General and Structural Chemistry
Quiz 1_M22
IIIT-Hyderabad

Q.1. (i) What is the trend in the electron affinity variation across a period and why?
(ii) Do the electron affinities of Si and P follow the above trend and why?   (2+3)

Q.2. Thallium, a neurotoxin, is the heaviest member of Group 13 of the periodic table and is found most usually in the +1 oxidation state. Aluminium, which causes anaemia and dementia, is also a member of the group but its chemical properties are dominated by the +3 oxidation state. Give two most probable reasons for this difference in their properties.   (4)

Q.3. (i) Name three properties of Li that are useful for the Lithium-Ion Batteries.
(ii) We know that sometimes Lithium-Ion Batteries catch fire. Cite a cause of Lithium-Ion Batteries catching fire.   (1.5+1.5)

Q.4. Briefly explain the following observations: (3+3)
(i) Nitric acid can dissolve Ag but not Au, although both these coinage metals are present in the same group.
(ii) Hg can form Hg_2^{2+} ion which is not common among metals.

Q.5. Below is pictured the reaction between an atom of magnesium and an atom of oxygen. Identify each **element** and the **ions** formed and **explain** your reasoning.
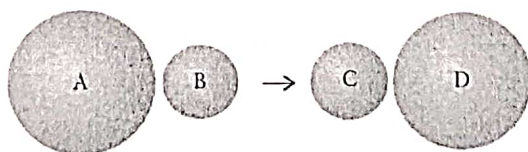
(4x2)

Q.6. Write a balanced chemical equation for the reaction of solid selenium dioxide, $SeO_2(s)$, with water.   (2)

Q.7. A metalloid has an acidic oxide of the formula R_2O_3. The element has no oxide of the formula R_2O_5. What is the name of the element? Give reasons in support of your answer. (4)

Q.8. Fill in the blanks (4x2)
(i)   The ……….. quantum number determines the energy of a hydrogenic atomic orbital.
(ii)   The square of the angular momentum determines the ……….. quantum number of a hydrogenic atomic orbital.
(iii) The z-component of the angular momentum determines the ………….. quantum number of a hydrogenic orbital.
(iv)   The orbital degeneracy of the levels in a hydrogen atom that have energy, $-hR/4$ (where R is the Rydeberg constant), is ………….

Q.9. The following plot shows the radial distribution function of the 3s- and 3p-orbitals of a hydrogen atom. **Identify** each curve and **explain** how you made your decision. (2x2)
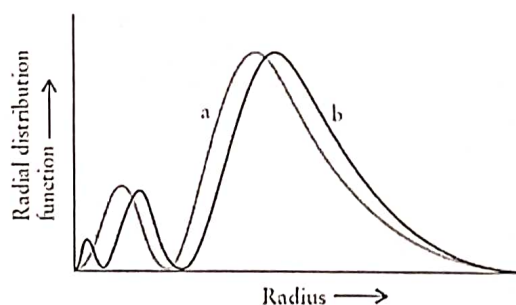
Q10. Two angular wavefunctions are given below. **Predict** the atomic orbitals and **explain** how you made your decision. (4+4)

(i) $\left(\dfrac{3}{4\pi}\right)^{1/2} \cos\varphi\theta$

(ii) $\left(\dfrac{3}{4\pi}\right)^{1/2} \sin\theta\cos\varphi$

*********End*********

Q1. If 8 atomic orbitals combine to form MOs (molecular orbitals), how many MOs will be formed? How many nodes are there in the 2nd lowest-energy molecular orbital (MO)?   (1,1)

Q2. Carbon monoxide (CO) forms an extensive series of carbonyl complexes with d-elements. Which end (O or C) usually forms coordination with the d-elements? Explain the carbonyl complex formation behavior by using the molecular orbital theory.   (1,3)

Q3. From a VBT perspective, explain why it is not possible to include any resonance structures of NO_3^- that include two N=O double bonds.   (5)

