1. Explain the following (Any Five)

(i) The bond angle of OF_2 < H_2O whereas Cl_2O > H_2O.

- In OF_2, the oxygen atom is sp³ hybridized with two lone pairs and two bond pairs. The electronegativity of fluorine (3.98) is much higher than that of oxygen (3.44). This pulls the shared electron pairs closer to the fluorine atoms, increasing the electron density around fluorine and reducing the electron-electron repulsion between the bonding pairs around oxygen. This leads to a smaller bond angle.

- In H_2O, the oxygen atom is sp³ hybridized with two lone pairs and two bond pairs. The electronegativity of oxygen (3.44) is higher than that of hydrogen (2.20). The shared electron pairs are pulled closer to the oxygen atom, but not as strongly as in OF_2.

- In Cl_2O, the oxygen atom is sp³ hybridized with two lone pairs and two bond pairs. The electronegativity of chlorine (3.16) is less than that of oxygen (3.44). This means the shared electron pairs are pulled closer to the oxygen atom. The larger size of chlorine atoms also contributes to greater steric repulsion between the lone pairs and bond pairs, pushing the bonding pairs further apart. This results in a larger bond angle compared to H_2O.

(ii) NF_3 has a dipole moment, while BF_3 has zero dipole moment.

- NF_3 has a trigonal pyramidal geometry due to the presence of a lone pair on the central nitrogen atom and three bond pairs with fluorine atoms. Nitrogen is less electronegative than fluorine, so the individual N-F bond dipoles are directed towards the fluorine atoms. The lone pair also contributes to the net dipole moment, which does not cancel out. Therefore, NF_3 has a net dipole moment.

- BF_3 has a trigonal planar geometry. The central boron atom is sp² hybridized and forms three identical B-F bonds. Fluorine is more electronegative than boron, so the individual B-F bond dipoles are directed towards the fluorine atoms. Due to the symmetrical trigonal

planar arrangement, these three bond dipoles are equal in magnitude and cancel each other out, resulting in a zero net dipole moment for BF_3.

(iii) PF_5 exists but PH_5 does not.

- For PF_5 to exist, phosphorus needs to expand its octet and form five bonds. Phosphorus has available d-orbitals in its valence shell (3d orbitals) which can be used for hybridization (sp^3d) to accommodate more than eight electrons and form five P-F bonds.

- Hydrogen, being a first-period element, does not have any d-orbitals. Therefore, it cannot accommodate more than two electrons in its valence shell. In PH_5, if phosphorus were to form five bonds with hydrogen, hydrogen would need to expand its valency beyond one, which is not possible. Thus, PH_5 does not exist.

(iv) Though the radii of Ag^+ is comparable with the radii of K^+, but the melting point of AgCl is much lower than that of KCl.

- Both AgCl and KCl are ionic compounds. The melting point of ionic compounds is related to the lattice energy.

- Ag^+ has a $[Kr]4d^{10}$ electron configuration (pseudo noble gas configuration), while K^+ has a $[Ar]$ noble gas configuration. The d-electrons in Ag^+ provide poor shielding of the nuclear charge, leading to a higher effective nuclear charge on Ag^+ compared to K^+.

- This higher effective nuclear charge makes Ag^+ more polarizing than K^+. According to Fajan's rule, a cation with higher polarizing power and an anion with higher polarizability lead to a greater covalent character in the bond. The chloride ion (Cl^-) is polarizable.

- Thus, the Ag-Cl bond in AgCl has a greater covalent character compared to the K-Cl bond in KCl, which is predominantly ionic. Covalent bonds are generally weaker than strong ionic bonds, leading to a lower lattice energy and consequently a lower melting point for AgCl compared to KCl.

(v) The first electron gain enthalpy of O is exothermic, whereas its second electron gain enthalpy is endothermic; still, it exists as O^{2-} in oxides.

- The first electron gain enthalpy ($\Delta_{eg}H_1$) of oxygen is exothermic because the incoming electron experiences attraction from the positively charged nucleus, and energy is released when a stable O^- ion is formed.

- The second electron gain enthalpy ($\Delta_{eg}H_2$) for oxygen ($O^- + e^- \rightarrow O^{2-}$) is endothermic. This is because the incoming electron has to be added to an already negatively charged O^- ion. There is a strong electrostatic repulsion between the negative charge of the O^- ion and the incoming electron, which requires energy input to overcome.

- Despite the endothermic nature of the second electron gain enthalpy, O^{2-} exists in metal oxides because the very high lattice energy released during the formation of the ionic crystal (e.g., MgO, CaO) more than compensates for the energy required to form the O^{2-} ion. The overall process of oxide formation is energetically favorable due to the strong electrostatic attractions between the highly charged cations and O^{2-} anions in the crystal lattice.

(vi) Electronic configuration of Cr is $3d^5 4s^1$ and not $3d^4 4s^2$.

- The electronic configuration of chromium (Cr, Z=24) is an exception to the Aufbau principle.

- The reason is the extra stability associated with half-filled and completely filled subshells.

- A $3d^5$ configuration represents a half-filled d-subshell, which is more stable than a partially filled $3d^4$ configuration due to symmetry and exchange energy effects.

- Therefore, one electron from the 4s orbital shifts to the 3d orbital to achieve the more stable $3d^5$ configuration, resulting in the observed electronic configuration of $[Ar]3d^5 4s^1$.

2. (a) Name the quantum numbers which arise as a consequence of the solution of the wave equation for H-atom. What idea do you get from all these quantum numbers?

- The quantum numbers which arise from the solution of the wave equation (Schrödinger equation) for the H-atom are:

  - Principal Quantum Number (n)

  - Azimuthal or Angular Momentum Quantum Number (l)

  - Magnetic Quantum Number (m_l)

  - Spin Quantum Number (m_s) (though not directly from the Schrödinger equation but required to fully describe an electron)

- Idea obtained from these quantum numbers:

  - **Principal Quantum Number (n):** It defines the main energy level or shell of an electron. It can have positive integer values (1, 2, 3, ...). It also determines the size and, to a large extent, the energy of an orbital. Higher 'n' means larger size and higher energy.

  - **Azimuthal or Angular Momentum Quantum Number (l):** It defines the subshell and the shape of an orbital within a given shell. Its values range from 0 to n-1.

    - l = 0 corresponds to an s-orbital (spherical shape).

    - l = 1 corresponds to a p-orbital (dumbbell shape).

    - l = 2 corresponds to a d-orbital (more complex shapes).

    - l = 3 corresponds to an f-orbital (even more complex shapes).

  - **Magnetic Quantum Number (m_l):** It describes the orientation of the orbital in space. Its values range from -l to +l, including 0. For a given 'l', there are (2l+1) possible values of m_l, indicating the number of orbitals in a subshell. For example, for l=1 (p-

subshell), m_l can be -1, 0, +1, meaning there are three p-orbitals (p_x, p_y, p_z).

- o **Spin Quantum Number (m_s):** It describes the intrinsic angular momentum of an electron, which is quantized and is referred to as "spin". An electron can spin in one of two directions, either clockwise or counter-clockwise. It has two possible values: +1/2 and -1/2. This quantum number is crucial for understanding the behavior of electrons in magnetic fields and for explaining the Pauli Exclusion Principle.

- In essence, these four quantum numbers collectively provide a unique set of identifiers for each electron in an atom, describing its energy, shape of its orbital, spatial orientation of the orbital, and its spin state.

(b) Write the Kapustinskii equation for lattice energy and define the terms involved. What are the advantages and disadvantages over Born-Lande equation?

- **Kapustinskii Equation:**

  - $U_L = \frac{1202 \times \nu Z^+ Z^-}{r_c + r_a}\left(1 - \frac{0.345}{r_c + r_a}\right)$

  - Where:

    - U_L is the lattice energy in kJ/mol.

    - ν(nu) is the number of ions per formula unit of the compound (e.g., for NaCl, ν= 2; for $MgCl_2$, ν = 3).

    - Z^+ is the charge on the cation.

    - Z^- is the charge on the anion.

    - r_c is the radius of the cation in Ångstroms (Å).

    - r_a is the radius of the anion in Ångstroms (Å).

- **Advantages over Born-Lande equation:**

- o **Does not require crystal structure data:** The biggest advantage of the Kapustinskii equation is that it does not require knowledge of the crystal structure (specifically, the Madelung constant), which is often difficult to determine experimentally. It assumes a simplified, idealized NaCl-type lattice.

- o **Can be used for hypothetical compounds:** Due to its independence from crystal structure, it can be used to estimate lattice energies for hypothetical compounds or those for which crystallographic data is unavailable.

- o **Simpler calculation:** It is mathematically simpler to apply compared to the Born-Lande equation, which requires the Madelung constant and the Born exponent.

- **Disadvantages over Born-Lande equation:**

  - o **Less accurate:** Since it is based on a simplified model and assumptions (like the idealized NaCl structure), the lattice energies calculated by Kapustinskii equation are generally less accurate than those obtained from the Born-Lande equation, especially for compounds with complex crystal structures or significant covalent character.

