

## 13.19: Solutions to Selected Problems

### Exercise 13.2.1:

When two s orbitals combine out-of-phase, destructive interference occurs.

There is a node between the atoms.

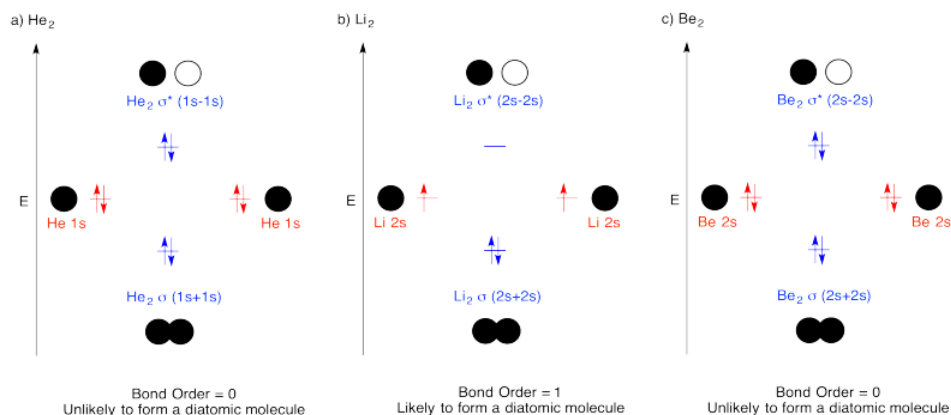
The energy of the electrons increases.

When two s orbitals combine in-phase, constructive interference occurs.

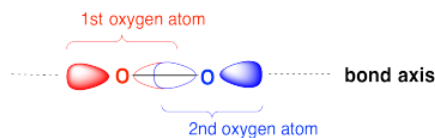
There is no node between the atoms; the electrons are found between the atoms.

The energy of the electrons decreases.

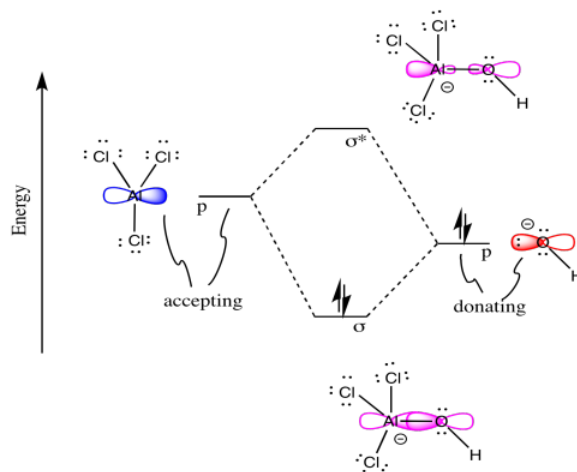
### Exercise 13.3.1:



### Exercise 13.4.1:

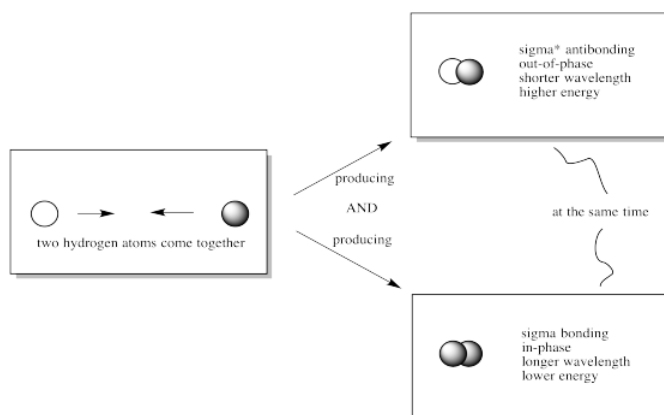


### Exercise 13.4.2:



### Exercise 13.5.1:

When 2 atomic orbitals are combined, 2 molecular orbitals are formed: one in-phase bonding orbital and one out-of-phase antibonding orbital.



#### Exercise 13.5.2:

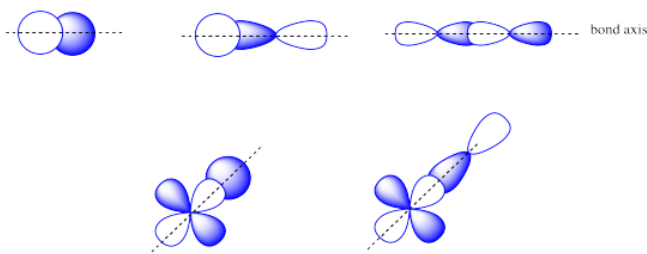
In-phase combinations of atomic orbitals give **bonding** orbitals.

#### Exercise 13.5.3:

Out-of-phase combinations of atomic orbitals give **antibonding** orbitals.

#### Exercise 13.5.4:

The combinations of  $s + s$  OR  $s + p$  OR  $p + p$  OR  $s + d$  OR  $p + d$  atomic orbitals can lead to  $\sigma$  orbitals.



#### Exercise 3.5.5:

The combinations of side by side  $p + p$  or  $p + d$  atomic orbitals leads to  $\pi$  orbitals.



e)  $\sigma^*$

#### Exercise 13.5.7:

$\text{Li}^+$  and  $\text{O}^{2-}$  are more similar in size than  $\text{K}^+$  and  $\text{O}^{2-}$ , so the bond between  $\text{Li}^+$  and  $\text{O}^{2-}$  is stronger.

The energy difference between the 1s orbitals and 2s orbitals is too large, so they cannot interact. In order for orbitals to interact, the orbitals need to have the same symmetry, be in the same plane, and be similar in energy.

#### Exercise 13.5.8:

When two parallel p orbitals combine out-of-phase, destructive interference occurs.

There is a node between the atoms.

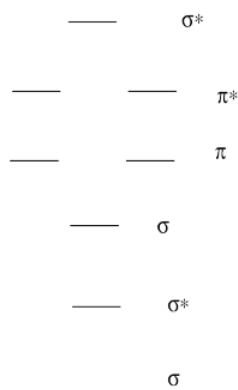
The energy of the electrons increases.

When two parallel p orbitals combine in-phase, constructive interference occurs.

There is no node between the atoms; the electrons are found above and below the axis connecting the atoms.

The energy of the electrons decreases.

