Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
First Semester 2016-2017
CHEM F213 Physical Chemistry - II
Mid-Semester Examination

Time: 90 minutes | **Date: 05.10.2016 (14.00 - 15.30 hrs.)** | **Max. Marks: 75**

Useful information: h = 6.626×10^{-34} J s, mass of electron (m_e) = 9.109×10^{-31} kg, c = 2.998×10^{8} m s^{-1}, 1 eV = 1.602×10^{-19} J, Charge of electron (e) = 1.602×10^{-19} C, k = 1.381×10^{-23} J k^{-1}, Constant in Wien's displacement law = 2.90×10^{-3} m K

---

1 (a) Calculate the de Broglie wavelength of an electron moving at a speed of 1×10^{6} m s^{-1}. **[2]**

(b) Solar spectrum can be approximated as a black body with λ_{max} at around 500 nm. Estimate the temperature of sun. **[2]**

(c) When a metal (X) is irradiated with light, one finds a stopping potential of 1.83 V for λ = 300 nm and 0.80 V for λ = 400 nm. Using this information answer the following: **[4+2+2]**
(i) Calculate the value of Planck's constant. (ii) Calculate threshold frequency. (iii) Calculate the work-function of the metal (X).

(d) An electron is confined to a linear region with a length of the same order as the diameter of an atom (~ 100 pm). Calculate the minimum uncertainties in it position and speed. **[3]**

2 (a) A certain one-particle, one-dimensional system has wavefunction, $\Psi = ae^{-ibt}e^{-bmx^2/\hbar}$, where a and b are constants and m is the mass of the particle. Find the potential energy function, V, for this system. **[5]**

(b) Evaluate g = $\widehat{A}\ f$ where $\widehat{A}$ = SQRT and f = x^4 **[1]**

(c) Consider the complex functions: $e^{+in\pi x/a}$ and $e^{-in\pi x/a}$, where n is an integer and i = $\sqrt{-1}$. **[4+3]**
(i) Demonstrate that these two functions are degenerate function of kinetic energy operator.
(ii) Show that any linear combination of the complex functions, $e^{+in\pi x/a}$ and $e^{-in\pi x/a}$, is an eigen function of the kinetic energy operator. Determine the eigen value.

(d) Consider $\widehat{A}$ to be a linear operator, such that $\widehat{A}^{\,n}$ = 1 (n is a positive integer). Assume no lower power of the operator equals to 1. Find the eigenvalue of $\widehat{A}$. **[2]**

3 (a) The energy of a particle of mass *m* in one-dimensional box of length l is measured. What are the possible values that can result from the measurement, if at the time of the measurement begins, the particle's state function is: **[2+1]**

(i) $\psi = \left(\frac{30}{l^5}\right)^{1/2} x(l-x) for\ 0 \le x\ \le l$ and (ii) $\psi = \left(\frac{2}{l}\right)^{1/2} \sin\left(\frac{3\pi x}{l}\right) for\ 0 \le x\ \le l$

(b) What would be the form of the time-dependent wavefunction for the particle which is having state function as represented in Part (ii) of previous question, i.e. **[5 × 2]**

$$\psi = \left(\frac{2}{l}\right)^{1/2} \sin\left(\frac{3\pi x}{l}\right) for\ 0 \le x\ \le l$$

(i) Does the time-dependent wavefunction represent stationary state of the system?
(ii) Is it an eigen function of the momentum operator?
(iii) Is it an eigen function of the $\widehat{p_x^2}$ operator?
(iv) If the time-dependent wavefunction is an eigen function of the momentum or $\widehat{p_x^2}$ operator, determine the eigen value(s).

(c) Show that in a rectangular box with sides L_1 = L and L_2 = 2L, there is an accidental degeneracy between the states (n_x=1 and n_y=4) and (n_x=2, n_y=2). **[3]**

(d) A crude treatment of the π-electron of a conjugated molecule regards these electrons as moving in a box of infinite potential wall - where the box length is somewhat more than the length of the conjugated chain. Consider Pauli exclusion principle. For, butadiene CH_2=CH-CH=CH_2, consider the box length as 7.0 Å. Use particle in a box model to estimate the wavelength of light absorbed when a π-electron is excited from the highest-occupied to lowest-vacant box level. **[4]**

4 (a) Determine the value of average momentum of a harmonic oscillator of mass m in one dimension. You may consider that the oscillator is in state n (vibrational quantum number) having wavefunction Ψ_n. **[3]**

(b) Lowering ($\hat{a}$) and raising ($\hat{a}^+$) operators are defined as, $\hat{a} = \frac{i}{2}(p - i\,x)$ and $\hat{a}^+ = \frac{1}{i\sqrt{2}}(p + i\,x)$. Consider an eigen state of simple harmonic oscillator which is having energy E_n. What would be the outcome, if $\hat{a}$ and $\hat{a}^+$ are applied separately to the eigen state having energy E_n? **[3]**

(c) The force constant of $^{79}Br^{79}Br$ is 240 N m^{-1}. Calculate the fundamental vibrational frequency (in cm^{-1}) and the zero point energy of $^{79}Br^{79}Br$. **[4]**

5 (a) Consider the following hydrogen-atom orbital: $\psi = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(Zr/a_0)\exp(-Zr/2a_0)\sin\theta\cos\phi$ **[2+4]**

Answer the following questions:

(i) What would be outcome of the energy operator ($\widehat{H}$)?

(ii) What would be the outcome of $\widehat{L_z}$ operator? Determine the probability of each outcome(s)

(b) Evaluate following integrals, where the functions are hydrogen like wavefunction: **[4]**

i) $\int 2p_1\widehat{L_z}2p_1\,d\tau$ and ii) $\int 3p_0\widehat{L_z}3p_0\,d\tau$

(c) Show that hydrogen atom like wavefunction $2p_x$ and $2p_1$ are not orthogonal. **[2]**

(d) Microwave spectrum of $H^{35}Cl$ consists of a series of equally spaced lines, separated by 6.26×10^{11} Hz. Calculate the bond length of $H^{35}Cl$. [Reduced mass of $H^{35}Cl$ is 1.61×10^{-27} kg] **[3]**

****** End ******