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

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 $(\sigma_{2s})^2(\sigma_{2p}^*)^2(\pi_{2p})^4(\pi_{2p}^*)^4$ with a bond order of 1, while F$_2^+$ is $(\sigma_{2s})^2(\sigma_{2p}^*)^2(\pi_{2p})^4(\pi_{2p}^*)^3$ 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. 

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Configuration</th>
<th>Bond Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$_2^+$</td>
<td>$\sigma^2\sigma^*^1$</td>
<td>0.5</td>
</tr>
<tr>
<td>HHHe$^+$</td>
<td>$\sigma^2$</td>
<td>1</td>
</tr>
<tr>
<td>H$_2^+$</td>
<td>$\sigma^1$</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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.

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:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Configuration</th>
<th>Bond Order</th>
<th>$D(X_z)$ kJ/mol</th>
<th>$d(X–X)$ pm</th>
<th>Magnetic Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$</td>
<td>$(\sigma_{2s})^2(\sigma^<em><em>{2s})^2(\sigma</em>{2p})^2(\pi_{2p})^4(\pi^</em>_{2p})^2$</td>
<td>2</td>
<td>494</td>
<td>120.75</td>
<td>para</td>
</tr>
<tr>
<td>$O_2^-$</td>
<td>$(\sigma_{2s})^2(\sigma^<em><em>{2s})^2(\sigma</em>{2p})^2(\pi_{2p})^4(\pi^</em>_{2p})^3$</td>
<td>1.5</td>
<td>395</td>
<td>135</td>
<td>para</td>
</tr>
<tr>
<td>$O_2^{2-}$</td>
<td>$(\sigma_{2s})^2(\sigma^<em><em>{2s})^2(\sigma</em>{2p})^2(\pi_{2p})^4(\pi^</em>_{2p})^4$</td>
<td>1</td>
<td>126</td>
<td>149</td>
<td>dia</td>
</tr>
</tbody>
</table>

Lewis structures:

\[
\begin{align*}
[\begin{array}{c}
\cdot \cdot \\
\cdot \cdot \\
\cdot \cdot \\
\cdot \cdot \\
\end{array}]
\end{align*}
\quad
[\begin{array}{c}
\cdot \cdot \\
\cdot \cdot \\
\cdot \cdot \\
\cdot \cdot \\
\end{array}]
\quad
[\begin{array}{c}
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\end{array}]
\quad
[\begin{array}{c}
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\end{array}]
\quad
[\begin{array}{c}
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\end{array}]
\quad
[\begin{array}{c}
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\end{array}]
\quad
[\begin{array}{c}
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\end{array}]
\quad
[\begin{array}{c}
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\end{array}]
\quad
[\begin{array}{c}
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\end{array}]
\end{align*}

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

<table>
<thead>
<tr>
<th>Formula</th>
<th>Configuration</th>
<th>bond order</th>
<th>$d(X–X)$ pm</th>
<th>Unpaired electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2^{2-}$</td>
<td>$(\sigma_{2s})^2(\sigma^*<em>{2s})^2(\pi</em>{2p})^4(\sigma_{2p})^2$</td>
<td>3</td>
<td>119</td>
<td>0</td>
</tr>
<tr>
<td>$O_2^{2-}$</td>
<td>$(\sigma_{2s})^2(\sigma^<em><em>{2s})^2(\sigma</em>{2p})^2(\pi_{2p})^4(\pi^</em>_{2p})^4$</td>
<td>1</td>
<td>122.4</td>
<td>2</td>
</tr>
<tr>
<td>$O_2$</td>
<td>$(\sigma_{2s})^2(\sigma^<em><em>{2s})^2(\sigma</em>{2p})^2(\pi_{2p})^4(\pi^</em>_{2p})^2$</td>
<td>2</td>
<td>120.75</td>
<td>2</td>
</tr>
</tbody>
</table>

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.
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 N₂, with which it is isoelectronic), and NO– has a bond order of 2 (like O₂, with which it is isoelectronic). Based on bond order, the bond lengths are predicted to be NO+ < NO < NO–. NO– is probably paramagnetic, like O₂, owing to two unpaired electrons in the doubly degenerate \( \pi^* \) 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.

\[
\begin{align*}
\sigma(2s) & \quad \sigma^*(2s) \\
\pi(2p_y) & \quad \pi^*(2p_y) \\
\pi(2p_x) & \quad \pi^*(2p_x)
\end{align*}
\]

