Chapter 4

4.1 Draw sketches of C, axes and a planes?
(a) NH$_3$?
In the drawings below, the circle represents the nitrogen atom of ammonia and the diamonds represent the hydrogen atoms. The mirror plane drawn is in the plane of the page, and it contains the nitrogen atom and the hydrogen atom on the left. The other two hydrogen atoms are out of this plane, one behind the page and one in front.

(b) The PtCl$_4^{2-}$ ion?
In the drawings below, the circle represents the platinum atom of the tetrachloroplatinate anion and the diamonds represent the chlorine atoms. The mirror plane drawn is in the plane of the page, and it contains all five atoms. This plane is also drawn on its side, so that all five atoms seem to lie on a single line. In addition, there are four more mirror planes perpendicular to the first plane.

4.2 $S_4$ or $i$:
(a) C0$_2$?
This linear molecule has a center of inversion. There are only two point groups for linear molecules, $D_h$ (has $i$) or $C$ (does not have $i$). Therefore, the point group is $D_h$.
(b) C$_2$H$_2$?
This linear molecule also has $i$. The point group is $D_h$.
(c) BF$_3$?
This molecule possesses neither $i$ nor $S_4$. It belongs to the $D_{3h}$ point group.
(d) SO$_4^{2-}$?
This ion has three different $S_4$ axes, which are coincident with three $C_2$ axes, but there is no $i$. The point group is $T_d$. 
4.3 Assigning point groups:
(a) $\text{NH}_2\text{Cl}$?
The only element of symmetry that this molecule possesses other than E is a mirror plane that contains the N and Cl atoms and bisects the H-N-H bond angle. The set of symmetry elements (E, $\sigma$) corresponds to the point group $C_s$ (the subscript comes from the German word for mirror, Spiegel).

(b) $\text{CO}_3^{2-}$?
The carbonate anion is planar, so it possesses at least one plane of symmetry. Since this plane is perpendicular to the major proper rotation axis, $C_3$, it is called $\sigma_h$. In addition to the $C_3$ axis, there are three $C_2$ axes coinciding with the three C-O bond vectors. There are also other mirror planes and improper rotation axes, but the elements listed so far (E, $C_3$, $\sigma_h$, 3$C_2$) uniquely correspond to the $D_{3h}$ point group (note that $\text{CO}_3^{2-}$ has the same symmetry as BF$_3$). A complete list of symmetry elements is E, $C_3$, 3$C_2$, $\sigma_h$, and 3$\sigma_v$.

(c) SiF$_4$?
This molecule has four $C_3$ axes, one coinciding with each of the four Si-F bonds. In addition, there are six mirror planes of symmetry (any pair of F atoms and the central Si atom define a mirror plane, and there are always six ways to choose a pair of objects out of a set of four). Furthermore, there is no center of symmetry. Thus, the set (E, 4$C_3$, 6$\sigma$, no $i$) describes this molecule and corresponds to the $T_d$ point group. A complete list of symmetry elements is E, 4$C_3$, 3$C_2$, 3$S_4$, and 6$\sigma_d$.

(d) HCN?
Hydrogen cyanide is linear, so it belongs to either the $D_{\text{\textendash}h}$ or the $C_{\text{\textendash}v}$ point group. Since it does not possess a center of symmetry, which is a requirement for the $D_{\text{\textendash}h}$ point group, it belongs to the $C_{\text{\textendash}v}$ point group.

(e) SiFC1BrI?
This molecule does not possess any element of symmetry other than the identity element, E. Thus, it is asymmetric and belongs to the $C_1$ point group, the simplest possible point group.

(f) BF$_4$?-
This anion is square planar. It has a $C_4$ axis and four perpendicular $C_2$ axes. It also has a $\sigma_h$ mirror plane. These symmetry elements uniquely correspond to the $D_{4h}$ point group. A complete list of symmetry elements is E, $C_4$, a parallel $C_2$, four perpendicular $C_2$, $S_4$, $i$, $\sigma_h$, 2$\sigma_v$, and 2$\sigma_d$.

4.4 The symmetry elements of orbitals?
(a) An s orbital?
An s orbital, which has the shape of a sphere, possesses an infinite number of $C_n$ axes where $n$ can be any number from 1 to infinity, plus an infinite number of mirror planes of symmetry. It also has a center of inversion, $i$. A sphere has the highest possible symmetry.
(b) A p orbital?
The + and - lobes of a p orbital are not equivalent and therefore cannot be interchanged by potential elements of symmetry. Thus, a p orbital does not possess a mirror plane of symmetry perpendicular to the long axis of the orbital. It does, however, possess an infinite number of mirror planes that pass through both lobes and include the long axis of the orbital. In addition, the long axis is a C axis; where n can be any number from 1 to infinity (in group theory this is referred to as a C axis).

(c) A d\textsubscript{xy} orbital?
The two pairs of + and - lobes of a orbital are interchanged by the center of symmetry that this orbital possesses. It also possesses three mutually perpendicular C\textsubscript{2} axes, each one coincident with one of the three Cartesian coordinate axes. Furthermore, it possesses three mutually perpendicular mirror planes of symmetry, which are coincident with the xy plane and the two planes that are rotated by 45° about the z axis from the x plane and the yz plane.

(d) A d\textsubscript{z^2} orbital?
Unlike a P\textsubscript{z} orbital, a d\textsubscript{z^2} orbital has two large + lobes along its long axis, and a - torus (or doughnut) around the middle. In addition to the symmetry elements possessed by a p orbital (see above), the infinite number of mirror planes that pass through both lobes and include the long axis of the orbital as well as the C axis, a d\textsubscript{z^2} orbital also possesses (i) a center of symmetry, (ii) a mirror plane that is perpendicular to the C axis, (iii) an infinite number of C\textsubscript{2} axes that pass through the center of the orbital and are perpendicular to the C axis, and (iv) an S\textsubscript{z} axis.

