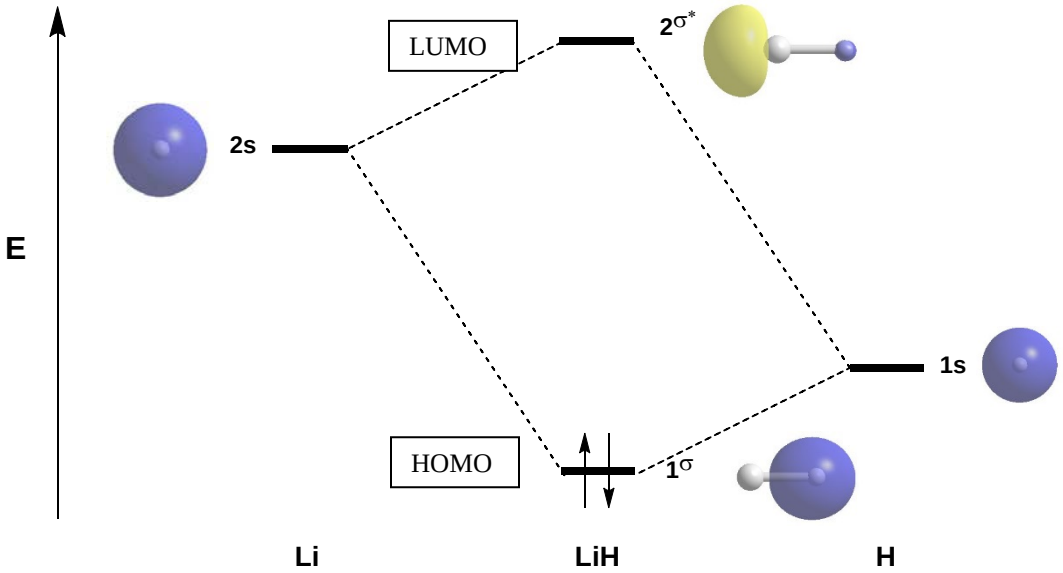
# Answers to Exercise 3.2
# Molecular Orbital Energy Level Diagrams: Heteronuclear Diatomics

1.

(a) The electron configuration for $Li$ is $1s^2 2s^1$, so $Li$ has 1 valence electron.
The electron configuration for $H$ is $1s^1$, so $H$ has 1 valence electron.
Therefore, $LiH$ has 2 valence electrons.



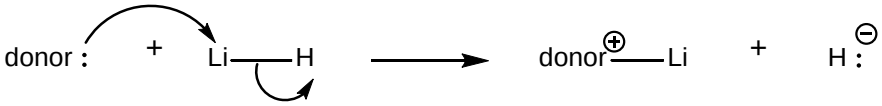

*If your pictures look the same as the ones on the diagram for $HHe^+$, that's fine.*
*The computer shows that the polarization is even stronger in $LiH$ than in $HHe^+$.*

(b) Li—H

The Lewis diagram gives a bond order of 1 since the Lewis diagram shows a single bond.
The bond order calculated from the molecular orbital energy level diagram is $\frac{2-0}{2} = \frac{2}{2} = 1$.
They match!

(c) H is more electronegative than Li, so the $Li - H$ bond is polar (with H as the negative end).
The electrons in $LiH$ are in the $1\sigma$ orbital which is strongly polarized toward H. As such, the electrons in $LiH$ spend more time near H than near Li. This means that H should be the negative end of the $Li - H$ bond, supporting the prediction based on electronegativities.

(d) If $LiH$ reacted as an electron pair acceptor in a reaction, the LUMO ($2\sigma^*$) would accept the electron pair. This orbital is strongly polarized toward Li, so Li would be the atom accepting the electrons:




Adding electrons to the antibonding $2\sigma^*$ orbital would reduce the $Li - H$ bond order from 1 to 0, resulting in breaking of the $Li - H$ bond.

2.

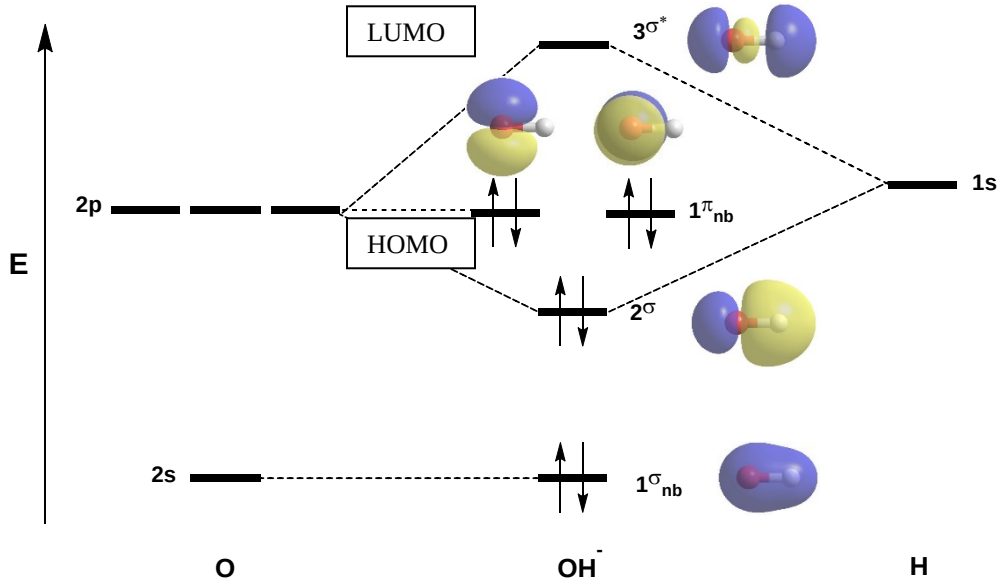
(a) The electron configuration for $O$ is $1s^2 2s^2 2p^4$, so $O$ has 6 valence electrons.

