CH107 End Semester Examination

27th February, 2021   **Time: 75 minutes**   **Full Marks: 20**

Q1. Considering Pauli exclusion principle to hold for 4 non-interacting electrons confined in a 1D infinite potential well of length L (V(x) = 0, 0<x<L), the total ground state energy of the system will be   **[1 mark]**

   A. $10h^2/8mL^2$
   B. $4h^2/8mL^2$
   C. $20h^2/8mL^2$
   D. $30h^2/8mL^2$
   E. I won't answer this question

Q2. Consider the following two electron slater determinant.
$$\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$$
In the absence of any external field, the energy degeneracy of the state is:
[1 mark]

   A. 1
   B. 2
   C. 3
   D. 4
   E. I won't answer this question

Q3. Suppose a quantum state of a Hydrogenic system is denoted by
$\psi = -\frac{\sqrt{5}}{3}\phi_{4,2,-1}(x,y,z) + \frac{2}{3}\phi_{3,2,1}(x,y,z)$, where $\phi_{n,l,m}$'s are eigenfunctions of H, L^2, and L_z. Here, ψ is an eigenfunction of   **[1 mark]**

   A. H only
   B. L^2 only
   C. L_z only
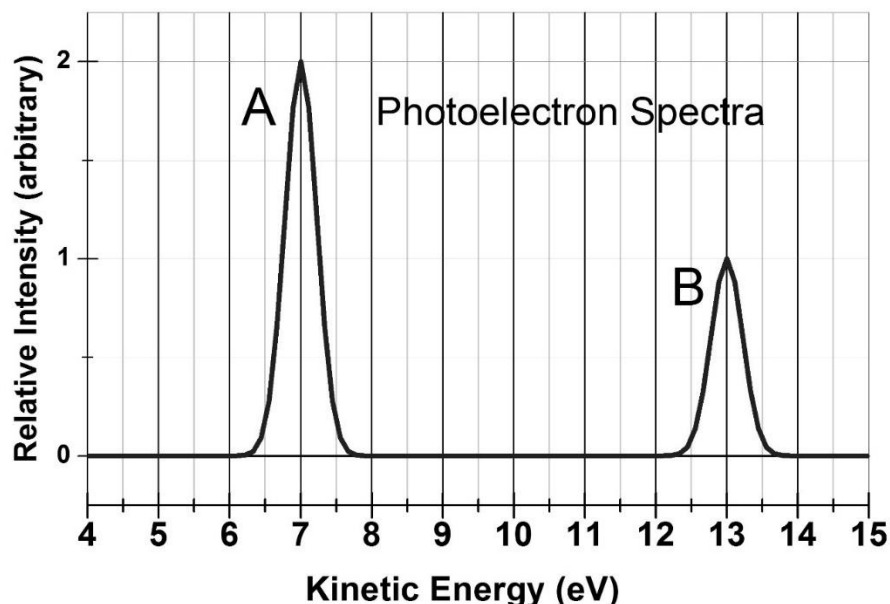   D. L_z and L^2 only
   E. I won't answer this question

Q4. Photoelectron spectrum of a diatomic molecule is shown below. Excitation light of wavelength (λ) 50 nm can eject one electron from each molecular orbital. The ratio of the ionization energies corresponding to peaks A and B is _____. Given, (E in eV) = 1250/(λ in nm).   **[1 mark]**

A. 3:2
B. 2:1
C. 3:4
D. 43:37
E. I won't answer this question

Q5. Which of the following is the correct electronic Hamiltonian for carbon atom?   **[1 mark]**

A. $\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{6}\nabla_i^2 - \sum_{i=1}^{6}\frac{6e^2}{4\pi\varepsilon_0 r_i} + \sum_{i=1}^{6}\sum_{\substack{j=1\\j>i}}^{6}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$

B. $\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{6}\nabla_i^2 + \sum_{i=1}^{6}\frac{6e^2}{4\pi\varepsilon_0 r_i} + \sum_{i=1}^{6}\sum_{\substack{j=1\\j>i}}^{6}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$

C. $\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{6}\nabla_i^2 - \sum_{i=1}^{6}\frac{6e^2}{4\pi\varepsilon_0 r_i} - \sum_{i=1}^{6}\sum_{\substack{j=1\\j>i}}^{6}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$

D. $\hat{H} = +\frac{\hbar^2}{2m_e}\sum_{i=1}^{6}\nabla_i^2 - \sum_{i=1}^{6}\frac{6e^2}{4\pi\varepsilon_0 r_i} + \sum_{i=1}^{6}\sum_{\substack{j=1\\j>i}}^{6}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$

E. I won't answer this question

Q6. A hybrid atomic orbital is expressed as:

$$\phi_h = 0.5\ 4s + 0.707\ 4p_x + 0.5\ d_{x^2-y^2}.$$

ϕ_h is _____ hybrid: **[1 mark]**

  A. sp^3d
  B. spd
  C. sp^3d^2
  D. sp^2d
  E. I won't answer this question

Q7. For a polyatomic system, if you do not consider the formation of non-bonding MOs, the coefficients of individual AOs in the normalized linear combination of AOs can be (select all that apply): **[1 mark]**

  A. non-zero integer
  B. rational number
  C. irrational number
  D. zero
  E. I won't answer this question

Q8. Consider the excited states of H_2 molecule where the two nuclei are separated by $2a_0$, formed by the promotion of 1 electron from HOMO (1σ) to LUMO ($1\sigma^*$). Which of the following statement(s) is/are correct? **[1 mark]**

