BITS Pilani, Pilani Campus; Semester-I, 2016-17

CHEM G553 : Advanced Physical Chemistry

Mid-semester Test (Closed book)

Duration: 90 min | Max. Total Marks: 60

Date: October 04, 2016 | Time: 4:00 pm-5:30 pm

Useful data: 1 a.m.u.=1.67×10^{-27} kg; h=6.626×10^{-34} Js; ħ=1.054×10^{-34} Js

1. A particle of mass m is confined to a one-dimensional translational motion between x=0 and x=L. **(a)** Plot qualitatively, the wavefunction corresponding to the third excited state. **(b)** Calculate the probability that the particle is located in the region between x=0 to x=L/4 when it is in the third excited state. **(c)** Show that the wavefunctions corresponding to n=1 and n=2 are mutually orthogonal. **[4+4+4]**

2. The microwave spectrum of $^{2}H^{127}I$ consists of a series of lines separated by 193.5 GHz. **(a)** Calculate the bond-length of the molecule using rigid rotor approximation. **(b)** What will be the separation between the spectral lines in the microwave spectrum of $^{1}H^{127}I$? **[6+4]**

3. (a) Show that the total energy of classical harmonic oscillator is conserved. **(b)** Arrange the molecules: ^{1}H-^{35}Cl, ^{1}H-^{37}Cl, ^{2}H-^{37}Cl and ^{2}H-^{35}Cl in the ascending order of their fundamental vibrational frequencies with explanation in no more than two sentences. **[8+4]**

4. Consider the following (unnormalized) orbitals of hydrogen atom and answer the questions:

$$\psi_a=\left(80-\frac{20r}{a_0}+\frac{r^2}{a_0^2}\right)re^{-r/4a_0}\cos\theta; \qquad \psi_b=\left(12-\frac{r}{a_0}\right)r^2e^{-r/4a_0}\sin2\theta\cos\phi$$

$$\psi_c=\left(6-\frac{r}{a_0}\right)re^{-r/3a_0}\sin\theta\sin\phi; \qquad \psi_d=re^{-r/2a_0}\cos\theta$$

(a) Identify the orbital(s) correspond to the energy level $-hcR_H/16$? **[2]**

(b) Identify the orbitals(s) with orbital angular momentum oriented along xy-plane? **[2]**

(c) Identify the orbital(s) with only one radial node. **[2]**

(d) Identify the orbital(s) with only one angular node. **[2]**

(e) Which of the electronic transitions is/are allowed? Why? **[4]**

(i) $\Psi_a\leftarrow\Psi_b$; **(ii)** $\Psi_a\leftarrow\Psi_c$; **(iii)** $\Psi_b\leftarrow\Psi_c$; **(iv)** $\Psi_a\leftarrow\Psi_d$; **(v)** $\Psi_b\leftarrow\Psi_d$;

5. (a) Derive all possible terms arising from the ground state electronic configuration of carbon atom. **(b)** Identify the ground term and state its degeneracy. **(c)** Identify the ground level and state its degeneracy. **[10+2+2]**

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