Quiz-1

Spring Semester 2024

General and Structural Chemistry

IIIT-Hyderabad

Max Marks: 55

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Q1. What four variables are required to fully describe the position of any object in space? In quantum mechanics, one of these variables is not explicitly considered. Which one?

[2,1]

Q2. What quantum number defines each of the following? [4x2]

(i) the overall shape of an orbital

(ii) the orientation of an electron with respect to a magnetic field

(iii) the orientation of an orbital in space

(iv) the average energy and distance of an electron from the nucleus

Q3. Which quantum numbers determine the energy of an electron in a multielectron atom?

[2]

Q4. What value of l corresponds to a g subshell? How many orbitals are in this subshell?

[2]

Q5. Write and comment on the quantum numbers of p_x, p_y and p_z orbitals. [3]

Q6. In a hydrogen-like atom, which one, 4*s*-electron or 3d-electron, has lower energy and why?

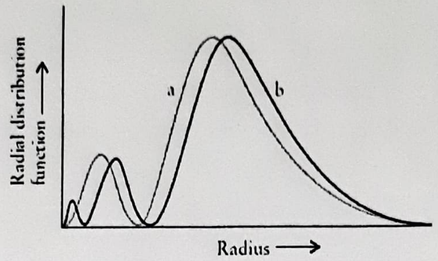
[2]

Q7. What is the degree of degeneracy of a hydrogen-like atom's first excited state? Name the degenerate orbitals. [2]

Q8. Correlate the angular wavefunctions, $Y_{0,0}$ (Y_0^0) and $Y_{1,0}$ (Y_1^0), with corresponding orbitals. Compare their angular (θ and φ) dependence. [2,2]

Q9. Write the complete eigen value equations showing the operations of L^2 and L_z angular momentum operators on the Spherical Harmonics eigenfunction, $Y_l^m(\theta,\varphi)$, and their corresponding eigen values. [2,2]

Q10. The following plot shows the radial distribution functions of some orbitals of a hydrogen atom. **Identify** each curve and **explain** how you made your decision. [3,3]



Q11. A *p* orbital is found to have one node in addition to the nodal plane that bisects the lobes. What would you predict to be the value of *n*? [3]

Q12. Angular wavefunction of an orbital is given below.

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

Predict the atomic orbital and **justify** your prediction. [4]

Q13. Is each set of quantum numbers allowed? Explain your answers. [6]

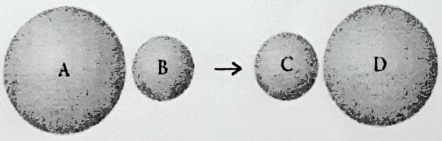
(i) $n = 2$; $l = 1$; $m = 2$; $s = +½$

(ii) $n = 3$, $l = 0$; $m = -1$; $s = -½$

(iii) $n = 2$; $l = 2$; $m = 1$; $s = +½$

Q14. 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.

[4,2]



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General and Structural Chemistry

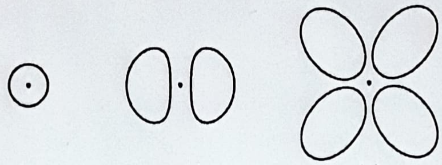
Mid-Semester Examination: Spring 2024

IIIT-Hyderabad

Full Marks: 60 **Time: 1:30 Hours**

Q.1. (a) What are all the types of atomic orbitals possible for $n = 6$? What would be the atomic number of the atom that would have all shells with $n = 6$ filled? [1,2]

(b) Consider the atomic orbitals shown here in the outline.



(i) What is the maximum number of electrons contained in a sub-shell of orbital of type (y)?

(ii) How many orbitals of type (z) are found in a shell with $n = 4$?

(iii) Write a set of quantum numbers for an electron in an orbital of type (z) in a shell with $n = 4$.

(iv) What is the smallest possible n value for an orbital of type (x)? Of type (z)?

