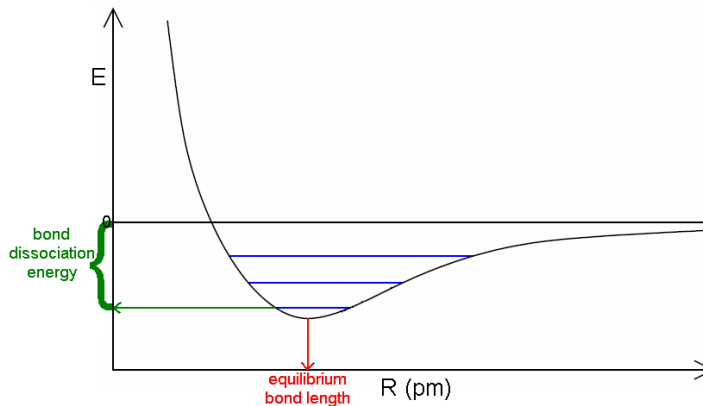# Answers to Practice Test Questions 2
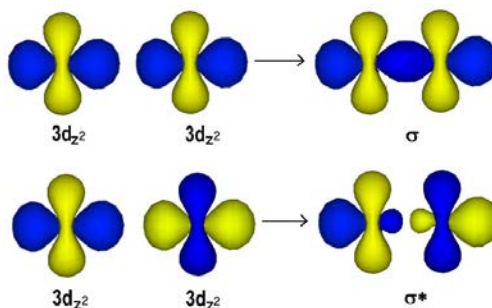# Molecular Orbital Theory: Homonuclear Diatomic Molecules

1.

Note that the bond dissociation energy (a positive value since energy is required to break a bond) is equal to the difference between E = 0 and the lowest energy vibrational energy level (close to the bottom of the energy curve but not exactly at the bottom).
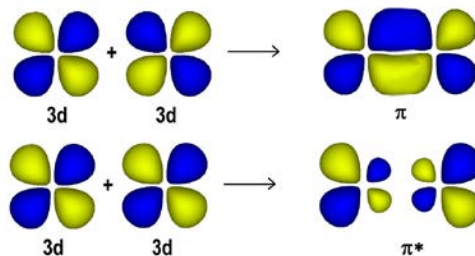
2.

(a)

$3d_{z^2}$ orbitals are used because the bond in a linear molecule is, by definition, along the z axis

(b)

The orbitals used are either both $3d_{xz}$ or both $3d_{yz}$ because the bond in a linear molecule is, by definition, along the z axis

3.

(a)   The $2s$ and $2p_z$ orbitals from each boron atom combine to form four sigma-symmetric MOs.

(b)   The $2p_x$ orbitals from each boron atom combine to form one pair of pi-symmetric MOs.

The $2p_y$ orbitals from each boron atom combine to form one pair of pi-symmetric MOs.

(c)
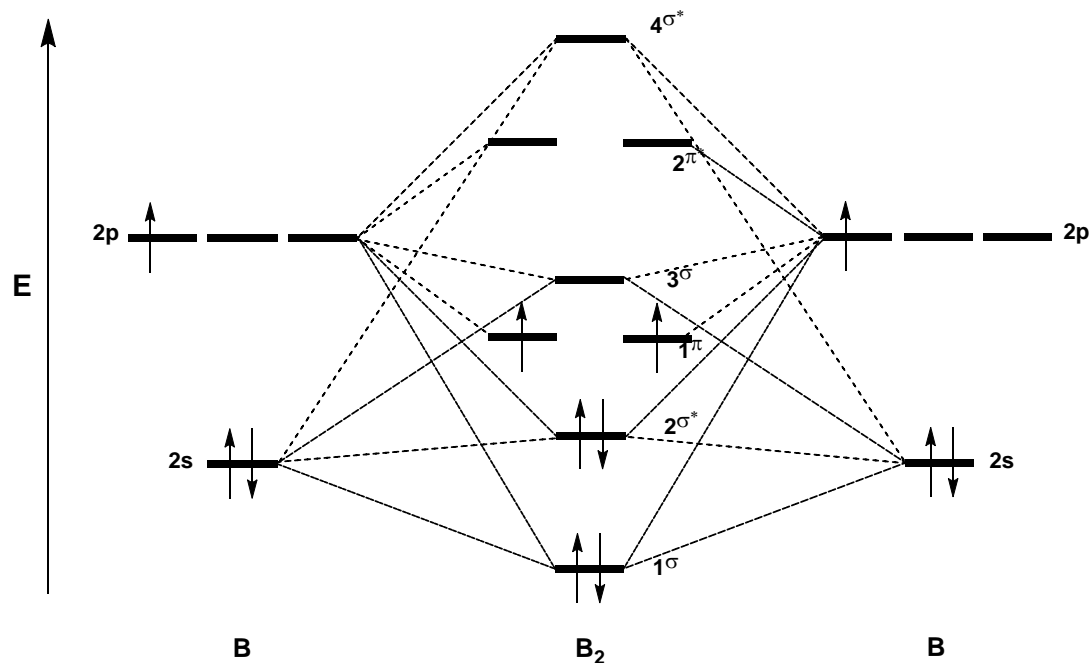
(d) $(1\sigma)^2(2\sigma^*)^2(1\pi)^2$

