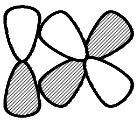
Chem 370 - Spring, 2019
Assignment 5 - Solutions

5.1 Additional combinations are $p_z \pm d_{z^2}$, $p_x \pm d_{xz}$, and $p_y \pm d_{yz}$.

$p_z \pm d_{z^2}$



$p_x \pm d_{xz}$ or $p_y \pm d_{yz}$

5.2 a. Li_2 has the configuration $(\sigma_{2s})^2$ with a bond order of 1, while Li_2^+ is $(\sigma_{2s})^1$ with a bond order of 0.5. Therefore, Li_2 has a shorter bond.

b. F_2 has the configuration $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$ with a bond order of 1, while F_2^+ is $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^3$ with a bond order of 1.5. Removing the electron from an antibonding MO strengthens the bond, so F_2^+ has a shorter bond.

c.

Molecule	Configuration	Bond Order
He_2^+	$\sigma^2\sigma^{*1}$	0.5
HHe^+	σ^2	1
H_2^+	σ^1	0.5

Both He_2^+ and H_2^+ have bond orders of 0.5, but H_2^+ would have the shorter bond length because hydrogen is smaller than helium. Nonetheless, HHe^+, with a bond order of 1 should be the shortest of the three.

5.3 The MO schemes for all these third-row homonuclear diatomic molecules would be similar to their second-row analogs, except that the highest energy MOs would be formed from combinations of AOs with $n = 3$.

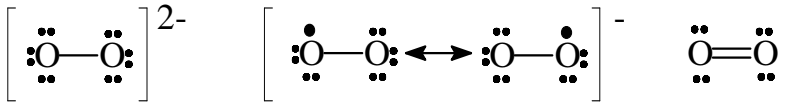
P_2 bond order = 3 (like N_2)
S_2 bond order = 2 (like O_2)
Cl_2 bond order = 1 (like F_2)

Therefore, Cl_2 has the weakest bond.

5.4 As shown in class:

Formula	Configuration	Bond Order	$D(X_2)$ kJ/mol	d(X–X) pm	Magnetic Property
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$	2	494	120.75	para
O_2^-	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^3$	1.5	395	135	para
O_2^{2-}	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	126	149	dia

Lewis structures:

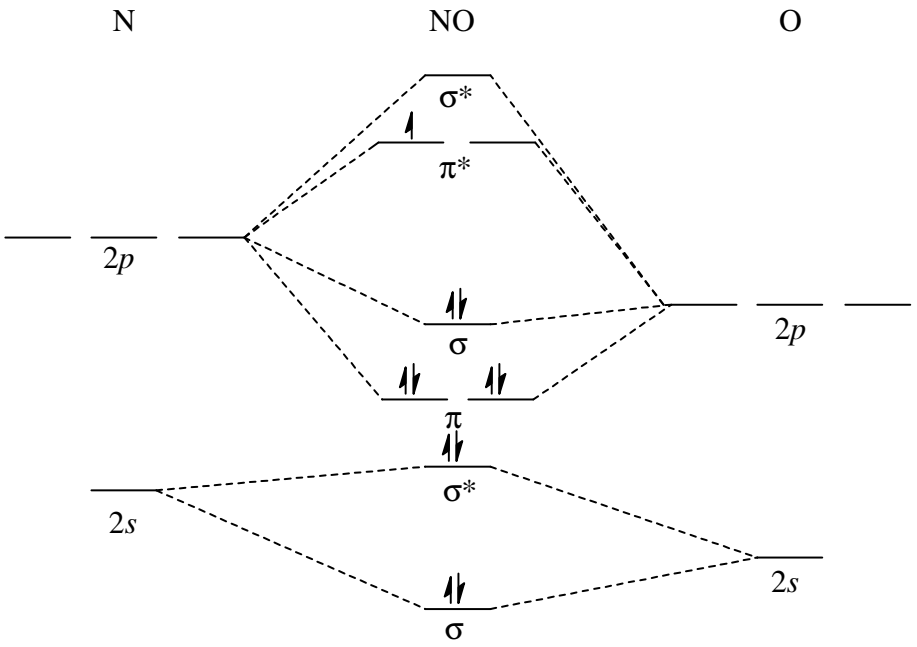


5.5 N_2^{2-} has 16 valence electrons, isoelectronic with O_2. Its bond distance (reported value 122.4 pm) should be about the same as O_2 (120.75 pm).

