1.6: Problems

1. Write octet structures (including formal charges, bond order, and molecular shape) for SeO_3^{2-}, SeF_4, XeF_4, $HClO_3$ (= $HOClO_2$), NO_3^-, and ClO_2^+.

2. Write octet structures (including formal charges, bond order, and molecular shape) for Al_2Cl_6, $SnCl_3^-$, BrF_4^-, HOClO, SO_3, and NO_2^+.

3. Show using resonance why the S-O bond is slightly shorter in SO_2F_2 than in SO_2.

4. Give the formulas for five stable molecules and/or ions that are isoelectronic with ammonia.

5. Name three well known molecules or ions that are isoelectronic with (a) O_3, (b) BF, (c) CO_3^{2-}, and (d) N_3^-.

6. Name three well known molecules or ions that are isoelectronic with (a) CN^-, (b) H_2O, (c) BF_3, and (d) CO_2.

7. The N-N bond distance is 1.10 Å in N_2. Using the Pauling bond length – bond strength formula, D(n) = D(1) - 0.6 log(n), calculate the bond distance in the N_2^+ cation.

8. In hydroxylamine, H_2NOH, the N-O bond distance is 1.46 Å. Using the Pauling bond length - bond strength formula, estimate the N-O bond distances in NO_2 and NO_3^-.

9. While PF_5 and SF_6 are stable molecules, NF_5 and OF_6 are unknown. Can you draw octet structures for these compounds? Why would these molecules be unstable?

10. Consider the compounds NH_3 and PH_3. The H-N-H bond angle in ammonia is 108° (close to the tetrahedral angle, 109.5°), but the analogous angle in PH_3 is 93°. Why is the angle in PH_3 closer to 90° than it is to the tetrahedral angle?

11. Two hypothetical structures for the $N_2F_3^+$ ion are $[N\text{-}NF_3]^+$ and $[F\text{-}N\text{-}NF_2]^+$. Which one is more stable? Explain. (Note: lines in the formulas can represent either single or multiple bonds)

12. Krypton difluoride, KrF_2, decomposes at dry ice temperature to Kr and F_2. However, several salts of the $[KrF]^+$ ion are relatively stable. Draw valence bond pictures for KrF_2 and $[KrF]^+$, showing lone pairs, possible resonance structures, formal charges, bond orders, and bond angles. Why is $[KrF]^+$ more stable than KrF_2?

13. Consider the molecule ClF_3O_2 (with Cl the central atom). How many isomers are possible? Which is the most stable?

14. The Br-F bond distance in the interhalogen compound BrF is 1.76 Å. Use this information to estimate the average bond lengths in BrF_3 and BrF_5.

15. The B-H bond distances are about the same in BH_3 and BH_4^-. however, the B-F bond distance in BF_3 is shorter than that in the BF_4^- ion. Explain.

16. The N-N bond dissociation energy in hydrazine ($H_2N\text{-}NH_2$) is 159 kJ/mol. The dissociation energy of the N-N triple bond in N_2 is 941 kJ/mol, i.e., much greater than three times the N-N single bond dissociation energy in hydrazine. Explain why the N-N bond in hydrazine is so weak, and why this effect is not seen in N_2.

17. Show that a set of three sp^2 hybrid orbitals satisfies the following criteria: (a) any two orbitals in the sp^2 set are orthogonal, and (b) the orbitals are properly normalized.

18. Quantum mechanically, the momentum (p) of a particle traveling in a specific direction (e.g., the x direction) can be obtained by operating on its wavefunction ψ with the **momentum operator**:

$$\hat{p}\psi = p\psi, \text{ where } \hat{p} = -i\hbar\frac{\delta}{\delta x} \tag{1.6.1}$$

Knowing the correct form of this operator was the key to Schrödinger's formulation of the Hamiltonian operator, $\hat{H} = \frac{\hat{p}^2}{2m} + V$, which operates on a wavefunction to give the total energy. The momentum operator must also be consistent with the **de Broglie relation**, $p = \frac{h}{\lambda}$, which relates the momentum to the particle wavelength.

By analogy to electromagnetic waves, Schrödinger knew that a wavelike particle (such as an electron) traveling in free space in the x-direction could be described by the wavefunction:

$$\psi(x,t) = Ae^{i(kx-\omega t+\varphi)} \tag{1.6.2}$$

where the **wavenumber** k is inversely related to the particle's **de Broglie wavelength** λ by $k = \frac{2\pi}{\lambda}$. Here A is a normalization constant, ω is the frequency of the wave, and φ represents its phase.

Show using the momentum operator $\hat{p}$ that the value of the momentum p we obtain for a free particle from $\hat{p}\psi = p\psi$ is consistent with the de Broglie relation, $p = \frac{h}{\lambda}$.
(Hint: k, ω, and φ are independent of x)

19. Which S-N bonds in the cyclic $S_4N_3^+$ ion would you predict to be the shortest? The atomic connectivity in the ring is: -S-S-N-S-N-S-N-. [*Hint:* determine the number of π-bonds in the molecule by electron counting and then find the most stable resonance structures].

20. F has a higher electronegativity than Cl, and F_2 is a much stronger oxidizing agent than Cl_2, despite the fact that the electron affinity of fluorine (-328 kJ/mol) is weaker than that of chlorine (-349 kJ/mol). Explain this apparent contradiction.

21. (a) Explain why C-H, N-H, and O-H bonds in chemical compounds are stronger than Si-H, P-H, and S-H bonds, respectively. (b) Explain why C-F, N-F, and O-F single bonds follow the opposite trend, namely, they are weaker than Si-F, P-F, and S-F single bonds, respectively.
