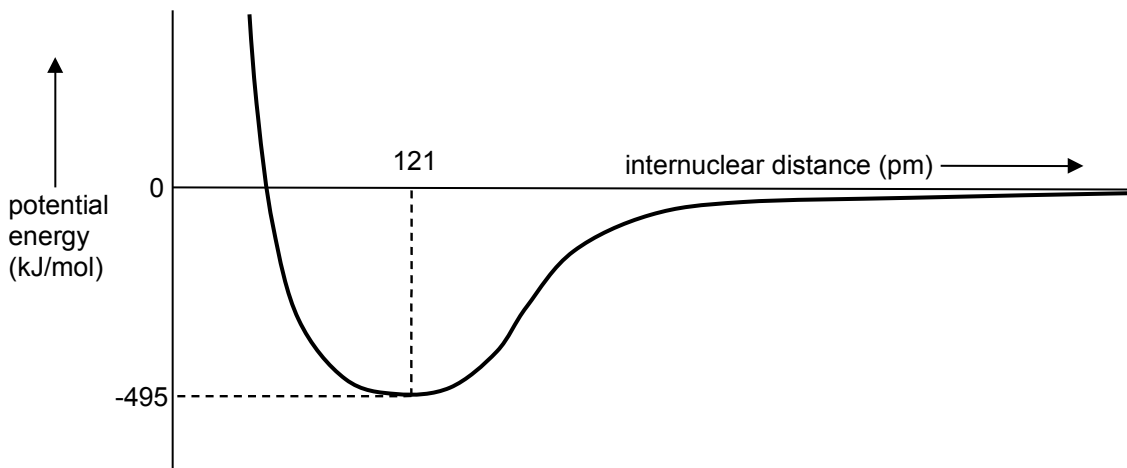
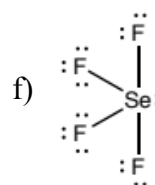
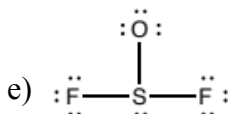
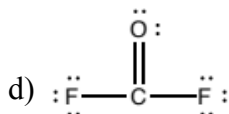
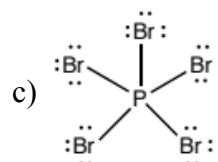
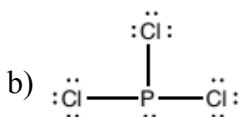
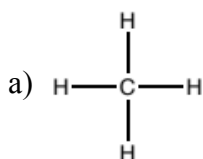


SOLUTIONS TO TOPIC F PROBLEMS

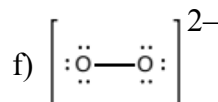
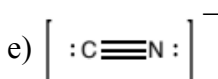
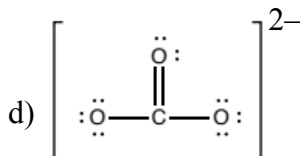
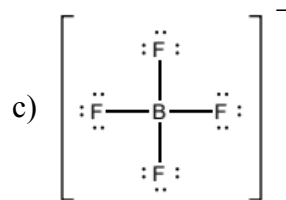
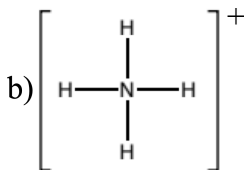
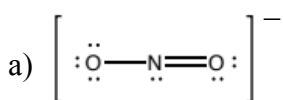
1)



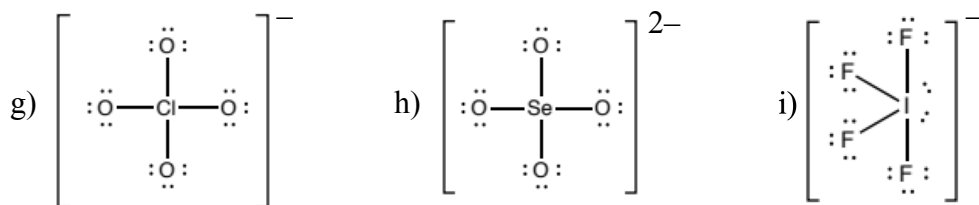
2) Drawing Lewis structures was covered extensively in the laboratory, so I will not write out explanations of how to draw structures in this answer key. If you need more assistance, talk to me.