Q4. Write down the correct VB bonding wave function to describe an electron-pair bond in F_2 (neglecting the ionic contribution).   (4)

Q5. Given the following bond angles, use the percent s-character in the lone pair to determine which PX$_3$ compound is the better Lewis base: PF$_3$ (97.8°), PCl$_3$ (100.4°), PBr$_3$ (101.0°), and PI$_3$ (102°).   (6)

Q6. Consider a coordinate complex, ML$_2$, with linear configuration. If the ligands lie in the ±z directions, show the d-orbitals crystal field energy-levels splitting (in the increasing order).   (4)

Q7. For each pair of the following complexes, predict which will have the larger CF splitting parameter and state the reason: (3×2)

(i) [NiCl$_4$]$^{2-}$ or [NiCl$_6$]$^{4-}$

(ii) [PtF$_6$]$^{2-}$ or [Pt(CN)$_6$]$^{2-}$

(iii) [Ru(NH$_3$)$_6$]$^{2+}$ or [Ru(NH$_3$)$_6$]$^{3+}$

Q8. For each of the following coordination compounds, sketch the CF splitting diagram, label the d-orbitals, label each energy level with its group theoretical symbol, fill in the electrons, and predict the magnetism.   (6+6)

(i) [CoCl$_4$]$^{2-}$
(ii) [FeF$_6$]$^{3-}$

Q9. Explain why [Co(H$_2$O)$_6$]$^{3+}$ is a strong enough oxidizing agent to oxidize H$_2$O, but [Co(NH$_3$)$_6$]$^{3+}$ is stable in an aqueous solution.   (5)

Q10. Most first-row transition metals in the 2+ oxidation state are octahedral. Being said that, predict which of the ions – between Co and Ni (at this oxidation state) – will show a higher preference for the tetrahedral complex. Why?   (6)

Q11. Which d^n electron configurations are expected to undergo a Jahn–Teller distortion in a tetrahedral coordination compound?   (6)

Q12. Predict the geometry and number of unpaired spins in the following four-coordinate complexes: [AuBr₄]⁻ and [NiBr₄]²⁻. Explain your reasoning. (4)

Q13. Walsh diagram for EH₂ type of molecule is shown below. The energy in the diagram increases from bottom to top. Use the Walsh diagram to predict the shape of the 'ground' and 'first excited' states of BeH₂. (6)

