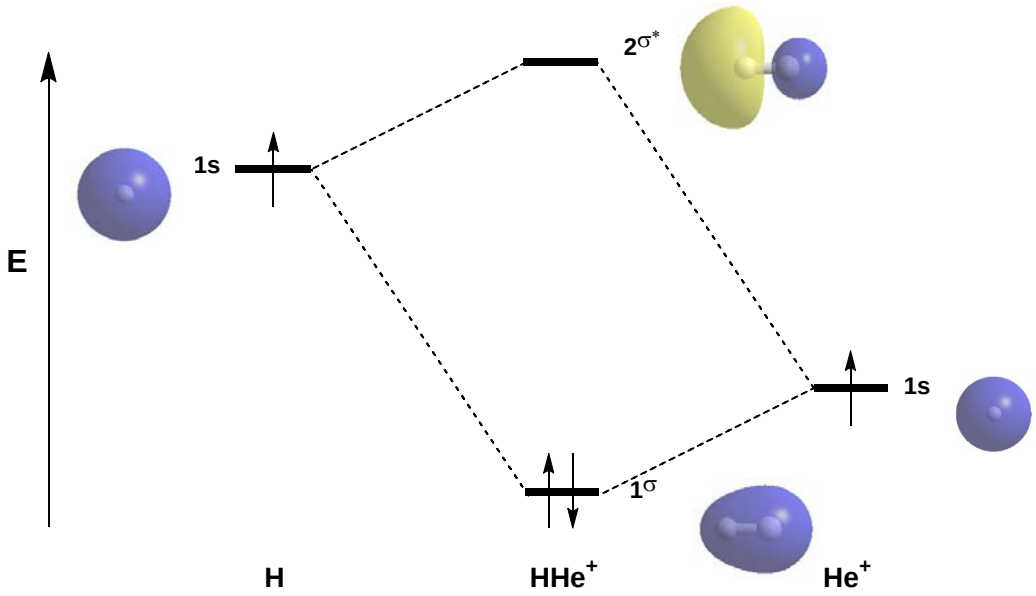
Answers to Practice Test Questions 3
Molecular Orbital Theory: Heteronuclear Diatomic Molecules

1.

(a) The electron configuration for H is $1s^1$, so H has 1 valence electron.
The electron configuration for He is $1s^2$, so He has 2 valence electrons.
Therefore, HHe would have 3 valence electrons, and HHe^+ has 2 valence electrons.



(b) $\frac{2-0}{2} = \frac{2}{2} = 1$

(c) diamagnetic
All electrons are spin-paired.

2.

(a) These energies would be obtained by photoelectron spectroscopy.
High-energy photons ionize a sample. Part of the energy of each photon goes into the ionization process, and the rest shows up as kinetic energy of the ejected electron. The ionization energy is E_i, where the orbital energy is $-E_i$. By measuring the kinetic energies of the ejected electrons and comparing to the energy of a photon, we can therefore calculate the corresponding orbital energies:

$$E_{photon} = E_i + E_k(ejected\ electron)$$

Therefore:

