CH107: Physical Chemistry Quiz 19th October, 2013 1.5 hours

Answer each question in a separate page. Calculators may be used. Use PEN to write all answers, including sketches. Read questions carefully and keep answers to-the-point. Provide arguments to earn full credit.

Answer all questions. Total 24 Marks – Will be graded on best 20 marks answered

h=6.626x10^{-34}Js; c=3x10^{8} ms^{-1};m_e=9.1x10^{-31}kg;m_p=1.672x10^{-27} kg; e=6x10^{-19}C; 1eV=1.6x10^{-19} J;k_B=1.308 x 10^{-23} JK^{-1}

1A. Assume the function Bx(a-x) is a solution for a particle in 1-D well potential of length *a* (limit 0-a); B = const.

(i) Does this function satisfy all the necessary conditions to be a well-behaved wavefunction? [1]
(ii) Obtain the energy expression for the particle (of mass *m*) and compare it with the one obtained using trigonometric functions. [2]
(iii) Evaluate the normalization constant for the wavefunction, if it can be normalized at all. [1]

1B. Draw contours of equal probability for (1,2) and (2,2) states of a particle in a 2D square-well potential. [2]

2A. What is the expression for energy of an un-normalized wavefunction? [1]

2B. Does the following wavefunction represent a stationary or a non-stationary state? Explain!

$$\Psi(x,t)=\varphi_1(x)\exp\left(-iE_1t/\hbar\right)+\varphi_2(x)\exp\left(-iE_2t/\hbar\right)$$; **Note: E_1, E_2 are constants [2]**

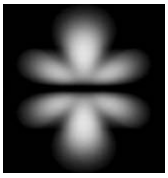
2C. Consider a single electron moving in a circular orbit of radius *r* around a nucleus. What percentage error is introduced in the value of energy of (a) *m* = 0 and (b) *m* = 1 states, if the mass of the electron, m_e is used in the energy expression instead of the reduced mass μ. Note: *m* is the relevant quantum number. [2]

3A. The force acting between the electron and the proton in H-atom is given by $F=-e^2/4\pi\varepsilon_0 r^2$ Calculate the expectation value (in terms of e,ε_0,a_0) of the force when an electron is in 1*s* state. $\psi_{1s}=\frac{1}{\sqrt{\pi}}\left(1/a_o\right)^{3/2}\exp\left(-r/a_o\right)$ **[2]**

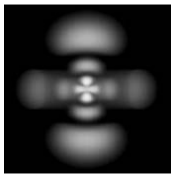
3B. Identify the radial and angular nodes in the following projections of electron density, and hence identify the orbitals.

Note: The vertical direction is the z-axis. [2]

(i)



(ii)



3C. The d orbitals have a nomenclature $d_{z^2},d_{xy},d_{yz},d_{xz},d_{x^2-y^2}$. Show how the following orbital

$\psi_{3d}=\left(\sqrt{2}/81\sqrt{2\pi}\right)\left(1/a_o\right)^{3/2}\left(r/a_o\right)^2\exp\left(-r/3a_o\right).\sin^2\theta\sin 2\phi$ **can be expressed in the form f(r).F(x,y). From the derived expression, identify the nodal line(s)/plane(s)/surface(s) for this 3d orbital. [3]**

4A. What is a spin orbital? [1]

4B. Express the electronic Hamiltonian of Li atom in terms of 1-e Hydrogenic Hamiltonians and other terms. Under what conditions of the Hamiltonian can the corresponding Schrodinger Equation be solved? [3]

4C. What are the possible (acceptable) spin-functions for a 3 electron system? Hint. Use symmetry arguments to nullify spin-functions which distinguish between electrons. [2]

