CH107: Physical Chemistry

20 November, 2013 **End Semester Exam 2 Hours, 30 Minutes**

Answer all questions. Total 32 Marks – Maximum Marks to be awarded 30. Answer each question in a separate page. Calculators may be used. Use PEN to write all answers, including sketches. Read questions carefully and keep answers to-the-point. Provide arguments to earn full credit.

$h=6.626\times10^{-34}$Js; $c=3\times10^{8}$ ms^{-1}; $m_e=9.1\times10^{-31}$kg; $m_p=1.672\times10^{-27}$ kg; $e=6\times10^{-19}$C; 1eV=1.6×10^{-19} J

1A. ψ_1, ψ_2 and ψ_3 are the only possible orthornormaleigenfunctions of an operator $\hat{A}$ and the corresponding eigenvalues are a_1=1, a_2=2 and a_3=3, respectively. When physical observable corresponding to $\hat{A}$ is measured for a particular system, there is a 50 percent chance of obtaining a value a_1 and there are equal probabilities for getting values a_2 and a_3. Write down the correct wavefunction for the system and calculate $\langle \hat{A} \rangle$. Note: Only answers using quantum mechanical concepts will be awarded marks. **2**

1B. Graphene is a single sheet of sp^2 hybridized carbon atoms forming a 2-dimensional array over which theπ-electrons are delocalized and are independent of each other. For a square graphene sheet of side L,calculate the state energies of π-electrons upton_x, n_y = 5 in terms of$h^2/8mL^2=\beta$. Assuming all transitions are equally allowed, sketch the absorption spectrum (Intensity vs. photon-energy) for the possible transitions from all the lower energy states to the [5,5] state. **3**

2A. Given $\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}\cos\theta$, where is the angular probability of finding an electron in $2p_z$ orbital the highest? **2**

2B. What is the magnetic quantum number of $4p_y$ orbital? **1**

2C. Sketch, on the same graph, the radial functions $R(r)$ for $4d_{xy}$ and $4d_{z^2}$ orbitals. **1**

2D. For an excited Helium atom with the electronic configuration $1s^1 2s^1$, write down the Slater determinant(s) for the $M_s = 0$ state. **2**

3A. Write down the Coulomb integral for the Helium atom. What is the physical interpretation of this Coulomb integral? **2**

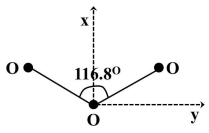
3B. Write spatial VBT and MOT wavefunctions of the H_2molecule. State the primary difference between the two. **3**

4A. What are hybrid and molecular orbitals? Explain. **2**

4B. Calculate the energies of the bonding and antibonding molecular orbitals generated by linear combination of hydrogen-$1s$ and fluorine-$2p_z$ atomic orbitals for various values of overlap integral $S_{12} = 0.1, 0.2$ and 0.6. Given $H_{11} = -13.6eV$, $H_{22} = -18.6eV$ and $H_{12} = -1.75S_{12}\sqrt{(H_{11}.H_{22})}$. Plot $E_{Bonding}$ and $E_{Antibonding}$ as a function of overlap integraland explain the trends. Note: Here H_{11} and H_{22} are constants and are independent of R. **3**

5A. Consider the hybridization of a $2s$ and a $2p_x$ orbital:with $\psi_{hybrid} = C_1 \cdot 2s - C_2 \cdot 2p_x$. , where C_1>0and C_2>0. Qualitatively plot the hybrid orbital. Mark all the regions including axes, signs of the wavefunction, nucleus and nodes. **2**

5B. For O_3 molecule (bond angle 116.8°, see Figure) obtain the normalizedwavefunction of hybrid orbitals for the given geometry, that house (a) bond pairs and (b) lone pair, in terms of $2s$ and $2p$ atomic orbitals on the central oxygen atom. **4**



6A Assuming all the proportionality constants to be identical for all intermolecular interactions, plot the potential energy as function of intermolecular distance for a *fixed* orientation in cases of ion-dipole, dipole-dipole and induced dipole-induced dipole interactions. **2**

6B. Write down the polarizability tensor matrix and explain the meaning of the diagonal and off-diagonal elements therein. Which of the intermolecular interaction(s) depend(s) on the electronic polarizability? **3**