The stronger the bond, the deeper the well. So to change Figure 1-1 to represent a weaker bond, simply move the lowest point up.

The key to this exercise is the understanding that there is an ionic bond involved where each of the partner ions has a filled shell. For the more electronegative partner this means a filled valence shell and a charge that corresponds to the number of additional electrons that were added to fill the shell. For the less electronegative partner, electrons have been lost so that the valence shell is empty, and, again, the number of electrons lost corresponds to the number of positive charges. Notice that because each of compounds given is neutral, the number of positive and negative charges for each must be equal.

The key to drawing structures is to know the "normal" valency for all of the atoms that are common in organic structures. The valency corresponds to the number of covalent bonds formed.

<table>
<thead>
<tr>
<th>Valency</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>I</td>
<td></td>
</tr>
</tbody>
</table>

Constructing structures is most straightforward starting with one of the atoms with the highest valency. In addition, none of the mono valent atoms can be connected to another mono valent atoms as that would result in a complete structure with no more valencies available to connect to other atoms.

For example, take CH₂Cl₂. We start by placing the carbon in the center of the structure and because the other four atoms are all mono valent, they all must be connected to the carbon.

\[
\begin{align*}
  & \vdots \quad \vdots \\
\text{Cl} & : C & : \text{Cl} \\
  & \vdots \\
\text{H} & 
\end{align*}
\]

At this point, it makes no difference where you place the hydrogen atoms and the chlorine atoms.

All that is required to answer this exercise is to know the electronegativities of the elements commonly found in organic structures.
For a bond between atoms of different electronegativity, the electrons are closer to the atom with greater electronegativity. We indicate this bond polarization with an arrow with a positive charge at the tail pointing at the more electronegative atom. Note that for these answers, ONLY the polarization is being indicated, not the number of bonds.

Thus, for SO, the arrow points at the more electronegative oxygen atom.

1-5 The most fundamental concept in chemistry is that electrons are attracted to protons (that make up the nucleus of atoms) and electrons repel electrons. In order to understand the shapes of molecules, it is important to consider ALL valence electrons that are present. For ammonia, this means we must consider all eight valence electrons about the nitrogen. These are present in four pairs, three of which are shared with the hydrogen atoms and one of which is present as a lone pair of electrons. Thus, to a first approximation, we would predicted that these four electron pairs would be as far from each other as possible, oriented at the corners of a tetrahedron. However, the lone pair is closer to the nitrogen than are the other three pairs which are shared with another nucleus. Thus, the lone pair "pushes" the three shared pairs closer to each other, decreasing the angle slightly from the tetrahedral angle of 109.54.

1-6 This exercise is an extension of 1-3 where now there is more than one atom present with a valency greater than 1. The procedure remains the same. Start with one of the atoms of highest valency and add to it another atom of high valency. Thus, for CH3CH2CH3, we start with a carbon atom, add another carbon atom to form C—C, and then add the third carbon (it makes no difference here which carbon the third is added to as both are the same). Finally, we add the 8 hydrogen atoms, filling the valence of each of the three carbon atoms.

1-7 This exercise is explained in WORKING WITH THE CONCEPTS on page 17 of the textbook.

1-8 (a) First, we must decide how the atoms are connected as the formula itself does not tell us. There are two clues we can use. First, nitrogen is trivalent so it is more likely to be connected to the other two atoms than is one of the oxygen atoms. Second, we can "learn" that an oxygen-oxygen bond is very weak (36 kcal/mole) and indeed, the weakest bond that we normally encounter in organic chemistry. So we start by attaching each of the oxygens to the nitrogen. Now we know that nitrogen usually has three bonds, so we can presume that there is a second bond between the nitrogen and one of the oxygen atoms. But which one, they seem to be identical---this is the first hint that there may be two resonance structures of equal importance). Let's evolve the structure in to two resonance structures by adding the second bond first to the left-hand oxygen and then to the one on the right. We add lone pairs of electrons to fill the valence shells of the atoms and then analyze if any atoms "own" more (or fewer) electrons than they do when they are neutral and we
arrive at the resonance structures on the right, below.

\[
\text{O--N--O} \quad \leftrightarrow \quad \text{O=N=O}
\]

Now to the question of geometry. Nitrogen is surrounded by three sets of electrons, two from bonds to the oxygen atoms and the lone pair of electrons. Thus, we conclude that the structure should be roughly trigonal planar (not exactly so as the three sets of electrons are not identical).

