

1. (5%) The ionization energy of an excited hydrogen atom, $H^*(2s^1)$, is equal to that of $H^*(2p^1)$. However, the first ionization of $H^-(1s^1 2s^1)$ is greater than that of $H^-(1s^1 2p^1)$. Explain.
2. (9%) When an atom of helium absorbs a photon to form the excited configuration of $1s^1 2s^1$ (He^*), a weak bond forms to give the diatomic molecule, He-He. Construct a molecular-orbital description of the bonding in this molecule.
3. (10%) Construct a Walsh diagram correlating the orbitals of a trigonal planar XH_3 (D_{3h}) molecule with those of a trigonal pyramidal XH_3 (C_{3v}) molecule.
4. (6%) (a) Discuss the relation between Pauling's scale of electronegativity of atom and valence bond theory. (b) Based on the definition of Pauling's electronegativity, how can one establish the electronegativity of all the element in the periodic table.
5. (10%) Consider the trigonal prismatic six-coordinate ML_6 complex with D_{3h} symmetry. Under the influence of ligand field, divide the d orbitals of the metal into sets of defined symmetry type assuming that the ligands are at the same angle relative to the xy plane as in a tetrahedral complex.
6. (6%) The diatomic cations, Br_2^+ and I_2^+ , are both known. Br_2^+ is red while I_2^+ is bright blue. (a) What electronic transition is probably responsible for absorption in these ions? (3%) (b) Which ion has the more closely spaced HOMO and LUMO? (3%)
7. (9%) Choose and explain: (a) Larger bond angle: NO_2^- or O_3 ; (b) Lower boiling point: H_2S or OF_2 ; and (c) Larger K_a value: K_a for the aqueous Fe^{3+} ion or K_a for the aqueous Al^{3+} ion.
8. (6%) Give the spin-only magnetic moment, and the crystal field stabilization energy (CFSE) of the following complexes: (a) FeF_6^{3-} , (b) $Mn(CN)_6^{3-}$ and (c) $CoCl_4^{2-}$.

9. (8%) In each of the following pairs of transition states, which would you expect to be more intense and why? (a) ${}^3A_{2g}$ to ${}^3T_{2g}$ in NiCl_6^{4-} or 3T_1 to 3T_2 in NiCl_4^{2-} and (b) The most intense d-d band in CoCl_4^{2-} or the most intense d-d band in MnCl_4^{2-} .
10. (12%) Describe in detail the bonding in the following compounds: (a) $(\text{SN})_x$ (a "one-dimensional" conductor), (b) $\text{B}_{12}\text{H}_{12}^{2-}$ (a regular icosahedron with 20 equilateral triangles forming the faces), and (c) $\text{Re}_2\text{Cl}_8^{2-}$ (eclipsed conformation; 75Re).
11. (9%) Chromate ion, CrO_4^{2-} , has T_d symmetry. Using the group theory method, predict the possible hybridization schemes for the chromate atom in CrO_4^{2-} . Which of these schemes would you expect to be most likely? Explain.

| D_{3h} | E | $2C_3$ | $3C_2$ | σ_h | $2S_3$ | $3\sigma_v$ | | |
|----------|---|--------|--------|------------|--------|-------------|--------------|-------------------|
| A_1' | 1 | 1 | 1 | 1 | 1 | 1 | | $x^2 + y^2, z^2$ |
| A_2' | 1 | 1 | -1 | 1 | 1 | -1 | R_z | |
| E' | 2 | -1 | 0 | 2 | -1 | 0 | (x, y) | $(x^2 - y^2, xy)$ |
| A_1'' | 1 | 1 | 1 | -1 | -1 | -1 | | |
| A_2'' | 1 | 1 | -1 | -1 | -1 | 1 | z | |
| E'' | 2 | -1 | 0 | -2 | 1 | 0 | (R_x, R_y) | (xz, yz) |

| T_d | E | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ | | |
|-------|---|--------|--------|--------|-------------|-----------|---------------------------------|
| A_1 | 1 | 1 | 1 | 1 | 1 | | $x^2 + y^2 + z^2$ |
| A_2 | 1 | 1 | 1 | -1 | -1 | | |
| E | 2 | -1 | 2 | 0 | 0 | | $(2z^2 - x^2 - y^2, x^2 - y^2)$ |
| T_1 | 3 | 0 | -1 | 1 | -1 | | |
| T_2 | 3 | 0 | -1 | -1 | 1 | (x, y, z) | (xy, xz, yz) |

| C_{3v} | E | $2C_3$ | $3\sigma_v$ | | |
|----------|---|--------|-------------|----------------------|---------------------------|
| A_1 | 1 | 1 | 1 | z | $x^2 + y^2, z^2$ |
| A_2 | 1 | 1 | -1 | R_z | |
| E_2 | 2 | -1 | 0 | (x, y)(R_x, R_y) | $(x^2 - y^2, xy)(xz, yz)$ |

12. (10%) Classify the following reactions into (I) Ligand Association (LA), (II) Ligand Dissociation (LD), (III) Oxidative Addition (OA), (IV) Reductive Elimination (RE), and (V) Migratory Insertion (MI):

For example, $\text{HRh}(\text{PPh}_3)_3 \rightarrow \text{HRh}(\text{PPh}_3)_2 + \text{PPh}_3$ Answer: **LD**