(e) B_2 is paramagnetic. It has two unpaired electrons, giving it a non-zero net spin. As such, B_2 would be attracted to a magnetic field.

(f) $\frac{2-2}{2} = \frac{0}{2} = 0$

σ bond order is calculated by subtracting electrons in σ^* MOs from electrons in σ MOs then dividing by 2.

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

π bond order is calculated by subtracting electrons in π^* MOs from electrons in π MOs then dividing by 2.

(h) $0 + 1 = 1$

Overall bond order is calculated by adding σ bond order and π bond order.

For questions 4 and 5, begin by drawing the valence molecular orbital energy level diagram for N_2. Remember that N_2^+ has one less electron than N_2 while N_2^- has one more electron than N_2.
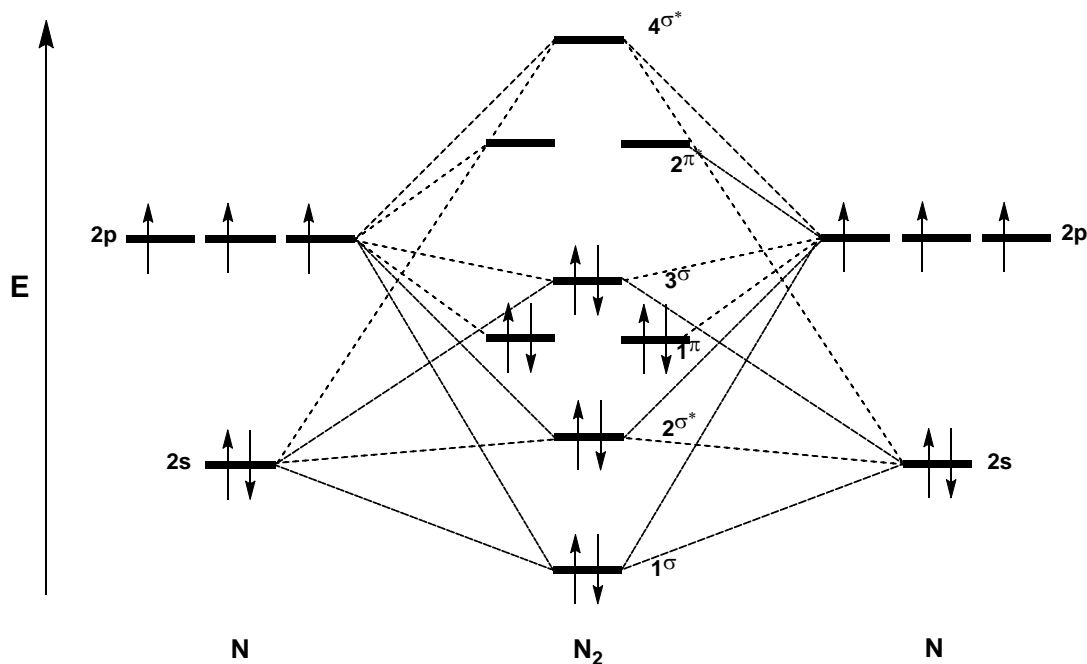
4. The valence orbital occupancy of N_2 is $(1\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^2$. As such, the $N - N$ bond order in N_2 is $\frac{8-2}{2} = \frac{6}{2} = 3$.

