, X will turn around and donate its nucleophilic electrons to the electrophilic carbocation, in a subsequent step.

Example 6 - An atom (carbon, below) loses two shared electrons from a covalent sigma bond that is broken. This reaction does not follow the patterns presented above where two electrons are donated and two electrons are lost simultaneously (two arrows in a single equation). In this example there is subsequent step that brings in two electrons to replace the electrons that were lost from carbon.
1. In step 1, the C-Br sigma bond is broken, with the more electronegative bromine atom taking both electrons with it. Bromine is the leaving group. This leaves a very electropositive carbon atom with only three sigma bonds and positive formal charge.

2. Carbon's electron credit went down by one when the sigma bond was broken and bromine took away both of the shared electrons ($0 \rightarrow +1$). The positive charge shows that this carbon is electron poor and needs two electrons to complete its octet. A carbon like this is called a carbocation. Carbocations are strong Lewis acids and electrophiles. Two electrons will be added back to the carbon in a subsequent step (step 2). Later, we will discover that these electrons are added back in, in one of three possible ways.

3. The bromine atom gained an additional lone pair from the electrons that were shared in the carbon-bromine sigma bond. Bromine's electron credit went up by one electron ($0 \rightarrow -1$). It is more electron rich as bromide.

4. In step 2 the electrophilic carbon lacking an octet is an obvious target for donation of a nucleophilic pair of electrons from the oxygen atom of the alcohol. The alcohol is a Lewis base and nucleophile. The positive charge moves from electropositive carbon to electronegative oxygen. At first this does not look like a good trade off, but the positively charged oxygen atom has a full octet, while the positively charged carbon had only six valence electrons. The full octet trumps the relative electronegativity differences. Also, if you count all of the sigma bonds in the reactants (five) you will see that an additional bond is created in this reaction step, as there are six sigma bonds in the products. It’s always better to have more bonds. The product of step 2 looks ready to donate a proton (it’s a strong acid), similar to examples 1, 2 and 5 above (…and it does).

Take another look at the example reactions above and contemplate what the curved arrows and formal charge are showing you. You might even consider placing those examples in front of you as you eat your morning breakfast and “meditating” on them. As you study the reactions in this book, you will see these ideas again and again and again…

This has been a long detour from formal charge rule 2 to rule 3, but a lot of important material was previewed. You are not expected to understand the details of the above reactions — yet (…except formal charge). All of these reactions, and more, will be studied in detail later in this book. Do try to see the similar features in each of these reactions. Seeing the similar themes is the secret to making sense of organic chemistry and biochemistry…and will make your life so much more enjoyable.

3. If the formal charge calculation shows excess electron credit over an atom’s normal number of valence electrons, a negative formal charge is added for each extra electron (anionic). There are a number of ways that this can occur. Several of them are shown in the examples above. Electrons can be retained by an atom from a broken sigma bond or a broken pi bond, giving an atom excess electron density and negative charge if it was neutral to begin with ($0 \rightarrow -1$). If the atom that retains the
electrons had a positive charge as a reactant, it would become neutral in the product structure \((+1 \rightarrow 0)\). In either case, formal charge will show that the atom gained electron density (neutral \(\rightarrow\) negative or positive \(\rightarrow\) neutral).

4. The total charge on a molecule, ion or free radical is the sum of all of the formal charges on the individual atoms. The overall charge on a molecule can be neutral, even though formal charge is present on specific atoms in its structure, if the charges cancel one another. Examples demonstrating this aspect in organic chemistry are shown below.

\[
\begin{align*}
\text{The overall formal charge on diazomethane is 0.} & \quad \text{The overall formal charge on nitromethane is 0.} \\
\text{The overall formal charge on azidomethane is 0.} & \quad \text{The overall formal charge on ozone is 0.}
\end{align*}
\]

Amino acids typically have formal charge present. Three examples are provided showing multiple charges totaling zero, negative one and positive one.

\[
\begin{align*}
\text{glycine overall charge = 0} & \quad \text{aspartic acid overall charge = -1} & \quad \text{histidine overall charge = +1}
\end{align*}
\]

Most of us like well-defined, unambiguous methods for solving problems, and the formal charge equation above will do this for you in this. However, the formal charge calculation is tedious to do over and over for every atom in a structure. As you use this equation, your intuition will grow. You will begin to recognize that when an atom gains an electron pair from what was a bond (sigma or pi), it becomes more negative by one, and when an atom shares an electron pair by making a bond (sigma or pi), it becomes more positive by one. If a sigma bond breaks and an atom keeps the electrons, it becomes more negative by one, while the atom that lost the electrons becomes more positive by one.

