Answers to Exercise 4.2
Molecular Orbital Energy Level Diagrams: Linear Polyatomic Molecules

1. *(a) and (b) were open-ended questions, and there are other reasonable answers to them; however, you must include more detail than "the diagram for BeF_2 is more complicated*

(a) BeF_2 and BeH_2 are both linear molecules, so they should both have two pi systems (two sets of pi-symmetric orbitals that are independent of each other). One set of pi-symmetric MOs is constructed from the $2p_x$ orbitals, and one set of pi-symmetric MOs is constructed from the $2p_y$ orbitals.

or Since the $2s(F)$ orbitals are too low in energy to combine with any other AOs, there will still only be one sigma-symmetric AO ($2p_z$) on each fluorine atom to combine with the sigma-symmetric $2s$ and $2p_z$ orbitals on beryllium.

(b) Fluorine atoms have more valence orbitals and more valence electrons than hydrogen atoms. The molecular orbital energy level diagram for BeF_2 will have more six more MOs and twelve more electrons than the molecular orbital energy level diagram for BeH_2.

or The molecular orbital energy level diagram for BeF_2 will have nonbonding sigma MOs from the $2s(F)$ orbitals (which are too low in energy to interact with any of the other valence atomic orbitals).

or Because fluorine has pi-symmetric valence atomic orbitals, the $2p_x$ and $2p_y$ orbitals on beryllium will interact with them, and there will be bonding and antibonding pi-symmetric MOs (whereas BeH_2 only had nonbonding pi-symmetric MOs).

(c) The electron configuration for Be is $1s^2 2s^2$, so Be has 2 valence electrons.

The electron configuration for F is $1s^2 2s^2 2p^5$, so each F has 7 valence electrons.
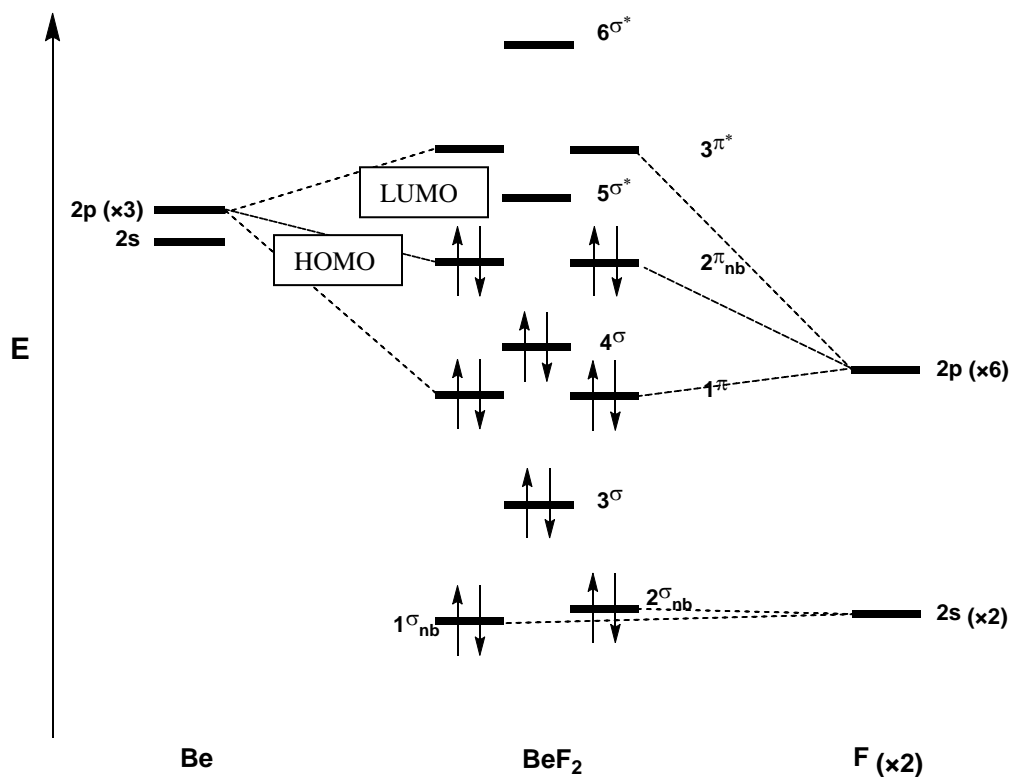
Therefore, BeF_2 has $2 + 2(7) = 16$ valence electrons.