3) For polyatomic ions, be sure that you get the correct total number of electrons, accounting for the charge on the ion. For example, NO_2^- has 18 electrons: 5 from the nitrogen atom, 6×2 from the oxygen atoms, and 1 additional electron to produce the -1 charge. Note that I have drawn structures that satisfy the octet rule wherever possible.



Continued on the next page



Note: structures that minimize the formal charge on the central atom are also acceptable, as long as they do not contain double bonds to a group 7A outer atom. For example, the following structures are also acceptable for parts g and h, because they have a zero formal charge on the central atom.



4) a) The bond order is the number of electron pairs in the bond (and it's also the number of lines you draw between the atoms):

Methanol: the carbon-oxygen bond order is 1

Formaldehyde: the carbon-oxygen bond order is 2

Carbon monoxide: the carbon-oxygen bond order is 3

b) Carbon monoxide has the largest carbon-oxygen bond energy. The bond energy is the energy you need to break the bond; the higher the bond order, the higher the bond energy.

c) Methanol has the largest carbon-oxygen bond distance. The higher the bond order, the shorter the bond distance.

d) The C–H bond distances in methanol and formaldehyde should be equal (or very close). The bond distance does not depend significantly on the rest of the molecule.

5) A covalent bond will be polar if the two atoms have different electronegativities. If the bond is polar, the atom with the lower electronegativity is positively charged (and the other atom is negatively charged).

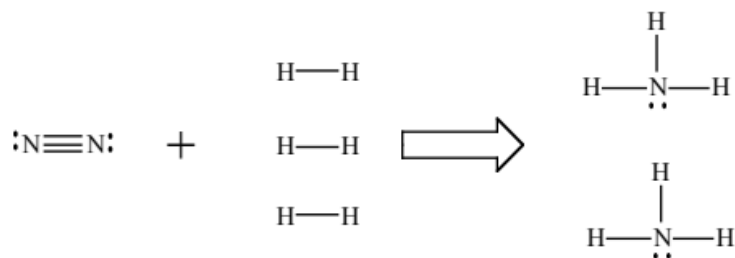
a) Each C–Cl bond is polar, and the carbon atom is positively charged. (The electronegativity of C is 2.5 and the electronegativity of Cl is 3.0.)

b) Each O–Cl bond is polar, and the chlorine atom is positively charged.

c) Each C–H bond is polar, and the hydrogen atom is positively charged.

d) The C–C bond is not polar, because both atoms have the same electronegativity.

6) To use bond energies, we must first determine the actual bonds in the products and reactants by drawing reasonable Lewis structures.



The ΔH for this reaction equals the sum of the bond energies in the reactants minus the sum of the bond energies in the products.

Reactants:

One $\text{N}\equiv\text{N}$: 1 mol \times 941 kJ/mol = 941 kJ

Three $\text{H}-\text{H}$: 3 mol \times 432 kJ/mol = 1296 kJ

Total = 2237 kJ

Products:

Six $\text{N}-\text{H}$: 6 mol \times 391 kJ/mol = 2346 kJ

$$\Delta H = 2237 \text{ kJ} - 2346 \text{ kJ} = \mathbf{-109 \text{ kJ}}$$

7) To use bond energies, we must draw Lewis structures for all of these:



For the reactants, we have 6 moles of $\text{Xe}-\text{O}$ bonds. We do not know the bond energy of a $\text{Xe}-\text{O}$ bond, so let's call it x .

$$6 \text{ mol} \times (x \text{ kJ/mol}) = 6x \text{ kJ}$$

For the products, we have 3 moles of $\text{O}=\text{O}$ bonds:

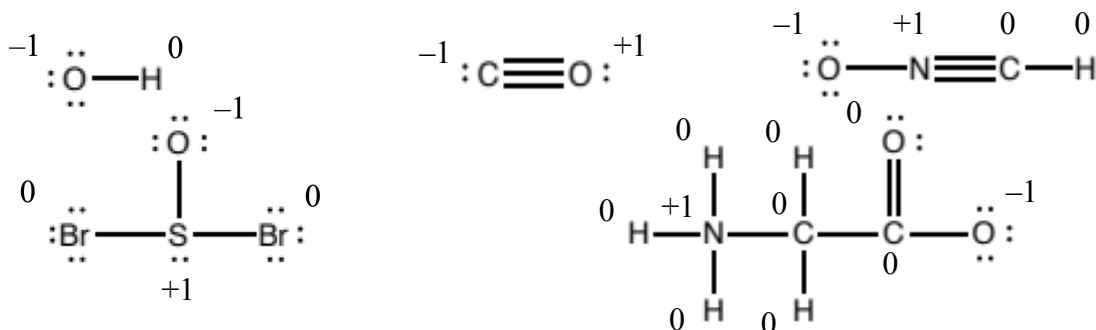
$$3 \text{ mol} \times 495 \text{ kJ/mol} = 1485 \text{ kJ}$$