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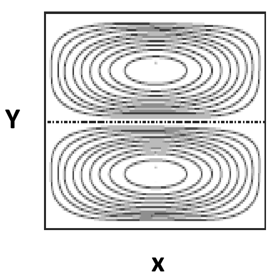
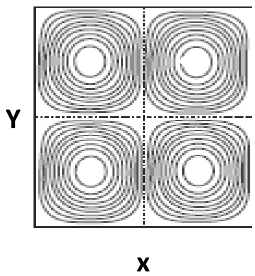
MODEL ANSWERS for the CH-107 Quiz

1A i)	***ψ = Bx(a-x)*** in the limits 0 to a a) ψ = 0 at x=0 and x=a (Vanishes at the boundaries) b) Continuous c) First derivative continuous d) square integrable e) Finite within the limits f) Single valued Point (a) is mandatory + any three from (b-f) **1 MARK**	
1A ii)	$E = \frac{\langle \psi \vert H \vert \psi \rangle}{\langle \psi \vert \psi \rangle} = \frac{\int_0^a Bx(a-x)\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}Bx(a-x)dx}{\int_0^a Bx(a-x)\cdot Bx(a-x)dx}$	**0.5 MARKS**
	$= \frac{\int_0^a Bx(a-x)\frac{-\hbar^2}{2m}(-2B)dx}{\int_0^a Bx(a-x)\cdot Bx(a-x)dx}$	
	$= \frac{\frac{\hbar^2 B^2}{m}\int_0^a x(a-x)dx}{B^2\int_0^a x(a-x)\cdot x(a-x)dx}$	**0.5MARKS**
	$= \frac{\frac{\hbar^2}{m}\int_0^a x(a-x)dx}{\int_0^a x(a-x)\cdot x(a-x)dx} = \frac{\frac{\hbar^2 a^3}{6m}}{\frac{a^5}{30}}$ $= \frac{5\hbar^2}{ma^2}$	**0.5MARKS**
	OR	
	$E = \langle \psi \vert H \vert \psi \rangle = \int_0^a Bx(a-x)\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}Bx(a-x)dx$	**0.5 MARKS**
	$= \int_0^a Bx(a-x)\frac{-\hbar^2}{2m}(-2B)dx$	**0.5 MARKS**
	$= \frac{\hbar^2 B^2}{m}\int_0^a x(a-x) = \frac{\hbar^2 B^2 a^3}{6m}$	**0.5 MARKS**

	Substituting value of B from 1A iii) $E = \frac{5\hbar^2}{ma^2}$ The energy obtained by the trigonometric function for n=1 state is $E = \frac{h^2}{8ma^2}$ in comparison shows same dependence $1/a^2$ 1/a2on length of the box. **OR** The energy expression is not a function of quantum number ***n*** **OR** $H\psi = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}Bx(a-x) = -2B$ not of the form $H\psi = E\psi$, hence energy cannot be evaluated.	 **<u>0.5 MARKS</u>** **<u>0.5 MARKS</u>** **<u>0.5MARKS</u>**
1A iii)	$1 = \langle\psi\|\psi\rangle = \int_0^a Bx(a-x)\cdot Bx(a-x)dx$ $= B^2\int_0^a x(a-x)\cdot x(a-x)dx = \frac{B^2a^5}{30}$ $B = \pm\sqrt{\frac{30}{a^5}}$	**<u>0.5 MARKS</u>** **<u>0.5 MARKS</u>** No marks if ± is not written
1B	  **<u>0.5 MARKS</u>** for the contours **<u>0.5 MARKS</u>** for axis **<u>0.5 MARKS</u>** for not writing +/- signs **<u>0.5 MARKS</u>** for getting nodes correct	