  - o **Approximation:** It is an empirical approximation and does not have the same theoretical rigor as the Born-Lande equation, which is derived from fundamental principles of electrostatics and repulsion.

(c) What do you understand by partial ionic character in a covalent bond? The electronegativity of hydrogen and bromine are 2.2 and 3.0 respectively. Calculate percent ionic character of HBr. Also predict the nature of HBr molecule.

- **Partial ionic character in a covalent bond:**

- o In a purely covalent bond, electrons are shared equally between two atoms with identical electronegativities.

- o In a purely ionic bond, there is a complete transfer of electrons from one atom to another due to a large electronegativity difference.

- o However, most chemical bonds are neither purely covalent nor purely ionic. When two atoms with different electronegativities form a covalent bond, the electron pair is not shared equally. The more electronegative atom pulls the shared electron pair closer to itself, acquiring a partial negative charge (δ^-), while the less electronegative atom acquires a partial positive charge (δ^+). This unequal sharing of electrons creates a dipole moment and gives the bond a "partial ionic character." The greater the difference in electronegativity, the greater the partial ionic character.

- **Calculate percent ionic character of HBr:**

  - o Given electronegativity of Hydrogen (χ_H) = 2.2

  - o Given electronegativity of Bromine (χ_{Br}) = 3.0

  - o Difference in electronegativity ($\Delta\chi$) = $\chi_{Br} - \chi_H$ = 3.0 - 2.2 = 0.8

  - o Percent ionic character can be calculated using the Pauling formula (or Hannay-Smith equation):

    - Percent Ionic Character = $(1 - e^{-0.25(\Delta\chi)^2}) \times 100\%$ *
      Percent Ionic Character = $(1 - e^{-0.25(0.8)^2}) \times 100\%$ *
      Percent Ionic Character = $(1 - e^{-0.25 \times 0.64}) \times 100\%$ *
      Percent Ionic Character = $(1 - e^{-0.16}) \times 100\%$ *
      Using $e^{-0.16} \approx 0.852$ * Percent Ionic Character = $(1 - 0.852) \times 100\%$ * Percent Ionic Character = $0.148 \times 100\%$

    - Percent Ionic Character = 14.8%

- o (Alternatively, using Hannay-Smith equation, % ionic character = $16|\chi_A - \chi_B| + 3.5|\chi_A - \chi_B|^2$)

    - % Ionic Character = $16(0.8) + 3.5(0.8)^2$ * % Ionic Character =$12.8 + 3.5(0.64)$ * % Ionic Character =$12.8 + 2.24$ * % Ionic Character =15.04%

- **Nature of HBr molecule:**

    - o Since the electronegativity difference is 0.8, and the calculated percent ionic character is approximately 14.8% to 15.04%, the HBr molecule is predominantly covalent but possesses a significant partial ionic character. This means the H-Br bond is polar covalent. The electron density is shifted towards the more electronegative bromine atom.

    (d) On the basis of the Slater's rule, explain why 4s orbital is filled before the filling up of 3d orbitals in potassium atom?

- **Slater's Rule and Shielding Effect:** Slater's rules are empirical rules used to estimate the effective nuclear charge (Z_eff) experienced by an electron in a multi-electron atom. The effective nuclear charge is given by Z_eff = Z - S, where Z is the atomic number (actual nuclear charge) and S is the shielding constant. The order of filling orbitals is determined by the (n+l) rule (Madelung rule) and modified by the shielding effect. Electrons in inner shells shield outer electrons from the full nuclear charge more effectively.

- **Potassium Atom (Z = 19):**

    - o Electronic configuration: 1s² 2s² 2p⁶ 3s² 3p⁶ 4s¹ (for K) and 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹ (hypothetically if 3d was filled before 4s)

- **Calculation of Z_eff for a 4s electron:**

    - o Grouping for 4s: (1s²)(2s²2p⁶)(3s²3p⁶)(4s¹)

    - o Contribution to S for a 4s electron:

- From (n-1) shell ($3s^2 3p^6$): 8 electrons * 0.85 = 6.80

- From (n-2) and deeper shells ($1s^2$)($2s^2 2p^6$): 8 electrons * 1.00 = 8.00 (from $2s^2 2p^6$) + 2 electrons * 1.00 = 2.00 (from $1s^2$) = 10 electrons * 1.00 = 10.00

- Total S for 4s = 6.80 + 10.00 = 16.80

- Z_eff (4s) = Z - S = 19 - 16.80 = 2.20

- **Calculation of Z_eff for a 3d electron (hypothetical case):**

  - Grouping for 3d: ($1s^2$)($2s^2 2p^6$)($3s^2 3p^6 3d^1$)($4s^0$)

  - Contribution to S for a 3d electron:

    - From electrons in the same (3d) group: (1-1) * 0.35 = 0 (since it's the first 3d electron, no other 3d electrons to shield it).

    - From electrons in groups to the left of 3d ($1s^2$)($2s^2 2p^6$)($3s^2 3p^6$): 18 electrons * 1.00 = 18.00

    - Total S for 3d = 0 + 18.00 = 18.00

  - Z_eff (3d) = Z - S = 19 - 18.00 = 1.00

- **Conclusion:**

  - The Z_eff for a 4s electron (2.20) is greater than the Z_eff for a 3d electron (1.00). A higher effective nuclear charge means the electron is more strongly attracted to the nucleus, resulting in lower energy and greater stability.

  - Although the principal quantum number of 4s is higher than 3d, the 4s orbital experiences a significantly higher effective nuclear charge due to its greater penetration power (meaning it spends more time closer to the nucleus and is less shielded by inner electrons compared to 3d). This makes the 4s orbital energetically more favorable (lower energy) than the 3d orbital.

- o Therefore, based on the lower energy associated with a higher effective nuclear charge, the 4s orbital is filled before the 3d orbital in potassium.

3. (a) Given the equation: $\Psi_{4,1,0} = R_{4,1} \cdot \theta_{1,0} \cdot \phi_0$. Based upon the equation, answer the following questions.

- (i) Name the equation.

    - o The given equation represents a **wave function** for an electron in a hydrogen-like atom in spherical polar coordinates. It is a specific solution to the time-independent Schrödinger equation for the hydrogen atom. It shows the separability of the wave function into radial and angular parts.

- (ii) Define the terms involved in the equation.

    - o $\Psi_{4,1,0}$: This is the **total wave function** of the electron. The subscripts (4, 1, 0) represent the values of the quantum numbers (n, l, m_l) respectively.

        - n = 4 (Principal Quantum Number)

        - l = 1 (Azimuthal Quantum Number)

        - m_l = 0 (Magnetic Quantum Number)

    - o $R_{4,1}$: This is the **radial part of the wave function**. It depends on the principal quantum number (n=4) and the azimuthal quantum number (l=1). This part describes how the wave function varies with the distance from the nucleus (r) and determines the size and energy of the orbital.

    - o $\theta_{1,0}$: This is the **angular part of the wave function (polar angle component)**. It depends on the azimuthal quantum number (l=1) and the magnetic quantum number (m_l=0). This part describes how the wave function varies with the polar angle (θ) and contributes to the shape of the orbital.

- ϕ_0: This is the **angular part of the wave function (azimuthal angle component)**. It depends only on the magnetic quantum number (m_l=0). This part describes how the wave function varies with the azimuthal angle (ϕ) and, along with θ, determines the orientation of the orbital in space.

- (iii) Which orbital is related with the equation?

  - Based on the quantum numbers (n=4, l=1, m_l=0):

    - n=4 indicates the 4th principal shell.

    - l=1 indicates a p-orbital.

    - m_l=0 indicates a specific orientation of the p-orbital, typically the p_z orbital.

  - Therefore, the equation is related to the **4pz orbital**.

  (b) Why the covalent radius of Ge (122 pm) is almost the same as that of Si. (117 pm) even though Ge has 18 electrons more than Si?

- **Atomic Size Trend in a Group:** Generally, as we move down a group in the periodic table, the atomic radius increases due to the addition of new electron shells, which increases the distance of the outermost electrons from the nucleus and enhances shielding by inner electrons.

- **The Case of Germanium (Ge) and Silicon (Si):**

  - Silicon (Si) is in Period 3, Group 14, with atomic number 14. Its electronic configuration is $[Ne]3s^2 3p^2$.

  - Germanium (Ge) is in Period 4, Group 14, with atomic number 32. Its electronic configuration is $[Ar]3d^{10}4s^2 4p^2$.

- **Role of d-Block Contraction (Lanthanoid Contraction Analogy):** The anomaly in the atomic radius of Ge compared to Si is primarily due to the presence of the **10 3d-electrons** in germanium.

- o When moving from Si to Ge, the 3d subshell is filled. These 3d electrons are located in an inner shell and are relatively poor at shielding the outermost (4s and 4p) electrons from the nuclear charge.

- o As a result, the increase in nuclear charge from Si (Z=14) to Ge (Z=32) is not fully compensated by the shielding effect of the 3d electrons. The effective nuclear charge experienced by the valence electrons in Ge is significantly higher than what would be expected based solely on the addition of a new shell.