Grouping the valence AOs by symmetry and energy gives:
*   three pi-symmetric $2p_x$ orbitals, one from each atom,
*   three pi-symmetric $2p_y$ orbitals, one from each atom,
*   two sigma-symmetric orbitals that are more than 1 Ry lower in energy than all other sigma-symmetric AOs: the $2s$ orbital on each fluorine atom,
*   four sigma-symmetric orbitals close enough in energy to combine: $2s(Be)$, $2p_z(Be)$ and two $2p_z(F)$ (one from each fluorine atom).
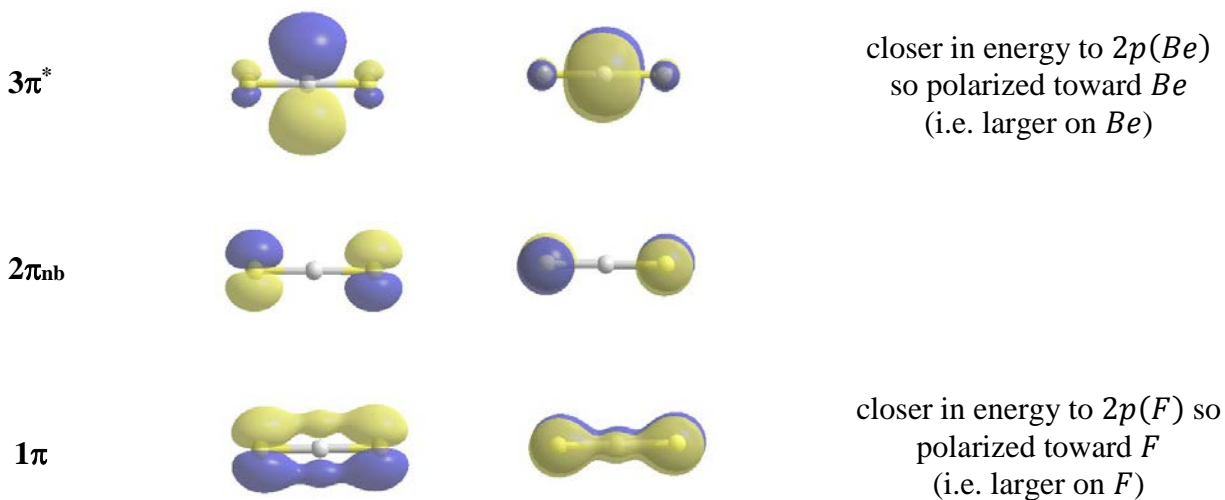
This results in:
*   three pi-symmetric MOs (one bonding, one nonbonding, one antibonding) from combination of the $2p_x$ orbitals,
*   three pi-symmetric MOs (one bonding, one nonbonding, one antibonding) from combination of the $2p_y$ orbitals,
*   two sigma-symmetric MOs with about the same energy as $2s(F)$ AOs; you may either show them with the same energy or show one with slightly higher energy and one with slightly lower energy; either way, they are both nonbonding; your choice will affect how you number the rest of the MOs; if you show them with the same energy, they are both $1\sigma_{nb}$; if you show different energies, they are $1\sigma_{nb}$ and $2\sigma_{nb}$),
*   four sigma-symmetric MOs from the last group of sigma-symmetric AOs (two bonding and two antibonding)

Tie lines to 3σ, 4σ, $5\sigma^*$ and $6\sigma^*$ have been omitted from the diagram below for clarity.

