CH 107 End Semester Examination

November 10, 2016 **Time: 2.5 hours** **Full Marks: 24**

Answer all the parts of the same question **together**. Answers should be brief and to the point. Use **only Pen** to write your answers (**including sketches**). Provide arguments to earn full credit.

$h = 6.63\text{x}10^{-34}$ Js; $c = 3\text{x}10^{8}$ ms^{-1}; $m_e = 9.1\text{x}10^{-31}$kg; $e = 6\text{x}10^{-19}$C; $k_B = 1.31 \text{ x } 10^{-23}$ JK^{-1}

Question 1

(a) What is orbital approximation? **1 mark**

(b) In the same graph (with same axes), qualitatively plot the *Radial Distribution Functions* for and orbitals of the same hydrogenic atom (identify each curve). **1 mark**

(c) Given the angular part of an orbital is , what are the values of $\boldsymbol{l}$ and $\boldsymbol{m_l}$? **1 mark**

(d). For which value of is the probability of finding an electron the greatest for the following orbital? **2 marks**

, Where N is a constant.

(e) Using the *negative* linear combination of two 1s orbitals of H-atom (normalization constant), evaluate (*derive*) the *average energy* of the <u>*anti-bonding*</u> molecular orbital in terms of the overlap (***S***), Coulomb (***J***) and Exchange (***K***) integrals, and the internuclear separation, ***R***. **3 marks**

Question 2

(a) Plot the overlap integral (***S***) as a function of internuclear distance (***R***) for *bonding* situation, between two $\boldsymbol{3d_{xz}}$ atomic orbitals where the two atoms approach **(*i*)** along z-direction and **(*ii*)** along y-direction. **2 marks**

(b) For a homonuclear diatomic molecule, qualitatively sketch the contours of *bonding* molecular orbitals (MOs) generated by linear combinations of **(*i*)** $\boldsymbol{3p_x}$ and $\boldsymbol{3p_x}$ and **(*ii*)** $\boldsymbol{3p_y}$ and $\boldsymbol{3p_y}$ atomic orbitals (AOs). Consider the y-axis to be the internuclear axis in both cases. Show three contours lines and signs of MOs for full credit. **2 marks**

(c) **(*i*)** Write the expressions for the delocalized *bonding* MOs of as linear combinations of valence atomic orbitals of appropriate symmetry. *Do not invoke s-p mixing*. Consider z-axis to be internuclear axis. **2+1+0.5 0.5 = 4 marks**

(*ii*) Assign gerade (g) and ungerade (u) symmetries to the MOs, if applicable.

(*iii*) How many spectral bands (or lines) do you expect to see in the *entire* photoelectron (PE) spectrum**?**

(*iv*) If there is more than one band in the *entire* PE spectrum, what will be the ratio of their intensities?

Question 3

(a) Carefully sketch the *contours* of the hybrid orbital: . For full credit, define axis, assign signs, show nuclear position and identify the node(s). **2 marks**

(b) The expressions for the wavefunctions for two rotational levels with quantum numbers and for a rigid rotor are and . Considering the electric field of microwave radiation to be along z–axis, evaluate the transition dipole moment integral for a spectroscopic transition involving these two wavefunctions and hence comment if is allowed or not. (<u>*Hint:*</u> Use only the z-component of the dipole moment). **3 marks**

(c) The equilibrium vibration frequency of a diatomic molecule is 500 cm^{-1} and the anharmonicity constant is 0.05. At 300 K, what is the relative intensity of the hot band (v = 1 to v = 2) transition compared to that of the fundamental (v = 0 to v = 1) transition? The energies of an anharmonic oscillator are cm^{-1}. **2 marks**

(d) The high-resolution infrared spectrum of HCl can provide information about bond strength and two other properties of the molecule. What are these two additional properties? **1 mark**