- o This increased effective nuclear charge pulls the valence electrons closer to the nucleus, causing a contraction in the atomic radius. This phenomenon is analogous to "lanthanoid contraction" observed in the 4f series.

- **Conclusion:** The poor shielding effect of the intervening 10 d-electrons in germanium counteracts the expected increase in size due to the addition of a new principal energy level. This results in the covalent radius of Ge being only slightly larger than, and almost comparable to, that of Si.

  (c) Arrange the following in order of increasing bond angles X - P - X and justify your answer.

- PF_3, PCl_3, PBr_3 and PI_3.

- **Order of increasing bond angles:** $PI_3 < PBr_3 < PCl_3 < PF_3$

- **Justification (based on electronegativity and steric effects):**

  - o All these molecules (PX_3, where X = F, Cl, Br, I) are derived from a central phosphorus atom bonded to three halogen atoms, and the phosphorus atom has one lone pair of electrons. According to VSEPR theory, they all have a trigonal pyramidal geometry, and their bond angles are expected to be less than the ideal tetrahedral angle of 109.5° due to lone pair-bond pair repulsions.

- o The key factor influencing the bond angle in this series is the **electronegativity of the halogen atom (X)**.

    - Electronegativity order: F > Cl > Br > I

- o **Electronegativity Effect:**

    - When the electronegativity of the surrounding atom (X) increases (from I to F), the shared electron pair in the P-X bond is pulled closer to the halogen atom.

    - This decreases the electron density in the bonding region around the central phosphorus atom.

    - As the electron density in the bond pair decreases, the bond pair-bond pair repulsion also decreases.

    - Consequently, the lone pair on phosphorus exerts a relatively stronger repulsive force on the bond pairs, pushing them closer together and decreasing the X-P-X bond angle.

- o **Steric Effect (Minor Contribution):** Although the electronegativity effect is dominant, steric hindrance (size of the halogen) also plays a role.

    - Iodine is the largest halogen, and fluorine is the smallest. Larger halogens might cause some steric repulsion, which would tend to increase the bond angle.

    - However, the electronegativity effect is more significant in determining the trend observed. If steric effects were dominant, PI_3 would have the largest bond angle, which is contrary to the experimental observation.

- o **Conclusion:** The observed trend of increasing bond angle from PI_3 to PF_3 (i.e., decreasing bond angle with increasing electronegativity of X) strongly supports the electronegativity effect as the primary factor. The decreasing electronegativity

from F to I means the bond pair electrons are progressively further from the central P atom, leading to less bond pair-bond pair repulsion and a smaller angle.

4. (a) Draw the radial probability distribution curves for 3s, 3p, and 3d orbitals. Based on these plots explain their shielding effect and penetration power.

- **Radial Probability Distribution Curves:**

    o (Note: As per instructions, I cannot draw diagrams. However, I will describe the key features of these curves.)

    o **General Shape:** A radial probability distribution curve plots $4\pi r^2 R^2(r)$ against r (distance from the nucleus). The peaks in the curve indicate regions where the probability of finding an electron is highest. The number of radial nodes for an orbital is given by n - l - 1.

    o **3s orbital (n=3, l=0):**

        ▪ Has $3 - 0 - 1 = 2$ radial nodes.

        ▪ The curve will show 3 maxima (peaks) separated by 2 points where the probability drops to zero (nodes).

        ▪ The innermost peak is closest to the nucleus, and the outermost peak is the largest.

    o **3p orbital (n=3, l=1):**

        ▪ Has $3 - 1 - 1 = 1$ radial node.

        ▪ The curve will show 2 maxima (peaks) separated by 1 node.

        ▪ The innermost peak is further from the nucleus than the innermost peak of 3s.

    o **3d orbital (n=3, l=2):**

- Has $3 - 2 - 1 = 0$ radial nodes.

- The curve will show 1 maximum (peak).

- This single peak is further out from the nucleus compared to the outermost peaks of 3s and 3p, and it is also narrower.

- **Shielding Effect and Penetration Power (based on the curves):**

  - **Penetration Power:**

    - Penetration power refers to the ability of an electron in a particular orbital to get closer to the nucleus, i.e., to "penetrate" the inner electron shells.

    - Looking at the radial probability curves, the 3s orbital has significant probability density very close to the nucleus (its innermost peak is closest). The 3p orbital has some probability density near the nucleus, but less than 3s. The 3d orbital, having no radial nodes and its single peak further away, has the least probability density near the nucleus.

    - Therefore, the order of penetration power is: **3s > 3p > 3d**.

  - **Shielding Effect:**

    - Shielding effect is the reduction in the effective nuclear charge experienced by an electron due to the repulsion from other electrons in the atom. Electrons in inner shells shield outer electrons.

    - An electron that penetrates closer to the nucleus experiences less shielding from inner electrons because it spends more time "inside" the inner electron shells. Conversely, an electron that penetrates less is more effectively shielded by inner electrons.

- Since the 3s orbital penetrates the most, it is least shielded by inner electrons and experiences a higher effective nuclear charge.

- The 3d orbital penetrates the least, meaning it is more effectively shielded by the inner (1s, 2s, 2p, 3s, 3p) electrons and experiences a lower effective nuclear charge.

- Therefore, the order of shielding effect on the valence electrons by inner electrons is: **3d > 3p > 3s**. (Meaning 3d is most shielded, 3s is least shielded by *other* electrons).

- When considering the shielding provided *by* these orbitals *to* outer orbitals, the order would be 3s > 3p > 3d because 3s is closest to the nucleus and therefore is more effective at shielding outer electrons. However, the question asks to explain their shielding effect and penetration power, implying the effect *on* these orbitals and *by* them in a general sense. The primary interpretation is how much they penetrate and how much they are shielded.

(b) Calculate the limiting radius ratio of cation to that of anion when coordination number is six. Given $r_{A^{3+}}$ = 59 pm and $r_{B^{2-}}$ = 170 pm, predict the geometry of AB.

- **Limiting Radius Ratio for Coordination Number 6:**

  o For coordination number six, the most common geometry is octahedral.

  o In an ideal octahedral arrangement, the cation sits in the center, and six anions surround it, touching both the cation and each other along the faces of the octahedron.

  o Consider a square plane of four anions, with the cation in the center. The distance from the center of the cation to the center

of an anion is $r_c + r_a$. The distance between the centers of two touching anions along the diagonal of the square is $2r_a$.

o Using the Pythagorean theorem for a right-angled triangle formed by the cation and two adjacent anions:

- $(r_c + r_a)^2 + (r_c + r_a)^2 = (2r_a)^2$ (This is incorrect. This formula is for coordination number 8, cubic.)

o For coordination number 6 (octahedral), consider the diagonal of the face of the octahedron. The two anions on the diagonal touch each other. The distance between them is $2r_a$. The distance from the cation to the corners is $r_c + r_a$.

o In a square planar arrangement within the octahedral structure:

- The distance from the center of the cation to the corner of the square (anion) is $r_c + r_a$.

- The diagonal of the square formed by four anions touching each other is $2r_a$.

- The distance from the center of the square to a corner (anion) is r_a.

- For the cation to fit perfectly, it must touch all six anions. In an ideal octahedral arrangement, the cation sits in the center, and the anions touch each other along the edges of the octahedron, but not necessarily along the face diagonals.

- The limiting condition is when the cation is just large enough to touch all six anions without the anions touching each other.

- Consider the cross-section. The cation is at the center, and four anions are in a square. The distance from the center to an anion is $r_c + r_a$. The distance from the center of the square to the corner (anion) is $r_a\sqrt{2}$.

- For the anions to just not touch, the cation must fill the space.

- Let's reconsider the standard derivation for CN=6 (octahedral):

  - Consider a central cation with radius r_c and four anions with radius r_a forming a square in a plane. The fifth and sixth anions are directly above and below the cation.

  - For the anions to just touch, the distance between the centers of two anions along the edge of the square is $2r_a$.

  - From the center of the cation to the center of an anion is $r_c + r_a$.

  - Consider a right-angled triangle formed by the center of the cation, the center of an anion in the square plane, and the midpoint between two adjacent anions. This is not the easiest way.

  - Let's use the standard result from geometry. For an octahedral void, the radius of the largest sphere that can fit into the void, when the host spheres are touching, is given by:

    - $r_c + r_a = r_a\sqrt{2}$ (This relates to face-centered cubic where the octahedral void is at the center of the cube edge or center of the cube).