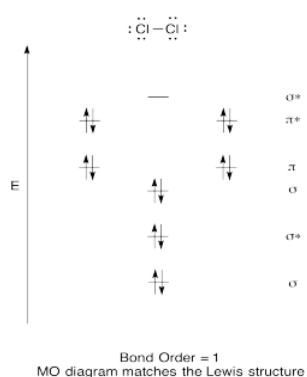
#### Exercise 13.6.1:



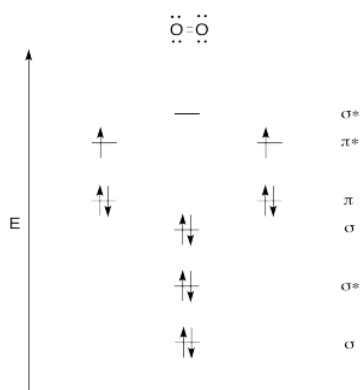
#### Exercise 13.6.2:

- Count the valence electrons on the molecule. That's the number of valence electrons on each atom, adjusted for any charge on the molecule. (eg  $C_2^{2-}$  has 10 valence electrons: 4 from each carbon -- that's 8 -- and two more for the 2- charge).
- Fill electrons into the lowest energy orbitals first.
- Pair electrons after all orbitals at the same energy level have one electron.

#### Exercise 13.6.3:

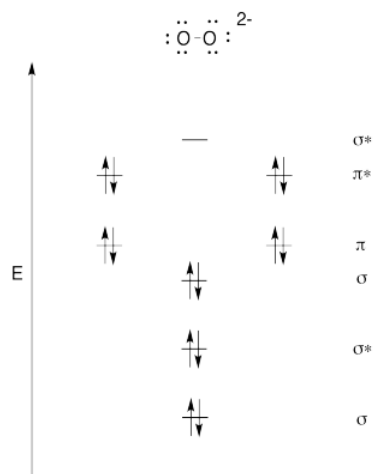


#### Exercise 13.6.4:



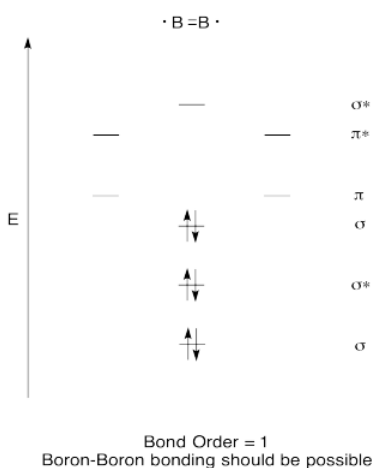
Bond Order = 2  
MO diagram indicates two unpaired electrons and therefore does not match the Lewis structure. Based on the MO diagram oxygen would be paramagnetic and would be attracted to a magnetic field

### Exercise 13.6.5:

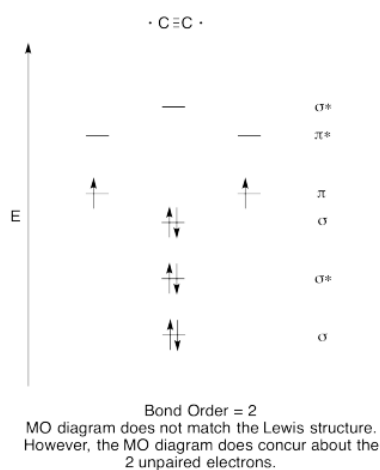


Bond Order = 1  
MO diagram matches the Lewis structure. Both predict a Bond Order of 1 and 6 lone pairs of electrons. The addition of two electrons to  $O_2$  to  $O_2^{2-}$  would be possible.

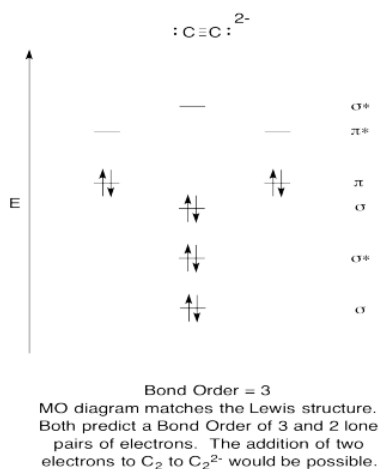
### Exercise 13.6.6:



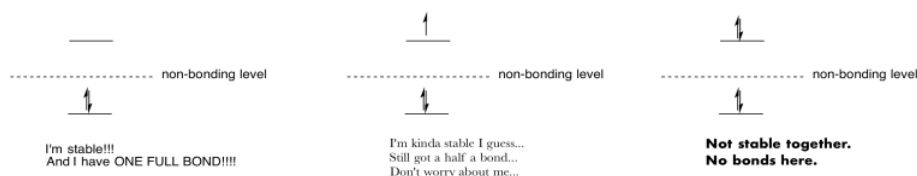
Exercise 13.6.7:



Exercise 13.6.8:

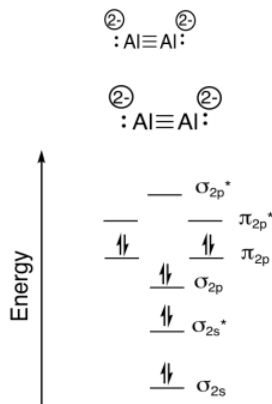


Exercise 13.6.9:



### Exercise 13.6.10

- Na, because Na has a lower ionization potential (and a lower electronegativity) than Al.
- Al
- 4-, because there are four  $\text{Na}^+$
- total  $e^- = 2 \times 3 e^-$  (per Al) +  $4 e^-$  (for the negative charge) =  $10 e^-$



$$\text{g) bond order} = \frac{\# \text{ bonding } e^- - \# \text{ antibonding } e^-}{2} = \frac{8-2}{2} = 3$$

### Exercise 13.7.1:

From MO6: 3. Diamagnetic (no unpaired electrons); 4. Paramagnetic; 5. Diamagnetic; 6. Diamagnetic; 7. Paramagnetic; 8. Diamagnetic

### Exercise 13.7.2:

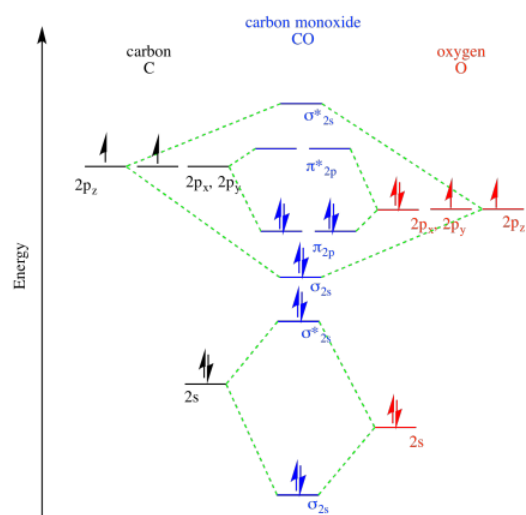
- $\text{N}_2^+$ . From the MO diagrams,  $\text{N}_2^+$  has one less bonding electron. Thus, the bond order will be lower and the bond will be longer than in  $\text{N}_2$ .
- $\text{N}_2^-$ . From the MO diagrams,  $\text{N}_2^-$  has one more antibonding electron. Thus the bond order will be lower and the bond will be longer than  $\text{N}_2$ .