(v) What are the possible l and m_l values for an orbital of type (x)? Of type (z)? [1,1,1,2,2]

Q.2. (a) What is meant by the degenerate energy levels? [1]

(b) Show that the n-th hydrogen-like energy level is n^2 degenerate. [2]

(c) The mathematical expression for an orbital (wave function of a one-electron atom) is given as $f = (2)^{1/2} (3/8\pi)^{1/2} \sin\theta \cos\phi$. Find out its nodal plane. [3]

(d) The electron configurations of 3d transition elements are generally given as $[Ar]3d^n4s^2$. Which subshell, 3d or 4s, has lower energy? Which subshell gets filled up first with electrons for these transition elements? Why? Among these subshells, which electron(s) are lost first during their ion formation? Why? [3]

(e) Potassium and magnesium are required in our diet. K^+ ion is isoelectronic as [Ar] and Mg^{2+} is with [Ne]. Can we use argon and neon elements in their places as diet? [1]

Q.3. (a) Compare the ionization energies of the atomic hydrogen (H) and molecular hydrogen (H_2). Justify your answer. [2]

(b) Rationalize the following observations based on the electronic structures of the halogen atoms and their ions. Iodide ions can be oxidized to elemental iodine by molecular oxygen: $4HI + O_2 \rightarrow$

$2I_2 + 2H_2O$ but the corresponding reaction does not occur with HCl: $HCl + O_2 \rightarrow$ no reaction.

[3]

(c) Briefly explain the following:

(i) Hg can form Hg_2^{2+} ion which is not common among metals. [2.5]

(ii) Lead favors the formation of lead(II) oxide when heated in the air whereas tin forms tin(IV) oxide?

[2.5]

Q.4. (a) Write down the Hamiltonian for the single electron in H_2^+. Define or schematically show the parameters involved in the Hamiltonian. [3]

(b) Define the terms Coulomb integral (J) and exchange integral (K) and state their significance.

[4]

(c) Draw schematic diagrams to show how an s-orbital and a p-orbital on two different atoms may combine to form molecular orbitals, one of their interactions giving rise to σ-bonding orbital and another a nonbonding orbital. Comment on the *values of their respective overlap integrals*.

[3]

Q.5. (a) Sketch the MO energy diagram for OH radical. Characterize the HOMO and LUMO as bonding, antibonding or nonbonding. What is the multiplicity (spin state) for this species?

[2,2,2]

(b) Show that the bonding and antibonding molecular orbitals formed from H 1s atomic orbitals for H_2 molecule are orthogonal to each other. [2]

(c) Why does carbon monoxide (CO) form so many carbonyl compounds with transition elements?

[2]

Q.6. (a) Derive the **Born–Mayer** equation for an ionic lattice:

$$E_{p,min} = -A\frac{N_A|z_A z_B|e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)$$

where the terms have their usual significance. [8]

(b) 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]

Given: Potassium (K): Z = 19. Magnesium (Mg): Z = 12.

$$E_{repulsion} = B\exp\left(\frac{-d}{d^*}\right)$$

Quiz-2
Spring Semester 2024
General and Structural Chemistry
IIIT-Hyderabad

Max Marks: 50

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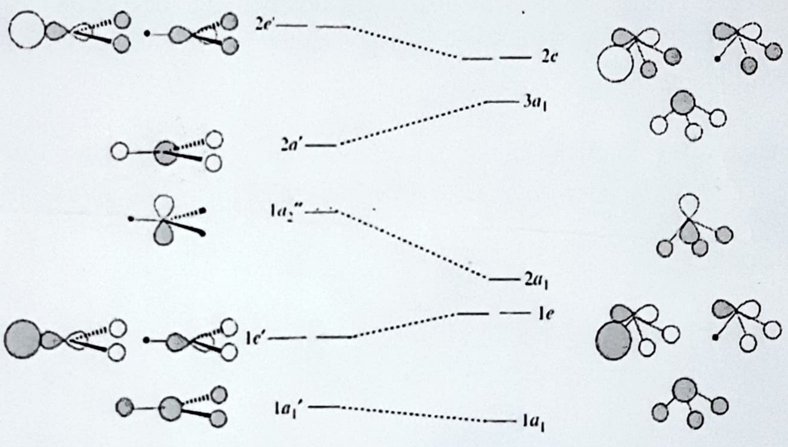
Q1. What is meant by the *symmetry adapted linear combinations* (SALCs)? Construct it for the ground state of BeH_2 molecule. [2,3]