(b) We can take the same approach for SO\textsubscript{2}, placing the sulfur in the middle because it uses the third shell and can many more bonds than can oxygen (recall from your previous courses in chemistry that there is SC\textsubscript{6}, where sulfur is bound by six bonds to six chlorines).

Although we have arrived at a structure that has no charges and all atoms have filled valence shells, we note that we are now dealing with bonds between atoms from different rows of the periodical table—sulfur is substantially larger than is oxygen (the Van der Waals radius for oxygen is 1.52 whereas that for sulfur is 1.80). Thus, we might anticipate that electron sharing between these two different size atoms might be reduced. As a result, we might consider additional resonance structures where there is only one oxygen with two bonds to sulfur and even a structure with only single bonds between sulfur and oxygen.

Based on the idea that charge separation is bad, atoms with unfilled valence shells are bad, and maximizing the number of bonds (that is, sharing of electrons between atoms) is good, we would conclude that the structure on the left is the dominant contributor. We can use analogy with SO (as the book does) only if we know the electron distribution is SO, which we do not. Nonetheless, we know experimentally that the dipole moment of SO is substantial (1.55 versus 1.11 for H—Cl) and thus there is a very significant positive charge on sulfur and negative charge on oxygen.

What about the shape? All of the resonance structures we have considered have three sets of electrons about sulfur, and thus we expect a roughly trigonal planar structure. We can tell that the structure is not linear from a simple measurement: the dipole moment of SO\textsubscript{2} is 1.63.

1-9 Recall that the reason that atoms are joined to form molecules is for sharing electrons, a process that we formalize as bonds. In general, the more bonds the better will be the resonance structure. For a) we presume that the connectivity of the atoms is as show in the formula, that is with the nitrogen bound to both carbon and oxygen.

Next we pick one pair of atoms, for example, nitrogen and oxygen, and establish as many bonds as we can up to the valency of one the lower valence atom which in this case is oxygen. Thus, be place two bonds between nitrogen and oxygen. We now turn to the other pair, nitrogen and carbon and add as many bonds as possible, in this case also two bonds which reaches the valence shell limit of 8 electrons for nitrogen (from
We can shift a lone pair of electrons from carbon to being shared with nitrogen if we move a carbon-nitrogen pair to oxygen at the same time. Doing so, we obtain the resonance structure on the right, above. There are three criteria for comparing and evaluating resonance structures: bonds (that is the number and type); charges (how many and where they are); and valence shells filling. Both resonance structures have all atoms with filled valence shells (place the appropriate number of lone pairs on oxygen and convince yourself that this is correct). Both have the same number of bonds-four (we will not delve into the difference that might result from the different kinds of bonds); As to charge, the left hand structure has two negative charges concentrated on carbon whereas the right hand structure has these negative charges on two atoms. Therefore, we conclude that the left hand structure is the greater contributor. Note that it is possible to write other resonance structures with fewer than four bonds but we can quickly conclude that these are likely to be minor contributors.

In much the same way we can derive the resonance structure on the left, below for (b):

It is not possible to have any more bonds between oxygen and nitrogen as both atoms have a filled valence shell. We can move one of the two bonds to oxygen but can conclude that doing so will decrease the number of bonds by one (bad) and will de-fill the valence shell of nitrogen (bad). Although this process does move the negative charge from the less to the more electronegative atom, the other two factors together out way the position of the charge and the left hand structure is the major contributor.

1-10 This exercise is explained in WORKING WITH THE CONCEPTS on page 22 of the textbook.

1-11 See the answer in the textbook. If you have trouble, revisit exercise 1-10.