### Exercise 13.7.3:

- $\text{O}_2^+$ . From the MO diagram,  $\text{O}_2^+$  has one less antibonding electron. Thus the bond order will be higher and the bond will be stronger than in  $\text{O}_2$ .
- $\text{O}_2$ . From the MO diagram,  $\text{O}_2$  has one less antibonding electron. Thus the bond order will be higher and the bond will be stronger than in  $\text{O}_2^-$ .

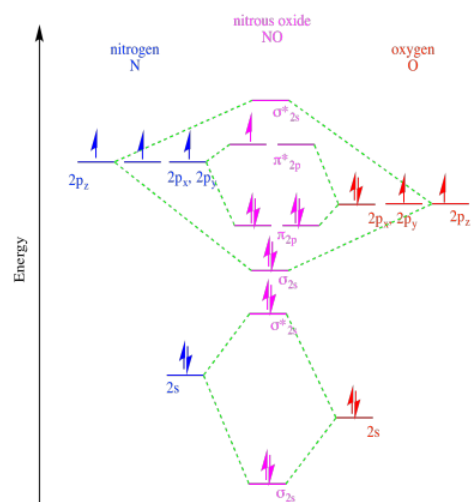
### Exercise 13.9.1:

-



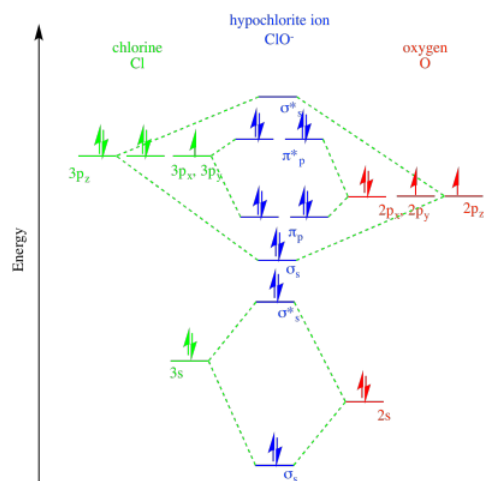
diamagnetic; bond order = 3 (3 net pairs bonding)

b)



paramagnetic (one electron unpaired);  
bond order = 2.5 (2 net pairs bonding; third bonding pair offset by one electron antibonding)

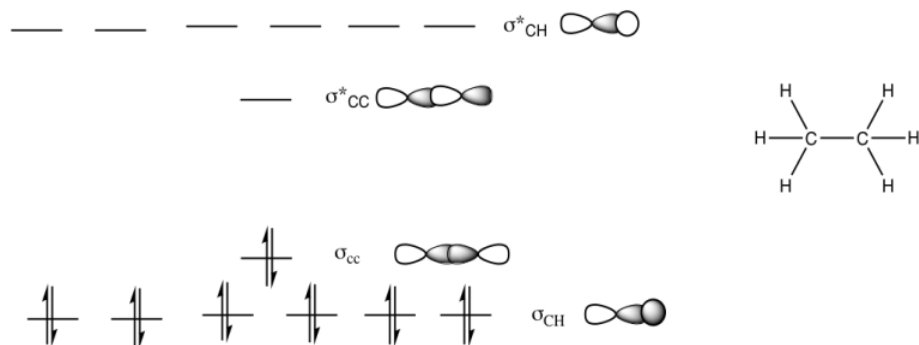
c)



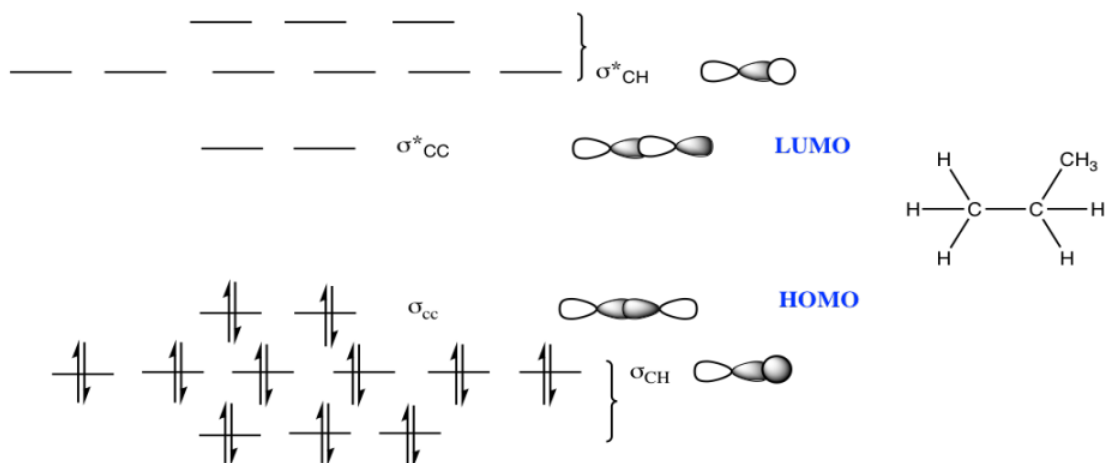
Note that the hypochlorite anion has one additional electron to make it negative.  
diamagnetic; bond order = 1 (1 net pair bonding)

### Exercise 13.11.1:

a)