    - This simplifies to $r_c/r_a = \sqrt{2} - 1$ * $r_c/r_a \approx 1.414 - 1 = 0.414$

- **Calculation of Radius Ratio for given ions:**

  - Given $r_{A^{3+}}$ (cation radius) = 59 pm

  - o Given $r_{B^{2-}}$ (anion radius) = 170 pm

  - o Radius Ratio (r_c/r_a) = 59 pm/170 pm

  - o Radius Ratio = 0.347

- **Predict the geometry of AB:**

  - o Compare the calculated radius ratio with the ranges for different coordination numbers:

    - § 0.155 - 0.225: Coordination Number 3 (Trigonal Planar)

    - § 0.225 - 0.414: Coordination Number 4 (Tetrahedral)

    - § 0.414 - 0.732: Coordination Number 6 (Octahedral)

    - § 0.732 - 1.000: Coordination Number 8 (Cubic)

  - o The calculated radius ratio is 0.347. This value falls within the range for **Coordination Number 4 (0.225 - 0.414)**.

  - o Therefore, the predicted geometry of AB is **Tetrahedral**.

  (c) Using VSEPR theory, predict the shapes of the following species: I_3^-, ClF_3, PCl_6^-, SF_4, ICl_4^-.

- **I_3^- (Triiodide ion):**

  - o Central atom: Iodine (I)

  - o Valence electrons on central I = 7

  - o Number of bonded atoms = 2 (to other I atoms)

  - o Negative charge adds 1 electron = 1

  - o Total electrons for bonding and lone pairs = 7 + 2 + 1 = 10 electrons or 5 pairs.

  - o Number of bond pairs = 2

  - o Number of lone pairs = (10 - 2*2) / 2 = 6 / 2 = 3

- o Steric number = Bond pairs + Lone pairs = 2 + 3 = 5

- o Hybridization based on steric number 5 is sp³d.

- o Ideal geometry for steric number 5 is trigonal bipyramidal.

- o Lone pairs occupy equatorial positions to minimize repulsion. With 3 lone pairs, they will occupy all three equatorial positions.

- o **Shape:** Linear

- **ClF$_3$ (Chlorine trifluoride):**

  - o Central atom: Chlorine (Cl)

  - o Valence electrons on central Cl = 7

  - o Number of bonded atoms = 3 (to F atoms)

  - o Total electrons for bonding and lone pairs = 7 + 3 = 10 electrons or 5 pairs.

  - o Number of bond pairs = 3

  - o Number of lone pairs = (10 - 3*2) / 2 = 4 / 2 = 2

  - o Steric number = Bond pairs + Lone pairs = 3 + 2 = 5

  - o Hybridization based on steric number 5 is sp³d.

  - o Ideal geometry for steric number 5 is trigonal bipyramidal.

  - o Lone pairs occupy equatorial positions to minimize repulsion. With 2 lone pairs, they will be in two of the three equatorial positions.

  - o **Shape:** T-shaped

- **PCl$_6$$^-$ (Hexachlorophosphate(V) ion):**

  - o Central atom: Phosphorus (P)

  - o Valence electrons on central P = 5

- o Number of bonded atoms = 6 (to Cl atoms)

- o Negative charge adds 1 electron = 1

- o Total electrons for bonding and lone pairs = 5 + 6 + 1 = 12 electrons or 6 pairs.

- o Number of bond pairs = 6

- o Number of lone pairs = (12 - 6*2) / 2 = 0 / 2 = 0

- o Steric number = Bond pairs + Lone pairs = 6 + 0 = 6

- o Hybridization based on steric number 6 is sp^3d^2.

- o Ideal geometry for steric number 6 is octahedral.

- o **Shape:** Octahedral

- **SF_4 (Sulfur tetrafluoride):**

  - o Central atom: Sulfur (S)

  - o Valence electrons on central S = 6

  - o Number of bonded atoms = 4 (to F atoms)

  - o Total electrons for bonding and lone pairs = 6 + 4 = 10 electrons or 5 pairs.

  - o Number of bond pairs = 4

  - o Number of lone pairs = (10 - 4*2) / 2 = 2 / 2 = 1

  - o Steric number = Bond pairs + Lone pairs = 4 + 1 = 5

  - o Hybridization based on steric number 5 is sp^3d.

  - o Ideal geometry for steric number 5 is trigonal bipyramidal.

  - o The lone pair occupies an equatorial position to minimize repulsion.

  - o **Shape:** See-saw (or distorted tetrahedron)

- **ICl_4^- (Tetrachloroiodate(III) ion):**

  - Central atom: Iodine (I)

  - Valence electrons on central I = 7

  - Number of bonded atoms = 4 (to Cl atoms)

  - Negative charge adds 1 electron = 1

  - Total electrons for bonding and lone pairs = 7 + 4 + 1 = 12 electrons or 6 pairs.

  - Number of bond pairs = 4

  - Number of lone pairs = (12 - 4*2) / 2 = 4 / 2 = 2

  - Steric number = Bond pairs + Lone pairs = 4 + 2 = 6

  - Hybridization based on steric number 6 is sp³d².

  - Ideal geometry for steric number 6 is octahedral.

  - Lone pairs occupy positions 180° apart (axial positions) to minimize repulsion.

  - **Shape:** Square Planar

5. (a) Give the mathematical expression for the conditions of orthogonality and normalization wave function. What is meant by well-behaved wave function?.

- **Conditions for Orthogonality of Wave Functions:**

  - Two wave functions, Ψ_i and Ψ_j, are said to be orthogonal if their integral over all space is zero, provided $i \neq j$.

  - Mathematical expression:

    - $\int \Psi_i^* \Psi_j d\tau = 0 \quad$ for $i \neq j$

    - Where:

- Ψ_i^* is the complex conjugate of the wave function Ψ_i.

- Ψ_j is another wave function.

- $d\tau$ represents integration over all spatial coordinates (e.g., $dxdydz$ in Cartesian coordinates, or $r^2\sin\theta dr d\theta d\phi$ in spherical polar coordinates).

- **Conditions for Normalization of Wave Functions:**

  o A wave function Ψ is said to be normalized if the probability of finding the particle somewhere in all space is equal to one.

  o Mathematical expression:

    ▪ $\int \Psi^*\Psi d\tau = 1$

    ▪ Where:

      - Ψ^* is the complex conjugate of the wave function Ψ.

      - $\Psi^*\Psi$ (or $|\Psi|^2$) represents the probability density of finding the particle.

      - $d\tau$ represents integration over all spatial coordinates.

- **Meaning of Well-behaved Wave Function:**

  o For a wave function to be physically acceptable and meaningful in quantum mechanics, it must satisfy certain mathematical conditions, often referred to as "well-behaved" or "acceptable" wave functions. These conditions ensure that the probability interpretation of the wave function is valid and that the results of calculations (like energy) are finite and single-valued.

  o A well-behaved wave function must be:

    i. **Single-valued:** For every set of coordinates (x, y, z), there must be only one value for the wave function Ψ.

This ensures that the probability of finding the particle at a given point is unambiguous.

ii. **Finite:** The wave function Ψ must be finite everywhere (i.e., its value should not go to infinity). If Ψ were infinite at some point, it would imply an infinite probability of finding the particle at that point, which is physically impossible.

iii. **Continuous:** The wave function Ψ and its first derivatives (with respect to spatial coordinates) must be continuous everywhere. This means there should be no abrupt jumps or breaks in the wave function, which would imply infinite momentum or acceleration, also physically impossible.

iv. **Square-integrable:** The integral of $|\Psi|^2$ over all space must be finite (and preferably equal to 1, i.e., normalized). This ensures that the total probability of finding the particle is finite and can be normalized to unity.

(b) Write the following in order of as mentioned in each case with suitable reasons:

- (i) Increasing acidity – Acetylene, ethane and ethene.

    o **Order of increasing acidity:** Ethane < Ethene < Acetylene

    o **Reasons:**

       ▪ Acidity of hydrocarbons is related to the stability of the conjugate base formed by the removal of a proton (H^+). The more stable the conjugate base, the stronger the acid.

       ▪ The stability of the conjugate base (carbanion) is influenced by the hybridization of the carbon atom bearing the negative charge.

       ▪ **Ethane (C_2H_6, $CH_3 - CH_3$):** The carbon atoms are sp³ hybridized. When a proton is removed, a sp³ hybridized

carbanion is formed. sp³ orbitals have 25% s-character. The s-orbital is closer to the nucleus, so sp³ orbitals are less effective at stabilizing the negative charge because of less s-character.

- **Ethene (C_2H_4, $CH_2 = CH_2$):** The carbon atoms are sp² hybridized. When a proton is removed, a sp² hybridized carbanion is formed. sp² orbitals have 33% s-character. This higher s-character means the electrons in the sp² orbital are held more tightly to the nucleus than in sp³ orbitals, leading to better stabilization of the negative charge compared to sp³ carbon.

- **Acetylene (C_2H_2, $CH \equiv CH$):** The carbon atoms are sp hybridized. When a proton is removed, a sp hybridized carbanion is formed. sp orbitals have 50% s-character. This highest s-character means the electrons in the sp orbital are held most tightly to the nucleus, resulting in the best stabilization of the negative charge among the three.

- Therefore, the stability of the carbanion increases in the order: $CH_3CH_2^- < CH_2 = CH^- < HC \equiv C^-$.

- Consequently, the acidity increases in the same order: Ethane < Ethene < Acetylene.