Adding one electron to N_2 gives N_2^-. The extra electron goes into a $2\pi^*$ orbital (which is antibonding). This reduces the $N - N$ bond order to $\frac{8-3}{2} = \frac{5}{2} = 2.5$.

The energy required to break a bond increases as the bond order increases. Since N_2 has a larger $N - N$ bond order than N_2^-, it follows that the bond dissociation energy for N_2 will be larger than the bond dissociation energy for N_2^-,

5.

(a) N_2 N_2^+ N_2^-

bond order = 3   predicted bond order = 3?   predicted bond order = 2

Since both of the ions are radicals, it is impossible to draw Lewis diagrams in which all atoms obey the octet rule. The best we are able to do is to have one nitrogen atom with 8 electrons and one with 7 electrons. Recall that you are never allowed to give more than 8 electrons to any atom of a second period element.

(b) The valence orbital occupancy of N_2^+ is $(1\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^1$. As such, the $N-N$ bond order in N_2^+ is $\frac{7-2}{2} = \frac{5}{2} = 2.5$.

The valence orbital occupancy of N_2^- is $(1\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^2(2\pi^*)^1$. As such, the $N-N$ bond order in N_2^- is $\frac{8-3}{2} = \frac{5}{2} = 2.5$.

In both cases, experimental data show that the bond orders predicted by molecular orbital theory are correct. Lewis diagrams are not always very good at describing radicals (molecules containing one or more unpaired electrons).

6. In MO theory, the core electrons form MOs which are either:
   - essentially identical to the original AOs (e.g. the single nonbonding MO formed from the $2s(F)$ orbital in HF), or
   - non-overlapping superpositions of core orbitals (e.g. the two $1s(F)$ orbitals in F_2 are physically far enough apart that when they "combine" to give two MOs, those MOs are both almost identical in energy to $1s(F)$ and are nonbonding).

   In either case, the molecular orbitals produced from core atomic orbitals are not involved in bonding. This justifies focusing on the valence electrons, both in MO theory and when drawing Lewis diagrams.
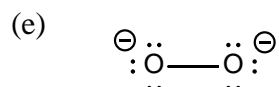
7.

(a)

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

(c)

$\ddot{\ddot{O}}\!=\!\ddot{\ddot{O}}$
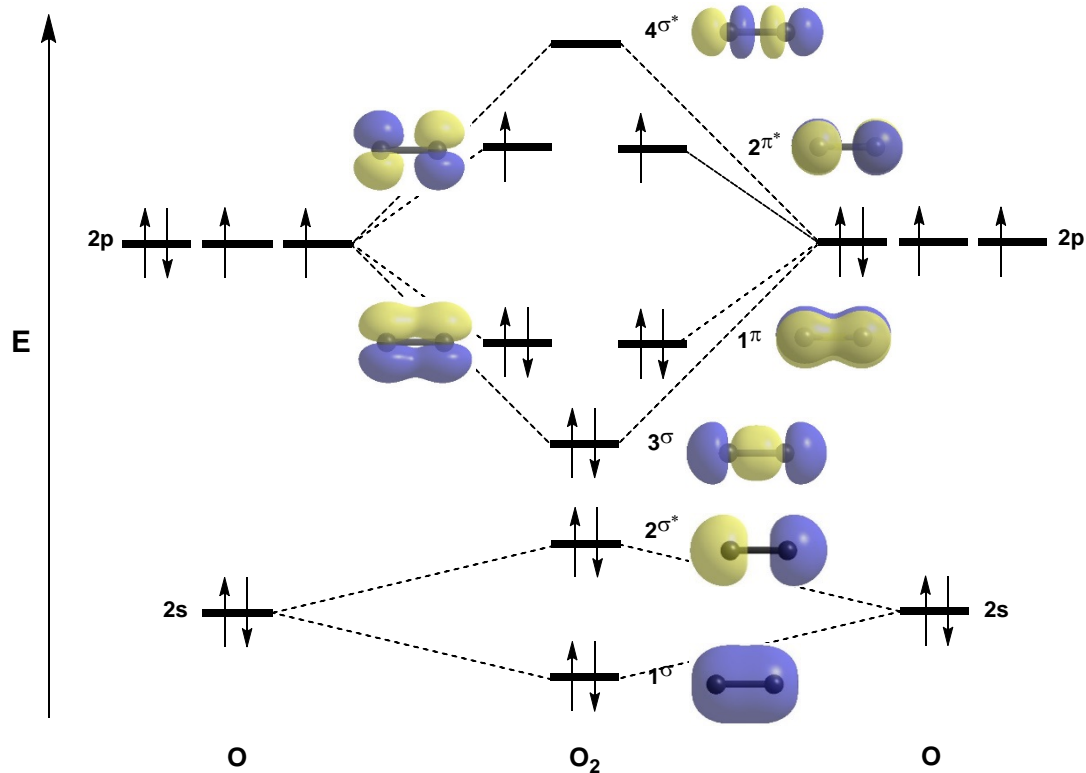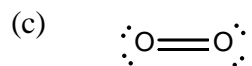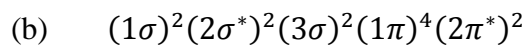
(d) O_2 has two unpaired electrons (shown by the MO diagram but not the Lewis diagram). This makes O_2 paramagnetic.