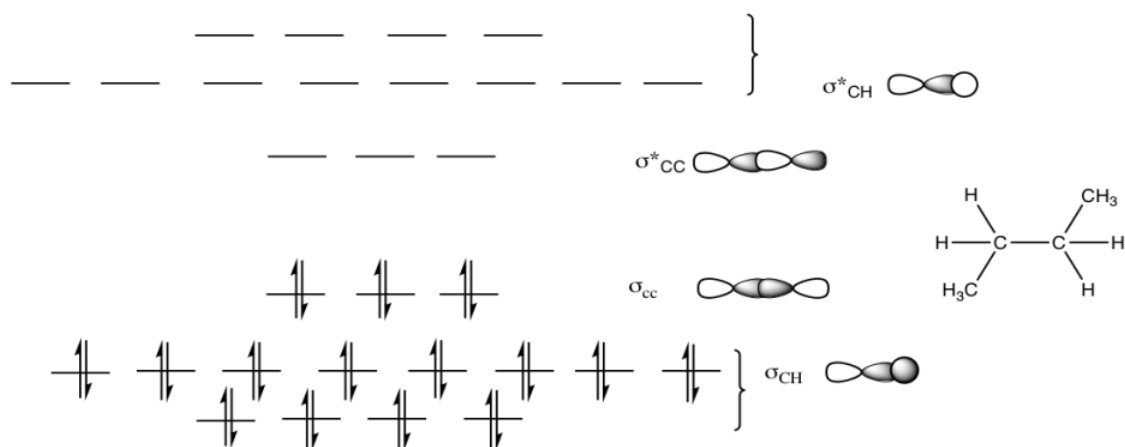


b)



c)

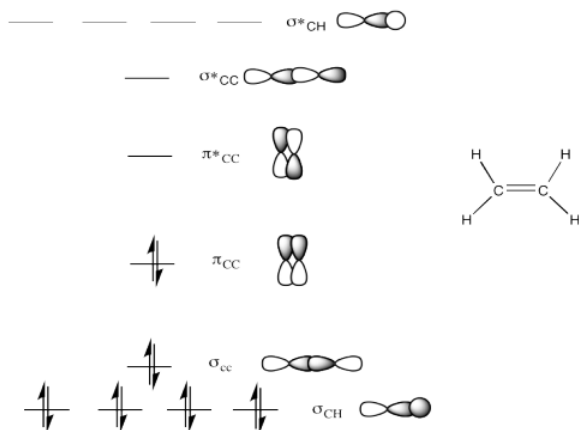




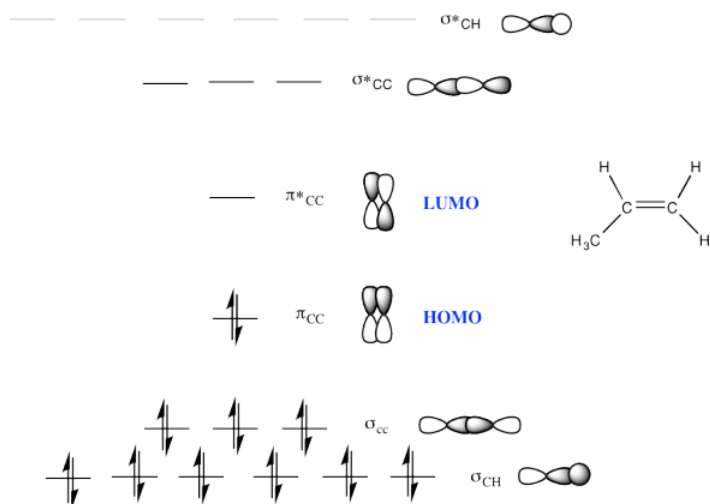
The number of orbitals = the number of bonds and the number of antibonds  
(thus twice as many orbitals as you would draw in a lewis structure).

Exercise 13.11.2:

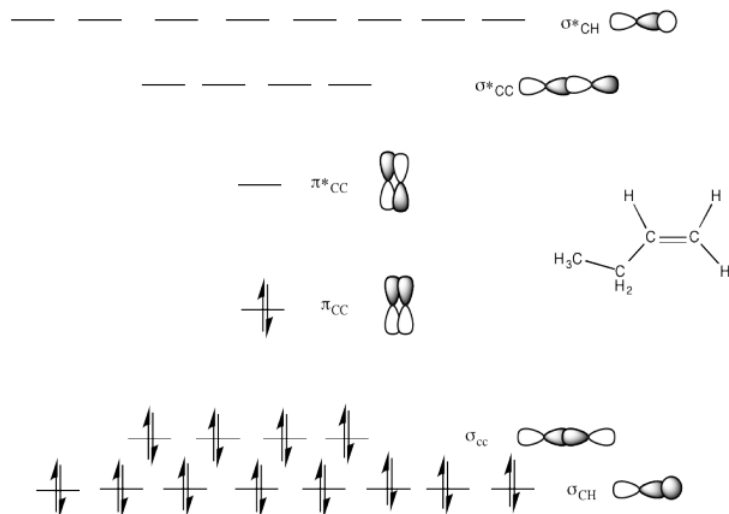
a)



b)

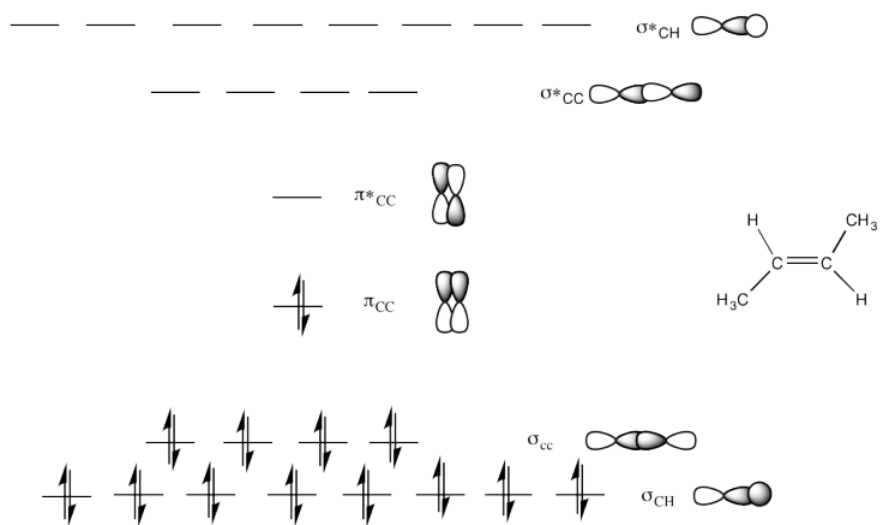


c)