Q2. The Walsh correlation diagram for the *valence electrons* of an AH_3 molecules is shown below. The left side of the diagram gives the energy ordering (increasing from bottom to top) of the molecular orbitals for an H-A-H bond angle for a trigonal planar geometry. The right side gives the energy ordering of the molecular orbitals for an H-A-H bond angle for a trigonal pyramidal geometry.



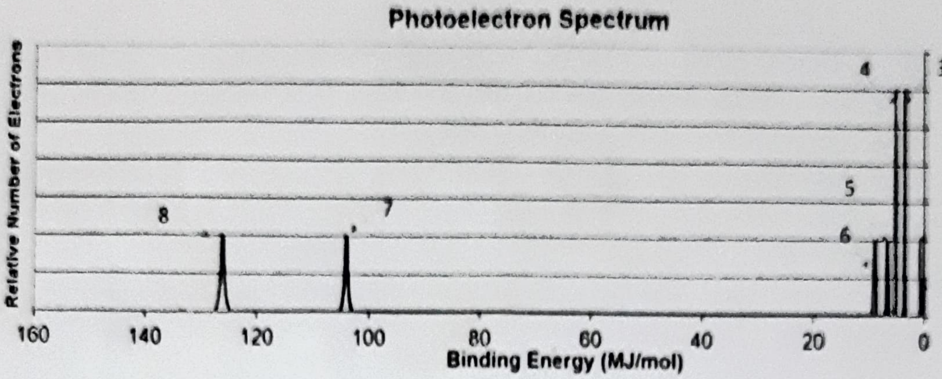
Trigonal planar (D_{3h}) Trigonal pyramidal (C_{3v})

Based on the above Walsh correlation diagram, answer the following: [1,1,1,3,1]

(a) What is the expected H-C-H bond angle in CH_3^+ ion?
(b) Give the MO electron distribution for the ground state CH_3^+ ion.
(c) What are the HOMO and LUMO of the CH_3^+ ion?
(d) When CH_3^+ ion shows its Lewis Acid character, which atoms act as the electron pair acceptor? Why? What will be the geometry of the Lewis Acid-Base adduct? Why?
(e) While changing trigonal planar to trigonal pyramidal geometry, which orbitals get stabilized, and which get destabilized?

Q3. (a) Compare PES and ESCA techniques. [3]

(b) PES line/peaks of Na and Mg are shown below. Identify the peaks (1 – 8) with corresponding element's AOs. [4]



Q4. When two molecules come into contact, there is always a possibility of bonding interactions between the two, since each molecule has filled MO's and vacant MO's. Explain why sometimes they form adducts and sometime not. [3]

Q5. Show the FMO diagram for the covalent interaction between the acceptor A and donor B when the donor HOMO is much higher in energy than the HOMO of the acceptor. Comment on the nature of interactions. [3,3]

Q6. Some metals are commonly found in nature as salts of chloride or as oxide ores while others are found in combination with sulfur. Use Pearson's HSAB principle to justify it. [4]

Q7. State true or false: [4×2]

(i) In general, a hard acid has a small ionic radius, high positive charge, no electron pairs in its valence shell, low EA, is strongly solvated, and/or has a high-energy HOMO.

(ii) Soft acids have small radii, have low or partial positive charge, have electron pairs in their valence shells, are easy to polarize and oxidize, and have low-energy LUMOs with large magnitude coefficients.