Formula	Configuration	bond order	d(X–X) pm	Unpaired electrons
C_2^{2-}	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$	3	119	0
N_2^{2-}	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2(\pi^*_{2p})^2$	2	122.4	2
O_2^{2-}	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	149	0
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$	2	120.75	2

5.6 The MO scheme for both Cl_2 and Ar_2^+ is analogous to that of F_2 and Ne_2^+, except that the highest energy combining AOs have $n = 3$ (cf. answer to problem 5.3). Therefore, Cl_2 has a bond order of 1 and Ar_2^+ has a bond order of 0.5. Therefore, the Ar_2^+ is expected to be much weaker and longer. The reference calculates it at >300 pm, compared to the Cl_2 bond length of 198.8 pm.

5.7 a.

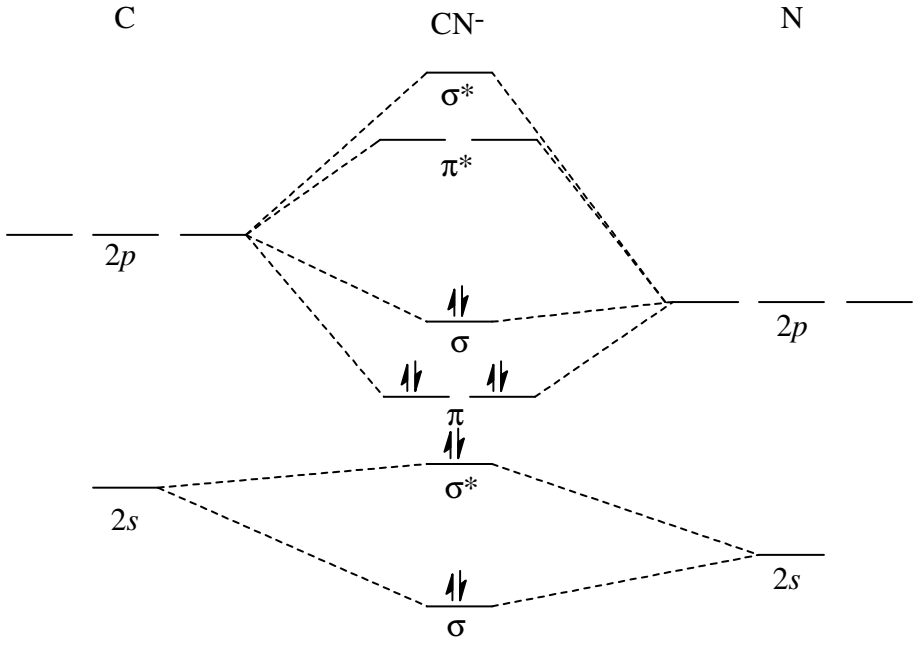


b. Oxygen is more electronegative than nitrogen, so its AOs lie lower in energy. As a result, oxygen contributes more to bonding MOs, and nitrogen contributes more to antibonding MOs.

c. Bond order is 2.5, and there is one unpaired electron.

d. NO^+ has a bond order of 3 (like N_2, with which it is isoelectronic), and NO^- has a bond order of 2 (like O_2, with which it is isoelectronic). Based on bond order, the bond lengths are predicted to be $NO^+ < NO < NO^-$. NO^- is probably paramagnetic, like O_2, owing to two unpaired electrons in the doubly degenerate π* MOs.