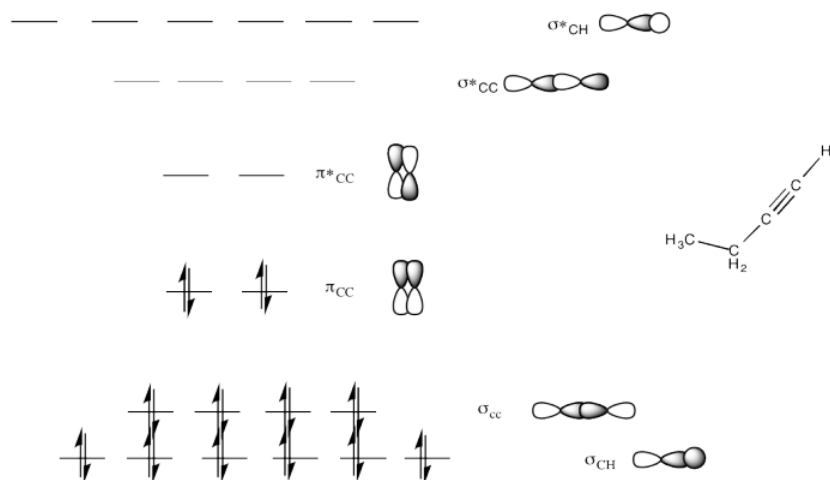
The number of orbitals = the number of bonds and the number of antibonds  
(thus twice as many orbitals as you would draw in a lewis structure.

d)



Location of pi bond makes little to no difference to the MO pattern.

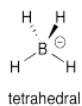
e)



It results in the addition of another pi bond with approximately the same energy level.

### Exercise 13.11.3:

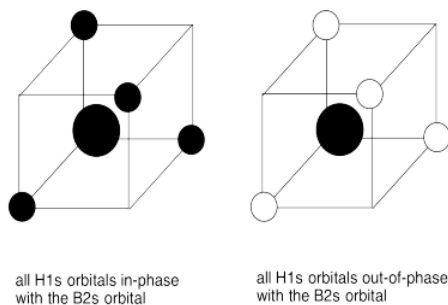
a)



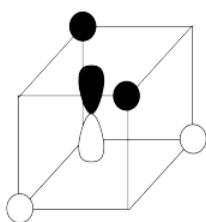
b)



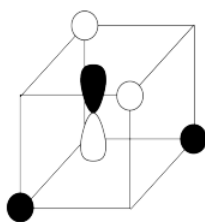
c)



d)

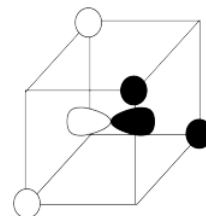


all H1s orbitals in-phase  
with the B2p<sub>z</sub> orbital

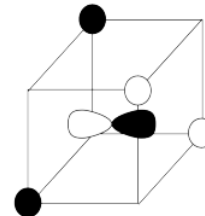


all H1s orbitals out-of-phase  
with the B2p<sub>z</sub> orbital

e)

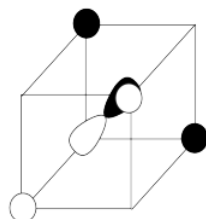


all H1s orbitals in-phase  
with the B2p<sub>y</sub> orbital

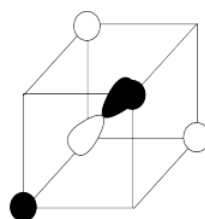


all H1s orbitals out-of-phase  
with the B2p<sub>y</sub> orbital

f)



all H1s orbitals in-phase  
with the B2p<sub>x</sub> orbital



all H1s orbitals out-of-phase  
with the B2p<sub>x</sub> orbital

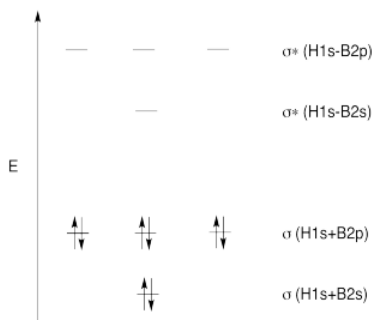
g) In each case all four H1s orbitals interact with each boron orbital.

h) The constructive overlap of the four H1s orbitals and the B2s orbital results in the lowest energy combination as it contains no nodes. (LOWEST ENERGY)

The constructive overlap of the four H1s orbitals with the three B2p orbitals results in bonding orbitals containing a single node. (MEDIUM-LOW ENERGY)

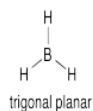
The destructive overlap of the four H1s orbitals with the B2s orbital results in an anti-bonding orbital. (HIGH ENERGY)

The destructive overlap of the four H1s orbitals with the three B2p orbitals results in anti-bonding orbitals. (HIGHEST ENERGY)



#### Exercise 13.11.4:

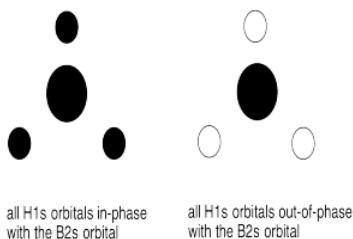
a)



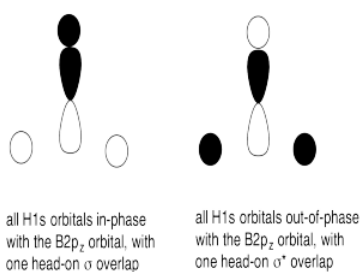
b)



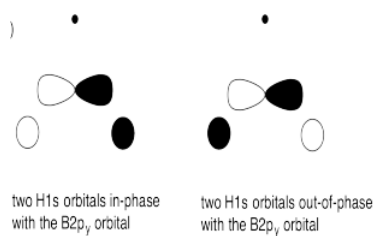
c)



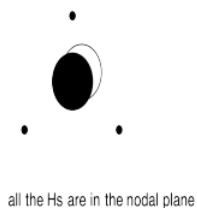
d)



e)



f)



g) In some of the cases the one or more Hs may be in a nodal plane

h) The constructive overlap of the H1s orbitals and the B2s orbital results in the lowest energy combination. (LOWEST ENERGY)

The constructive overlap of the three H1s orbitals with the B2p orbital results in a bonding orbital (MEDIUM-LOW ENERGY)

