Birla Institute of Technology & Science, Pilani, Rajasthan 333031
First Semester 2015-2016

Course Number: CHEM F111 Course Title: General Chemistry Marks: 10
Tutorial Problem Set 2 (based on Lecture No.'s: 10-13 in the course hand out)

Instructions to the student: *The following problems should be solved as home assignment within a week of display. Any one problem will be assigned as a closed book class test in the following tutorial hour.*

Q. 1 (a) What atomic terms are possible for the electron configuration np^1nd^1? Which term is likely to lie lowest in energy? (b) Give the possible term symbols for (a) Sc: [Ar]$3d^1 4s^2$, (b) Br: [Ar]$3d^{10}4s^2 4p^5$ **[4+2+2+2]**

Q. 2 (a) Suppose that an atom has 2 electrons in different orbitals. What are the possible values of the total spin quantum number *S*? What is the multiplicity in each case? **[2+2]**

(b) What values of *J* may occur in the terms (i) ^{2}P, (ii) ^{3}P? How many states (distinguished by the quantum number M_J) belong to each level? **[3+3]**

Q. 3 (a) Arrange the species O_2^+, O_2, O_2^-, O_2^{2-} in order of increasing bond length. (b) From the ground-state electron configurations of B_2 and C_2, predict which molecule should have the greater bond dissociation energy. **[4+4]**

Q. 4 (a) Show that the sp^2 hybrid orbital $(s + 2^{1/2}p)/3^{1/2}$ is normalized to 1 if the *s* and *p* orbitals are normalized to 1. (b) Normalize the molecular orbital $\psi_A + \lambda\psi_B$ in terms of the parameter λ and the overlap integral *S*. **[4+4]**

Q. 5 (a) Write the term(s) corresponding to the ground state electronic configuration of Cu^{2+} ion ([Ar]$3d^9$) and identify the lowest energy level. (b) Which of the following molecules N_2, C_2 and O_2 would you expect to be stabilized by (i) the addition of an electron to form A_2^-; (ii) the removal of an electron to form A_2^+? **[5+5]**

Q. 6 (a) Obtain all possible terms and the levels arising from the excited electronic configuration $1s^12s^1$ of helium atom. State the degeneracy of each term and each level. **[2+2+2]**

(b) Write the wavefunctions (ignoring normalization) corresponding to the M_S=0-triplet and singlet states arising from this configuration if the wavefunction corresponding to M_S=1-triplet is

$\Psi^{triplet}(1,2)(M_S=1) = [\varphi_{1s}(1)\,\varphi_{2s}(2) - \varphi_{2s}(1)\varphi_{1s}(2)]\alpha(1)\alpha(2)$ **[2+2]**

Q. 7 (a) Determine the hybridization of each of the following hybrid atomic orbitals formed from combination of two pure atomic orbitals: φ_s and φ_{pz}. **[2+2+2]**

(I) $\chi_1 = 2^{-1/2}(\varphi_s + \varphi_{pz})$ (II) $\chi_1 = 3^{-1/2}(\varphi_s - 2^{1/2}\varphi_{pz})$ (III) $\chi_1 = 0.5(\varphi_s + 3^{1/2}\varphi_{pz})$

(b) Write the ground state electronic configuration of O_2 molecule using LCAO-MO orbitals. What will be the bond order of the molecule if one of the electrons in the highest occupied MO (HOMO) is excited to one of the lowest occupied MO (LUMO) ?

[2+2]

Q. 8 (a) Does the bond order of a molecule in the given electronic state depend on the spin-multiplicity of the state? Justify your answer using the excited electronic configuration of H_2 molecule: $\sigma_g^1\sigma_u^1$.

[2+2]

(b) Using LCAO-MO approximation, express the molecular orbitals σ_g and σ_u of H_2 molecule as linear combination of atomic orbitals $1s_a$ and $1s_b$ centered on atoms a and b.

[2]

(c) Express the normalized ground state wavefunction of H_2 in terms of the molecular orbitals and explicitly written spin-part. Calculate the bond order.

[2+2]

Q. 9 (a) A valence bond of a diatomic molecule is expressed by the following normalized wavefunction:

$\Psi(1,2) = c_{covalent}\,\Psi_{covalent} + c_{ionic}\,\Psi_{ionic}$

(I) Assuming that $\Psi(1,2)$, $\Psi_{covalent}$ and Ψ_{ionic} are normalized, state whether the bond is dominantly covalent or ionic if $c_{covalent} = 0.6$. Calculate the % ionic character of the bond.

[3]

(II) If φ_a and φ_b are the atomic orbitals (centered on the atoms, A and B) involved in the valence bond, express the $\Psi_{covalent}$ in terms of φ_a and φ_b ignoring the normalization constant and the spin-part.

[1]

(b) Can a wavefunction of a two-electron system be antisymmetric with respect to both spatial and spin parts simultaneously? What is the spin multiplicity of a two-electron wavefunction corresponding to symmetric with spin-part? Explain using the spin expressions**.** **[6]**

Q. 10 (a) How many electronic states of an atom are represented by the term ^4G.

[1]

(b) Determine all the possible levels corresponding to this term.

[4]

(c) State the degeneracy of all the levels.

[4]

(d) Assuming the given term to be ground term corresponding to electronic configuration with a less than half-full subshell and the rest of the subshell either full or empty, identify the ground level.

[1]

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