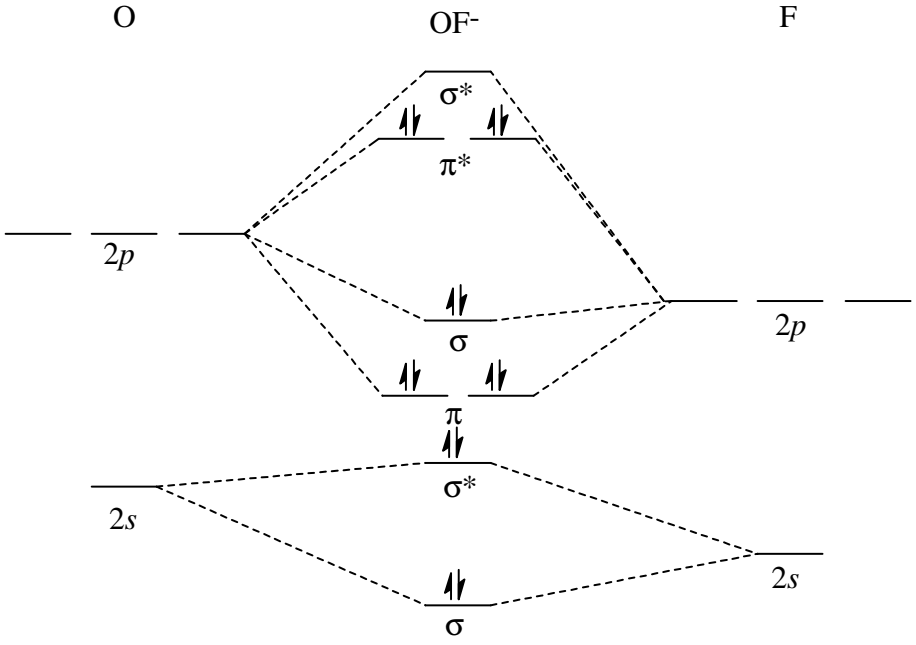
5.8 a. CN^- is isoelectronic with N_2, so its MO scheme is similar. However, nitrogen is more electronegative than carbon, so its AOs lie lower than carbon's. Nitrogen contributes more to bonding MOs, and carbon contributes more to antibonding MOs.



b. Bond order is 3, and there are no unpaired electrons.

c. In forming the HCN molecule from H^+ and CN^-, the proton will interact most strongly with the HOMO of the cyanide ion, the $\sigma(2p)$ MO. N being more electronegative, we might assume that the σ HOMO would have more electron density on that atom. However, with mixing, it appears that the C $2p_z$ only contributes to the σ_{2p} and not to the same symmetry σ_{2s}, because the C $2p_z$ AO is closer in energy. This is analogous to the case of CO (see text, p. 137/138). Thus, H^+ adds to the C end of CN^- to form HCN.

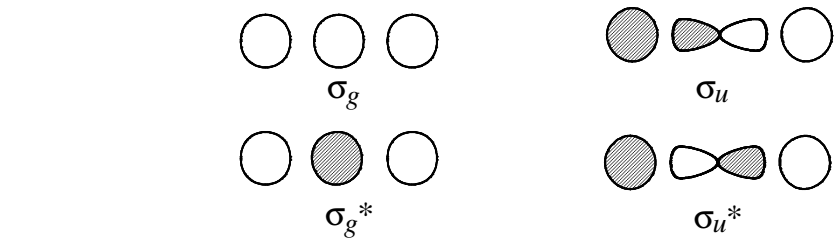
5.10 a. OF^- is isoelectronic with F_2, so the MO schemes are similar. Fluorine is more electronegative than oxygen, so its AOs contribute more to bonding MOs, and oxygen's AOs contribute more to antibonding MOs. The shown ordering of the filled π and σ levels assumes that OF^- is like other second-row heteronuclear cases, which tend to have ordering analogous to the lighter homonuclear cases (e.g., C_2, N_2).