$$E_i = E_{photon} - E_k(ejected\ electron)$$

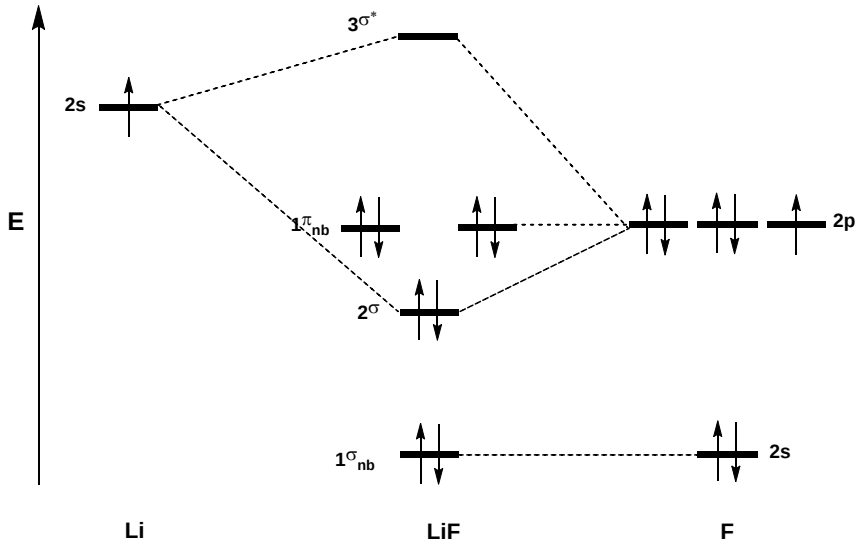
(b) The electron configuration for Li is $1s^2 2s^1$, so Li has 1 valence electron.

The electron configuration for F is $1s^2 2s^2 2p^5$, so F has 7 valence electrons.

Therefore, LiF has 8 valence electrons.

Grouping the valence AOs by symmetry and energy gives:

- one pi-symmetric $2p_x$ orbital on F,
- one pi-symmetric $2p_y$ orbital on F,
- one sigma-symmetric $2s$ orbital on F that is more than 1 Ry away from the nearest other sigma-symmetric orbital, and
- two sigma-symmetric AOs close enough in energy to combine: $2s(Li)$ and $2p_z(F)$.

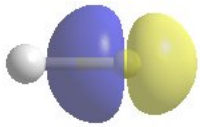


The valence orbital occupancy for LiF is $(1\sigma_{nb})^2(2\sigma)^2(1\pi_{nb})^4$

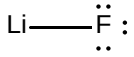
The $Li - F$ bond order is $\frac{2-0}{2} = \frac{2}{2} = 1$