Knowing what an atom’s normal bonding pattern is makes it easier to recognize when it’s not normal and what the difference is (e.g. \(\text{H}_3\text{O}^+\) has fewer lone pairs than water and \(\text{HO}^-\) has more lone pairs than water). As a quick reminder of neutral atom bonding patterns, hydrogen atoms always form one bond, carbon atoms form four bonds, nitrogen atoms form three bonds and have one lone pair or electrons, oxygen atoms form two bonds and have two lone pairs of electrons (sulfur often bonds similarly) and fluorine atoms form one bond and have three lone pairs of electrons (the other halogens bond similarly).
In the following formal charge problems you will find many structures similar to those you will see on your journey through organic chemistry. You may instantly recognize the formal charge in some of these, or you may be flummoxed by the formal charge on an atom. When you don’t know what the formal charge is, use the above equation to calculate it. However, first try to use your intuition to speculate upon an atom’s formal charge. When you find that you are consistently correct on your guesses at formal charge, it is probably safe to begin using your intuition to estimate formal charge. This will happen naturally from your experience of working many problems. The formal charge equation is always there, whenever you feel puzzled about an atom’s formal charge.

As you work through the problems, you will see that some of the structures have been grouped together and have identical skeletal arrangements and overall formal charge. The only difference between the grouped structures is where the formal charge is placed and where the pi bonds are drawn. These are resonance structures, which are necessary variations to show how charge is distributed in a given structure. In many organic structures, a single 2D or 3D representation cannot show the actual charge distribution. Resonance structures are used to collectively reveal where charges (or partial charges) are located. A double headed arrow is placed between all resonance structures to indicate what they are. We will discuss this topic more in the next section and it will be used often throughout this book. This is just a little up-front notice about one your most important concepts.

Before we actually calculate a formal charge, I need to make a disclaimer. When we write a positive charge on oxygen in $H_3O^+$, it seems that oxygen is carrying the entire load of the positive charge. What it really means is that the oxygen atom is electron deficient relative to a normal oxygen having two bonds and two lone pairs of electrons. When we write a negative charge on hydroxide, HO⁻, we really mean that the hydroxide oxygen atom is carrying a larger amount of electron density than a “neutral” oxygen atom. Computational calculations can estimate the amount of positive and negative charges present on each atom in a molecule or ion. If we perform such calculations on hydroxide, water and hydronium ion (thanks Herb), we find that in all of them the oxygen atom carries a partial negative charge that is balanced by the positive charge of the hydrogen atoms (H₂O⁺ and H₂O) or hydrogen atom (HO⁻). Even in H₂O⁺, there is no positive charge on the oxygen atom. What we can see is that the oxygen atom is less negative in the hydronium ion than water and less negative in water than in hydroxide.

Formal charge is useful to us, if we just remember that it indicates an electron deficiency or an excess of electron density on an atom compared with its neutral bonded state. An electron poor oxygen in $H_3O^+$ induces a base to attack a proton, which then releases the electrons in the O-H sigma bond to the oxygen atom, so that it has the usual amount of electron density it needs. Electron deficient atoms will tend to attract negative charge towards them and electron rich atoms will tend to push their electron density towards positive sites. It is somewhat paradoxical that in all of the structures that we study, hydrogen atoms will always have one bond and zero formal charge, even as they carry the partial positive charge, when bonded to electronegative atoms like nitrogen, oxygen or the halogens.

\[
\begin{align*}
\text{formal charge} &= -1 \\
\text{formal charge} &= 0 \\
\text{formal charge} &= +1
\end{align*}
\]

Calculated partial charges

\[
\begin{align*}
oxygen &= -1.214 \\
hydrogen &= +0.214
\end{align*}
\]

Calculated partial charges

\[
\begin{align*}
oxygen &= -0.664 \\
hydrogen &= +0.332
\end{align*}
\]

Calculated partial charges

\[
\begin{align*}
oxygen &= -0.291 \\
hydrogen &= +0.430
\end{align*}
\]

Perhaps a more accurate way to represent $H_3O^+$, but not as practical for drawing structures.
Problem 16 – Write in the formal charge wherever present in the atoms below. Resonance structures are shown within parentheses and have double headed arrows between them. All of the resonance structures must be considered together to evaluate the true nature of a particular structure.