- (ii) Decreasing melting points – KF, KCl, KBr, KI

  - **Order of decreasing melting points:** KF > KCl > KBr > KI

  - **Reasons:**

    - These are all ionic compounds (alkali halides). The melting point of ionic compounds is primarily determined by the **lattice energy (U_L).** Higher lattice energy means stronger electrostatic forces between ions, requiring more energy to break the lattice, thus higher melting point.

- Lattice energy is directly proportional to the product of the charges of the ions (which is constant for K^+X^- series) and inversely proportional to the sum of their ionic radii ($U_L \propto \frac{Z^+Z^-}{r_c+r_a}$).

- In the series KF, KCl, KBr, KI, the cation K^+ is common. The anions are F^-, Cl^-, Br^-, and I^-.

- As we move from F^- to I^-, the size of the halide anion increases: F^- (133 pm) < Cl^- (181 pm) < Br^- (196 pm) < I^- (220 pm).

- Since the size of the anion increases, the sum of the ionic radii ($r_K^+ + r_{X^-}$) increases.

- As the denominator ($r_c + r_a$) in the lattice energy equation increases, the lattice energy decreases.

- Lower lattice energy implies weaker electrostatic forces of attraction, which requires less energy to overcome, leading to lower melting points.

- Therefore, the melting points decrease as the anion size increases: KF > KCl > KBr > KI.

(c) Ψ_A and Ψ_B are wave functions of two atomic orbitals A and B. Draw the molecular orbital diagrams obtained by combination of the atomic orbitals when

- (i) $\chi_A = \chi_B$

  - (Note: As per instructions, I cannot draw diagrams. I will describe the molecular orbital diagram.)

  - **Description for $\chi_A = \chi_B$ (Homodiatomic Molecule, e.g., H₂):**

    - When two atomic orbitals (A and B) of equal energy and equal electronegativity combine, they form two molecular

orbitals (MOs): one bonding MO and one antibonding MO.

- **Energy Levels:** The atomic orbitals (A and B) will be at the same energy level.

- **Bonding Molecular Orbital (σ or π):** This MO will be lower in energy than the original atomic orbitals. It results from the constructive interference of the atomic orbitals. The electron density is concentrated between the nuclei, leading to stabilization.

- **Antibonding Molecular Orbital (σ^* or π^*):** This MO will be higher in energy than the original atomic orbitals. It results from the destructive interference of the atomic orbitals. There is a nodal plane between the nuclei, leading to repulsion and destabilization.

- **Symmetry:** The energy diagram will be symmetrical, with the bonding MO stabilized to the same extent that the antibonding MO is destabilized relative to the original atomic orbitals.

- **Filling:** Electrons fill the MOs according to the Aufbau principle, Hund's rule, and Pauli exclusion principle, starting from the lowest energy MO.

- (ii) $\chi_A < \chi_B$ where χ_A and χ_B are the electronegativities of atoms A and B.

  - (Note: As per instructions, I cannot draw diagrams. I will describe the molecular orbital diagram.)

  - **Description for $\chi_A < \chi_B$ (Heterodiatomic Molecule, e.g., HF):**

    - When two atomic orbitals (A and B) combine, and atom B is more electronegative than atom A (meaning atom B's atomic orbital is lower in energy), the resulting molecular

orbitals are unequally contributed by the two atomic orbitals.

- **Energy Levels:** The atomic orbital of the more electronegative atom (B) will be at a lower energy level than the atomic orbital of the less electronegative atom (A).

- **Bonding Molecular Orbital (σorπ):** This MO will be lower in energy than both original atomic orbitals. However, it will be closer in energy to, and have a greater contribution from, the atomic orbital of the more electronegative atom (B). This means the electron density in the bonding MO is more localized towards the more electronegative atom.

- **Antibonding Molecular Orbital (σ^*orπ^*):** This MO will be higher in energy than both original atomic orbitals. It will be closer in energy to, and have a greater contribution from, the atomic orbital of the less electronegative atom (A).

- **Polarity:** The unequal contribution of atomic orbitals to the molecular orbitals is the basis for bond polarity. The bonding electrons spend more time near the more electronegative atom, resulting in a partial negative charge on that atom and a partial positive charge on the less electronegative atom.

6. (a) (i) What is a radial node? How many radial nodes are there in a 3s orbital?

- **Radial Node:**

  - A radial node (also known as a spherical node) is a spherical surface within an atomic orbital where the probability of finding an electron is zero. At a radial node, the radial part of the wave function, R(r), is zero.

o These nodes occur at specific distances from the nucleus where the wave function changes its sign.

- **Number of radial nodes in a 3s orbital:**

    o The number of radial nodes for any orbital is given by the formula: $n - l - 1$, where 'n' is the principal quantum number and 'l' is the azimuthal (angular momentum) quantum number.

    o For a 3s orbital:

        ▪ n = 3 (principal quantum number)

        ▪ l = 0 (for an s-orbital)

    o Number of radial nodes = $3 - 0 - 1 = 2$

    o Therefore, a 3s orbital has **2 radial nodes**.

(a) (ii) What is radial probability distribution function? Explain it for 1s orbital.

- **Radial Probability Distribution Function:**

    o The radial probability distribution function (RPDF), denoted as $4\pi r^2 R^2(r)$, represents the probability of finding an electron within a thin spherical shell of radius 'r' and thickness 'dr' at a distance 'r' from the nucleus.

    o It is obtained by multiplying the square of the radial wave function ($R^2(r)$) by the volume of a spherical shell ($4\pi r^2 dr$).

    o $R^2(r)$ itself gives the probability density at a given point 'r', but $4\pi r^2 R^2(r)$ gives the total probability of finding the electron at a particular distance 'r' from the nucleus, summed over all directions.

- **Explanation for 1s orbital:**

    o For a 1s orbital (n=1, l=0):

- The radial wave function R(r) for a 1s orbital is a decaying exponential function (e.g., $R_{1,0} \propto e^{-Zr/a_0}$). This means the probability density ($R^2(r)$) is maximum at the nucleus (r=0) and decreases exponentially as 'r' increases.

- However, the volume of the spherical shell ($4\pi r^2$) is zero at r=0 and increases as 'r' increases.

- The radial probability distribution function ($4\pi r^2 R^2(r)$) is a product of these two terms.

- At r=0, $4\pi r^2 R^2(r)$ is 0 (because r^2 is 0).

- As 'r' increases from 0, the r^2 term rapidly increases, causing the RPDF to increase initially.

- Eventually, the exponential decay of $R^2(r)$ dominates, causing the RPDF to decrease and approach zero as 'r' approaches infinity.

- This results in a single maximum (peak) in the radial probability distribution curve for the 1s orbital. This peak corresponds to the distance from the nucleus where there is the highest probability of finding the electron. This maximum value occurs at $r = a_0/Z$ (for hydrogen atom, Z=1, so at a_0, the Bohr radius).

- The 1s orbital has $n - l - 1 = 1 - 0 - 1 = 0$ radial nodes, which is consistent with its single peak.

(b) "In case of B_2, C_2 and N_2 molecules s-p$_2$ mixing cannot be neglected while in case of O_2 and F_2, MO diagrams explain most of the characteristics of these molecules without considering s-p$_2$ mixing." Justify the statement. Draw MO diagram of N_2 molecule using s-p$_2$ mixing.

- **Justification of s-p mixing:**

- o **s-p mixing (or s-p interaction)** refers to the phenomenon where atomic orbitals of similar energy and appropriate symmetry can interact and mix. Specifically, in diatomic molecules, the 2s atomic orbital and 2p_z atomic orbital (which both have sigma symmetry) can interact. This interaction affects the relative energies of the resulting molecular orbitals.

- o **For B_2, C_2, and N_2 (up to Z=7, Nitrogen):**

    - The energy difference between the 2s and 2p atomic orbitals is relatively small.

    - Due to this small energy difference, there is significant s-p mixing between the 2s and 2p atomic orbitals.

    - This mixing causes the energy of the σ_{2s} bonding MO to decrease and the energy of the σ_{2s}^* antibonding MO to increase.

    - More importantly, it pushes up the energy of the σ_{2p} bonding MO above the π_{2p} bonding MOs.

    - So, the MO energy order becomes: $\sigma_{2s} < \sigma_{2s}^* < \pi_{2p} < \sigma_{2p} < \pi_{2p}^* < \sigma_{2p}^*$

    - This altered energy order is crucial for correctly predicting properties like bond order and magnetic behavior (e.g., B_2 is paramagnetic, which is only explained with s-p mixing). For N_2, it correctly explains its high bond order and diamagnetism.

- o **For O_2 and F_2 (from Z=8, Oxygen, onwards):**

    - As we move across the period from nitrogen to oxygen and fluorine, the effective nuclear charge increases significantly.

- This increase in effective nuclear charge causes the 2s and 2p atomic orbitals to contract and their energies to decrease.

- Crucially, the energy difference between the 2s and 2p atomic orbitals becomes much larger.

- Due to this large energy difference, the s-p mixing becomes negligible.