All four of those molecular orbitals are made by combining the $2s(Be)$, $2p_z(Be)$ and $2p_z(F)$ orbitals. 3σ, 4σ, $5\sigma^*$ and $6\sigma^*$ would therefore have tie lines to $2s(Be)$, $2p_z(Be)$ and $2p_z(F)$.
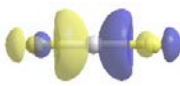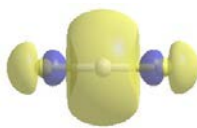

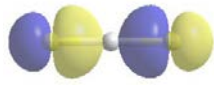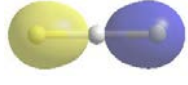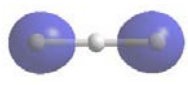*For clarity, the pictures of the orbitals are shown below:*

$3\pi^*$ — closer in energy to $2p(Be)$ so polarized toward Be (i.e. larger on Be)

$2\pi_{nb}$

1π — closer in energy to $2p(F)$ so polarized toward F (i.e. larger on F)

Each pi-symmetric MO has one more node than the next lowest energy pi-symmetric MO.

There are two degenerate pi-symmetric MOs of each type: one made from $2p_x$ orbitals and one made from $2p_y$ orbitals.

$6\sigma^*$		$2p_z(Be)$ combined out-of-phase with $2p_z(F)$; closer in energy to $2p_z(Be)$ therefore polarized toward Be
$5\sigma^*$		$2s(Be)$ combined out-of-phase with $2p_z(F)$; closer in energy to $2s(Be)$ therefore polarized toward Be
4σ		$2p_z(Be)$ combined in-phase with $2p_z(F)$; closer in energy to $2p_z(F)$ therefore polarized toward F
3σ		$2s(Be)$ combined in-phase with $2p_z(F)$; closer in energy to $2p_z(F)$ therefore polarized toward F
$2\sigma_{nb}$		$2s(F)$ combined out-of-phase; large distance between atoms therefore not much overlap
$1\sigma_{nb}$		$2s(F)$ combined in-phase; large distance between atoms therefore not much overlap

Note that there is <u>not</u> a node in $1\pi_{nb}$ because the phases on both sides of the gap are the same! The gap is just a function of what percentage of electron density we chose to look at. If we looked for a higher percentage of electron density (e.g. 99% instead of 95%), the lobes would appear larger and the gap would fill in.

Keeping that in mind, we can see that each sigma-symmetric MO has one more node than the next lowest energy sigma-symmetric MO.

(d)   The HOMO and LUMO are labeled on the molecular orbital energy level diagram in part (c).

The HOMO is $2\pi_{nb}$ which has all its electron density on the two fluorine atoms. This tells us that if BeF_2 were to act as an electron donor, it would donate a lone pair from a fluorine atom.

The LUMO is $5\sigma^*$ which is largest on the beryllium atom. This tells us that if BeF_2 were to act as an electron acceptor (which it is more likely to do since it is a good Lewis acid), it would accept electrons at the beryllium atom.

2.

(a)   The electron configuration for N is $1s^2 2s^2 2p^3$, so each N has 5 valence electrons. Therefore, N_3 would have $3(5) = 15$ valence electrons and N_3^- has 16 valence electrons. Grouping the valence AOs by symmetry and energy gives:

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

This results in:

- three pi-symmetric MOs (one bonding, one nonbonding, one antibonding) from combination of the $2p_x$ orbitals,
- three pi-symmetric MOs (one bonding, one nonbonding, one antibonding) from combination of the $2p_y$ orbitals,
- six sigma-symmetric MOs from the sigma-symmetric AOs (three bonding and three antibonding)

Tie lines to 1σ, 2σ, $3\sigma^*$, 4σ, $5\sigma^*$and $6\sigma^*$ have been omitted from the diagram below for clarity. All six of those molecular orbitals are made by combining the $2s(N)$ and $2p_z(N)$orbitals. 1σ, 2σ, $3\sigma^*$, 4σ, $5\sigma^*$and $6\sigma^*$ would therefore have tie lines to $2s(N)$ and $2p_z(N)$.