The overall ΔH for this reaction is -804 kJ, so we have:

$$6x \text{ kJ} - 1485 \text{ kJ} = -804 \text{ kJ}$$

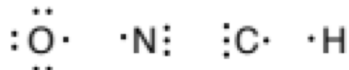
Solving this equation gives us $x = \mathbf{113.5 \text{ kJ/mol}}$ (or 114 kJ/mol). This is a very low bond energy; as a result, XeO_3 is not very stable and readily breaks down into Xe and O_2 if it is heated.

8) I will show how the formal charges in fulminic acid are calculated in detail; for the other four species, I will just give the answers.



Detailed explanation for fulminic acid.

To determine formal charges, start by breaking every covalent bond in the molecule. Each atom gets one of the two electrons from each bond. Doing this with fulminic acid gives:



Note that when we break the triple bond, each atom gets three electrons, because a triple bond is a total of six electrons.

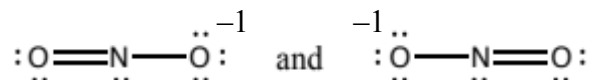
Next, you compare the number of valence electrons in each atom with the “normal” number of valence electrons, which equals the group number. If the atom has extra electrons, it is negatively charged; if it has too few, it is positively charged.

Oxygen:	normally has 6 valence electrons has 7 valence electrons in this structure = 1 extra electron charge = -1
Nitrogen:	normally has 5 valence electrons has 4 valence electrons in this structure = 1 missing electron charge = +1
Carbon:	normally has 4 valence electrons has 4 valence electrons in this structure = the normal number charge = 0
Hydrogen:	normally has 1 valence electron has 1 valence electron in this structure = the normal number charge = 0

9) a) This statement is **not accurate**. When you have two resonance structures, the actual molecule behaves like the average of the two. In this case, the two oxygen-oxygen bonds are the same strength, somewhere between a single and a double bond.

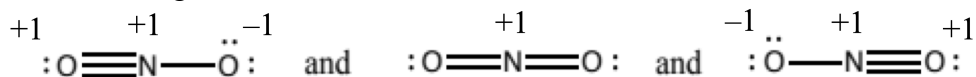
b) This statement is **not accurate**. Ozone never looks like structure #1 (or structure #2). It always looks like the average of the two. Each bond has a bond order of 1.5, so the two bonds are always the same length.

10) a) NO_2^- requires two resonance structures. Here they are, with the non-zero formal charges.



The actual structure of NO_2^- is the average of these two resonance structures.

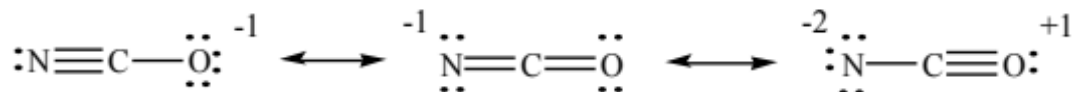
b) NO_2^+ can be represented by three resonance structures. Here they are, with the non-zero formal charges.



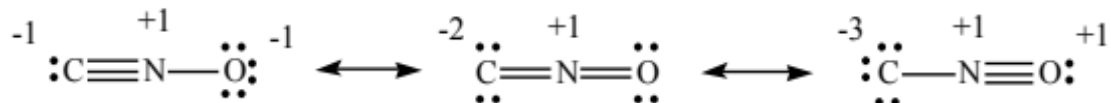
c) The first and third structures effectively cancel each other out, so the average of the three structures is identical to the second structure (with two double bonds). As a result, we do not need to draw all three structures; the middle structure (with two double bonds) is an accurate representation of NO_2^+ .

d) The two N–O bonds in NO_2^- are equal to each other, with a bond order of 1.5 (the average of 1 and 2). The two N–O bonds in NO_2^+ are equal to each other, with a bond order of 2. The larger the bond order, the shorter the bond distance, so **the bond distances in NO_2^+ are shorter than the bond distances in NO_2^- .**

11) a) For cyanate, we have the following possibilities. Note that in this case, we must include the structures that contain one single and one triple bond, because they are not equivalent to one another.