- Therefore, the original energy order of MOs (without considering strong mixing) is observed: $\sigma_{2s} < \sigma_{2s}^* < \sigma_{2p} < \pi_{2p} < \pi_{2p}^* < \sigma_{2p}^*$ * This order correctly predicts the properties of O_2 (paramagnetic due to two unpaired electrons in π_{2p}^* orbitals) and F_2 (diamagnetic).

- **Conclusion:** The extent of s-p mixing is inversely related to the energy difference between the 2s and 2p atomic orbitals. This difference is small for lighter elements (B, C, N), leading to significant mixing and altered MO energy order, but large for heavier elements (O, F), making s-p mixing negligible and leading to a "normal" MO energy order.

- **MO Diagram of N_2 molecule using s-p mixing:**

  o (Note: As per instructions, I cannot draw diagrams. I will describe the energy levels and electron filling for N_2 MO diagram with s-p mixing.)

  o **Atomic Orbitals (on left and right):**

    - Each Nitrogen atom has 2s and 2p (2px, 2py, 2pz) atomic orbitals.

  o **Molecular Orbitals (in the center):**

    - **From 2s orbitals:**

      - σ_{2s} (bonding, lower energy)

- σ_{2s}^* (antibonding, higher energy)

  - **From 2p orbitals (with s-p mixing):**

    - Due to s-p mixing, the σ_{2p} orbital is pushed up in energy, becoming higher than the π_{2p} orbitals.

    - π_{2p} (bonding, two degenerate orbitals, lower than σ_{2p})

    - σ_{2p} (bonding, higher than π_{2p})

    - π_{2p}^* (antibonding, two degenerate orbitals, higher energy)

    - σ_{2p}^* (antibonding, highest energy)

- **Complete Energy Order (with s-p mixing):**

  - $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$

- **Electron Filling for N₂ (Total 14 electrons: 7 from each N):**

  - Fill 1s electrons: $\sigma_{1s}^2 \sigma_{1s}^{*2}$ (4 electrons)

  - Fill 2s electrons: $\sigma_{2s}^2 \sigma_{2s}^{*2}$ (4 electrons)

  - Remaining electrons for 2p orbitals = 14 - 8 = 6 electrons.

  - Fill 2p MOs: $\pi_{2p_x}^2 \pi_{2p_y}^2 \sigma_{2p_z}^2$ (6 electrons)

- **Resulting Configuration:** $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_x}^2 \pi_{2p_y}^2 \sigma_{2p_z}^2$ * **Bond Order:** $BO = \frac{1}{2}$ (Number of bonding electrons − Number of antibonding electrons) * BO $= \frac{1}{2}[(2 + 2 + 6) − (2 + 2)] = \frac{1}{2}[10 − 4] = \frac{6}{2} = 3$

- o **Magnetic Properties:** All electrons are paired, so N_2 is diamagnetic.

(c) On which law is the Born-Haber cycle based? Set up a Born Haber cycle for the formation of MgO from magnesium metal and oxygen, i.e. Mg(s) + ½ O_2(g) → MgO (s)

- **Law on which Born-Haber cycle is based:**

  - o The Born-Haber cycle is based on **Hess's Law of Constant Heat Summation**. Hess's Law states that the total enthalpy change for a chemical reaction is independent of the pathway taken, provided the initial and final conditions are the same. In other words, if a reaction can be expressed as a series of steps, the overall enthalpy change for the reaction is the sum of the enthalpy changes for each step.

- **Born-Haber cycle for the formation of MgO:**

  - o The formation of magnesium oxide (MgO) from its constituent elements in their standard states is represented by the enthalpy of formation ($\Delta_f H°$).

  - o Overall reaction: $Mg(s) + \frac{1}{2} O_2(g) \rightarrow MgO(s) \quad \Delta H = \Delta_f H°(MgO)$

  - o The Born-Haber cycle breaks this overall reaction into a series of hypothetical steps, each with a known or measurable enthalpy change:

    - v. **Sublimation of Magnesium:** The energy required to convert solid magnesium into gaseous magnesium atoms.

      - $Mg(s) \rightarrow Mg(g) \quad \Delta H_{sub}$ (Enthalpy of sublimation)

    - vi. **Ionization of Gaseous Magnesium:** The energy required to remove two electrons from a gaseous

magnesium atom to form a gaseous magnesium ion (Mg^{2+}). This occurs in two steps:

- $Mg(g) \rightarrow Mg^+(g) + e^-$ IE_1 (First ionization enthalpy)

- $Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$ IE_2 (Second ionization enthalpy)

- Total ionization energy = $IE_1 + IE_2$

vii. **Dissociation of Oxygen:** The energy required to break the O_2 molecule into individual oxygen atoms. Since we need only one oxygen atom for MgO, it's half the bond dissociation energy.

- $\frac{1}{2}O_2(g) \rightarrow O(g)$ $\frac{1}{2}D_{O_2}$ (Half of the bond dissociation energy of O_2)

viii. **Electron Gain by Gaseous Oxygen Atoms:** The energy change when two electrons are added to a gaseous oxygen atom to form a gaseous oxide ion (O^{2-}). This also occurs in two steps:

- $O(g) + e^- \rightarrow O^-(g)$ EA_1 (First electron gain enthalpy, usually exothermic)

- $O^-(g) + e^- \rightarrow O^{2-}(g)$ EA_2 (Second electron gain enthalpy, always endothermic due to repulsion)

- Total electron gain enthalpy = $EA_1 + EA_2$

ix. **Formation of Ionic Lattice:** The energy released when gaseous magnesium ions and oxide ions combine to form solid magnesium oxide. This is the lattice energy.

- $Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s)$ U_L (Lattice energy, always exothermic)

- o **Applying Hess's Law:**

  - ▪ According to Hess's Law, the enthalpy of formation of MgO is equal to the sum of the enthalpy changes of all these steps:

    - $\Delta_f H°(MgO) = \Delta H_{sub} + IE_1 + IE_2 + \frac{1}{2}D_{O_2} + EA_1 + EA_2 + U_L$

7. (a) The bond angle in water molecule is 104.5°. Calculate the S character used by the oxygen atom directed to the two bonded orbitals and two non-bonded orbitals.

- **Understanding the Concept:**

  - o The bond angle in water (H_2O) is 104.5°, which is less than the ideal tetrahedral angle of 109.5°. This deviation is due to the presence of two lone pairs on the central oxygen atom.

  - o The oxygen atom in water is sp^3 hybridized. In a perfectly sp^3 hybridized molecule, the s-character is 25%. However, due to lone pair-bond pair repulsions, the hybridization is slightly distorted, meaning the s-character is not uniformly distributed among all four hybrid orbitals.

  - o Bent's Rule states that lone pairs prefer orbitals with more s-character, and bond pairs (especially with more electronegative atoms) prefer orbitals with more p-character. However, for a bond angle calculation based on hybridization, we can use a simpler relationship relating bond angle to s-character.

- **Formula Relating Bond Angle and S-character in Hybrid Orbitals:**

  - o For a hybrid orbital involved in a bond (specifically, the angle between two equivalent hybrid orbitals), the fractional s-character (f_s) can be related to the bond angle (θ) using the formula:

- $cos\theta = \frac{f_s - 1}{f_s}$ (This formula is for fractional p-character, or for the angle between two equivalent hybrid orbitals that are pure p-orbitals in character if f_s = 0, and pure s-orbital if f_s=1).

- A more common and useful formula derived from orthogonality is: $1 + \lambda^2 cos\theta = 0$, where λ is the ratio of p-character to s-character (i.e., hybrid orbital is of the form $s + \lambda p$). Then, fractional s-character is $f_s = \frac{1}{1+\lambda^2}$ and fractional p-character is $f_p = \frac{\lambda^2}{1+\lambda^2}$.

- From $1 + \lambda^2 cos\theta = 0$, we get $\lambda^2 = -\frac{1}{cos\theta}$.

- So, $f_s = \frac{1}{1 - \frac{1}{cos\theta}} = \frac{cos\theta}{cos\theta - 1}$.

- Let's use the relation for bond angle (angle between two bond orbitals):

  - $cos\theta = \frac{\%s_{orbital}}{100} - 1$ (This is for the angle between hybrid orbitals, if the lone pair contributions are simplified).

    - A more direct approach for the s-character in the bond orbitals:

      - Let $f_{s(bond)}$ be the fractional s-character in the hybrid orbitals forming the O-H bonds.

      - Then $f_{p(bond)} = 1 - f_{s(bond)}$.

      - The percentage s-character is given by:

        - $\%s = \frac{cos\theta}{cos\theta - 1} \times 100$ (This formula gives the %s-character in a hybrid orbital if it were an sp hybrid of a given angle,

typically not used for multiple hybrid orbitals with lone pairs.)

- The formula for percentage s-character in the bonding orbitals, considering only the angle, is approximately:

  - $\%s_{bond} = \frac{-cos\theta}{1-cos\theta} \times 100$ * Given $\theta = 104.5°$.