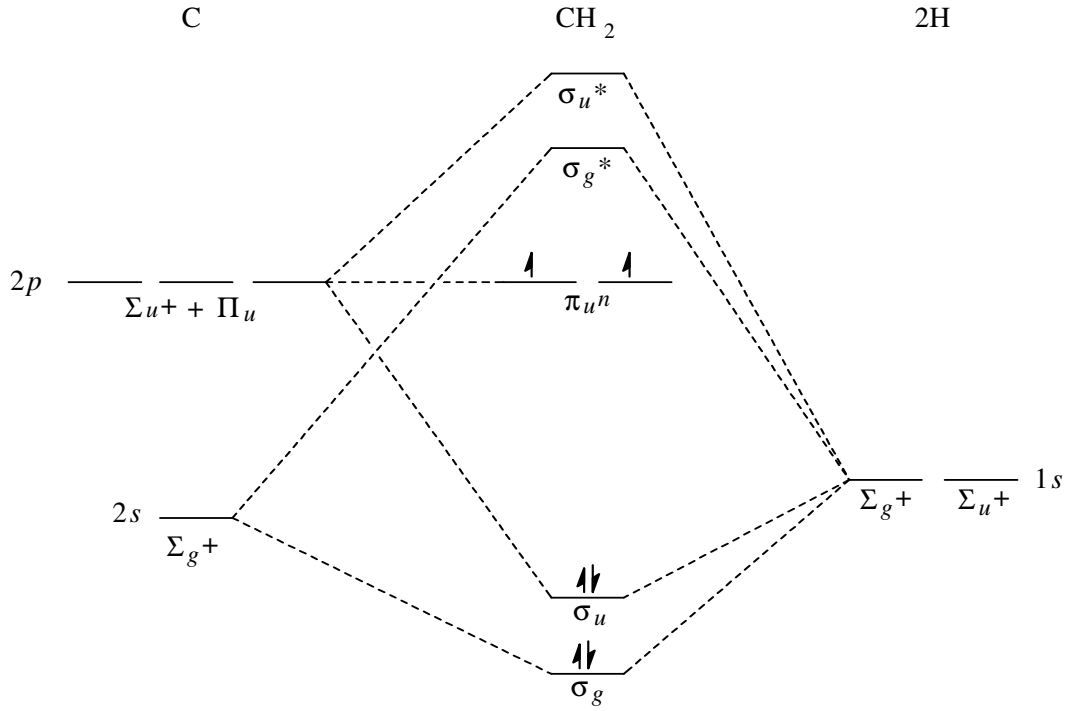


b. Like F_2, the net bond order for OF^- is one, and there are no unpaired electrons.

c. The electron density in the π* MOs is weighted more heavily toward the oxygen atom. Therefore, it is more likely that H^+ would be attracted to that end of OF^-. In HOF, the H–O–F angle is 97°, as if the hydrogen were bonded to a 2*p* orbital on oxygen.

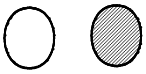
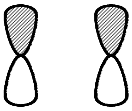
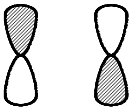
5.14 a. The construction of a qualitative MO scheme for linear CH_2 ($D_{\infty h}$) follows the same approach as the MO scheme of BeH_2 (see class notes). The two hydrogen 1*s* orbitals form SALCs of Σ_g^+ and Σ_u^+. On the central carbon atom, the 2*s* orbital has the symmetry of the totally symmetric representation (Σ_g^+), as always. From the unit vector listings in the $D_{\infty h}$ character table, the $2p_z$ orbital transforms as Σ_u^+ and the $2p_x$ and $2p_y$ orbitals transform degenerately as Π_u. The Σ_g^+ SALC forms σ_g and σ_g^* bonding and antibonding MOs with the carbon 2*s* AO. The Σ_u^+ SALC forms σ_u and σ_u^* bonding and antibonding MOs with the carbon $2p_z$ AO. The carbon $2p_x$ and $2p_y$ orbitals (Π_u) have no matching SALCs and so remain nonbonding. The bonding and antibonding combinations and the resulting MO scheme are shown below.



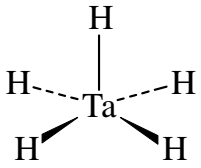


b. With two unpaired electrons in the π_u^n level, the molecule would be paramagnetic.

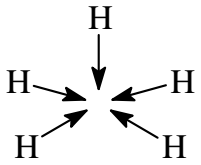
5.17 Disregarding the 1*s* orbitals on fluorine, which are assumed to be nonbonding core electrons, the orbitals available to form SALCs are 2*s* and 2*p*. Pairs of 2*s* orbitals and pairs of $2p_z$ will form four sigma-type SALCs. Pairs of $2p_x$ orbitals and pairs of $2p_y$ orbitals will form four pi-type SALCs.

	SALC	Xe AO match	MO Types	Symmetry
$2s + 2s$		$5s$, $4d_{z^2}$	σ & σ*	Σ_g^+
$2s - 2s$		$5p_z$	σ & σ*	Σ_u^+
$2p_z + 2p_z$		$5p_z$	σ & σ*	Σ_u^+
$2p_z - 2p_z$		$5s$, $4d_{z^2}$	σ & σ*	Σ_g^+
$2p_y + 2p_y$		$5p_y$	π & π*	Π_u
$2p_y - 2p_y$		$4d_{yz}$	π & π*	Π_g
$2p_x + 2p_x$		$5p_x$	π & π*	Π_u
$2p_x - 2p_x$		$4d_{xz}$	π & π*	Π_g

5.18 Describing TaH_5 as having a C_{4v} structure implies that it is square pyramidal.



Use a set of five vectors pointing in towards the central Ta atom as a basis for a representation of the sigma-bonding SALCs.