For fulminate, we have the following possibilities.



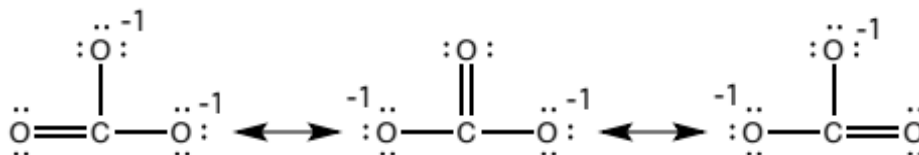
b) For cyanate, the **first and second structures** should make significant contributions to the actual structure of the cyanate ion. Each of these structures has a single -1 charge on an atom that has a fairly high electronegativity. (The first structure would be expected to make a somewhat higher contribution than the second, but both are important.) The third structure has charge separation (positive and negative charges in the same structure), a high charge on nitrogen (-2), and a positive charge on oxygen (which has a very high electronegativity), all of which make it much less important as a contributor to the overall behavior of cyanate.

For fulminate, the **first structure** should be the largest contributor by far. The second structure, with similar charge separation but with a high negative charge on carbon and no charge on oxygen, should be a minor contributor. The third structure, with larger charge separation, a positive charge on oxygen, and an extremely high charge on carbon, should be an extremely minor contributor to the overall behavior of fulminate.

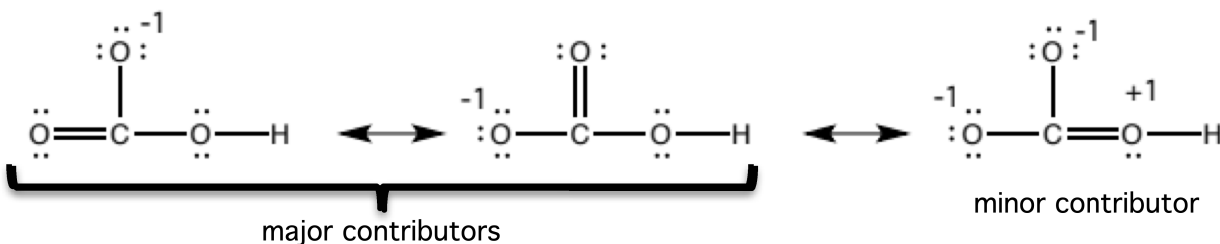
c) Since the actual structure of cyanate is roughly the average of resonance structures 1 and 2 above, **the nitrogen atom and the oxygen atom will share the negative charge.**

d) Since the actual structure of fulminate is quite close to resonance structure #1 above, **the carbon atom and the oxygen atom will share the negative charge.**

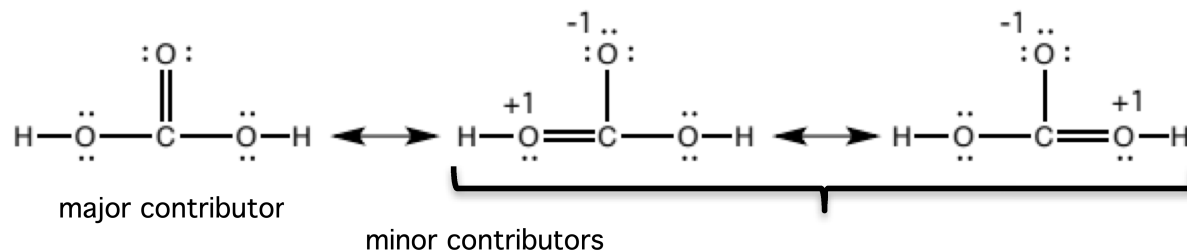
12) a) For CO_3^{2-} , there are three reasonable resonance structures. These structures are equivalent to each other, so the actual ion is an average of these three structures.



b) For HCO_3^- , there are also three reasonable resonance structures, but only two of them are major contributors. The other one has more atoms with nonzero formal charges, and it has a positively charged oxygen atom. The actual ion essentially looks like the average of the first two structures.



c) For H_2CO_3 , there are also three reasonable resonance structures, but now, just one of them is a major contributor. The other two have atoms with nonzero formal charges and a positively charged oxygen atom. The actual molecule essentially looks like the first structure.