- $cos(104.5°) \approx -0.2504$ * $\%s_{bond} = \frac{-(-0.2504)}{1-(-0.2504)} \times 100$ * $\%s_{bond} = \frac{0.2504}{1.2504} \times 100$ * $\%s_{bond} \approx 0.20025 \times 100 \approx 20.025\%$

- **S-character in Bonded Orbitals:**

  - Each of the two O-H bond orbitals has approximately **20.0% s-character** and 80.0% p-character.

- **S-character in Non-bonded (Lone Pair) Orbitals:**

  - Since oxygen uses one 2s and three 2p orbitals for hybridization, the total s-character is 100%.

  - The total s-character distributed among all four hybrid orbitals must be 25% (i.e., 1/4th of the s-orbital).

  - Let $f_{s(bond)}$ be the s-character in each bond orbital and $f_{s(lonepair)}$ be the s-character in each lone pair orbital.

  - We have 2 bond orbitals and 2 lone pair orbitals.

  - Total s-character = $2 \times f_{s(bond)} + 2 \times f_{s(lonepair)} = 1$ (as fraction)

  - Total s-character = $2 \times 20.025\% + 2 \times f_{s(lonepair)} = 100\%$ * $40.05\% + 2 \times f_{s(lonepair)} = 100\%$ * $2 \times f_{s(lonepair)} =$

$$100\% - 40.05\% = 59.95\% * f_{s(lonepair)} = 59.95\%/2 = 29.975\% \approx 30.0\%$$

- o **Conclusion:**

  - The s-character used by the oxygen atom for each of the two **bonded orbitals (O-H bonds)** is approximately **20.0%**.

  - The s-character used by the oxygen atom for each of the two **non-bonded orbitals (lone pairs)** is approximately **30.0%**.

- o This result is consistent with Bent's Rule, which states that orbitals directed towards more electronegative atoms (H, here) have less s-character, and lone pair orbitals have more s-character to minimize electron-electron repulsion and maximize stability.

(b) Arrange the following in increasing order of dipole moment: BF_3, NH_3, NF_3. Justify your answer.

- **Order of increasing dipole moment:** BF_3 < NF_3 < NH_3

- **Justification:**

  - o **BF₃:**

    - Molecular geometry: Trigonal planar.

    - Hybridization of central B atom: sp².

    - Bond polarity: B-F bonds are polar (F is more electronegative than B), with bond dipoles pointing towards F.

    - Net dipole moment: Due to the symmetrical trigonal planar arrangement, the three equal B-F bond dipoles cancel each other out.

- **Dipole moment = 0 D**.

- NF_3:

  - Molecular geometry: Trigonal pyramidal.

  - Hybridization of central N atom: sp^3 (with one lone pair).

  - Bond polarity: N-F bonds are polar (F is more electronegative than N), with bond dipoles pointing towards F.

  - Lone pair contribution: The lone pair on nitrogen contributes a dipole moment pointing away from the nucleus (towards the lone pair).

  - Net dipole moment: The bond dipoles point away from the lone pair. The vector sum of the N-F bond dipoles is in the opposite direction to the lone pair dipole moment. This results in a relatively small net dipole moment (0.23 D). The lone pair's contribution largely counteracts the bond dipoles.

- NH_3:

  - Molecular geometry: Trigonal pyramidal.

  - Hybridization of central N atom: sp^3 (with one lone pair).

  - Bond polarity: N-H bonds are polar (N is more electronegative than H), with bond dipoles pointing towards N.

  - Lone pair contribution: The lone pair on nitrogen contributes a dipole moment pointing away from the nucleus (towards the lone pair).

  - Net dipole moment: Both the N-H bond dipoles (which point towards the nitrogen) and the lone pair dipole moment are directed in the same general direction

(upwards, away from the base of the pyramid). They reinforce each other.

- **Dipole moment = 1.47 D**.

- **Summary:** BF_3 is non-polar due to symmetry. Both NH_3 and NF_3 are polar. In NH_3, the lone pair dipole and bond dipoles add up, leading to a large dipole moment. In NF_3, the lone pair dipole and bond dipoles largely cancel each other, leading to a small dipole moment.

  (c) Define Bent's Rule. How does it help to decide the bond angles of CH_2F_2?

- **Bent's Rule Definition:**
  - Bent's Rule states that in a molecule, atomic s-character concentrates in hybrid orbitals directed towards less electronegative substituents (or lone pairs), while p-character concentrates in hybrid orbitals directed towards more electronegative substituents.
  - Alternatively, hybrid orbitals used to form bonds with more electronegative atoms will have more p-character (and less s-character), whereas hybrid orbitals used to form bonds with less electronegative atoms (or to accommodate lone pairs) will have more s-character.

- **How it helps to decide bond angles of CH_2F_2:**
  - In CH_2F_2 (difluoromethane), the central atom is carbon. It is sp³ hybridized, leading to a distorted tetrahedral geometry.
  - The molecule has two C-H bonds and two C-F bonds.
  - Fluorine (electronegativity ≈ 3.98) is significantly more electronegative than hydrogen (electronegativity≈ 2.20).
  - According to Bent's Rule:

- The hybrid orbitals forming the **C-F bonds** will have more **p-character** (and thus less s-character) because fluorine is highly electronegative and pulls electron density away from carbon.

- The hybrid orbitals forming the **C-H bonds** will have more **s-character** (and thus less p-character) because hydrogen is less electronegative than fluorine, and the carbon 'prefers' to direct its s-character towards it.

- **Impact on Bond Angles:**

  - **C-H bond angle (H-C-H):** Since the C-H bond orbitals have more s-character, and larger s-character implies a wider angle, the H-C-H bond angle will be **greater than 109.5°**.

  - **C-F bond angle (F-C-F):** Since the C-F bond orbitals have more p-character, and more p-character implies a smaller angle (approaching 90° as p-character increases), the F-C-F bond angle will be **less than 109.5°**.

- **Experimental Verification:** Indeed, the H-C-H bond angle in CH_2F_2 is approximately 111.8°, and the F-C-F bond angle is approximately 108.0°, which is consistent with Bent's Rule. This rule effectively explains the deviations from ideal bond angles in molecules with varying electronegativity of substituents.

(d) What is the expected change in Bond order during the following ionization processes:

- (i) $O_2 \rightarrow O_2^+ + e^-$

  - **O_2 (Oxygen molecule):**

    - Total valence electrons = 6 (from each O) x 2 = 12 valence electrons.

- MO configuration (without s-p mixing):
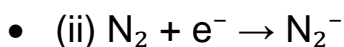 $\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_z}^2 \pi_{2p_x}^2 \pi_{2p_y}^2 \pi_{2p_x}^{*1} \pi_{2p_y}^{*1}$
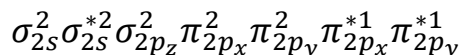
- Bonding electrons = 2 + 2 + 4 = 8

- Antibonding electrons = 2 + 2 = 4 (from σ_{2s}^* and π^*)

- Bond Order (BO) = $\frac{1}{2}(8 - 4) = 2$

- **O₂⁺ (Oxygen molecular ion):**

  - Formed by removing one electron from O_2. The electron is removed from the highest occupied molecular orbital (HOMO), which is the π_{2p}^* antibonding orbital.

  - MO configuration: $\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_z}^2 \pi_{2p_x}^2 \pi_{2p_y}^2 \pi_{2p_x}^{*1}$ (or $\pi_{2p_y}^{*1}$)

  - Bonding electrons = 8

  - Antibonding electrons = 3

  - Bond Order (BO) = $\frac{1}{2}(8 - 3) = 2.5$

- **Change in Bond Order:** From 2 to 2.5. The bond order **increases**.

- (ii) $N_2 + e^- \rightarrow N_2^-$

  - **N₂ (Nitrogen molecule):**

    - Total valence electrons = 5 (from each N) x 2 = 10 valence electrons.

    - MO configuration (with s-p mixing): $\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_x}^2 \pi_{2p_y}^2 \sigma_{2p_z}^2$

    - Bonding electrons = 2 + 6 = 8

    - Antibonding electrons = 2

    - Bond Order (BO) = $\frac{1}{2}(8 - 2) = 3$

- o **N₂⁻ (Nitrogen molecular ion):**

    - Formed by adding one electron to N_2. The electron is added to the lowest unoccupied molecular orbital (LUMO), which is the π_{2p}^* antibonding orbital.

    - MO configuration: $\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_x}^2 \pi_{2p_y}^2 \sigma_{2p_z}^2 \pi_{2p_x}^{*1} (\text{or} \pi_{2p_y}^{*1})$

    - Bonding electrons = 8

    - Antibonding electrons = 3

    - Bond Order (BO) = $\frac{1}{2}(8-3) = 2.5$

  - o **Change in Bond Order:** From 3 to 2.5. The bond order **decreases**.

- (iii) NO → NO⁺ + e⁻

  - o **NO (Nitric Oxide molecule):**

    - Total valence electrons = 5 (from N) + 6 (from O) = 11 valence electrons.