Since you weren't provided with the energy for the $2p(Li)$ orbitals, it was expected that you would leave them off the MO diagram. If you wanted to include them, they would be slightly higher in energy than the $2s(Li)$ orbital - approximately -0.3 Ry or so. This would introduce three more unoccupied nonbonding MOs (two π_{nb} and one σ_{nb}) with energies approximately equal to $2p(Li)$.

(c) The bonding MO (2σ) is much closer in energy to $2p_z(F)$ than it is to $2s(Li)$. As such, it is strongly polarized toward the fluorine atom, looking like:



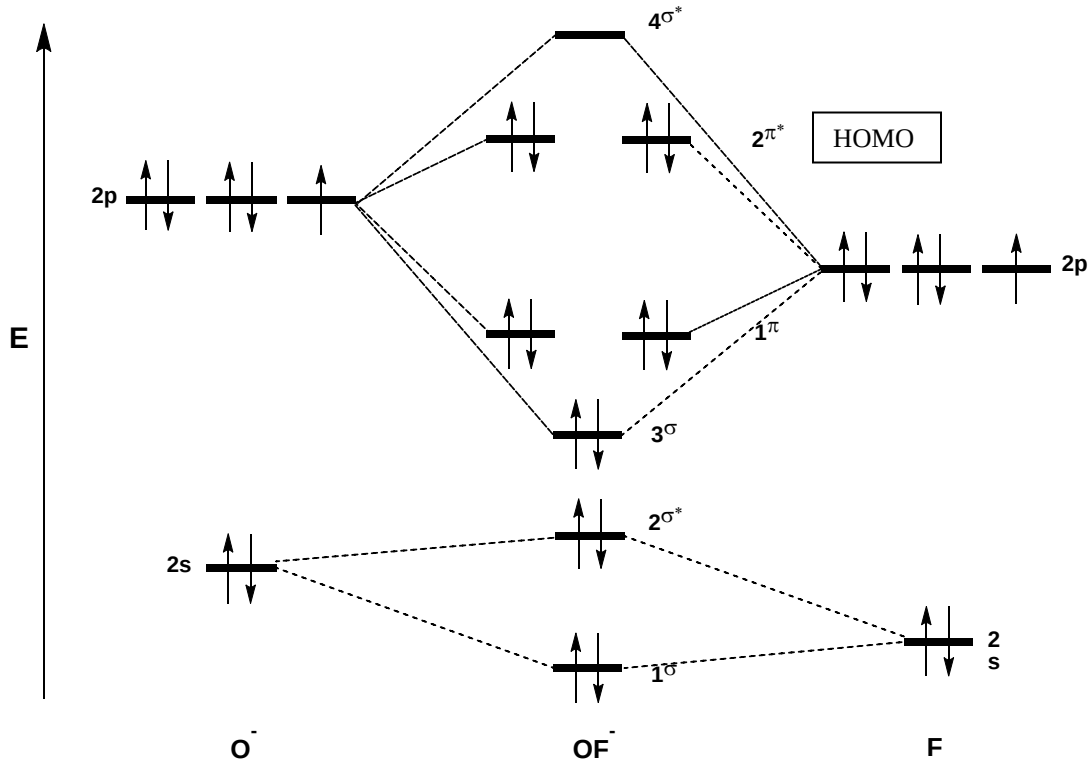
This translates to a polar $Li - F$ bond with more electron density on the fluorine atom, giving fluorine a partial negative charge and lithium a partial positive charge. This is consistent with substantial ionic character (i.e. a strong dipole) for the $Li - F$ bond.

