

CH 107 End-Sem

November 15, 2019

Time: 2 Hours

Full marks: 24

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

Question 1

- (a) Mark these statements as either true or false (no justification necessary): **3.0 marks**
- (i) The greater the bond order of a molecule, the shorter and stronger is the bond.
 - (ii) The orbitals of H-atom are exact eigenfunctions of the electronic Hamiltonian, without any approximations.
 - (iii) The average (expectation) value is always equal to an eigen value.
- (b) Consider an orbital given by the wavefunction, $\psi(r, \theta, \phi) = N \cdot r^3 \sin^2 \theta \cos \theta \sin 2\phi e^{-r/4a_0}$
- (i) Compute the numerical value(s) of r , θ , and ϕ , for which the probability of finding the electron is maximum? **3.0 marks**
 - (ii) Draw the polar plot of $\Theta(\theta)$ against θ for the above wavefunction. Indicate the sign(s) of lobe(s) and position(s) of node(s) in this plot, if any. **2.0 marks**

Question 2

- (a) Show that the bonding and antibonding molecular orbitals for the H_2 molecule formed using linear combination of 1s atomic orbitals are orthogonal to each other. Show your work for full credit. **2.0 marks**
- (b) For the following hybrid orbitals: $\psi_1 = -0.55\psi_{2s} - 0.45\psi_{2p_z} + 0.71\psi_{2p_x}$, and $\psi_2 = -0.45\psi_{2s} - 0.55\psi_{2p_z} + 0.71\psi_{2p_y}$, evaluate, showing your work, **2.0 marks**
- (i) % s character for ψ_1 , and
 - (ii) the bond angle in degrees between the above two hybrid orbitals.
- (c) Construct the labeled MO energy level diagram for linear BeH_2 molecule considering s-p mixing in Be. Write the expressions for the two bonding orbitals in terms of linear combination of the atomic orbitals. Sketch the two corresponding bonding MO's showing proper signs and label them according to their symmetries. **3.0 marks**

Question 3

- (a) Consider two electrons trapped in a 1D box of length L , which interact via Coulomb potential.
- i) Write the complete Hamiltonian of the system. Denote the position of the two electrons by x_1 and x_2 . **1.0 mark**
 - ii) Applying orbital approximation to the above system, write down the total lowest energy wavefunction for this system (including spatial and spin components) wherein both the electrons have α spin. **2.0 marks**
 - iii) Write down the corresponding normalized Slater determinant of the wavefunction in (ii). **1.0 mark**
- (b) For an electron in the α spin state, calculate the value of angle θ in degrees that the spin angular momentum vector makes with the z-axis. Show your work for full credits. **2.0 marks**
- (c) A water molecule at equilibrium geometry is oriented along x-y plane with one O-H bond along x-axis. Consider the 1s atomic orbitals centered on the 2 H atoms, and 2s and 2p orbitals centered on the O atom. **3.0 marks**
- (i) Identify the atomic orbital that will have an overlap integral of 0 with all other atomic orbitals. Provide proper justification for full marks. This orbital is called non-bonding orbital.
 - (ii) Consider the two lone-pair hybrid orbitals on oxygen atom. Find the correct linear combination of these lone pairs that will give the non-bonding orbital in (i). Justify your answer.

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Constants:

$$h = 6.6 \times 10^{-34} \text{ J s}; c = 3 \times 10^8 \text{ m/s}; m_e = 9.1 \times 10^{-31} \text{ kg}; e = 1.6 \times 10^{-19} \text{ C}; k_B = 1.38 \times 10^{-23} \text{ J/K}$$

1. Particle in a 1D box with length L :

$$E_n = \frac{h^2 n^2}{8mL^2}$$

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad 0 < x < L$$

2. Hydrogen atom:

$$\text{Laplacian} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

$$\psi_e(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi)$$

$$\hat{H}_e \psi_e(r, \theta, \phi) = E_n \psi_e(r, \theta, \phi), \text{ with } E_n = -\frac{Z^2 \mu e^4}{8\epsilon_0^2 h^2 n^2} = -\frac{13.6 Z^2}{n^2} \text{ eV, with } n = 1, 2, \dots$$

$$\hat{L}^2 \psi_e(r, \theta, \phi) = \hbar^2 l(l+1) \psi_e(r, \theta, \phi), \text{ with } l = 0, 1, \dots, n-1,$$

$$L_Z \psi_e(r, \theta, \phi) = \hbar m \psi_e(r, \theta, \phi), \text{ with } m = -l, \dots, 0, \dots, l$$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$$

3. Hydrogen molecule:

$$E_\sigma = E_{1s} + \frac{Qe^2}{R_{AB}} - Qe^2 \frac{J+K}{1+S}$$

$$E_{\sigma^*} = E_{1s} + \frac{Qe^2}{R_{AB}} - Qe^2 \frac{J-K}{1-S}$$

$$J = \int d\tau_e |1s_A|^2 / r_{1B}; K = \int d\tau_e 1s_A 1s_B / r_{1B}$$