    - MO configuration (considering the energy difference, generally no strong s-p mixing like N_2, but some interaction, simplified for bond order calculation, usually follows O_2 pattern but with slight asymmetry due to unequal electronegativity):

        - $\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_z}^2 \pi_{2p_x}^2 \pi_{2p_y}^2 \pi_{2p_x}^{*1}$

    - Bonding electrons = 2 + 2 + 4 = 8

    - Antibonding electrons = 2 + 1 = 3 (from σ_{2s}^* and π_{2p}^*)

    - Bond Order (BO) = $\frac{1}{2}(8-3) = 2.5$

  - o **NO⁺ (Nitrosyl Cation):**

- Formed by removing one electron from NO. The electron is removed from the highest occupied molecular orbital (HOMO), which is the π^*_{2p} antibonding orbital.

- MO configuration: $\sigma^2_{2s}\sigma^{*2}_{2s}\sigma^2_{2p_z}\pi^2_{2p_x}\pi^2_{2p_y}$

- Bonding electrons = 8

- Antibonding electrons = 2

- Bond Order (BO) = $\frac{1}{2}(8-2) = 3$

  o **Change in Bond Order:** From 2.5 to 3. The bond order **increases**.

8. (a) What do you understand by the term effective nuclear charge? Calculate the shielding constant and effective nuclear charge (Zeffe) for the electron present in 4s and 3d of Scandium (Z = 21).

- **Effective Nuclear Charge (Z_eff):**

  o The effective nuclear charge (Z_eff) is the net positive charge experienced by an electron in a multi-electron atom.

  o In a multi-electron atom, the electrons are attracted to the positively charged nucleus, but they are also repelled by other electrons in the atom. This repulsion by other electrons "shields" or "screens" the outer electrons from the full attractive force of the nucleus.

  o Therefore, the effective nuclear charge is always less than the actual nuclear charge (atomic number, Z).

  o It is calculated as: $Z_{eff} = Z - S$, where Z is the atomic number (number of protons) and S is the shielding constant (or screening constant). The shielding constant quantifies the extent to which other electrons reduce the nuclear charge felt by a particular electron.

- **Calculation for Scandium (Sc, Z = 21):**

  - Electronic configuration of Sc: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$

  - **For an electron in the 4s orbital:**

    - Grouping of electrons for Slater's rules: $(1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^1)(4s^2)$

    - Considering one of the 4s electrons:

      - **Electrons in the same (n=4) group (4s^1):** There is 1 other electron in the 4s orbital. Contribution = $1 \times 0.35 = 0.35$ * **Electrons in the (n-1) group (3s^{2}3p^6):** There are 8 electrons in the 3s and 3p orbitals. Contribution = $8 \times 0.85 = 6.80$ * **Electrons in the (n-1) group (3d^1):** There is 1 electron in the 3d orbital. Contribution = $1 \times 0.85 = 0.85$ (Note: When calculating for s/p electrons, d/f electrons in the same principal shell contribute 0.85, even if they are in a different group according to the Slater's grouping. However, the rule states that electrons to the right of the current electron contribute 0, so we count 3d electrons in the (n-1) shell if they are considered "inner" for 4s. A more consistent grouping would be $(1s^2)(2s^2 2p^6)(3s^2 3p^6 3d^1)(4s^2)$.)

      - Let's use the most common Slater's grouping which treats (ns,np) and (nd) as separate groups within a shell if they are valence electrons. But for screening of 4s by 3d, 3d acts as an inner shell.

      - Let's apply the standard rules:

        - Group: $(1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^1)(4s^2)$

        - For a 4s electron:

- Other 4s electrons (1 electron): $1 \times 0.35 = 0.35$

- (n-1) shell ($3s^2 3p^6$, $3d^1$): 8 electrons (3s,3p) + 1 electron (3d) = 9 electrons.

  - $9 \times 0.85 = 7.65$ * (n-2) shell ($2s^2 2p^6$): 8 electrons. $8 \times 1.00 = 8.00$ * (n-3) shell ($1s^2$): 2 electrons. $2 \times 1.00 = 2.00$ * Total Shielding Constant (S) for 4s $= 0.35 + 7.65 + 8.00 + 2.00 = 18.00$ * Effective Nuclear Charge (Z_{eff}) for 4s $= Z - S = 21 - 18.00 = 3.00$

- **For an electron in the 3d orbital:**

  - Grouping of electrons for Slater's rules: $(1s^2)(2s^2 2p^6)(3s^2 3p^6 3d^1)(4s^2)$

  - For a 3d electron:

    - Other 3d electrons: There are no other 3d electrons in this case (it's the first one). Contribution = $0 \times 0.35 = 0$

    - Electrons in groups to the left of the (nd, nf) group contribute 1.00.

    - All electrons in inner shells (n-1, n-2, etc. and all (ns, np) electrons for d-electron calculation) shield by 1.00.

    - Total electrons in inner shells ($1s^2$ $2s^2 2p^6$ $3s^2 3p^6$) = 2 + 8 + 8 = 18 electrons.

    - Contribution = $18 \times 1.00 = 18.00$

- Electrons in outer shells (4s²): These do not shield the inner 3d electron. Contribution = 0.

- Total Shielding Constant (S) for 3d = $0 + 18.00 = 18.00$ * Effective Nuclear Charge (Z_{eff}) for 3d = $Z - S = 21 - 18.00 = 3.00$

- **Summary for Sc:**

  - **For 4s electron:** Shielding Constant (S) = 18.00, Effective Nuclear Charge (Z_{eff}) = 3.00

  - **For 3d electron:** Shielding Constant (S) = 18.00, Effective Nuclear Charge (Z_{eff}) = 3.00

- **Note on Interpretation:** While the calculated Z_eff is the same by Slater's rules, experimentally and based on energy levels, the 4s electron is higher in energy than the 3d electron in Sc⁺, but the 4s orbital is filled first in the neutral atom due to its higher penetration and lower initial energy. The Z_eff calculation here shows that the screening effect makes them experience a similar effective charge, but subtle differences in penetration power and orbital shape still dictate filling order.

(b) Differentiate between:

- (i) Orbit and orbital.

  - **Orbit:**

    - **Concept:** Based on Bohr's model of the atom.

    - **Description:** A well-defined, circular, two-dimensional path or trajectory around the nucleus in which an electron is believed to revolve.

    - **Nature:** Classical concept. Assumes electrons move in fixed, planetary-like paths.

- **Predictability:** The exact position and momentum of an electron in an orbit can be simultaneously determined (deterministic).

- **Shape:** Always circular or elliptical.

- **Maximum Electrons:** No fixed limit on the number of electrons per orbit in Bohr's original theory, though later shells could hold $2n^2$ electrons.

- **Orbital:**

  - **Concept:** Based on quantum mechanical model of the atom (Schrödinger wave equation).

  - **Description:** A three-dimensional region of space around the nucleus where there is a high probability (typically > 90-95%) of finding an electron with a specific energy. It represents a wave function.

  - **Nature:** Quantum mechanical concept. Does not describe a definite path, but rather a probability distribution.

  - **Predictability:** The exact position and momentum of an electron cannot be simultaneously determined (Heisenberg's Uncertainty Principle applies). Only the probability of finding an electron in a given region is known.

  - **Shape:** Can have various shapes (spherical for s-orbitals, dumbbell for p-orbitals, cloverleaf for d-orbitals, etc.).

  - **Maximum Electrons:** Each orbital can hold a maximum of two electrons, provided they have opposite spins (Pauli Exclusion Principle).

- (ii) Electronegativity and electron affinity

  - **Electronegativity:**

- **Definition:** It is a qualitative measure of the tendency of an atom in a chemical bond (or molecule) to attract a shared pair of electrons towards itself.

- **Nature:** A property of an atom when it is *part of a bond* within a molecule. It cannot be measured for an isolated atom.

- **Units:** Dimensionless (though scales like Pauling scale, Mulliken scale exist).

- **Trend (Periodic Table):** Generally increases across a period (from left to right) and decreases down a group. Fluorine is the most electronegative element.

- **Factors Affecting:** Nuclear charge, atomic size, shielding effect, and hybridization state.

- **Relevance:** Helps predict bond polarity, reaction mechanisms, and properties of compounds (e.g., acidity, basicity).

o **Electron Affinity (or Electron Gain Enthalpy):**

- **Definition:** It is the enthalpy change (energy change) that occurs when an electron is added to a neutral gaseous isolated atom to form a gaseous anion.

- **Nature:** A quantitative property of an *isolated gaseous atom*. It can be experimentally measured.

- **Units:** kJ/mol or eV/atom.

- **Trend (Periodic Table):** Generally increases (becomes more negative/exothermic) across a period and generally decreases (becomes less negative/exothermic or more positive/endothermic) down a group. Halogens typically have high electron affinities.

- **Factors Affecting:** Nuclear charge, atomic size, electronic configuration (stability of anion).

- **Relevance:** Indicates the ease with which an atom accepts an electron to form an anion; relevant for ionic bond formation and redox reactions.

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