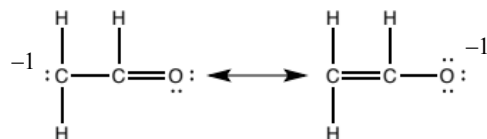


13) In CO_3^{2-} , **all three bonds are the same length**. The structures are equivalent, so each C–O bond is the average of a double bond and two single bonds (bond order = $\frac{4}{3}$ for each bond).

In HCO_3^- , **two of the C–O bonds are the same length**; they are the one on the left and the one above the C as I've drawn the structures in part b above. The real ion is essentially the average of the first two structures, so the left-hand and upper C–O bonds are the average of a double and a single bond (bond order = $\frac{3}{2}$ for each bond). The right-hand C–O bond is essentially a single bond.

In H_2CO_3 , **two of the C–O bonds are the same length**; they are the bonds on the left and right sides of the carbon atom as I've drawn the structures in part c above. The real molecule essentially looks like the first structure, in which the left-hand and right-hand bonds are single bonds and the upper bond is a double bond.

14) For the first two molecules, no resonance is possible, so bond A is a single bond and bond B is a double bond. For the third and fourth molecules, we can draw two resonance structures. Here are the two resonance structures for the third molecule, with non-zero formal charges included:



The second structure will be the major contributor, because it puts the negative charge on oxygen, which is more electronegative than carbon. Therefore, bond C is between a single and a double bond, but closer to a double bond.

Here are the two resonance structures for the fourth molecule, with non-zero formal charges included:



These structures are equivalent, so for both bond D and bond E, the order of bond D is 1.5 (the average of 1 and 2).

Now we can rank the four bonds. Starting with the shortest bond (i.e. the bond with the highest bond order), we get:

Shortest: Bond B (bond order = 2)
 Bond C (bond order between 1.5 and 2)
 Bond D (bond order = 1.5)
Longest: Bond A (bond order = 1)

15) **A: 120° B: 109.5° C: 90° D: 120° E: 180°**

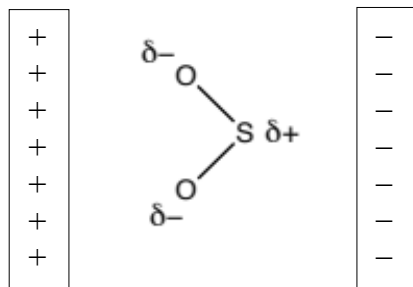
The left-hand carbon atom (at angles A and D) has three electron domains, making it trigonal planar, with all three angles around it being about 120°. The third carbon atom (at angle B) has four electron domains, making it tetrahedral, with all four angles around it being about 109.5°. The fourth carbon atom (at angle E) has two electron domains, making it linear, with the bond angle being 180°. The sulfur atom (at angle C) has six electron domains, making it octahedral, with all of the F-S-F and F-C-F angles around it being about 90°.

16) VSEPR is covered extensively in the laboratory, so I will not show detailed explanations for the molecular shapes.

a) **CO₂ is nonpolar and SO₂ is polar.** Here are the Lewis structures for the two molecules.



CO₂ has two electron domains, so it is linear, and therefore nonpolar. SO₂ has three electron domains, one of which is a lone pair, so it is bent, and therefore polar. (If SO₂ is placed into a box with charged sides, it has a preferred orientation, as shown below.)

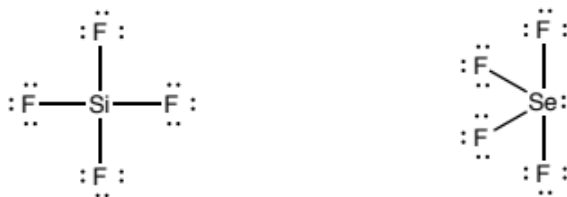


b) **NCl_3 is polar and BCl_3 is nonpolar.** Here are the Lewis structures for the two molecules.