Walsh Diagram:
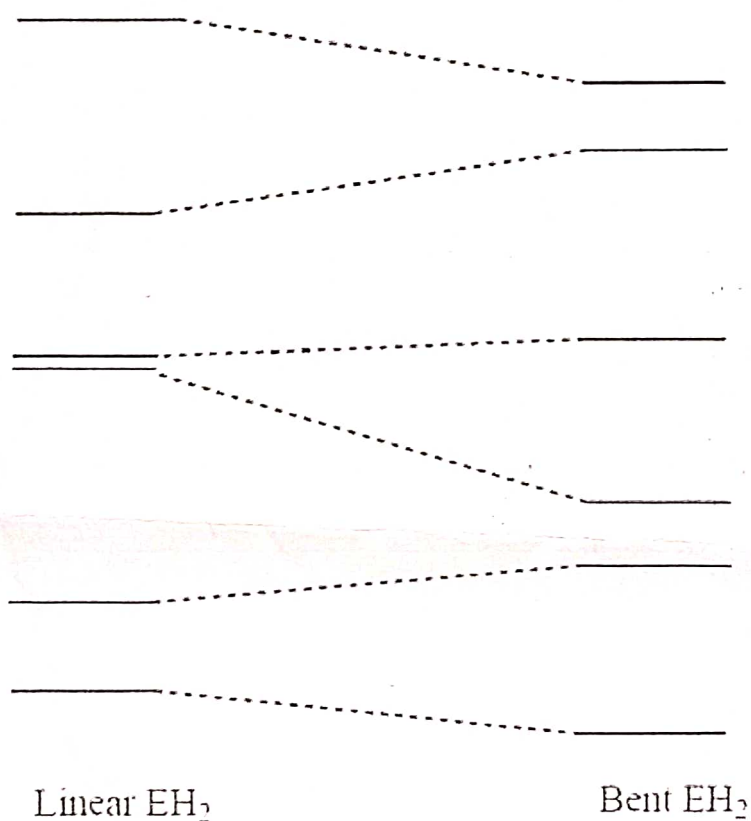
Linear EH₂   Bent EH₂

Full Marks: 60

Time: 1:30 Hours

Q.1. (a) The four spheres below represent the four ions (Mg^{2+}, Cl^-, K^+, and Se^{2-} ions), scaled according to the ionic size. Match each ion to its appropriate sphere. Explain how you arrive at your conclusions.
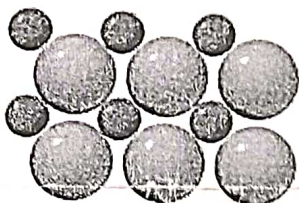
[5]

(b) One of the following pictures represents NaCl and one represents MgO. Which is which? Give reasoning.

[3]

(a)

(b)

(c) The Na^+ and Mg^{2+} ions have the same electronic configuration as the noble gas neon, but neon does not show a tendency to form compounds like the Na^+ and Mg^{2+} ions. Why?   [2]

Q.2. Consider the molecules N_2, N_2H_4, and N_2F_2. Write the electron-dot formulas for the molecules. Predict the qualitative molecular potential energy curves for the NN bond by making rough *sketches* on one graph for the above molecules. Justify (compare) the predicted sketches for the energy and the internuclear distance at the lowest point on each curve.   [3,4,3]

Q.3. The molecular orbital energy-level diagram of the cyanide ion, CN^-, is similar to that for N_2.

(a) Draw the energy-level diagram for CN^-. How will the molecular orbital energy-level diagram of CN^- differ from that of N_2?

[3,1]

(b) Write the ground-state valence electron configuration of cyanide ion, CN^-, and calculate the bond order of the species.

[2,1]

(c) Could you suggest whether the negative charge is at C or N? Why?

[2]

(d) Compare the dipole moments of the excited state with the ground state?

[1]

Q.4. Let us consider the bonding in a heteronuclear diatomic molecule. The MO ψ is written as the linear combination: $\psi = c_A \psi_A + c_B \psi_B$, where the terms have their usual significance.

Based on the above state whether the following statements are true or false: [5×2]

(i) The coefficients c_A and c_B are equal.

(ii) When c_A^2 is large, then the molecular orbital looks more like the atomic orbital of A and the electron density is greater near A.

(iii) The atom with the atomic orbitals of lower energy dominates the molecular orbitals and the electron density is greater closer to that atom.

(iv) If $c_A^2 = c_B^2$, then the electron pair is shared equally between the two atoms.

(v) If atom A forms a cation and atom B forms an anion in an ionic bond, the c_A^2 is nearly zero.

Q.5. (a) Which properties of Li are useful in the Lithium-Ion Batteries? Justify your answer with the help of a schematic diagram of a typical Lithium-Ion Battery. [1.5, 3]

(b) What is the trend in the electron affinity variation across a period and why? Explain the correct trend of the electron affinities of C and N. [1.5,2]

(c) Thallium, a neurotoxin, is the heaviest member of Group 13 of the periodic table and is found most usually in the +1 oxidation state. Aluminium, which causes anaemia and dementia, is also a member of the group but its chemical properties are dominated by the +3 oxidation state. Give two distinct reasons for this difference in behavior. [2]

Q.6. (a) The following reaction, known as the thermite reaction, was used during the Civil War to repair torn-up railroad tracks.

$$2\, Al\ (s) + Fe_2O_3\ (s) \rightarrow 2\, Fe\ (s) + Al_2O_3\ (s)$$
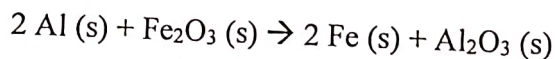
What is the main thermodynamic driving force for the above reaction and why does it arise? [2.5]