(d) 

Both the Lewis diagram and the MO diagram show the $Li - F$ bond as a single bond (bond order = 1) and three pairs of nonbonding electrons on fluorine.

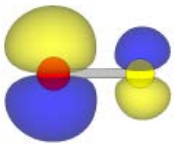
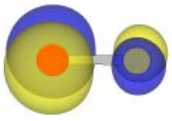
3. The electron configuration for O is $1s^2 2s^2 2p^4$, so O has 6 valence electrons.
The electron configuration for F is $1s^2 2s^2 2p^5$, so F has 7 valence electrons.
Therefore, OF would have 13 valence electrons, and OF^- has 14 valence electrons.
Grouping the valence AOs by symmetry and energy gives:

- two pi-symmetric $2p_x$ orbitals, one from each atom,
- two pi-symmetric $2p_y$ orbitals, one from each atom,
- two sigma-symmetric $2s$ orbitals, one from each atom, and
- two sigma-symmetric $2p_z$ orbitals, one from each atom.



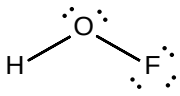
Combining O and F^- would be equally acceptable.

(b) The HOMOs have been labeled in the answer to part (a).

 and 

The red atom is O. The yellow atom is F.

(c)



(d) Electrons in the HOMO will be donated to H^+ to make the new bond. As can be seen in part (b), the HOMO is polarized toward the oxygen atom (i.e. more electron density lies around the oxygen atom than the fluorine atom), so the oxygen atom will be the reactive site, and the new bond will be from oxygen to hydrogen.

4.

(a) The Cl nucleus contains 17 protons while the H nucleus contains only 1 proton. So, the $1s$ electrons in Cl are more strongly attracted to the nucleus than the $1s$ electrons in H.