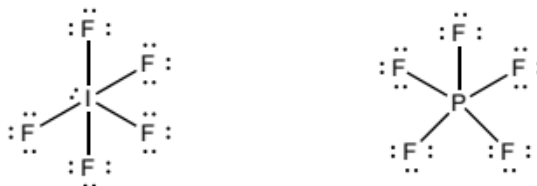
NCl_3 has four electron domains, one of which is a lone pair, so it is trigonal pyramidal, and therefore polar. The nitrogen atom is not centered between the three Cl atoms; it's somewhat above them. BCl_3 has three electron domains, so it is trigonal planar, and therefore nonpolar. The boron atom is exactly centered between the three Cl atoms, and the Cl atoms are spaced out evenly around the boron.

c) **SiF_4 is nonpolar and SeF_4 is polar.** Here are the Lewis structures for these molecules:



SiF_4 has four electron domains, so it is tetrahedral, and therefore nonpolar. The four fluorine atoms are spaced out evenly, with the Si atom exactly centered between them. SeF_4 has five electron domains, one of which is a lone pair, so it is see-saw shaped, and therefore polar. The four fluorine atoms are spread out unequally.

d) **IF_5 is polar and PF_5 is nonpolar.** Here are the Lewis structures for these molecules:



IF_5 has six electron domains, one of which is a lone pair, so it is square pyramidal, and therefore polar. The fluorine atom on the top of the pyramid is not balanced by a fluorine atom on the bottom. PF_5 has five electron domains, so it is trigonal bipyramidal, and therefore nonpolar. The five fluorine atoms are spread out evenly around the phosphorus atom.

17) To determine the hybridization, count the number of electron domains around the central atom. Two electron domains gives sp hybridization, three electron domains gives sp^2 hybridization, four electron domains gives sp^3 hybridization, five electron domains gives sp^3d hybridization, and six electron domains gives sp^3d^2 hybridization.

a) The nitrogen atom is **sp^3 hybridized**. It has four electron domains around it: the three bonds to the hydrogen atoms and one lone pair.

b) The phosphorus atom is **sp^3d hybridized**. It has five electron domains around it: the five bonds to the phosphorus atoms.

c) The carbon atom is **sp hybridized**. It has two electron domains around it: the two double bonds to the oxygen atoms. Remember that a double bond or a triple bond is just one electron domain.

d) The carbon atom is **sp^2 hybridized**. It has three electron domains around it: the two single bonds to hydrogen and the double bond to oxygen.

e) The iodine atom is **sp^3d^2 hybridized**. It has six electron domains around it: the five bonds to fluorine atoms and one lone pair.

f) The nitrogen atom is **sp^2 hybridized**. It has three electron domains around it: a single bond to one oxygen atom, a double bond to the other oxygen atom, and a lone pair.

18) a) The nitrogen atom has **four sp^3 orbitals**.

b) The phosphorus atom has **five sp^3d orbitals**.

c) The carbon atom has **two sp orbitals and two $2p$ orbitals**.

d) The carbon atom has **three sp^2 orbitals and one $2p$ orbital**.

e) The iodine atom has **six sp^3d^2 orbitals**.

f) The nitrogen atom has **three sp^2 orbitals and one $2p$ orbital**.

19) To answer this question, you must first determine the hybridization on each atom that is bonded to two or more other atoms. For outer atoms, you can either leave them unhybridized or you can hybridize them in the usual way (by counting electron domains). In this answer key, I will give both options.

Atoms that are hybridized use their hybrid orbitals to form all of the sigma bonds; atoms that are not hybridized use their outermost orbital (usually a p orbital).

a) The hydrogen uses its **$1s$ orbital**. The bromine uses a **$4p$ orbital** (or an sp^3 orbital if you use hybrid orbitals on outer atoms).

b) Each iodine atom uses a **$5p$ orbital** (or an sp^3 orbital if you use hybrid orbitals on outer atoms).

c) The carbon uses an **sp^3 orbital**. The fluorine uses a **$2p$ orbital** (or an sp^3 orbital if you use hybrid orbitals on outer atoms).

d) The carbon uses an **sp orbital**. The hydrogen uses its **$1s$ orbital**.

e) The carbon uses an **sp^2 orbital**. The chlorine uses a **$3p$ orbital** (or an sp^3 orbital if you use hybrid orbitals on outer atoms).

f) The left-hand carbon uses an **sp^3 orbital**, and the right-hand carbon uses an **sp^2 orbital**.

g) The carbon uses an **sp^2 orbital** and the oxygen uses an **sp^3 orbital**.