(iii) Hard bases have small radii, are hard to oxidize, are weakly polarizable, have very electronegative centers, are strongly solvated, and/or have low-energy HOMOs.

(iv) Soft bases tend to have large radii, have intermediate values for the electronegativity, are easily polarized and oxidized, and have low-energy HOMOs with large magnitude coefficients.

Q8. Define the valence and conduction bands. What are the conduction bands in Na and Mg metals respectively. [2,2]

Q9. (a) State the rules for orbital hybridization. [4]

(b) Calculate the bond angle on the central atom which undergoes sp^2 hybridization. [2]

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International Institute of Information Technology, Hyderabad

End Semester Examination: Spring 2024

GENERAL and STRUCTURAL CHEMISTRY

Max. Time: 3 Hr **Max. Marks: 100**

Q1. (a) Draw the MO energy diagram for H_2O molecule and label each MO. Schematically show the contour diagrams of the ligand group orbitals (LGOs) (on the right side of the diagram), central atom orbitals (on the left side) and MOs (at the centre). [3]

(b) Comment on the natures of the MOs (sigma or pi and as bonding, nonbonding, or antibonding). [2]

(c) Fill in the electrons and determine the HOMO and LUMO. [1]

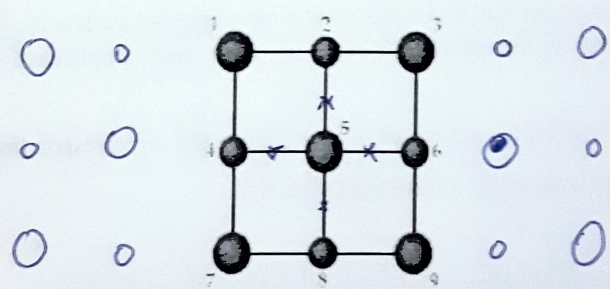
(d) The photoelectron spectrum of water shows four MO energy peaks with some vibrational fine structures. How does it compare with the VBT based unshared and shared electron pairs? [2]

(e) The two atomic orbitals that contribute to the antibonding orbital are each proportional to e^{-r/a_0}, where r is the distance of the point from its parent nucleus. Show that there is a nodal plane lying halfway between the two nuclei. [2]

Q2. (a) Apply the molecular orbital theory to explain the conducting properties of metallic solids and the insulating properties of ionic solids (use schematic diagrams as required). [3,3]

(b) Describe how photoelectron spectroscopy (PES) can be used to determine the nature of MOs as the bonding, antibonding and nonbonding. [4]

Q3. In the following, a portion of a two-dimensional "slab" of NaCl(s) is shown here in which the ions are numbered.



(a) Which balls must represent sodium ions? Which balls must represent chloride ions? Give reasons. [2]

(b) Consider ion 5. How many attractive electrostatic interactions are shown for it? How many repulsive interactions are shown? [2]

(c) Is the sum of the attractive interactions larger or smaller than the sum of the repulsive interactions? Explain. [2]

(d) If this pattern of ions was extended indefinitely in two dimensions, would the lattice energy be positive or negative? Justify your answer. [2]

(e) Prove that the total probability density for the three 2p orbitals is a sphere. [2]

Q4. (a) While silver dissolves in HNO_3 (aq.), gold dissolves in aqua regia but not in HNO_3 (aq.). Explain. [3]

(b) Write *simple* valence bond wave function for the formation of covalent bonds between B and H atoms. What B-H molecule (B_xH_y) and molecular geometry does the simple VB model predict? [2, 1, 1]

(c) The bond angles of the following PX_3 compounds are given in the parenthesis: PF_3 (97.8°), PCl_3 (100.4°), PBr_3 (101.0°), and PI_3 (102°). Determine the percent *s*-character of their lone pairs and based on it explain which PX_3 compound will behave as better Lewis base. [3]