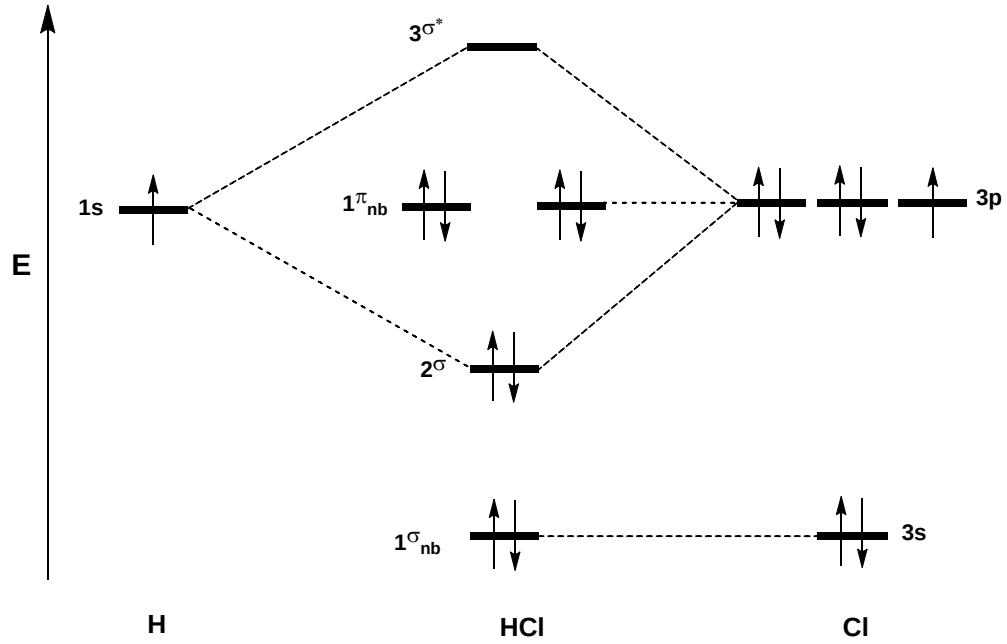
(b) The electron configuration for H is $1s^1$, so H has 1 valence electron.

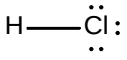
The electron configuration for Cl is $1s^2 2s^2 2p^6 3s^2 3p^5$, so Cl has 7 valence electrons..

Therefore, HCl has 8 valence electrons.

Grouping the valence AOs by symmetry and energy gives:

- one pi-symmetric $3p_x$ orbital on Cl,
- one pi-symmetric $3p_y$ orbital on Cl,
- one sigma-symmetric $3s$ orbital on Cl that is more than 1 Ry away from the nearest other sigma-symmetric orbital, and
- two sigma-symmetric AOs close enough in energy to combine: $1s(H)$ and $3p_z(Cl)$.



(c) 

(d) The Lewis diagram shows an $H - Cl$ bond order of 1 (single bond).

The $H - Cl$ bond order calculated from the MO diagram is $\frac{2-0}{2} = \frac{2}{2} = 1$.

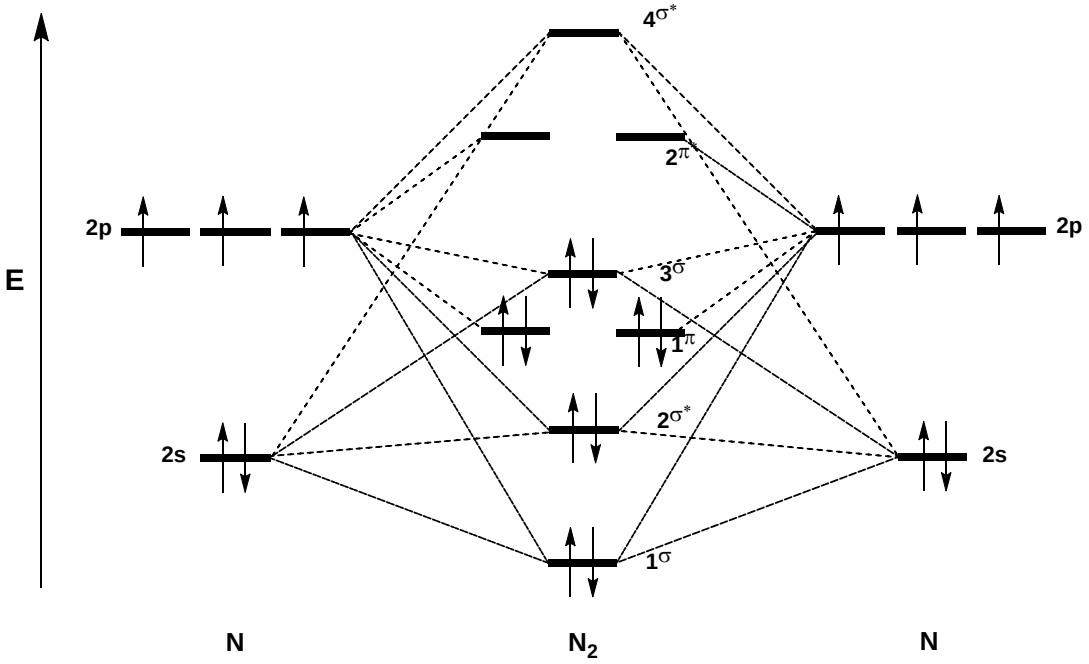
The Lewis diagram shows three pairs of nonbonding electrons on Cl.