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 \(\sigma\) HOMO would have more electron density on that atom. However, with mixing, it appears that the C \(2p_z\) only contributes to the \(\sigma_{2s}\) and not to the same symmetry \(\sigma_{2s}\), because the C \(2p_z\) AO is closer in energy. This is analogous to the case of CO (see text, p. 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 \(\pi\) and \(\sigma\) 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 \(\pi^*\) 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 2p orbital on oxygen.
5.14 a. The construction of a qualitative MO scheme for linear CH$_2$ ($D_{sh}$) follows the same approach as the MO scheme of BeH$_2$ (see class notes). The two hydrogen 1s orbitals form SALCs of $\Sigma_g^+$ and $\Sigma_u^+$. On the central carbon atom, the 2s orbital the symmetry of the totally symmetric representation ($\Sigma_g^+$), as always. From the unit vector listings in the $D_{sh}$ character table, the 2$p_z$ orbital transforms as $\Sigma_u^+$ and the 2$p_x$ and 2$p_y$ orbitals transform degenerately as $\Pi_u$. The $\Sigma_g^+$ SALC forms $\sigma_g$ and $\sigma_g^*$ bonding and antibonding MOs with the carbon 2s AO. The $\Sigma_u^+$ SALC forms $\sigma_u$ and $\sigma_u^*$ bonding and antibonding MOs with the carbon 2$p_z$ AO. The carbon 2$p_x$ and 2$p_y$ orbitals ($\Pi_u$) 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 $\pi_u^*$ level, the molecule would be paramagnetic.
5.17 Disregarding the 1s orbitals on fluorine, which are assumed to be nonbonding core electrons, the orbitals available to form SALCs are 2s and 2p. Pairs of 2s 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.

<table>
<thead>
<tr>
<th>SALC</th>
<th>Xe AO match</th>
<th>MO Types</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s + 2s</td>
<td>5s, 4d_{z^2}</td>
<td>σ &amp; σ*</td>
<td>(\Sigma_g^+)</td>
</tr>
<tr>
<td>2s - 2s</td>
<td>5p_z</td>
<td>σ &amp; σ*</td>
<td>(\Sigma_u^+)</td>
</tr>
<tr>
<td>2p_z + 2p_z</td>
<td>5p_z</td>
<td>σ &amp; σ*</td>
<td>(\Sigma_u^+)</td>
</tr>
<tr>
<td>2p_z - 2p_z</td>
<td>5s, 4d_{z^2}</td>
<td>σ &amp; σ*</td>
<td>(\Sigma_g^+)</td>
</tr>
<tr>
<td>2p_y + 2p_y</td>
<td>5p_y</td>
<td>π &amp; π*</td>
<td>(\Pi_u)</td>
</tr>
<tr>
<td>2p_y - 2p_y</td>
<td>4d_{yz}</td>
<td>π &amp; π*</td>
<td>(\Pi_g)</td>
</tr>
<tr>
<td>2p_x + 2p_x</td>
<td>5p_x</td>
<td>π &amp; π*</td>
<td>(\Pi_u)</td>
</tr>
<tr>
<td>2p_x - 2p_x</td>
<td>4d_{xz}</td>
<td>π &amp; π*</td>
<td>(\Pi_g)</td>
</tr>
</tbody>
</table>
5.18 Describing TaH₅ as having a \( C_{4v} \) structure implies that it is square pyramidal.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{Ta} \\
\text{H} & \quad \text{H}
\end{align*}
\]

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

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

<table>
<thead>
<tr>
<th>( C_{4v} )</th>
<th>( E )</th>
<th>( 2C_4 )</th>
<th>( C_2 )</th>
<th>( 2\sigma_v )</th>
<th>( 2\sigma_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_{\text{SALC}} )</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

\[
\Gamma_{\text{SALC}} = 2A_1 + B_1 + E
\]

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

\[
A_1 = s, p_z, d_2 \quad B_1 = d_{x^2-y^2} \quad E = (p_x, p_y), (d_{x^2}, d_{y^2})
\]

The two \( A_1 \) SALCs combine the five hydrogen 1s orbitals in the following ways:

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

The other \( A_1 \) SALC is a match for either 6p₂ or 5d₂. 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 $5d_z$ orbital:

![Diagram showing overlap](image)

The $B_1$ SALC, which matches with the $5d_{x^2-y^2}$ orbital on Ta, is a combination of $1s$ 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:

![Diagram showing overlap](image)

The axial $1s$ 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:

![Diagram showing overlap](image)

The other combinations would be oriented at $90^\circ$ about the $z$ axis to those shown above, and would involve $6p_y$ and $5d_{yz}$. Note that, once again, the axial $1s$ 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.
The normalized wave functions for the three MOs are as follows:

\[
\Phi_1(a_1') = \frac{1}{\sqrt{3}} (\varphi_1 + \varphi_2 + \varphi_3)
\]

\[
\Phi_2(e') = \frac{1}{\sqrt{6}} (2\varphi_1 - \varphi_2 - \varphi_3)
\]

\[
\Phi_3(e') = \frac{1}{2} (\varphi_2 - \varphi_3)
\]