CH 107 End Semester Examination

November 15, 2017 **Time: 3 Hours** **Full marks: 24**

Answer all parts of the same question **together**. Use **Pen** to write your answers (**including sketches**).

$h = 6.63\times10^{-34}$ Js; $c = 3\times10^{8}$ ms^{-1}; $m_e = 9.1\times10^{-31}$ kg; $e = 6\times10^{-19}$C; $k_B = 1.38\times10^{-23}$ JK^{-1}

Question 1

(a) $\psi_1 = xyz.e^{-\left(\sqrt{x^2+y^2+z^2}/2a_0\right)}$, where, *x*, *y*, z are Cartesian coordinates. a_0 = Bohr radius.

i) Find the expression for the θ–dependent part of ψ_1, i.e. $\Theta(\theta)$. **1.0 mark**

ii) Make a table with values of $\Theta(\theta)$ for the entire range of θ, at intervals of 10°. **1.0 mark**

iii) Construct a plot of $\Theta(\theta)$ against θ in the provided graph paper, using the points in the table made in ii) **1.5 marks**

iv) Indicate the sign(s) of lobe(s) and position(s) of node(s), in this plot, if any. **1.0 mark**

(b) For the following orbital: $\psi = Ne^{-r/a_0}$,

i) Find the normalization constant, *N*. Given: $\int_0^\infty x^n e^{-\alpha x}dx = \frac{n!}{\alpha^{n+1}}$ **1.5 mark**

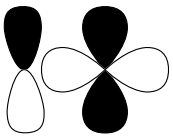
ii) Calculate the average and most probable values of *r*. **2.0 marks**

Question 2

(a) Determine the hybridization of the following orbital: $\psi_{h1} = 0.408\,\phi_{4s} - 0.707\,\phi_{4p_z} + 0.577\,\phi_{4d_z^2}$ **2.0 marks**

(b) Find the angle (degree, correct to the first place of decimal) between the hybrid orbitals: **2.0 marks**

$$\psi_{h2} = -0.55\phi_{2s} + 0.71\phi_{2p_x} - 0.45\phi_{2p_z}; \qquad \psi_{h3} = -0.45\phi_{2s} + 0.71\phi_{2p_y} + 0.55\phi_{2p_z}$$

(c) Plot the overlap integral as a function of internuclear distance for the following:  **1.0 mark**

(d) Explain whether a bonding molecular orbital is the same as a chemical bond or not. **1.0 mark**

(e) Derive an expression for the quantum number (J_{max}) of the energy level of a rigid rotor, which has the maximum population at a given temperature *T*. Energy of the J^{th} rotational level (in cm^{-1}), ϵ_J, is given by: **2.0 marks**

$\epsilon_J = BJ(J+1)$, where $B = \frac{h}{8\pi^2 Ic}$. Here *h* = Planck's constant, *I* = moment of inertia and *c* = speed of light.

Question 3

(a) Consider a BH_3 molecule in *xy* plane, with one of the B–H bonds along the *x*-axis. .

i) Draw the combinations of *1s* orbitals of the H atoms, which can give bonding and antibonding interactions with the 2s orbital of B atom. **0.5 mark**

ii) Draw a schematic energy level diagram for BH_3, using Molecular Orbital Theory. Energies of H atom 1s orbital and B atom 2s orbital are approximately the same. **2.0 marks**

iii) Sketch the photoelectron spectrum of BH_3, as you would expect from this energy level diagram. **1.5 marks**

(b) Write the total wavefunction for the lowest energy electronic state of triangular H_3^+ ion. **1.5 mark**

(c) Equilibrium vibration frequency ($\bar{\nu}_e$) of I_2 is 215 cm^{-1}. Its anharmonicity constant (x_e) is 0.003. Energy of a vibrational level with quantum number *v*, in cm^{-1}, is: $\epsilon_v = \left(v+\frac{1}{2}\right)\bar{\nu}_e - \left(v+\frac{1}{2}\right)^2 x_e\bar{\nu}_e$ **2.5 marks**

Calculate the intensity of the hot band (v=1 → v=2) relative to that of the fundamental (v=0 → v=1) at 300 K.

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