The MO diagram shows three pairs of nonbonding electrons in MOs localized on Cl.

The two bonding theories therefore give the same picture of HCl.

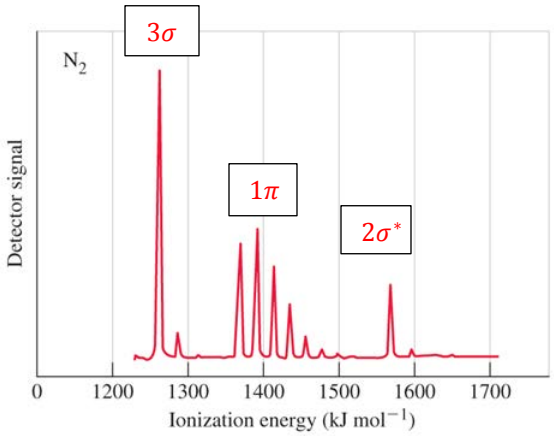
5.

(a)



(b) $\frac{8-2}{2} = \frac{6}{2} = 3$

(c)

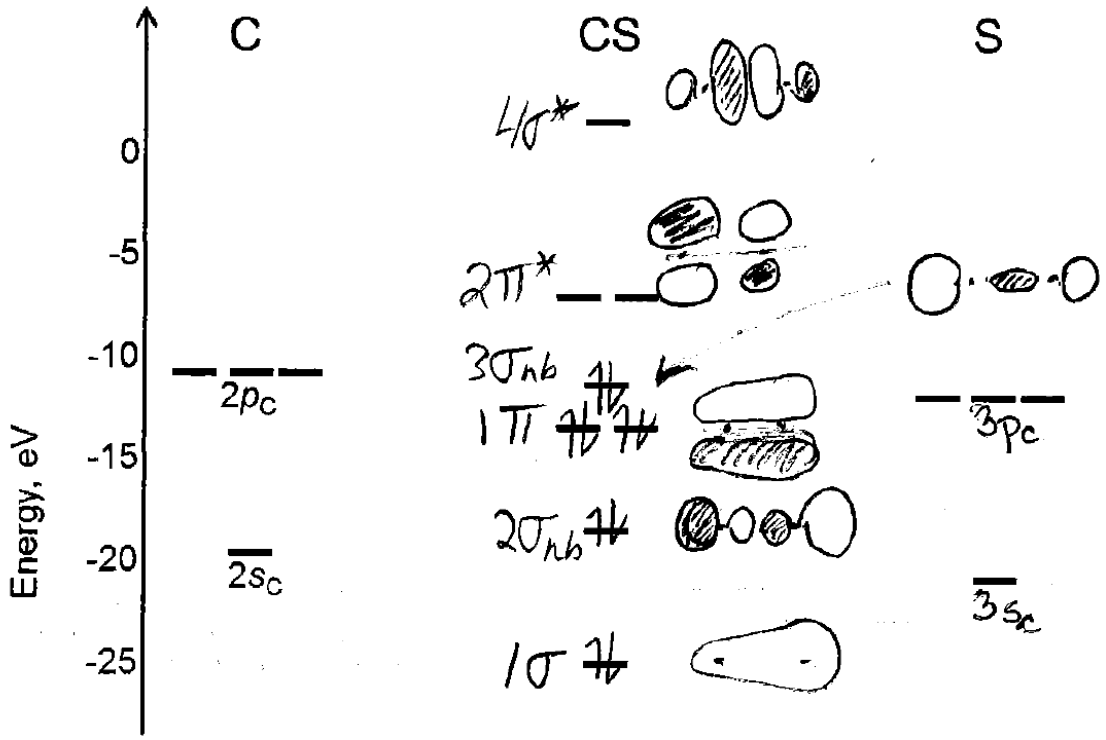


(d) The UV-photoelectron spectrum provides the energy of electrons in each orbital. The energy of a MO is equal to $0 - E_i$ where E_i is the ionization energy on the x-axis of the diagram above. *The answer to 2(a) gives more detail about how the ionization energy is obtained.*

In some cases, we can also deduce whether an orbital is bonding, nonbonding or antibonding from the width of the space between the lines in a signal. Signals corresponding to bonding MOs tend to consist of narrowly spaced lines whereas signals corresponding to antibonding MOs tend to consist of widely spaced lines. Signals corresponding to nonbonding MOs tend to just have a single line. This deduction is easiest when the spectrum shows both bonding and antibonding MOs whose line spacing can be directly compared.

6.

(a)



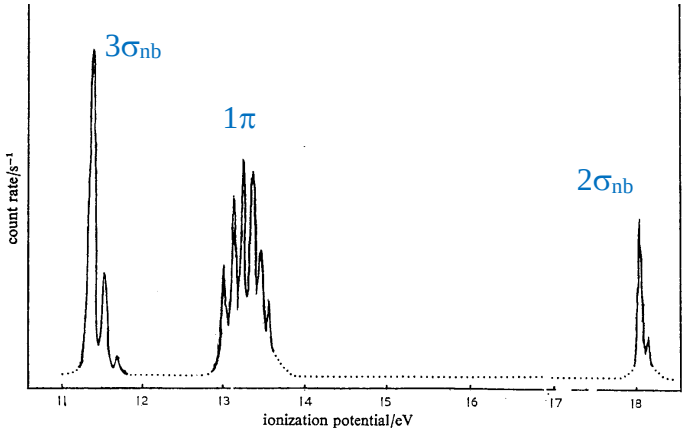
(b) $(1\sigma)^2(2\sigma_{nb})^2(1\pi)^4(3\sigma_{nb})^2$

(c)

i. HOMO is $3\sigma_{nb}$ therefore this is the peak at 11.4 eV

ii. peak at 13.3 eV (corresponds to 1π)

This peak shows extensive fine splitting due to vibrational energy levels, indicating a strong change in bond order after the molecule is ionized by exciting an electron out of this MO.



Simplified UV-PES spectrum of carbon monosulfide (22.2 eV photons)

iii. peaks at 11.4 eV and 18 eV (correspond to $2\sigma_{nb}$ and $3\sigma_{nb}$ respectively)

