CHEM 20100 (Inorganic Chemistry I) Problem Sets

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Contents

0 Course Prep Problems

9/13: **2.8** The details of several steps in the particle-in-a-box model in this chapter have been omitted. Work out the details of the following steps:

a. Show that if $\Psi = A\sin rx + B\cos sx$ (A, B, r, and s are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE}\left(\frac{2\pi}{h}\right)$$

Solution.

$$\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial^2\Psi(x)}{\partial x^2} = E\Psi(x)$$
$$\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial^2}{\partial x^2}(A\sin rx + B\cos sx) = E(A\sin rx + B\cos sx)$$
$$\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial}{\partial x}(Ar\cos rx - Bs\sin sx) = E(A\sin rx + B\cos sx)$$
$$\frac{-h^2}{8\pi^2 m}\cdot\left(-Ar^2\sin rx - Bs^2\cos sx\right) = E(A\sin rx + B\cos sx)$$
$$\frac{Ar^2h^2}{8\pi^2 m}\sin rx + \frac{Bs^2h^2}{8\pi^2 m}\cos sx = AE\sin rx + BE\cos sx$$
$$0 = \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(\frac{Bs^2h^2}{8\pi^2 m} - BE\right)\cos sx$$

Choose $x = 0$.

$$= \frac{Bs^2h^2}{8\pi^2 m} - BE$$
$$E = \frac{s^2h^2}{8\pi^2 m}$$
$$\frac{8\pi^2 mE}{h^2} = s^2$$
$$s = \sqrt{\frac{8\pi^2 mE}{h^2}}$$
$$\boxed{s = \sqrt{2mE}\frac{2\pi}{h}}$$

With this result ...

$$0 = \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(\frac{Bs^2h^2}{8\pi^2 m} - BE\right)\cos sx$$
$$= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(B\left(\frac{s^2h^2}{8\pi^2 m}\right) - BE\right)\cos sx$$
$$= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + (BE - BE)\cos sx$$
$$= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx$$

Choose $x = \frac{\pi}{2r}$.

$$= \frac{Ar^2h^2}{8\pi^2 m} - AE$$

$$\boxed{r = \sqrt{2mE}\frac{2\pi}{h}}$$

□

d. Show that substituting the value of r given in part c into $\Psi = A \sin rx$ and applying the normalizing requirement gives $A = \sqrt{2/a}$.

Solution.

$$\begin{aligned}
1 &= \int_{\text{all space}} \Psi\Psi^* \, \mathrm{d}\tau \\
&= \int_0^a \left(A \sin \frac{n\pi x}{a}\right)\left(A \sin \frac{n\pi x}{a}\right) \mathrm{d}x \\
&= \int_0^a A^2 \sin^2 \frac{n\pi x}{a} \, \mathrm{d}x
\end{aligned}$$

Use $\sin^2 u = \frac{1-\cos 2u}{2}$.

$$\begin{aligned}
&= A^2 \int_0^a \frac{1 - \cos \frac{2n\pi x}{a}}{2} \, \mathrm{d}x \\
&= \frac{A^2}{2}\left(\int_0^a \mathrm{d}x - \int_0^a \cos \frac{2n\pi x}{a} \, \mathrm{d}x\right) \\
&= \frac{A^2}{2}\left([x]_0^a - \left[\frac{a}{2n\pi} \sin \frac{2n\pi x}{a}\right]_0^a\right) \\
&= \frac{A^2}{2}\left((a-0) - \left(\frac{a}{2n\pi} \sin 2n\pi - \frac{a}{2n\pi} \sin 0\right)\right) \\
&= \frac{A^2}{2}\left(a - \left(\frac{a}{2n\pi} \sin 2n\pi\right)\right)
\end{aligned}$$

Since n is an integer, $\sin 2n\pi = 0$.

$$\begin{aligned}
&= \frac{aA^2}{2} \\
\frac{2}{a} &= A^2 \\
\boxed{A &= \sqrt{\frac{2}{a}}}
\end{aligned}$$

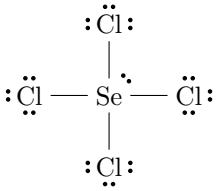
□

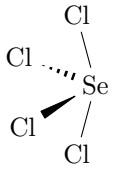
1 VSEPR and Point Groups

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

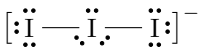
3.8 Give Lewis dot structures and sketch the shapes of the following:

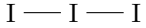
a. $SeCl_4$



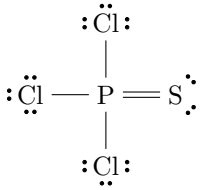


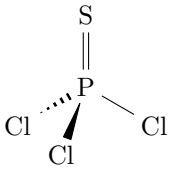
b. I_3^-



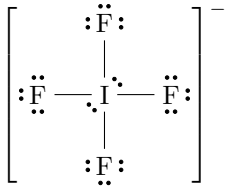


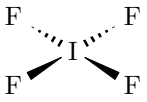
c. $PSCl_3$



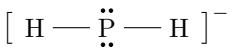


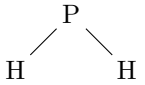
d. IF_4^-



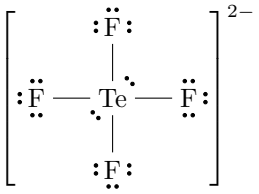


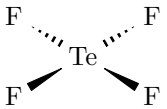
e. PH_2^-



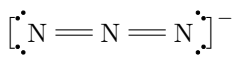


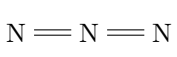
f. TeF_4^{2-}





g. N_3^-





h. $SeOCl_4$

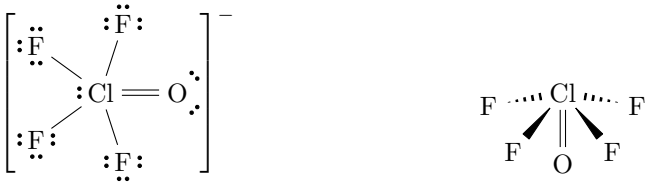
i. PH_4^+

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

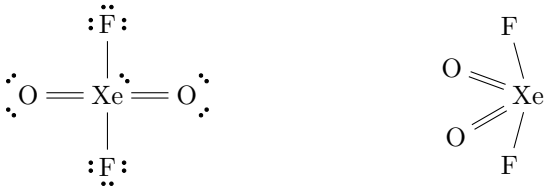
f. $IO(OH)_5$

g. $SOCl_2$

h. $ClOF_4^-$ [1]

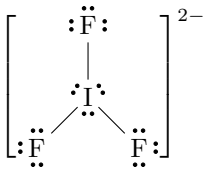


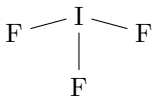
i. XeO_2F_2



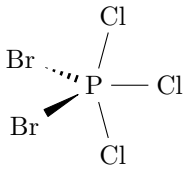
[1]Note that it is unclear whether the equatorial fluorines will be bent away from the lone pair and toward the oxygen, or the other way around. Hence, I arbitrarily chose to show them pointed away from the lone pair.

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 C_{2v} point group. □

b. I_3^-

Answer. I_3^- is of the $D_{\infty h}$ 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 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 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 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 D_{4h} point group. □

g. N_3^-

Answer. N_3^- is of the $D_{\infty h}$ 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 C_{2v} point group. □

i. PH_4^+

Answer. PH_4^+ is of the 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 C_{4v} point group. □

g. $SOCl_2$

Answer. $SOCl_2$ is of the C_s point group. □

h. $ClOF_4^-$

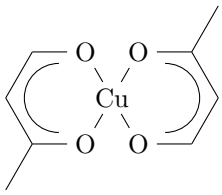
Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes and two perpendicular σ_d planes.
Therefore, $ClOF_4^-$ is of the C_{4v} point group. □

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 C_{2v} point group. □

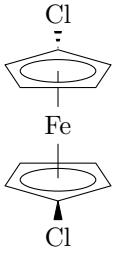
III) Assign the symmetry point group of the following molecules and objects. Ignore the H atoms in (a), (e), and (g). Note that (e) has pseudooctahedral geometry and (g) is square-planar.

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 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 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 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 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 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 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 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 C_{4v} point group. □

i) BFClBr

Answer. BFClBr is of the 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 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. If the described change is made, the point group changes from O_h to D_{4h}. In this change, every C_3 and S_6 axis, two of the three C_4 axes, four C_2 axes, and every σ_d that does not contain the axis along which the F ions are stretched are destroyed. □