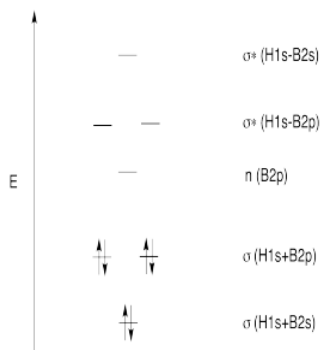
The constructive overlap of the two H1s orbitals with the B2p orbital results in a bonding orbital. (MEDIUM-LOW ENERGY)

The B2p orbital that is perpendicular to the plane of hydrogen atoms results in a non-bonding orbital. (MEDIUM ENERGY)

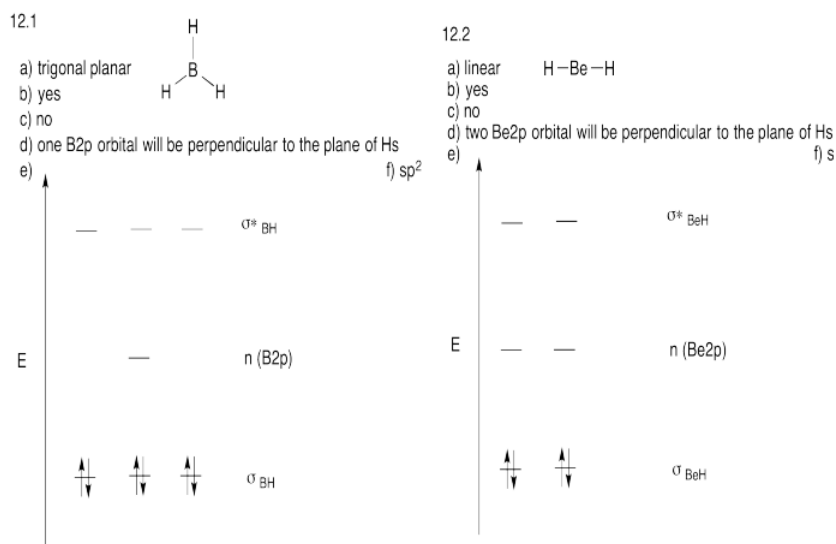
The destructive overlap of the two H1s orbitals with the B2p orbital results in an anti-bonding orbital (HIGH ENERGY)

The destructive overlap of the three H1s orbitals with the B2p orbital results in an anti-bonding orbital (HIGH ENERGY)

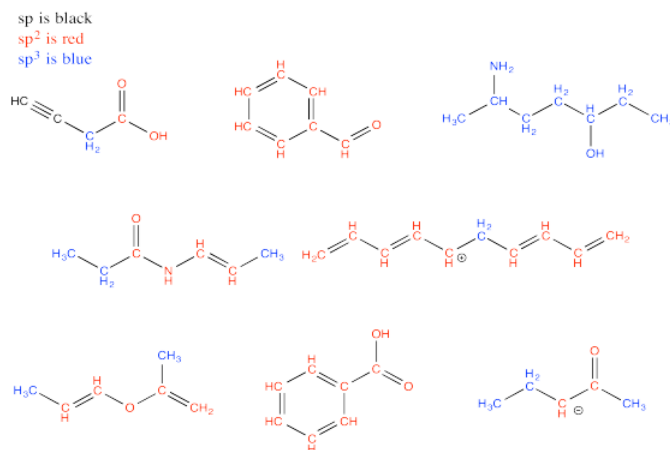
The destructive overlap of the three H1s orbitals with the B2p orbital results in an anti-bonding orbital (HIGHEST ENERGY)



### Exercises 13.12.1 & 13.12.2:

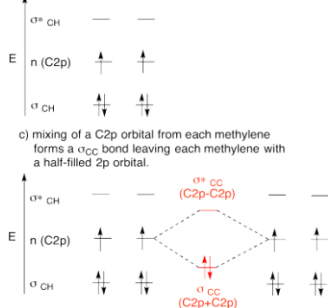


### Exercise 13.12.3:



### Exercises 13.13.1-13.13.3:

13.1 a) linear  $\cdot\dot{\text{C}}\text{H}_2$   
b) one 2s and one 2p orbital

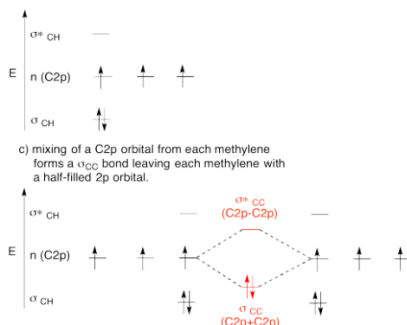


c) mixing of a C2p orbital from each methylene forms a  $\sigma_{\text{CC}}$  bond leaving each methylene with a half-filled 2p orbital.

d) The half-filled 2p orbitals on each methylene could mix with each other to form a  $\pi$  bond. NOTE: the carbon geometry changes to trigonal planar.



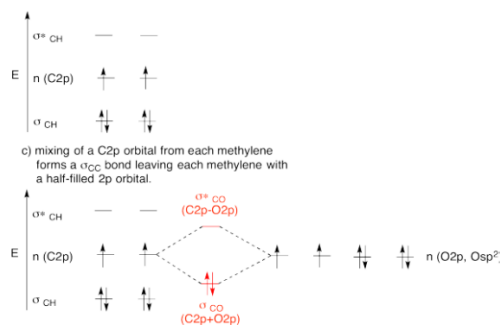
13.2 a) linear  $\cdot\dot{\text{C}}\text{H}$   
b) one 2s



c) mixing of a C2p orbital from each methylene forms a  $\sigma_{\text{CC}}$  bond leaving each methylene with a half-filled 2p orbital.

d) The two half-filled 2p orbitals on each methyne mix with each other to form a  $2\pi$  bonds.  $\text{HC}\equiv\text{CH}$

13.3 a) linear  $\cdot\dot{\text{C}}\text{H}_2$   
b) one 2s and one 2p orbital

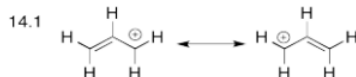


c) mixing of a C2p orbital from each methylene forms a  $\sigma_{\text{CC}}$  bond leaving each methylene with a half-filled 2p orbital.

d) The half-filled 2p orbitals on each methylene could mix with each other to form a  $\pi$  bond. NOTE: the carbon geometry changes to trigonal planar.