(b) The mathematical forms of the angular part of the wave functions for the 2p orbitals are given as follow:

$p_z = (3/4\pi)^{1/2} \cos\theta$

$p_x = (2)^{1/2} (3/8\pi)^{1/2} \sin\theta \cos\phi$

$p_y = (2)^{1/2} (3/8\pi)^{1/2} \sin\theta \sin\phi$

The terms bear their usual significance. Prove that the total probability density for the three 2p orbitals is a sphere. [3]

(c) Show a schematic plot of the variation of the effective potential energy of an electron in the hydrogen atom vs. radius for the $l = 0$ and $l \neq 0$ wavefunctions. Explain the nature of the curves. [3]

(d) "A 4s-electron may even have lower energy than that of a 3d-electron of the same atom." Justify the above statement. [1.5]

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Max. Marks: 100   Time: 3 hr

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Note: 1. Use of a non-programmable scientific calculator is allowed.
2. Answers must be to the point.

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Q1. (a) Name the three-dimensional primitive lattices that have a unit cell where none of the internal angles is 90°. [1]

(b) Which would you expect to be the more ductile element: Ag or Cr? Give reasoning. [2]

(c) Explain why X-rays can be used to measure atomic distances in crystals but visible light cannot be used for this purpose. [1]

(d) X-rays from a copper X-ray tube that have a wavelength of 154 pm are diffracted at an angle of 14.22 degrees (glancing angle) by crystalline silicon. Calculate the distance between the planes of atoms responsible for the diffraction in this crystal, assuming n = 1 (first-order diffraction). [1]

(e) Germanium has the same structure as silicon. If you were to repeat the experiment described in the previous problem but replace the Si crystal with a Ge crystal, would you expect the X-rays to be diffracted at a larger or smaller angle θ? [1]

(f) Mention the major differences one observes in the temperature effects on the electrical resistance of a normal metallic conductor, a semiconductor, and a superconductor. [1]

(g) What is Meissner effect? Mention one application of this effect. [2]

(h) How is a 'Cooper pair' different from two electrons (Fermions) in an orbital? [1]

Q2. (a) Using the mathematical expression for the $2p_z$ wave function of a one-electron atom, determine the probability of finding an electron in that orbital anywhere in the x-y plane. [2]

(b) Mathematical form of the radial wave function, $R(r)$, of the 2s orbital for the hydrogen-like atom is given as follows:

$$\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)^{3/2}e^{-\frac{Zr}{2a_0}}$$

where Z is the atomic number and $a_0 = 52.9$ pm, the Bohr radius.

At what distance from the nucleus does the radial node in a 2s orbital occur in the hydrogen atom? [4]

(c) Based on the building-up principle, or the Aufbau principle, write down the shells and subshells arranged in order of increasing energy for the occupation of electrons in multielectron atoms. [2]

(d) When Cu (Z=29) is oxidized by one electron, will the electron be removed from the 4s or the 3d orbital first? Explain your answer. [2]

Q3. (a) What is the Born-Oppenheimer (BO) Approximation? Discuss its use in the molecular orbital theory (taking the H_2 molecule as an example)? [2,4]

(b) What is the 'overlap integral'? Draw a schematic plot showing the variation of the overlap integral with the internuclear distance for an H_2 molecule. Explain the nature of the plot. [2,1,1]

Q4. *Draw* the schematic molecular orbital energy diagram for LiF (showing the relationship between the atomic and molecular orbital energy levels for the valence electrons). *Label* all molecular orbitals appropriately, and specify whether they are mostly *bonding, non-bonding,* or *antibonding*. Identify the *HOMO and LUMO. Sketch* the approximate shapes of all orbitals.[1] Based on the MO diagram, comment on the *bond order* and *polarity* of the molecule. Given the energies of the AOs are: -5.5 eV 2s(Li); -46.37 eV 2s(F) and -18.7 eV 2p(F). [2,1,2,2,1,2]