  A. The singlet excited state corresponds to an ionic form
  B. The triplet excited state corresponds to an ionic form
  C. The singlet excited state corresponds to a covalent form
 D. The triplet excited state corresponds to a covalent form
  E. I won't answer this question

Q9. The linear combination of two $3d_{xz}$ atomic orbitals on two different atoms can form: (select all that apply)　　　　　　　　　　　　　　　**[1 mark]**

    A. π bonding and anti-bonding MOs if 2 atoms approach along z-direction
    B. π bonding and anti-bonding MOs if 2 atoms approach along x-direction
    C. π bonding and anti-bonding MOs if 2 atoms approach along y-direction
    D. δ bonding and anti-bonding MOs if 2 atoms approach along y-direction
    E. δ bonding and anti-bonding MOs if 2 atoms approach along x-direction
    F. δ bonding and anti-bonding MOs if 2 atoms approach along z-direction
    G. I won't answer this question

Q10. Consider BH_3 molecule in the xy-plane, as shown below. A linear combination of H 1s orbitals $(c_1 1s_a + c_2 1s_b + c_3 1s_c)$ forms a bonding/antibonding MO with $2p_x$ orbital of B. The allowed values of coefficients c_1, c_2 and c_3 is/are:　　　　　　　　　　　**[1 mark]**
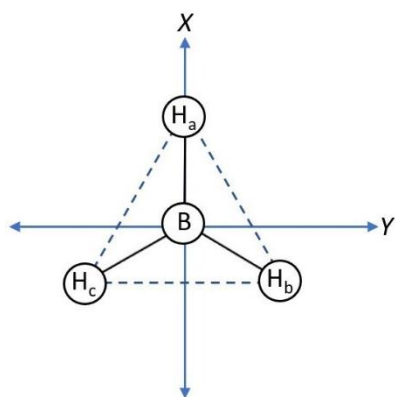
A. $c_1 = \sqrt{\frac{2}{3}}; c_2 = -\sqrt{\frac{1}{6}}, c_3 = -\sqrt{\frac{1}{6}}$

B. $c_1 = \sqrt{\frac{1}{6}}; c_2 = -\sqrt{\frac{2}{3}}, c_3 = \sqrt{\frac{2}{3}}$

C. $c_1 = -\sqrt{\frac{2}{3}}; c_2 = \sqrt{\frac{1}{6}}, c_3 = \sqrt{\frac{1}{6}}$

D. $c_1 = -\sqrt{\frac{2}{3}}; c_2 = \sqrt{\frac{1}{6}}, c_3 = -\sqrt{\frac{1}{6}}$

E. I won't answer this question

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Q11. The force acting between the electron and the nucleus in a Hydrogenic atom is given by $F = -\dfrac{Ze^2}{4\pi\epsilon_0 r^2}$. Evaluate the average (expectation) value of the force (consider $e, \epsilon_0, a_0 = 1$) when the electron is in the 1s state, for **Z = 2**. Given $\psi_{1s} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}\exp(-Zr/a_0)$.   **[2 marks]**

(Write "99999" if you do not want to answer this question.)

Q12. Calculate the electronic energy (in eV) of the Li$^+$ atom in ground state within the orbital approximation. Use $E_{1s} = -122.4\ eV$ and
$\left\langle 1s(1)1s(2)\left|\dfrac{e^2}{4\pi\epsilon_0 r_{12}}\right|1s(1)1s(2)\right\rangle = 57.0\ eV$.   **[2 marks]**
(Write "99999" if you do not want to answer this question.)

Q13. For H$_2$ molecule, assume that the normalized VBT wavefunction of the ground state is given by $\psi(1,2) = 0.95\phi_{covalent} + 0.1\phi_{ionic}$. If $\phi_{covalent}$ and ϕ_{ionic} are normalized covalent and ionic wavefunctions, respectively, the atomic overlap integral S= _____. **Important: Write your answer to 2 decimal places.**   **[2 marks]**
(Write "99999" if you do not want to answer this question.)

Q14. Consider the H$_2^+$ molecule. If the overlap integral is 0.1, the magnitude of energy difference (in eV, correct up to 1st place of decimal) between the bonding and antibonding MOs generated by linear combination of two 2s AOs, is _____.
Given, $\langle\psi_{2sA}|H|\psi_{2sA}\rangle = -4\ eV$,

$\langle\psi_{2sA}|H|\psi_{2sB}\rangle = 15\langle\psi_{2sA}|\psi_{2sB}\rangle\langle\psi_{2sA}|H|\psi_{2sA}\rangle$.   **[2 marks]**
(Write "99999" if you do not want to answer this question.)

Q15. For the molecule CH_2Cl_2, the central carbon atom forms two non-equivalent sets of hybrid orbitals using 2s and 2p AOs. The expressions of the two normalized hybrids which bond with 1s orbitals of the H atoms are: (*Note: for your calculations, make sure you go up to 3rd place of decimal for coefficients*).

$$\phi_{H_A}^{C} = 0.522\psi_s - 0.477\psi_{p_x} - 0.707\psi_{p_y}$$

$$\phi_{H_B}^{C} = 0.522\psi_s - 0.477\psi_{p_x} + 0.707\psi_{p_y}$$

The Cl-C-Cl angle (*in degrees, correct to the 2nd place of decimal*) is _____.
(Write "99999" if you do not want to answer this question.) **[2 marks]**