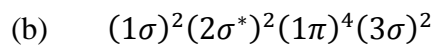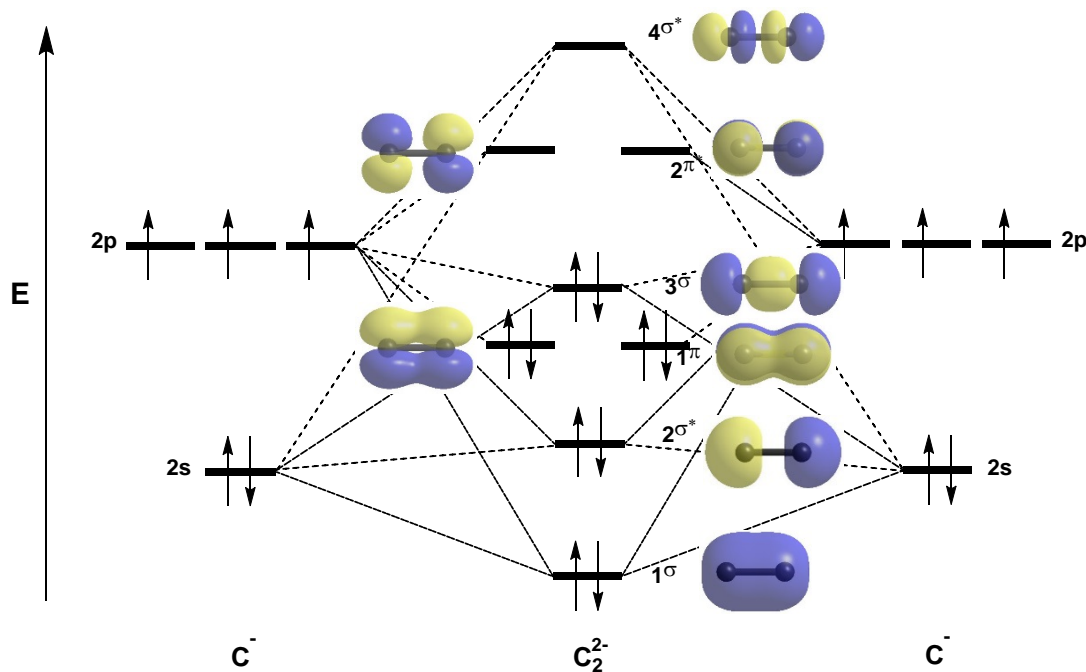(e)

$^{\ominus}\!:\!\ddot{O}\!-\!\ddot{O}\!:^{\ominus}$

When O_2 accepts two electrons from the sodium atoms to make the peroxide anion, they go into the $2\pi^*$ MOs.

Since the two electrons are added to antibonding MOs, they reduce the bond order:

- The bond order of O_2 is $\frac{8-4}{2} = \frac{4}{2} = 2$.
- The bond order of O_2^{2-} is $\frac{8-6}{2} = \frac{2}{2} = 1$

8.
(a)

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

(c)   The carbide anion will have a larger bond dissociation energy than C_2.

The bond order for C_2^{2-} is 3. The bond order for C_2 is 2.

Bond dissociation energy increases with increasing bond order.

(d) N_2 and CO