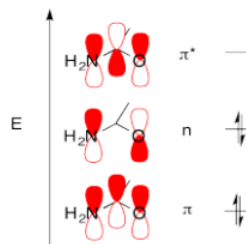
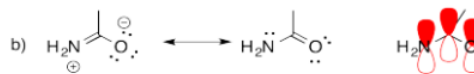
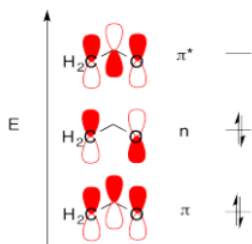
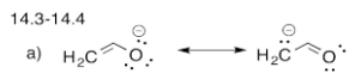
### Exercises 13.14.1-13.14.5:



These two resonance structures follow the Lewis rules, but both are necessary to illustrate the delocalize electrons



These two resonance structures follow the Lewis rules, but both are necessary to illustrate the delocalize electrons





14.5

a) acetone, no conjugation as the oxygen lone pair electrons are perpendicular to the  $\pi$  orbital



b) bicarbonate, this is a conjugated system as the oxygen lone pair electrons align with the  $\pi$  orbital



c) acetonitrile, this is not a conjugated system as the oxygen lone pair electrons are perpendicular to the  $\pi$  orbital



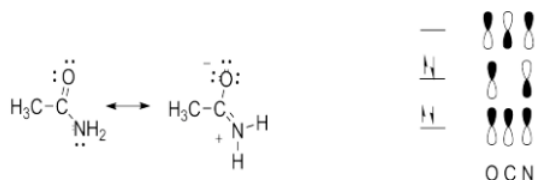
(NOTE: second perpendicular  $\pi$  orbital is not shown)

d) dinitrogen tetroxide, this is a conjugated system as the oxygen lone pair electrons align with the  $\pi$  orbital



### Exercise 13.14.6:

All of the answers depend on an understanding of the contributions of two resonance structures to the overall picture of acetaminde, or alternatively, that acetamide forms a conjugated pi system with four electrons delocalized over the O, C and N.



a. Contribution of the second resonance structure introduces some double bond character to the C-N bond and some single bond character to the C-O bond. Thus, both of these bonds are intermediate in length between single and double bonds.

b. Since the C, N and O atoms are  $\text{sp}^2$  hybridized, the C-N pi bond can only form if the remaining p orbitals on these atoms align. This places the atoms participating in the  $\text{sp}^2$  sigma bonds in the same plane.

c. Because of the partial double bond character there is a larger barrier to rotation than is typically found in molecules with only single bonds.

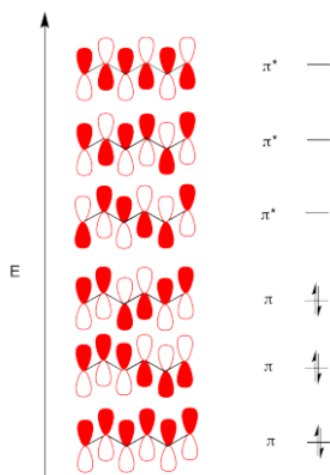
d. Because of the partial double bond character and the restricted rotation, the two H's are not identical. (One is nearer the O and one is nearer the CH<sub>3</sub> and the restricted rotation prevents their interconversion.)

### Exercises 13.15.1-13.15.3:



15.1 Cis-alkenes in the carbon chains cause the packing to be less orderly than in saturated carbon chains

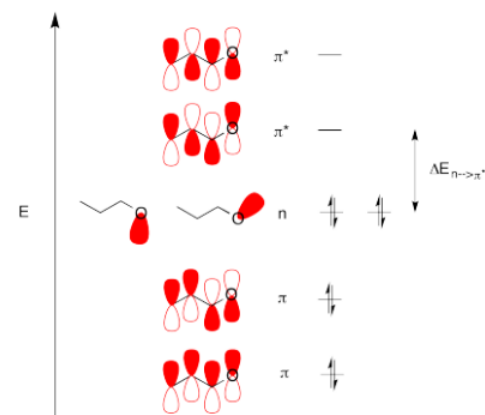
15.2 



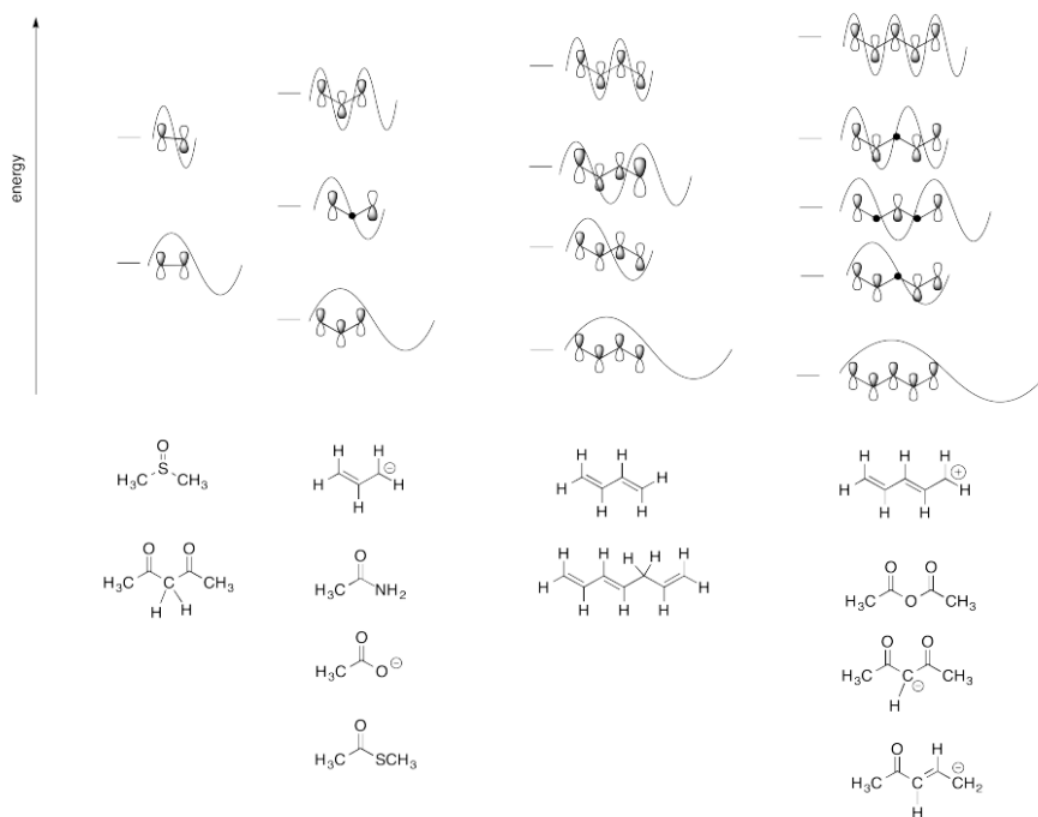
15.3



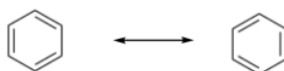
The  $n \rightarrow \pi^*$  energy gap will be smaller for propenal as the LUMO will be lower in energy due to conjugation effects. Therefore, the absorption wavelength will be shorter for propanal and longer for propenal.