20) The nonbonding electrons are in **sp^3 orbitals**.

21) a) Any single bond is a sigma bond. A double bond contains one sigma bond and one pi bond, and a triple bond contains one sigma bond and two pi bonds. Here, we have eight single bonds, two double bonds, and one triple bond, so we have

$$8 + 2 + 1 = \mathbf{11 \text{ sigma bonds}}$$

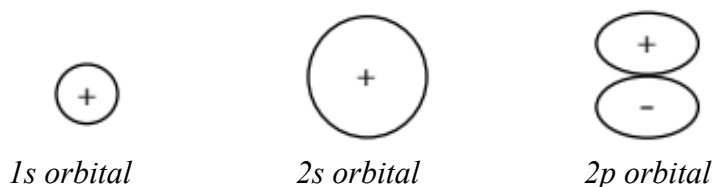
$$1 + 1 + 2 = \mathbf{4 \text{ pi bonds}}$$

b) Both atoms are sp^2 hybridized, because both have three electron domains around them. Therefore, each atom has three sp^2 orbitals and one 2p orbital. The double bond between them is made up of a sigma bond, which is formed by hybrid orbitals, and a pi bond, which is formed by p orbitals. Therefore, **the sigma bond is formed by an sp^2 orbital on each atom, and the pi bond is formed by a 2p orbital on each atom.**

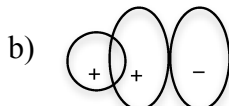
c) The carbon atom is sp hybridized, because it has two electron domains, so it has two sp orbitals and two 2p orbitals. The nitrogen atom is an outer atom, so it is not hybridized; it has one 2s orbital (which is filled) and three 2p orbitals (each of which is half-filled). The triple bond is made up of a sigma bond and two pi bonds, which are formed as follows: **the sigma bond is formed by an sp orbital on C and a 2p orbital on N, and each pi bond is formed by a 2p orbital on each atom.** (*If you hybridized the nitrogen atom, then the sigma bond is formed by an sp orbital on C and an sp orbital on N; the pi bond is as described above.*)

d) The nonbonding pair on the left-hand nitrogen is in an **sp^2 orbital**, and the nonbonding pair on the right-hand nitrogen is in a **2s orbital**. (*If you hybridized the right-hand nitrogen atom, its nonbonding pair is in an sp orbital.*)

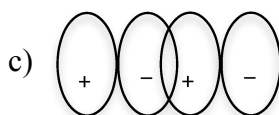
22) To answer this question, you need to know what each of the atomic orbitals looks like, and what the sign of the wave function is for each lobe.



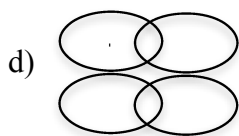
(Note: the 2s orbital has a second lobe that has a negative sign, but it is entirely inside the main lobe that is pictured here, and it can be ignored. Also, you can change the signs of the lobes in any orbital – make the 1s orbital's lobe negative, or exchange the signs of the two lobes of the 2p orbital.)



(Note that the 2p orbital must be turned sideways here.)



(The + lobe of one orbital overlaps with the – lobe of the other to form the antibonding MO.

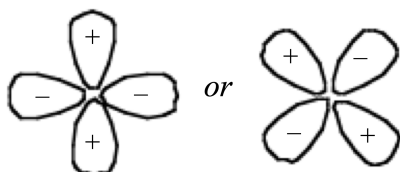


(Each orbital's + lobe must overlap the – lobe of the other orbital to form the antibonding MO. For the pi MO, the orbitals must overlap side-by-side instead of end-to-end as in part c.)

Note: p orbitals are typically drawn as shown to the right, but this is not accurate. A p orbital is not “tall and narrow.”

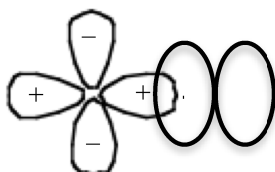


23) A d orbital has four lobes, which can be arranged in either of the following orientations:

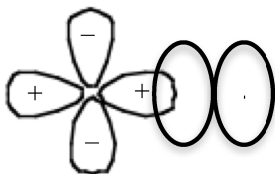


Note that the signs of the lobes alternate as you go around the orbital. In the first orientation, the positive lobes can be on the sides and the negative lobes can be on the top and bottom; you can similarly switch all of the signs on the second orientation.