C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_{SALC}	5	1	1	3	1

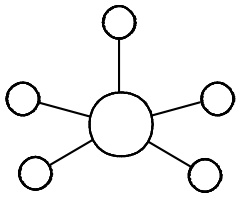
$$\Gamma_{SALC} = 2A_1 + B_1 + E$$

Looking at the unit vector and direct product listings, we have the following AO symmetries on Ta:

$$A_1 = s, p_z, d_{z^2} \qquad B_1 = d_{x^2-y^2} \qquad E = (p_x, p_y), (d_{xz}, d_{yz})$$

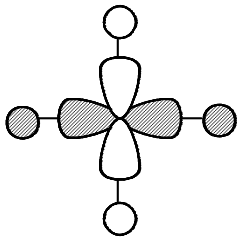
The two A_1 SALCs combine the five hydrogen 1*s* orbitals in the following ways:

The SALC on the left is a best match for the 6*s* orbital on Ta:



The other A_1 SALC is a match for either $6p_z$ or $5d_{z^2}$. The four basal hydrogens are in a plane below the Ta, which allows some overlap with the same-sign portion of the central $6p_z$ orbital or the annular ring ("doughnut") of the $5d_{z^2}$ orbital:

The B_1 SALC, which matches with the $5d_{x^2-y^2}$ orbital on Ta, is a combination of 1*s* orbitals of the basal positions only; i.e., in a plane parallel to the *xy* plane. The combination of this SALC and the Ta $5d_{x^2-y^2}$ orbital is shown below:

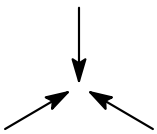


The axial 1*s* orbital (above the plane of the drawing above) is not a part of this combination, because it would have $S = 0$ overlap with the $5d_{x^2-y^2}$ orbital.

The pairs of *E* SALCs are identical to each other, except for orientation. Each SALC can overlap with either the $6p_x$ or $6p_y$ orbital, or with the $5d_{xz}$ or $5d_{yz}$ orbital, depending on orientation. The SALC-AO combinations that match with $6p_x$ and $5d_{xz}$ are shown below:

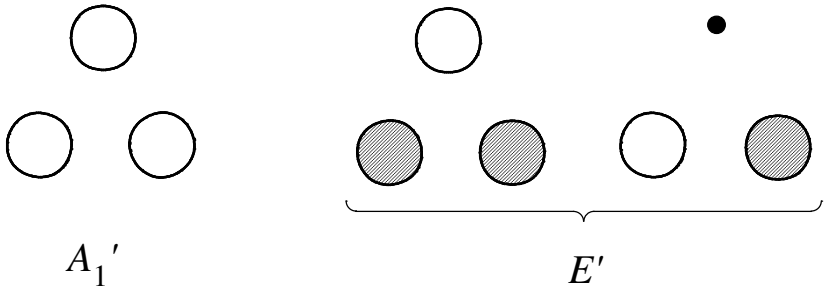
The other combinations would be oriented at 90° about the *z* axis to those shown above, and would involve $6p_y$ and $5d_{yz}$. Note that, once again, the axial 1*s* orbital is omitted from either SALC, because it would have $S = 0$ overlap with the symmetry-matched AOs. The bonding interaction between these SALCs and the appropriate *d* AOs is zero if the Ta atom is in the same plane as four hydrogen atoms. It only has effect because the four hydrogens are in a plane below that of the Ta. Indeed, the potential for forming this interaction can be seen as a driving force to draw the hydrogen plane down below the Ta atom.

5.21



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{3H}	3	0	1	3	0	1

$$\Gamma_{3H} = A_1' + E'$$



The normalized wave functions for the three MOs are as follows:

$$\Phi_1(a_1') = 1/\sqrt{3}\ (\varphi_1 + \varphi_2 + \varphi_3)$$
$$\Phi_2(e') = 1/\sqrt{6}\ (2\varphi_1 - \varphi_2 - \varphi_3)$$
$$\Phi_3(e') = 1/2\ (\varphi_2 - \varphi_3)$$