2A	$E = \frac{\langle \psi \| H \| \psi \rangle}{\langle \psi \| \psi \rangle} =$ or $E = \frac{\int_{allspace} \psi^* H \psi d\tau}{\int_{allspace} \psi^* \psi d\tau}$ **1.0 MARK**
2B	For stationary state the probability density should be constant $\psi^*(x,t)\psi(x,t) =$ $= \left[\varphi_1(x)\exp(-iE_1 t/\hbar) + \varphi_2(x)\exp(-iE_2 t/\hbar)\right]^* \left[\varphi_1(x)\exp(-iE_1 t/\hbar) + \varphi_2(x)\exp(-iE_2 t/\hbar)\right]$ **<u>0.5MARKS</u>** $= \left[\varphi_1(x)\exp(iE_1 t/\hbar) + \varphi_2(x)\exp(iE_2 t/\hbar)\right]\left[\varphi_1(x)\exp(-iE_1 t/\hbar) + \varphi_2(x)\exp(-iE_2 t/\hbar)\right]$ $= \varphi_1^2 + \varphi_2^2 + \varphi_1\varphi_2 \exp(i(E_1 - E_2)t/\hbar) + \varphi_1\varphi_2 \exp(i(E_2 - E_1)t/\hbar)$ **<u>1.0 MARK</u>** $\psi^*\psi$ is not independent of time. **<u>0.5MARKS</u>** **OR** $i\hbar \frac{\partial}{\partial t}\psi = i\hbar \frac{\partial}{\partial t}\left[\varphi_1(x)\exp(-iE_1 t/\hbar) + \varphi_2(x)\exp(-iE_2 t/\hbar)\right]$ $= E_1\varphi_1(x)\exp(-iE_1 t/\hbar) + E_2\varphi_2(x)\exp(-iE_2 t/\hbar)$ **<u>0.5 MARKS</u>** $\neq E_1(\text{or } E_2)\cdot\psi(x,t)$ **<u>1.0 MARK</u>** ψ is not a eigenfunction of the Energy operator **<u>0.5MARKS</u>**

2C	$-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\psi + V\psi = E\psi$ **Particle on a ring Schrodinger Equation** $-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\psi = (E-V)\psi$ $\psi = A\exp(im\phi)$ **Solution for the Schrodinger Equation** $\frac{\partial^2}{\partial\phi^2}\psi = -m^2 \cdot A\exp(im\phi)$ $\quad (E-V) = \frac{\hbar^2 m^2}{2I}$ $(E-V)_1 = \frac{\hbar^2 m^2}{2r^2 m_e}$ $\quad (E-V)_2 = \frac{\hbar^2 m^2}{2r^2 \mu}$ E1 **<u>0.5 MARKS</u>** E2 **<u>0.5 MARKS</u>** Error for m=0 state 0/0 Not Defined or 0 **<u>0.5 MARKS</u>** Error for m=1 state $(E_1 - E_2)/E_2 = \left(\frac{1}{\mu} - \frac{1}{m_e}\right)\Big/\frac{1}{m_e} = m_e/(m_e + m_p) \approx m_e/m_p = 0.054\%$ **<u>0.5 MARKS</u>**

3A

$$\langle F\rangle = \langle \psi_{1s}|F|\psi_{1s}\rangle = \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\exp(-r/a_0)\cdot\frac{e^2}{4\pi\varepsilon_0 r^2}\cdot\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\exp(-r/a_0)r^2dr\cdot\sin\theta\cdot d\theta\cdot d\phi =$$

$$=\frac{e^2}{4\pi^2\varepsilon_0 a_0^3}\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\exp(-2r/a_0)\cdot\frac{1}{r^2}\cdot r^2dr\cdot\sin\theta\cdot d\theta\cdot d\phi$$

$$=\frac{e^2}{4\pi^2\varepsilon_0 a_0^3}\int_{r=0}^{\infty}\exp(-2r/a_0)dr\int_{\theta=0}^{\pi}\sin\theta\cdot d\theta\int_{\phi=0}^{2\pi}d\phi$$

$$\frac{e^2}{4\pi^2\varepsilon_0 a_0^3}\cdot 4\pi\int_{r=0}^{\infty}\exp(-2r/a_0)dr$$

$$=\frac{e^2}{\pi\varepsilon_0 a_0^3}\left(\frac{-a_0}{2}\right)=\frac{-e^2}{2\pi\varepsilon_0 a_0^2}$$