Row 1
- methane
- methyl free radical
- methyl carbocation
- methyl carbanion
- methyl singlet carbene
- methyl doublet carbene

Row 2
- \( \text{H} \)
- \( \text{H} - \text{N} - \text{H} \)
- \( \text{H} - \text{N} : \)
- \( \text{H} - \text{N} \) 

Row 3
- \( \text{H} - \text{O} - \text{H} \)
- \( \text{H} - \text{O} : \)
- \( \text{H} - \text{O} \)

Row 4
- \( \text{H} - \text{F} - \text{H} \)
- \( \text{H} - \text{F} : \)
- \( \text{H} - \text{F} \) 

Row 5
- \( \text{H} - \text{C} = \text{C} - \text{H} \)
- \( \text{H} - \text{C} = \text{C} : \)
- \( \text{C} = \text{C} \)
- \( \text{C} = \text{C} : \)
- \( \text{C} = \text{C} \)

Row 6
- \( \text{H} - \text{C} = \text{N} : \)
- \( \text{C} = \text{N} : \)
- \( \text{H}_2\text{C} = \text{C} - \text{N} : 

Row 7
- \( \text{H} - \text{C} = \text{N} - \text{H} \)
- \( \text{H} - \text{C} = \text{N} - \text{H} \) 
- \( \text{H} - \text{C} = \text{O} : \)
- \( \text{H} - \text{C} = \text{O} : \)
The first two structures violate the octet rule, but are often rationalized based on sulfur's 3d orbitals to accept additional electron density. The first structure of the second group also violates the octet rule. Not all chemists agree on this point.
Which atoms from row 19 would you suspect are most likely to donate electrons in a chemical reaction?

Problem 17 - Which connection of atoms appears to be more reasonable in each pair below? Why? Assume that all nonhydrogen atoms have full octets. That means you have to add in lots of lone pairs of electrons. Some of these structures have different connections of the atoms (they are isomeric) and some have the same connections of the atoms, but have different electron distributions (they are resonance structures). Can you tell the difference?
Problem 18 – Add in any necessary formal charge to atoms in the equations below and then add in curved arrows to show electron movement in bond formation and bond breakage (review problem 10 on page 21 and the examples starting on page 52). Two arrows are required on the left side of each equation. Which atom donates electrons in each of the following chemical equations and what atom accepts those electrons? What is the polarity of each atom in the bond forming reaction? Do the products support your answers? Classify the reactants as Lewis acids and bases, and as electrophiles and nucleophiles.

a. \( \text{CH}_3\text{CN} \quad \text{CH}_3\text{NH} \)

b. \( \text{Cl}_2\text{O} \quad \text{Cl}_2\text{O} \)

c. \( \text{NO}_2\text{O} \quad \text{NO}_2\text{H} \)

d. \( \text{H}_2\text{C} \quad \text{H}_2\text{C} \)

e. \( \text{H}_2\text{O} \quad \text{H}_2\text{O} \)

f. \( \text{NO}_2\text{O} \quad \text{NO}_2\text{H} \)

g. \( \text{C} = \text{O} \quad \text{C} = \text{O} \)

h. \( \text{NO}_2\text{O} \quad \text{NO}_2\text{H} \)

Problem 19 – Even relatively simple formulas require clues about the connectivity of the atoms. These clues can come from the way a structure is drawn or from a chemical name. Using a very simple formula,
CH₃NO₂, some possible sigma skeletons have been generated. How many total valence electrons are there for bonding and lone pairs? (1xC, 1xN, 2xO, 3xH = ? electrons) Is there any formal charge? In some examples below, it depends how you add in the electrons. One way generates structures without formal charge and another generates structures with formal charge. These are called resonance structures, (developed in the next topic) Are there pi bonds, rings or lone pairs? Count the number of sigma bonds in the bottom row and compare it to the number of sigma bonds in the top row. In which row do we find resonance structures? What type of orbitals are necessary for resonance structures? (Hint: They are found in pi bonds.) There should be the same total number of bonds and lone pairs in every structure.

This row has potential resonance structures.

This row does not have potential resonance structures.