CH 107 End-Semester Examination

November 13, 2018   **Time: 2.5 hours**   **Full Marks: 24**

<u>Answer all the parts of the same question **together**</u>. Answer should be to the point, however, arguments have to be provided for full credit. Use **only Pen** to write your answers (**including sketches**).

An equation sheet is provided along with the question paper

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Question 1

(a) Write the complete Hamiltonian for an *anti*-He atom, with a negatively charged nucleus (*Z=-2*) and two positrons (electron with a positive charge) around it. *The mass of anti-particles to be same as that of the particles.*   1 mark

(b) What are all the possible spinorbitals for H-atom in the ground (lowest energy) state?   1 mark

(c) For what values of $[\theta,\varphi]$ are there angular nodes for the $3d_z^2$ orbital of H-atom? Show your work.   1 mark

(d) What is the value of θ for which the probability of finding an electron is greatest for the $3d_z^2$ orbital? Evaluate.   2 marks

(e) Qualitatively sketch, <u>*in the same plot*,</u> the radial distribution functions of $3d_{x^2-y^2}$ orbital for H and He^+ atoms. Label each curve appropriately.   1 mark

Question 2

(a) Consider the *triangular* H_3^+ with equal H-H bond-lengths. The *spatial part* of the ground state (lowest energy) *1-electron* MO is σ_b. (*No marks for considering a linear H_3^+ molecule*)

  (i)   Write the expression of σ_b in terms of 1s Atomic Orbitals (AOs). *No need for normalization constant.*   1 mark
  (ii)   Sketch the contour plot of σ_b. Show at least three contour lines, signs, nuclei and nodes if any.   1 mark
  (iii) Write the expression for the spin wavefunction of this molecule in the ground state.   1 mark
  (iv)   Express the ground state wavefunction of this molecule as a <u>*single*</u> Slater determinant.   1 mark

(b) Find the normalization constant **N** in terms of the *1-electron* overlap integral (S_{AB}) for the following *2-electron* molecular wavefunction: $\psi(1,2) = N\big[\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)\big]$, where ψ_A and ψ_B are normalized and are real *1-electron* wavefunctions.   2 marks

Question 3

(a) Qualitatively sketch, <u>*in the same plot*,</u> the potential energy curves for H_2, H_2^- and H_2^{2-} as a function of internuclear distance, R_{ab}. Label curves/axes appropriately. *No reasoning is necessary*.   2 marks

(b) The ground state MO of H_2^+ is $\psi = 0.6(1s_A + 1s_B)$. Evaluate the probability of finding the electron in a sphere of radius *$0.1a_0$* around <u>one of the nuclei</u> when the internuclear separation, R_{ab}, is *$2a_0$*. Assume that the value of $1s_A$ and $1s_B$ orbitals remain constant over the sphere of radius $0.1a_0$.   2 marks

(c) In the planar molecule formaldehyde ($H_2C=0$), the H-C-O bond angles are 121°. Evaluate the expressions for the hybrid AOs (in terms of the valence shell AOs of Carbon) which are used for σ-bonding. Consider the geometry where $H_2C=0$ is in *xz* plane with the C-O bond along positive z-axis (***hybrid orbital h_1 is defined along +z***).   2 marks

Question 4

(a) What is Born-Oppenheimer approximation? *Answer in ONE sentence/equation* (no more than two lines!)   1 mark

(b) If one considers the bond in H_2 as an anharmonic oscillator and a non-rigid rotor, will the vibrational (infrared) and rotational (microwave) transitions be allowed for the H_2 molecule? *Justify in one sentence/equation.*   1 mark

(c) For HCl^{35}, the transition (*v=0, J=1*)→(*v=1, J=2*) occurs at 2926 cm⁻¹, while the oscillation (vibrational) frequency (ω_{osc}) is 2886 cm⁻¹. Evaluate the transition energy (in cm⁻¹) of (*v=0, J=1*)→(*v=1, J=2*) for HCl^{37}. Assume (*i*) rigid rotor and harmonic oscillator models, and (*ii*) bond lengths are unchanged for HCl^{35} and HCl^{37}.   2 marks

(d) Predict whether an electronic transition from an occupied 1s-1s σ* (*anti-bonding*) MO to an unoccupied 2s-2s σ* (*anti-bonding*) MO in a homonuclear diatomic molecule is allowed or not? Show your work.   2 marks

------------SEE NEXT PAGE FOR THE EQUATION SHEET------------

Useful constants

h=6.64x10^{-34} Js; c=3x10^8 m/s; m_e=9.1x10^{-31} kg; e=6x10^{-19}C; k_B=1.31x10^{-23} J/K

Useful equations

1. $\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$

2. $\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$

3. $\psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0} \left(3\cos^2\theta - 1\right)$

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

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

6. $L_Z \psi_e(r, \theta, \phi) = \hbar m \psi_e(r, \theta, \phi)$, with $m = -l, ..., 0, ..., l$

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

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

9. $J = \int d\tau_e \frac{|1s_A|^2}{r_{1B}}$

10. $K = \int d\tau_e \frac{1s_A 1s_B}{r_{1B}}$

11. Rotational constant (in cm^{-1}): $B = \frac{h}{8\pi^2 c \mu r_0^2}$

12. Rotational energy: $E_J = BJ(J+1)$

13. Vibrational frequency (in cm^{-1}): $\omega_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

14. Vibrational energy (harmonic oscillator): $E_v = \omega_{osc}(v + 1/2)$

15. Vibrational energy (anharmonic oscillator): $E_v = \omega_{osc}(v + 1/2) - \omega_{osc}x_e(v + 1/2)^2$, $x_e = \omega_{osc}/(4D_e)$

16. Electronic dipole moment operator: $\vec{\mu} = q\vec{r}$