I MARK for right expression (line 1) and **1 MARK** for Right Answer

3B

Angular nodes = ***l***
Radial nodes = ***n-l-1***

i) Angular nodes = 3 $\Rightarrow$ ***l =3***
Radial Nodes = 0 $\Rightarrow$ ***n=4*** **0.5 MARKS**

4f orbital **0.5 MARKS**

ii) Angular nodes = 2 $\Rightarrow$ ***l =2***
Radial Nodes = 2 $\Rightarrow$ **n=5** **0.5 MARKS**
5d orbital **0.5 MARKS**

3C	$\psi_{3d} = \dfrac{\sqrt{2}}{81\sqrt{2\pi}}\left(\dfrac{1}{a_0}\right)^{3/2}\left(\dfrac{r}{a_0}\right)^2 \exp\left(-r/3a_0\right)\sin^2\theta\sin 2\phi$ $= \dfrac{\sqrt{2}}{81\sqrt{2\pi}}\left(\dfrac{1}{a_0}\right)^3 \cdot \exp\left(-r/3a_0\right) r^2 \sin^2\theta \cdot 2\sin\phi\cos\phi$ $= \dfrac{2\sqrt{2}}{81\sqrt{2\pi}}\left(\dfrac{1}{a_0}\right)^3 \cdot \exp\left(-r/3a_0\right) \cdot r\sin\theta\cos\phi \cdot r\sin\theta\sin\phi$ $= \dfrac{2\sqrt{2}}{81\sqrt{2\pi}}\left(\dfrac{1}{a_0}\right)^3 \cdot \exp\left(-r/3a_0\right) \cdot x \cdot y$ $= \dfrac{2\sqrt{2}}{81\sqrt{2\pi}}\left(\dfrac{1}{a_0}\right) \cdot f(r) \cdot F(x,y)$ $\psi = 0 \Rightarrow F(x,y) = 0$ X=0; YZ plane is the node Y=0; XZ plane is the node	**1.0 MARK** **1.0 MARK** **0.5 MARK** **0.5 MARK**

4A	The one electron wavefunction (or orbital) which includes the spin wavefunction is called spin orbital OR $\Psi = \psi_{space} \cdot \phi_{spin}$ **<u>1.0 MARK</u>**
4B	$H = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2+\nabla_2^2+\nabla_3^2\right) - \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}+\frac{1}{r_3}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right)$ $H = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r_2} - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r_3} + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right)$ $H = H_{1e}(1) + H_{1e}(2) + H_{1e}(3) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right)$ All three correct **<u>1 MARK</u>**; 2 correct **<u>0.5 MARKS</u>**; 1 Correct **<u>No MARKS</u>** (Line-1) Expressing in terms of one electron Hamiltonian **<u>1 MARK</u>** (Line-3) Directly writing in terms of one electron Hamiltonian **<u>2 MARK</u>** (Line-3) The electron-electron repulsion terms have to be modified in terms of Effective Nuclear Charge **<u>1 MARK</u>** The electron-electron repulsion terms have to neglected or variable separable form **<u>0.5 MARKS</u>**

4C	$\phi_1 = \alpha(1)\alpha(2)\alpha(3)$	**<u>0.5 MARKS</u>**
	$\phi_2 = \sqrt{1/3}\left[\alpha(1)\alpha(2)\beta(3)+\alpha(1)\beta(2)\alpha(3)+\beta(1)\alpha(2)\alpha(3)\right]$	**<u>0.5 MARKS</u>**
	$\phi_3 = \sqrt{1/3}\left[\alpha(1)\beta(2)\beta(3)+\beta(1)\alpha(2)\beta(3)+\beta(1)\beta(2)\alpha(3)\right]$	**<u>0.5 MARKS</u>**
	$\phi_4 = \beta(1)\beta(2)\beta(3)$	**<u>0.5 MARKS</u>** Normalization constant not necessary