Relative energies were calculated using HyperChem. It's expected that you can predict the correct order within each symmetry type (i.e. all the sigma MOs in the right order and all the pi MOs in the right order). It's also expected that you realize that 1σ and 2σ have the lowest energy while $6\sigma^*$ has the highest energy. It's not expected that you can predict exactly how the energies of $3\sigma^*$, 4σ and $5\sigma^*$ compare to the energies of the pi-symmetric MOs.
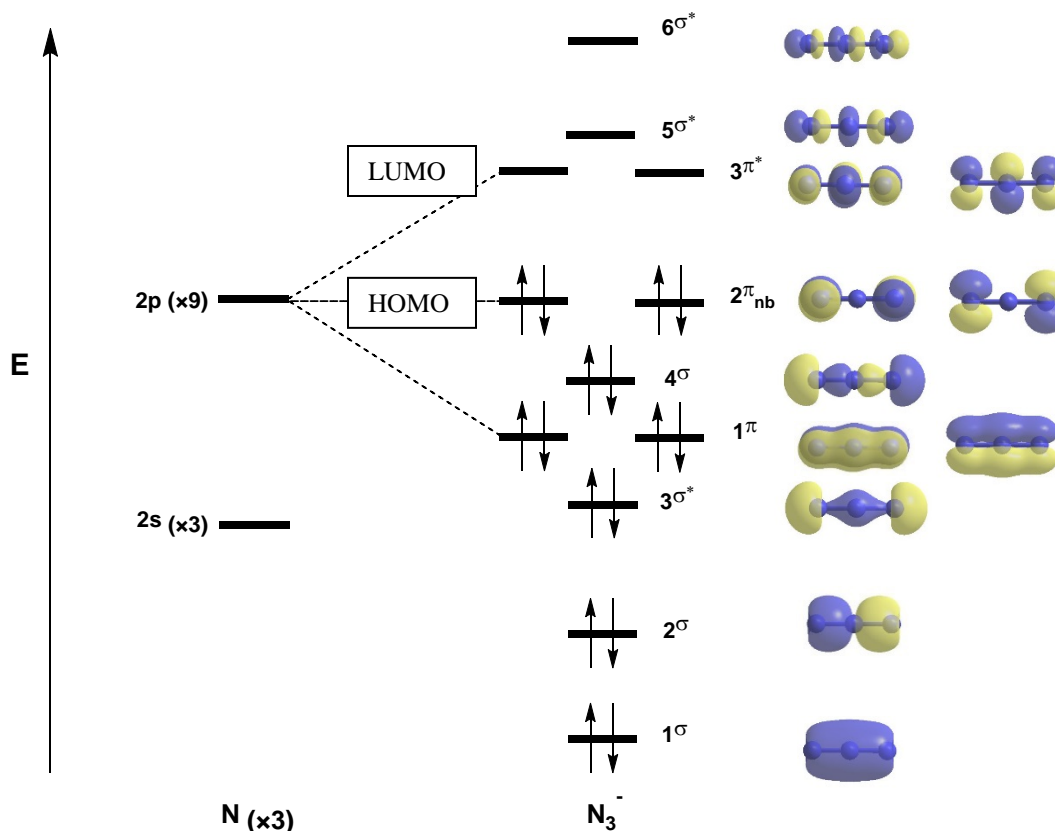
(b)   The HOMO and LUMO are labeled on the molecular orbital energy level diagram in part (a).

Since N_3^- is an anion, it is more likely to act as an electron pair donor than an electron pair acceptor. As such, its HOMO is more relevant to its reactivity.

The HOMO is $2\pi_{nb}$ which has all its electron density on the two terminal nitrogen atoms. This tells us that if N_3^- were to act as an electron donor (Lewis base), it would donate a lone pair from one of the terminal nitrogen atoms.