4.5 Which species are polar?
(a) The criteria?
The sets of symmetry elements that independently require that a molecule is nonpolar are (i) a C\textsubscript{n}, axis and a perpendicular C\textsubscript{2} axis (i.e. a D point group), (ii) a C\textsubscript{n}^- axis and a \sigma\textsubscript{h} plane (i.e., a C\textsubscript{nh} point group), (iii) a center of inversion, i, or (iv) multiple non collinear C\textsubscript{n} axes with n > 2. The first two sets, (i) and (ii), were discussed in the text. An example of a species that has a center of symmetry but not a C\textsubscript{n}, axis and a perpendicular C\textsubscript{2} axis is the planar conformation of H\textsubscript{2}O\textsubscript{2}. This molecule belongs to the C\textsubscript{2h} point group and is nonpolar. The fourth set (iv) includes the tetrahedron, the octahedron, and the icosahedron. For these symmetries, there is no distinction between the x, y, and z directions (i.e. x, y, and z are triply degenerate).

(b) Examples:
NH\textsubscript{3}Cl?
This molecule does not meet any of the four 4’ criteria stated above, and so it is polar.
CO\textsubscript{3}\textsuperscript{2-}?
The point group is D\textsubscript{3h}, so on the basis of criterion (i) it is nonpolar.
SiF\textsubscript{4}?
The point group is T\textsubscript{d}, so on the basis of criterion (iv) it is nonpolar.
HCN?
This molecule does not meet any of the four criteria stated above, and so it is polar.

\textbf{SiFClBrI?}

This molecule too does not meet any of the four criteria stated above, and so it is polar.

\textbf{BrF\textsubscript{4}⁻?}

This ion belongs to the D\textsubscript{4h} point group, so on the basis of criterion (i) it is nonpolar.

\textbf{4.6 Which species are chiral?}

\textbf{(a) The criteria.}

The symmetry criterion for chirality is the absence of an S\textsubscript{n} element of symmetry. Recall that S\textsubscript{1} = \sigma and S\textsubscript{2} = i.

\textbf{(b) Examples:}

\textbf{NH\textsubscript{2}Cl?}

This molecule does possess a mirror plane of symmetry, so it is not chiral.

\textbf{CO\textsubscript{3}\textsuperscript{2⁻}?}

The carbonate anion possesses four different planes of symmetry, so it is not chiral.

\textbf{SiF\textsubscript{4}?}

This molecule, belonging to the T\textsubscript{d} point group, possesses six different planes of symmetry, so it is not chiral. You should note that a tetrahedron also possesses three S\textsubscript{4} improper rotation axes that coincide with its C\textsubscript{2} axes.

\textbf{HCN?}

Since this molecule possesses an infinite number of mirror planes of symmetry, it is not chiral.

\textbf{SiFClBrI?}

This molecule does meet the criterion stated above for chirality since it does not possess any S\textsubscript{n} element of symmetry (since it is C\textsubscript{1}, or asymmetric, it does not possess any element of symmetry other than E).

\textbf{BrF\textsubscript{4}⁻?}

This D\textsubscript{4h} ion possesses many S\textsubscript{n} elements of symmetry, including \sigma\textsubscript{h}, i, 2\sigma\textsubscript{v}, 2\sigma\textsubscript{d}, and S\textsubscript{4}. Therefore, it is not chiral.

\textbf{4.7 Point group and degenerate MOs of the SO\textsubscript{3}\textsuperscript{2⁻} ion?}

\textbf{(a) Point group?}

Using the decision tree shown in Figure 4.9, you will find the point group of this anion to be C\textsubscript{3v} (it is nonlinear, it only has one proper rotation axis, a C\textsubscript{3} axis, and it has three \sigma\textsubscript{v}, mirror planes of symmetry).

\textbf{(b) Degenerate MOs?}

Inspection of the C\textsubscript{3v} character table (Appendix 3) shows that the characters under the column headed by the identity element, E, are 1 and 2. Therefore, the maximum degeneracy possible for molecular orbitals of this anion is 2.

\textbf{(c) Which p orbitals have the maximum degeneracy?}

According to the character table, the S atom 3s and 3P\textsubscript{z} orbitals are each singly degenerate (and belong to the A\textsubscript{1} symmetry type), but the 3P\textsubscript{x} and 3P\textsubscript{y} orbitals are doubly degenerate.
degenerate (and belong to the E symmetry type). Thus, the $3P_x$ and $3P_y$ atomic orbitals on sulfur can contribute to molecular orbitals that are two-fold degenerate.

4.8 Point group and degenerate MOs of PF$_5$:

(a) Point group?
As above, you use the decision tree to assign the point group, in this case concluding that PF$_5$ has D$_{3h}$ symmetry (it has a trigonal bipyramidal structure, by analogy with PCl$_5$ (see Table 3.7); it is nonlinear, has only one high-order proper rotation axis, a C$_3$ axis, it has three C$_2$ axes that are perpendicular to the C$_3$ axis, and it has a $\sigma_h$ mirror plane of symmetry).

(b) Degenerate MOs?
Inspection of the D$_{3h}$ character table (Appendix 3) reveals that the characters under the E column are 1 and 2, so the maximum degeneracy possible for a molecule with this symmetry is 2.

(c) Which p orbitals have the maximum degeneracy?
The P atom $3p_x$ and $3p_y$ atomic orbitals, which are doubly degenerate and are of the E’ symmetry type (i.e. they have E’ symmetry), can contribute to molecular orbitals that are two-fold degenerate. In fact, if they contribute to molecular orbitals at all, they must contribute to two-fold degenerate ones.