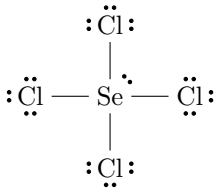
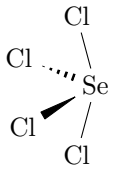
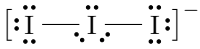
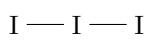
1/21: I) Do the following (VSEPR) problems from your text (Miessler et al. (2014)): Chapter 3: #8, 9f-i, 20, 29.

3.8 Give Lewis dot structures and sketch the shapes of the following:

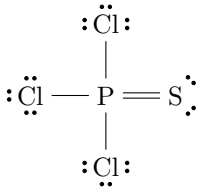
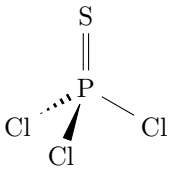
a. $SeCl_4$

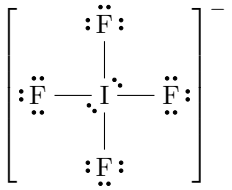
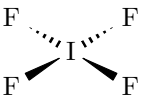
b. I_3^-

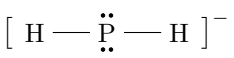
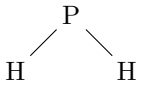
c. $PSCl_3$

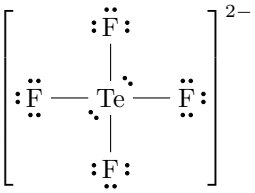
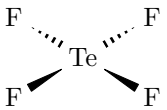
d. IF_4^-

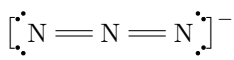
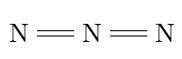
e. PH_2^-

f. TeF_4^{2-}

g. N_3^-

h. $SeOCl_4$

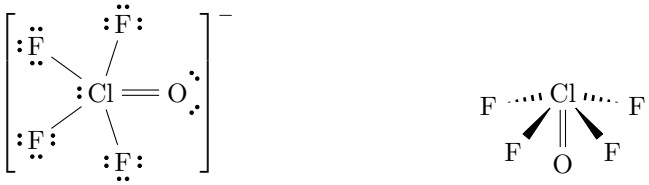
i. PH_4^+

3.9 Give Lewis dot structures and sketch the shapes of the following.

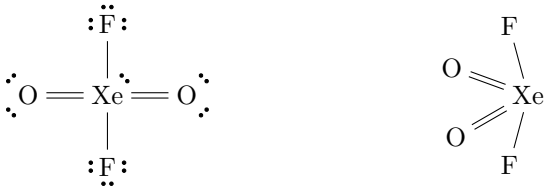
f. $IO(OH)_5$

g. $SOCl_2$

h. $ClOF_4^-$ [1]

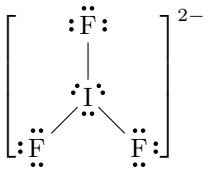


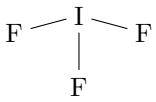
i. XeO_2F_2



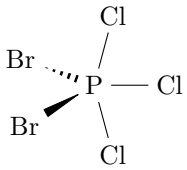
[1]Note that it is unclear whether the equatorial fluorines will be bent away from the lone pair and toward the oxygen, or the other way around. Hence, I arbitrarily chose to show them pointed away from the lone pair.

3.20 Predict and sketch the structure of the (as yet) hypothetical ion $IF_3{}^{2-}$.





3.29 Sketch the most likely structure of PCl_3Br_2 and explain your reasoning.



Answer. Bromine is more electropositive than chlorine. Thus, by Bent's rule, the bromines will bond to the hybrid orbitals with greater s-character (the equatorial sp^2 ones) first. □

II) Assign the symmetry point group to the 13 ions and molecules in problems #8, 9f-i in Chapter 3 of your text.

3.8

a. $SeCl_4$

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, $SeCl_4$ is of the $\boxed{C_{2v}}$ point group. □

b. I_3^-

Answer. I_3^- is of the $\boxed{D_{\infty h}}$ point group. □

c. $PSCl_3$

Answer. Not low or high symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h. Has three σ_v planes all offset by 60°.
Therefore, $PSCl_3$ is of the $\boxed{C_{3v}}$ point group. □

d. IF_4^-

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h.
Therefore, IF_4^- is of the $\boxed{D_{4h}}$ point group. □

e. PH_2^-

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, PH_2^- is of the $\boxed{C_{2v}}$ point group. □

f. TeF_4^{2-}

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h.
Therefore, TeF_4^{2-} is of the $\boxed{D_{4h}}$ point group. □

g. N_3^-

Answer. N_3^- is of the $\boxed{D_{\infty h}}$ point group. □

h. $SeOCl_4$

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, $SeOCl_4$ is of the $\boxed{C_{2v}}$ point group. □

i. PH_4^+

Answer. PH_4^+ is of the $\boxed{T_d}$ point group. □

3.9

f. $IO(OH)_5$

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes and two perpendicular σ_d planes.
Therefore, $IO(OH)_5$ is of the $\boxed{C_{4v}}$ point group. □

g. $SOCl_2$

Answer. $SOCl_2$ is of the $\boxed{C_s}$ point group. □

h. $ClOF_4^-$

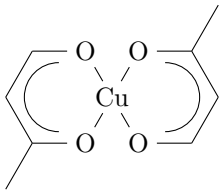
Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes and two perpendicular σ_d planes.
Therefore, $ClOF_4^-$ is of the $\boxed{C_{4v}}$ point group. □

i. XeO_2F_2

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, XeO_2F_2 is of the $\boxed{C_{2v}}$ point group. □