Exercise 13.15.4:



Exercise 13.16.1:



Because the two resonance structures shows double bonds in two different places, the implication is that all of the bonds in benzene have some double bond and some single bond character. You can think of them all as being about 1.5 bonds.

Exercise 13.16.2:

a) non-aromatic b) non-aromatic c) aromatic d) aromatic e) anti-aromatic f) anti-aromatic

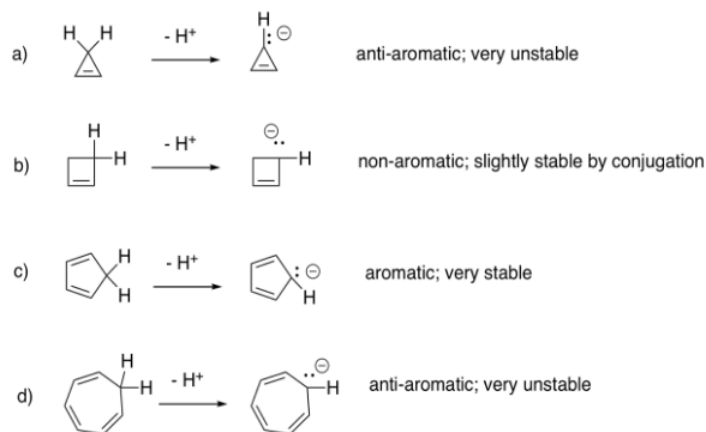
Exercise 13.16.3:

a) aromatic b) non-aromatic c) anti-aromatic d) aromatic

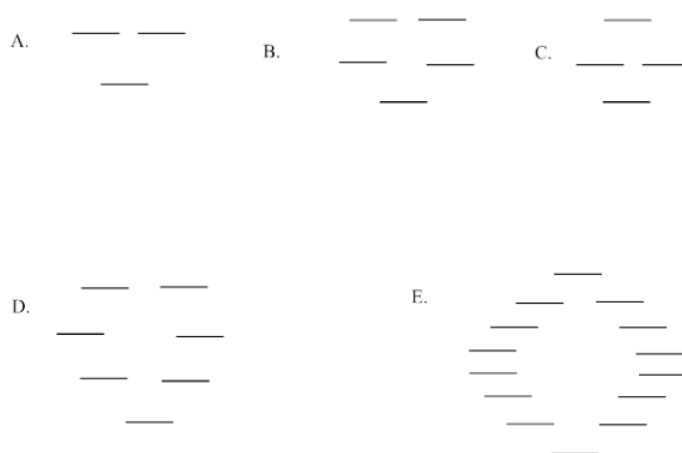
Exercise 13.16.4:

a) aromatic b) anti-aromatic c) aromatic d) anti-aromatic

Exercise 13.16.5:

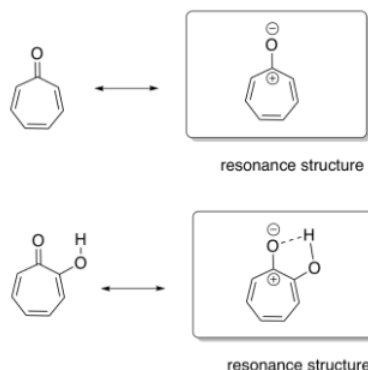


#### Exercise 13.16.6:



#### Exercise 13.16.7:

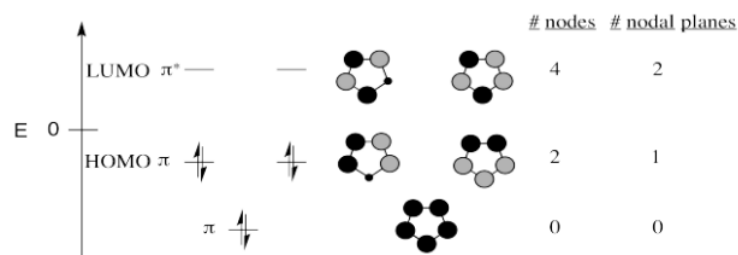
In tropone, the resonance structure on the right shows more aromatic character, because it clearly shows a fully-conjugated ring with an odd number of electron pairs in the pi system. The carbonyl in the picture on the left makes that conjugation less obvious: does its carbonyl pi bond contribute to the conjugated system of the ring? If it does, that would mean four pairs of electrons in the pi system, and that would be an even number, so it would be anti-aromatic.



The hydroxy group in hydroxytropone would stabilize the compound in the structure shown on the right, via an ion-dipole interaction with the anionic oxygen. That makes the right-hand, explicitly aromatic structure the dominant one.

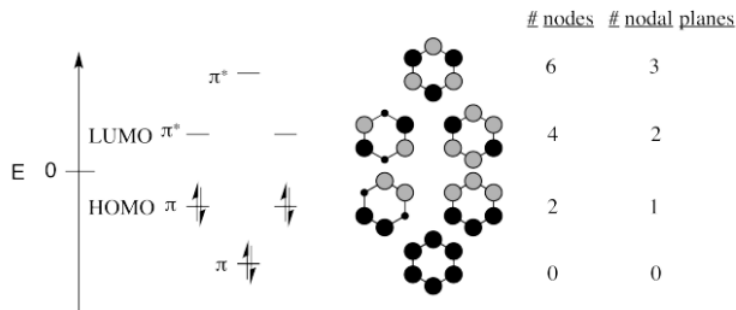
#### Exercise 13.17.1:

All of the compounds are aromatic and have the same Hückel MO diagram.



Exercise 13.17.2:

All of the compounds are aromatic and have the same Hückel MO diagram.



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