Q5. (a) Consider a linear coordinate complex, ML_2, with the two ligands lying on the z axis. Sketch the splitting pattern for the *p*-orbitals that would result. [2]

(b) Calculate the crystal field stabilization energy (CFSE) for a low spin d^7 octahedral complex? [2]

(c) While Cr^{2+} shows a tendency to oxidize to Cr^{3+}, Mn^{3+} has a tendency to reduce to Mn^{2+}. Explain. [3]

(d) What is meant by the (first order) Jahn–Teller effect/distortion? Give an example that shows compression as the preferred distortion. Justify it. [3]

Q6. (a) The compound $[M(H_2O)_6]^{2+}$ has a single electronic transition in its d^4 UV/VIS spectrum.

(i) Is this an HS or an LS complex? Explain. [2]

(ii) Given that the energy of this electronic transition is 709 nm, calculate the splitting parameter for M. [4]

(b) When $Ni(NO_3)_2$ is dissolved in water, it forms a green-colored solution. Addition of concentrated NH_4OH changes the color of the solution to blue while addition of ethylenediamine changes it to violet. Predict formulas for each of the coordination compounds and explain the trends in the colors of the compounds. [4]

Q7. (a) Compare the ligand field strengths of π-acid ligands and π-base ligands based on the ligand field theory (use appropriate schematic diagrams for the comparison purpose). Give one example each of a π-acid ligand and a π-base ligand. [4,1]

(b) Name a conducting polymer and draw the structures of the polymer and its corresponding monomer. [2]

(c) Describe the conduction mechanisms in the conducting polymers. [3]

Q8. (a) Describe the common structural features of molecules that form liquid crystals. [3]

(b) What kind of intermolecular interactions are most likely to result in a long-chain molecule that exhibits liquid crystalline behavior? Does an electrical field affect these interactions? [1.5, 0.5]

(c) Compare the natures and extents of order in the smectic and nematic liquid-crystal phases. [2]

(d) Which is more anisotropic—a cholesteric liquid crystal or a nematic liquid crystal? Why? [1]

(e) Mention one use of a cholesteric liquid crystal and one use of a nematic liquid crystal. Explain. [2]

Q9. (a) Define the absolute hardness of a species. How is it related to the reactivity of the species? [2]

(b) Will the equilibrium constant for $CH_3HgI + HCl \Leftrightarrow CH_3HgCl + HI$ be greater or less than 1? Explain. [2]

(c) The ambidentate ligand, SCN^- ligand, when S-bound, it has the name thiocyanate and the M–S–C bond angle is bent, but when N-bound, it has the name isothiocyanate and the M–N–C bond angle is ~180°. Explain why the S-bound species is bent. Predict the structures (linear or bent) of the metal–ligand bonding when the SCN^- ligand reacts with Fe^{3+} to form the bright red complex ion $[FeSCN]^+$. Predict the method of bonding when Cr^{3+} reacts with the SCN^- ligand. Justify your answers. [3]

(d) The proton affinities for PH_3, H_2S, HCl are 789, 712 and 564 kJ/mol, respectively. Explain this trend in terms of the energies of the bonding MOs in the acid–base interaction diagrams of each species with H^+. [3]

Q10. (a) If you are asked to produce visible light by using an invisible light source of wavelength 980 nm, mention the requirements/conditions for the conversion. What wavelength visible light will you produce? Prove it. [1,1,2]

(b) Describe the mechanisms of superconducting behaviour in superconductors. [2]

(c) What is Meissner effect? Why does it arise? Mention one application of this effect. [1,0.5,0.5]

(d) What are piezoelectric crystals? Which type of crystals show piezoelectricity? [1,1]

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The terms bear their usual significance.

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

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

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

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

$h = 6.63 \times 10^{-34}$ J.s

$c = 3.00 \times 10^{8}$ m/s

$N_A = 6.02 \times 10^{23}$ ions/mol

1 nm = 10^{-9} m

$$\cos\theta = \frac{S}{S-1}$$