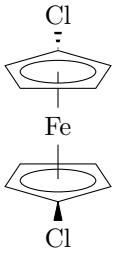
III) Assign the symmetry point group of the following molecules and objects. Ignore the H atoms in (a), (e), and (g). Note that (e) has pseudooctahedral geometry and (g) is square-planar.

a) The molecule pictured below.



Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. Has a σ_h.
Therefore, the above molecule is of the $\boxed{C_{2h}}$ point group. □

b) The molecule pictured below.



Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. Has a σ_h
Therefore, the above molecule is of the $\boxed{C_{2h}}$ point group. □

c) $POCl_3$

Answer. Not low or high symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h. Has three σ_v planes all offset by 60°.
Therefore, $POCl_3$ is of the $\boxed{C_{3v}}$ point group. □

d) Tennis ball (including the seam)

Answer. Not low or high symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. No σ_h. Has two perpendicular σ_d planes.
Therefore, a tennis ball is of the $\boxed{D_{2d}}$ point group. □

e) *trans*-$[CrCl_2(H_2O)_4]^+$

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h.
Therefore, *trans*-$[CrCl_2(H_2O)_4]^+$ is of the $\boxed{D_{4h}}$ point group. □

f) 1,3,5-trichlorobenzene.

Answer. Not low or high symmetry. Has a C_3 axis. Has 3 perpendicular C_2 axes. Has σ_h.
Therefore, 1,3,5-trichlorobenzene is of the $\boxed{D_{3h}}$ point group. □

g) *trans*-$Pt(NH_3)_2Cl_2$

Answer. Not low or high symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. Has σ_h.
Therefore, *trans*-$Pt(NH_3)_2Cl_2$ is of the $\boxed{D_{2h}}$ point group. □

h) SF_5Cl

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes and two perpendicular σ_d planes.
Therefore, SF_5Cl is of the $\boxed{C_{4v}}$ point group. □

i) BFClBr

Answer. BFClBr is of the $\boxed{C_s}$ point group. □

j) $PF_2{}^+$

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, $PF_2{}^+$ is of the $\boxed{C_{2v}}$ point group. □

IV) In the octahedral ion FeF_6^{3-}, what symmetry elements are destroyed if two *trans* F ions are moved away from the Fe^{3+} center in an equidistant fashion?

Answer. From the O_h character table, we have that the O_h symmetry *operations* are

$$E \qquad 8\,C_3 \qquad 6\,C_2 \qquad 6\,C_4 \qquad 3\,C_2(=C_4^2) \qquad i \qquad 6\,S_4 \qquad 8\,S_6 \qquad 3\,\sigma_h \qquad 6\,\sigma_d$$

Most of these operations are in one-to-one correspondence with a symmetry element. For example, each of the six C_2 rotations happens about a different C_2 axis. However, some symmetry elements have multiple symmetry operations happen about them. For example, each of the four C_3 axes has two (conjugate) C_3 symmetry operations (C_3 and C_3^2) occur about it. Thus, accounting for changes like this, we have that the O_h symmetry *elements* are

$$E \qquad 4\,C_3 \qquad 6\,C_2 \qquad 3\,C_4 \qquad 3\,C_2(=C_4^2) \qquad i \qquad 3\,S_4 \qquad 4\,S_6 \qquad 3\,\sigma_h \qquad 6\,\sigma_d$$

Similarly, we can determine that the D_{4h} symmetry elements are

$$E \qquad C_4 \qquad C_2(=C_4^2) \qquad 2\,C_2' \qquad 2\,C_2'' \qquad i \qquad S_4 \qquad \sigma_h \qquad 2\,\sigma_v \qquad 2\,\sigma_d$$

Between the two sets of symmetry elements, some are relabeled and some are lost entirely.

We will first discuss the relabeled ones. In particular...

- The two C_2 axes that lie in the xy plane become $2\,C_2''$;
- The two $C_2(=C_4^2)$ axes that do not become the principal axis of the D_{4h} molecule become $2\,C_2'$[2];
- The two σ_h planes that are not perpendicular to the principal axis of the D_{4h} molecule become $2\,\sigma_v$.

We now discuss the ones that are lost entirely. These include (of the O_h molecule)...

- All four C_3/S_4 axes;
- The four C_2 axes that do not lie in the xy plane;
- The two C_4/S_4 axes that do not become the principal axis of the D_{4h} molecule;
- The four σ_d planes that do not contain the principal axis of the D_{4h} molecule.

□

[2]The prime notation is explained in the discussion associated with Figure II.6b of my notes.