1-12 To do this, we must move the waves so that their nodes (that is, where they have a value of zero on the y axis) are at the same point:
First, we must determine the total number of electrons that will occupy the atomic orbitals. For neutral the number of electrons equals the number of protons in the nucleus which is equal the neutral atoms, the number of electrons equals the number of protons in the nucleus which is equal to the atomic number. For sulfur this is 16 and for phosphorus 15. We add electrons, starting at the bottom and filling each orbital before proceeding to the next. When there is more than one orbital of equal energy, we place one electron in each until each has one and then proceed to add the second. However, we can simplify this process by remembering that all second row elements have two electrons in the 1s orbital (a filled first level) and all third row elements (as are sulfur and phosphorus) have both the first and second levels filled, which requires a total of 10 electrons. Thus, for sulfur we need to add 6 more (in addition to the filled first two levels). We place 2 in the 3s, and 4 in the 3p, adding one to each of the p orbitals and then adding the 4th to one of them (it makes no difference which). For phosphorus we need to add 5 to the third level, 2 in the 3s and one in each of the 3p orbitals.

This exercise is explained in WORKING WITH THE CONCEPTS on page 31 of the textbook.

If you had any trouble with 1-5, go revisit it before taking on this exercise. Recalling that molecular shape is dictated by valence electron repulsion, our first task is to assess the number of electrons that surround an atom and then determine what shape allows for the maximum separation of the electrons. The carbon atom of the methyl cation has a total of 6 valence electrons in 3 pairs where each pair is shared with a hydrogen atom. The shape that provides maximum separation of these pairs is trigonal planar, with 120 degrees between each pair of electrons and the other two pairs. For the methyl anion, there are eight valence electrons (to move from a carbon with a positive charge to one with a negative charge, we need to add two electrons). Three pairs are shared with hydrogen atoms and the 4th is a lone pair, very much like the situation with ammonia, where the angle between the hydrogens is slightly less than the tetrahedral angle.

Of course, you must do this yourself.

After we have connected all of the four carbon atoms together, it is time to add the ten hydrogen atoms, being sure that we complete but do not go beyond carbons valency of 4.

Condensed formulas are used often in organic chemistry as they take less space than does a Kekule representation. Bond-Line formulas are very important as they greatly aid in seeing the connection between the atoms present that have a valency greater than 1. It is very important that you understand that the end of any line and the junction of multiple lines in a bond-line formula represents a carbon atom unless so other
element is explicitly represented. To proceed from a Kekule representation to a bond line formula it is necessary to remove all of the hydrogen atoms and the bonds that connect each to a carbon atom. We must also remove all of the carbon labels but the junctions of multiple bonds must be bent—otherwise we would not know that there was a junction! But rather than starting with a Kekule representation, we can take the same approach as in exercise 1-6 and 1-15 where we systematically build the structure. However, there is no way to represent as single carbon atom with bond-line formulas and we must start with two carbon atoms. We add a third, and then a fourth.

1-22 Dashed-wedged line formulas are use to try and represent organic structures in three-dimensions. This is where your model set will be very useful. Let's start by focusing on the left-hand carbon atom in the bond-line formula below. We know that the end of the line is a carbon atom that is represented as being bound to one other carbon (which is at the junction of the two lines). We also know that valence of all carbon atoms is filled to four by hydrogen atoms unless something else is represented. Thus, this left-hand carbon has three unrepresented hydrogen atoms. We will assume that all of the bonds between carbons are in the plane of the paper and add one hydrogen atom to the end carbon so that it is also in that plane (there are two ways to do this). Because we know that carbon is tetrahedral, one of the remaining two hydrogen atoms must be behind the plane of the paper and the other must be in front. Note that there will often be more than one way to do this.

Why is there more than one way to represent the hydrogen atoms that are in front and behind the plane of the paper? That is because the front one is directly on top of the one in the back. To be able to see both, we must move them away from each other, pushing the front hydrogen either to the left or to the right and the back hydrogen in the other direction.