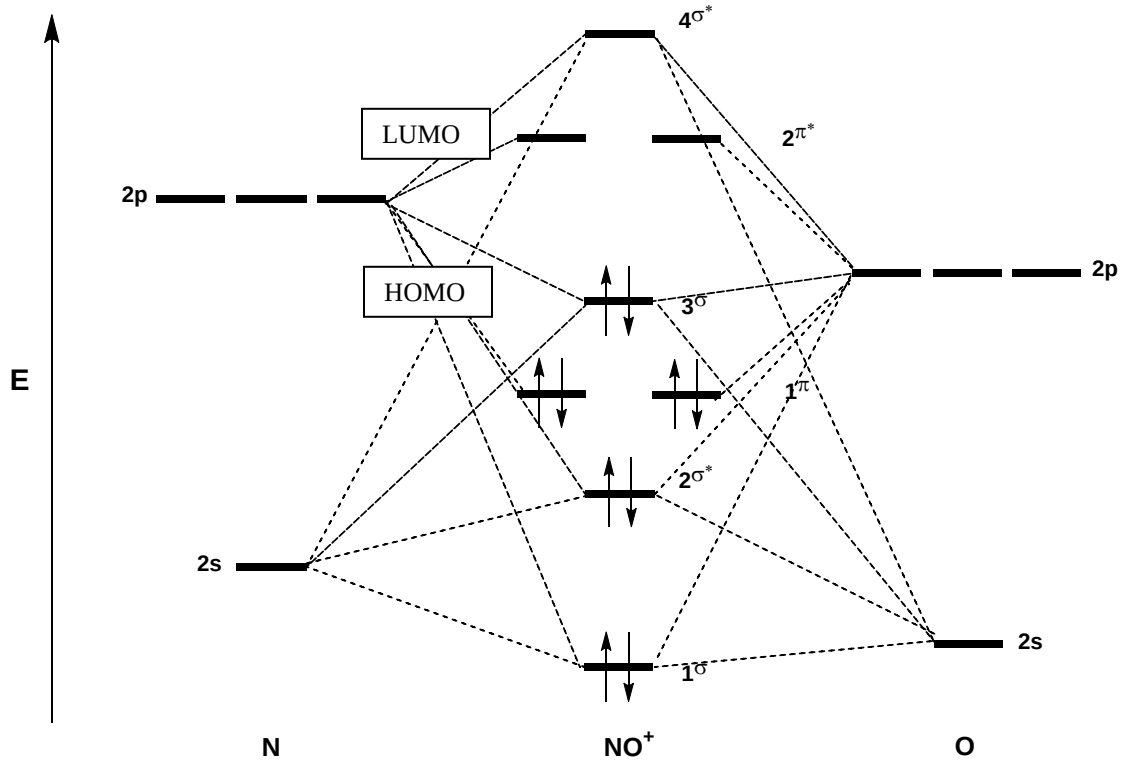
These peaks are sharp single peaks, indicating little change in bond order after the molecule is ionized by exciting an electron out of one of these MOs.

If you hadn't initially designated 2σ and 3σ as nonbonding, this part of the question provided evidence that they were, and you should have gone back to change that on your MO diagram.

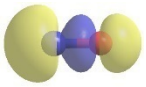
7.

(a) The electron configuration for N is $1s^2 2s^2 2p^3$, so N has 5 valence electrons.
The electron configuration for O is $1s^2 2s^2 2p^4$, so O has 6 valence electrons.
Therefore, NO would have 11 valence electrons, and NO^+ has 10 valence electrons.
Grouping the valence AOs by symmetry and energy gives:

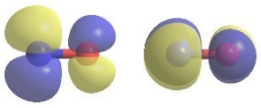
- two pi-symmetric $2p_x$ orbitals, one from each atom,
- two pi-symmetric $2p_y$ orbitals, one from each atom,
- four sigma-symmetric orbitals close enough in energy to combine: $2s(N)$, $2s(O)$, $2p_z(N)$ and $2p_z(O)$.



(b) The HOMO is labeled on the diagram in part (a).



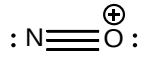
(c) The LUMO is labeled on the diagram in part (a).



You need to show both $2\pi^*$ MOs.

(d) $(1\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^2$

(e) N_2 or CO

(f) 

triple bond therefore predicted bond order is 3

(g) $\frac{8-2}{2} = \frac{6}{2} = 3$

This is the same as the bond order predicted from the Lewis diagram

(h) If an electron is added to NO^+, it goes in $2\pi^*$ (an antibonding MO). This reduces the bond order from 3 to 2.5.

$\frac{8-3}{2} = \frac{5}{2} = 2.5$

(i) Since the bond order of NO is smaller than the bond order of NO^+, adding an electron to NO^+ weakens the $N-O$ bond.

(j) NO and NO^- are both paramagnetic. They each contain at least one electron that is not spin-paired.