Q5. (a) Write simple (valence bond wave functions) for formation of bonds between B atoms and H atoms. What B-H compound (B_xH_y) does the simple VB model predict? What geometry does it predict for the molecule? [1.5,0.5,0.5]

(b) Assuming sp^n hybridization (n = 1–3), calculate the *p*-character of the S—H bond in H_2S (H—S—H bond angle = 92.1°). How does it differ from the *p*-character of the O—H bonding in H_2O molecule (H—O—H bond angle = 104.5°)? Explain the origin of the difference. [1.5,1.5,1.5]

(c) Predict the number of unpaired spins in the $[Cr(en)_3]^{2+}$ ion. If the complex ion is diamagnetic, use ideas from the crystal field theory to speculate on its probable structure. Give reasons. [1.5,1.5]

Q6. (a) What are ionic liquids? Give one example. How are they structurally different from the common ionic solids? Mention one application (along with properties used for that application) of the ionic liquids. [1,1,2,1]

(b) What is the "inert-pair effect"? Discuss various causes of the inert-pair effect in detail. [1,4]

Q7. (a) Consider a coordinate complex, ML_2, with linear configuration. If the ligands lie in the $\pm z$ directions, show the p-orbitals crystal field energy levels splitting (in the increasing order). Label the orbitals. [2]

(b) A d^4-electron transition metal forms an octahedral complex with a field splitting, Δ_o, of 16,000 cm^{-1}. Calculate the crystal (ligand) field stabilization energies (in cm^{-1}, neglecting the pairing energy) for the high-spin and low-spin complexes and discuss whether HS or LS complex is favored.

If the estimated pairing energy is of 20,000 cm^{-1}, which one – HS or LS – will be favored and why? [2.5,2.5]

(c) While taking IR spectra of metal carbonyls, namely $[Ni(CO)_4]$, $[Fe(CO)_4]^{2-}$, and $[Co(CO)_4]^-$, an undergraduate student forgot to label which spectrum belonged to which compound. The recorded IR spectral data of the metal carbonyl complexes showed $v(CO) = 1790$, 1890, and 2060 cm^{-1}. Assign the compounds to the correct spectra. Justify your answer. [3]

Q8. (a) Why are an aqueous solution of zinc nitrate, $[Cr(CO)_6]$, and compounds of Ti(IV) colorless. Explain. [3×1.5]

(b) Of the two complexes (a) $[CoF_6]^{3-}$ and (b) $[Co(en)_3]^{3+}$, one appears yellow and the other appears blue. Match the complex to the color and explain your choice. [3.5]

(c) Name three factors on which the magnitude of the lattice energy of an ionic solid depends. Briefly explain how they influence the lattice energy. [2]

Q9. (a) Using concepts of the ligand field theory, explain the following:

(i) Water is a weaker field ligand than ammonia.

(ii) Ethylenediamine is a weaker field ligand than CO. [2×3]

(b) Is the best description of the t_{2g}-orbitals in $[Co(OH_2)_6]^{3+}$ (i) bonding, (ii) antibonding, or (iii) nonbonding? Explain how you reached your conclusion. [2.5]

(c) Which d-orbitals on the metal ion are used to form π-bonds between metal ions and ligands in an octahedral complex? [1.5]

Q10. (a) Name a conducting polymer. Write down the skeletal structures of the polymer and its monomer. [1,2]

(b) What is meant by 'doping' of the conducting polymers? What is the usefulness of doping a conducting polymer? [1.5,1]

(c) Compare the natures and extents of order in the cholesteric, nematic, and smectic liquid-crystal phases of a substance. [3]

(d) Write the name of the experimental techniques that provide the following information:

(i) The core levels do not participate in chemical bond formation and can be neglected in the MO analysis of bond formation.

(ii) The number of unpaired electrons in a transition metal ion.

(iii) The bond lengths and bond angles of molecules in the gas phase. [3×0.5]