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

Therefore, $OH$ would have 7 valence electrons, and $OH^-$ has 8 valence electrons.

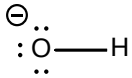
Grouping the valence AOs by symmetry and energy gives:

- one pi-symmetric $2p_x$ orbital on $O$,
- one pi-symmetric $2p_y$ orbital on $O$,
- one sigma-symmetric $2s$ orbital on $O$ 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 $2p_z(O)$.




*If your picture of $1\sigma_{nb}$ just looks like a $2s$ orbital on $O$, that's fine.*

(b)



The Lewis diagram gives a bond order of 1 since the Lewis diagram shows a single bond.

The bond order calculated from the molecular orbital energy level diagram is $\frac{2-0}{2} = \frac{2}{2} = 1$.

They match!

(c) The HOMO and LUMO have been labeled on the diagram in part (a).

Since $OH^-$ is an anion, it is more likely to react as an electron pair donor.

As an electron pair donor, $OH^-$ will react with its HOMO.

The HOMO $(1\pi_{nb})$ is polarized toward O, so $OH^-$ will tend to donate an electron pair from the oxygen atom. Since the HOMO is nonbonding, donating a pair of electrons from it will not change the $O - H$ bond order.

3.

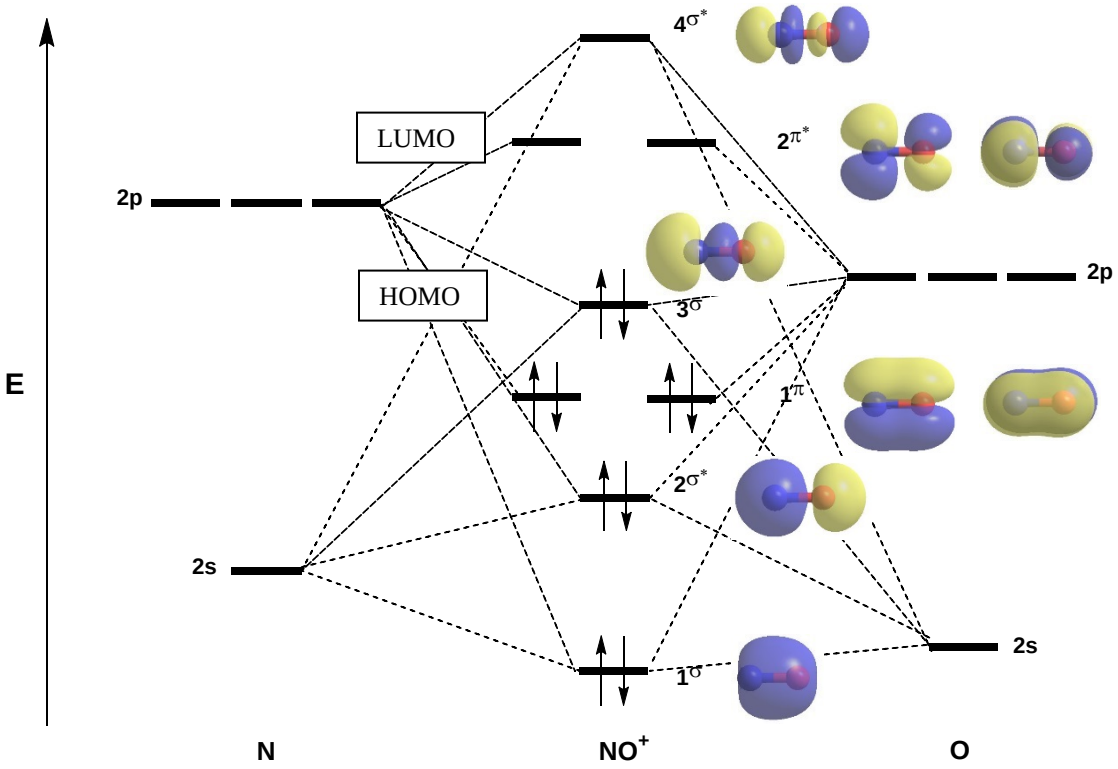
(a) The electron configuration for $N$ is $1s^2 2s^2 2p^3$, so $N$ has 5 valence electrons.

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 $2p_z(O)$.




*$1\sigma$ and $1\pi$ are slightly polarized toward O. $4\sigma^*$ and $2\pi^*$ are slightly polarized toward N. Because the difference in energy between the AOs of N and the AOs of O is not very large, this polarization is not very easy to see (except in $2\pi^*$). It is even harder to predict and see the polarization in $2\sigma^*$ and $3\sigma$ (since they are made from both $2s$ and $2p_z$ orbitals from both N and O).*

(b) The HOMO and LUMO have been labeled on the diagram in part (a).

Since $NO^+$ is a cation, it is more likely to react as an electron pair acceptor.

As an electron pair acceptor, $NO^+$ will react with its LUMO.

The LUMO ($2\pi^*$) is polarized toward N, so $NO^+$ will tend to accept an electron pair at the nitrogen atom. Since the LUMO is antibonding, adding a pair of electrons to it will reduce the bond order from 3 to 2.