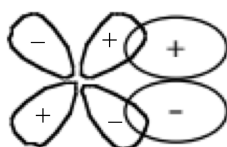
a) To make a sigma bonding MO, we must put a d and a p orbital together so they overlap in only one region (sigma overlap), and so the signs of the two lobes that overlap are the same (bonding overlap). Here is one way to do so:



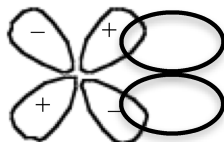
b) For a sigma antibonding MO, we simply reverse the signs of the lobes on one of the orbitals, so opposite signed lobes overlap.



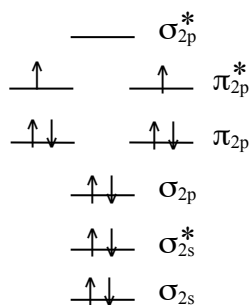
c) For a pi bonding MO, we must put the d orbital in a different orientation, so we get two regions of overlap, as shown on the next page. Note that again, lobes that are in contact must have the same sign.



d) For the pi antibonding MO, we reverse the signs of the lobes on one of the orbitals. I've reversed the signs on the p orbital here.



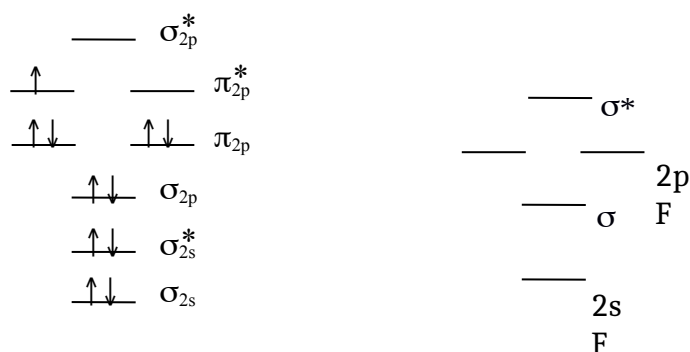
24) a) To determine the bond order in NO^- , we start by adding electrons to the MO diagram. NO^- has a total of 12 valence electrons, which fill the molecular orbitals as shown below.



Now we can determine the bond order. There are 8 bonding electrons and 4 antibonding electrons in NO^- , which gives us $8 - 4 = 4$ net bonding electrons. Since it takes 2 electrons to form a single bond, the bond order is $4/2 = 2$. In other words, NO^- has a double bond.

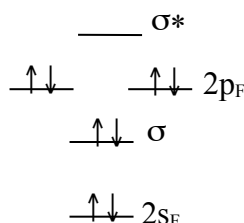
b) Any substance that has at least one unpaired electron is paramagnetic. NO^- has two unpaired electrons, so it is paramagnetic. It will be attracted by a magnet. (Diamagnetic substances are very weakly repelled by magnetic fields, but the effect can only be detected by sensitive measurements.)

c) NO has 11 valence electrons, which fill the molecular orbitals in this fashion:



There are 8 bonding and 3 antibonding electrons in NO, so we have 5 net bonding electrons, giving us a bond order of 2.5. The bond order in NO is larger than the bond order in NO^- , so the bond distance in NO^- is larger than the bond distance in NO.

25) a) Again, we begin by filling the molecular orbitals. There are 8 valence electrons in HF (1 from H and 7 from F), so we have:

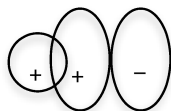


There are three occupied orbitals, but the $2s_F$ and $2p_F$ orbitals are nonbonding orbitals, meaning that they do not affect the bond order in any way. Therefore, HF has two bonding electrons (in the σ orbital) and no antibonding electrons. **The bond order in HF is 1.**

b) HF is **diamagnetic**, because it has no unpaired electrons.

c) There are **6 nonbonding electrons** in the HF molecule. (This does not include the core electrons on F, which are in a $1s$ orbital and are not shown on the MO diagram.)

d) The σ orbital is formed by the overlap of the $1s$ orbital of H and a $2p$ orbital on F.



e) The electron would come out of one of the $2p_F$ orbitals, which have no effect on bonding. Therefore, **there would be no effect on the bond energy.**