Chem 20A-1

2nd MIDTERM, November 19, 2012

NAME SOLUTIONS

DISCUSSION SECTION________________

Problem	Points possible	Points scored
1(a)	15	
1(b)	5	
1(c)	5	
1(d)	5	
2	20	
3	20	
4(a)	5	
4(b)	5	
4(c)	5	
4(d)	5	
4(e)	10	
	100	

BE SURE TO SHOW ALL YOUR WORK, I.E., MAKE CLEAR THE REASONING BEHIND YOUR SOLUTION TO EACH PROBLEM.

BE CAREFUL TO WRITE UNITS FOR EVERY QUANTITY WITH DIMENSIONS, WITHOUT EXCEPTION.

A COLLECTION OF USEFUL FACTS AND EQUATIONS, ARE PROVIDED ON THE LAST PAGE OF THE EXAM.

1. (30 points) Consider a mass m confined in a one-dimensional (1D) box of length L, *centered at x=0*. (NOTE: This system is identical to the one we considered at length in class, except for the allowed x-values ranging from $-L/2$ to $+L/2$, rather than from 0 to L. Recall that the allowed wavefunctions and energies were identified by finding solutions to the Schroedinger equation

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

that satisfy the boundary conditions, i.e., $\psi(x)$ must vanish at the boundaries of the box.

(a) (15 pts) Find the allowed wavefunctions and energies of this "new" particle-in-a-box problem, i.e., a particle confined in 1D between the boundaries $x=-L/2$ and $x=+L/2$. (YOU DON'T HAVE TO BOTHER HERE WITH EVALUATING THE NORMALIZATION CONSTANT.)

The solutions are $A\sin kx$ and $B\cos kx$, because

$$-\frac{h^2}{8\pi^2 m}\underbrace{\frac{d^2}{dx^2}\boxed{B\cos kx}}_{-Bk^2\cos kx} = \underbrace{+\frac{h^2k^2}{8\pi^2 m}}_{E}\boxed{B\cos kx}$$

and similarly for $A\sin kx$

BUT, to satisfy $\underbrace{\text{the boundary conditions}}_{\psi(\pm\frac{L}{2})=0}$, we need

$$\cos\left(-\frac{kL}{2}\right) = \cos\left(\frac{kL}{2}\right) = 0, \text{ i.e., } \frac{kL}{2} = \frac{n_{odd}\,\pi}{2} = \frac{2n+1}{2}\pi, \quad n = 0, 1, 2, 3, \ldots$$

OR

$$\sin\left(-\frac{kL}{2}\right) = -\sin\left(\frac{kL}{2}\right) = 0, \text{ i.e., } \frac{kL}{2} = \frac{n_{even}\,\pi}{2} = \frac{2n}{2}\pi, \quad n = 1, 2, 3, \ldots$$

Thus, smallest value of k -- and hence smallest E -- is $\frac{\pi}{L}$ ($\leftrightarrow B\cos\frac{\pi x}{L}$); next smallest is $\frac{2\pi}{L}$ ($\leftrightarrow A\sin\frac{2\pi x}{L}$); next is $\frac{3\pi}{L}$ ($\leftrightarrow B\cos\frac{3\pi x}{L}$); and next is $\frac{4\pi}{L}$ ($\leftrightarrow A\sin\frac{4\pi x}{L}$)...

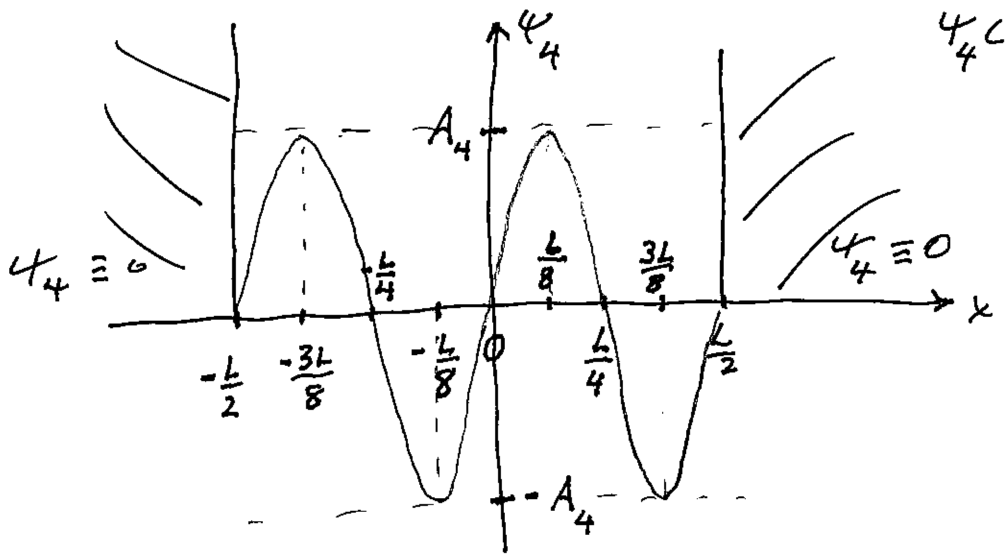
Corresponding energies are $\frac{h^2}{8\pi^2 m}k_n^2$, with

$$k_1 = \frac{\pi^2}{L^2},\ k_2 = \frac{2^2\pi^2}{L^2},\ k_3 = \frac{3^2\pi^2}{L^2},\ \ldots,$$

$$\text{i.e., } E_n = \frac{h^2}{8mL^2}n^2, \quad n = 1, 2, 3, \ldots$$

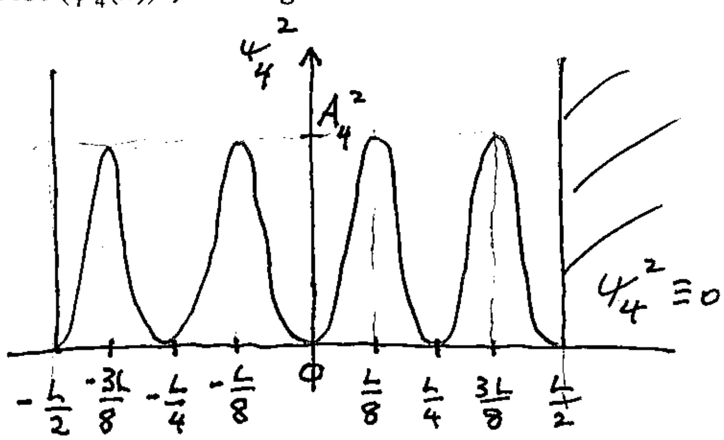
(b) (5 pts) The wavefunction corresponding to the 4[th]-lowest allowed energy of this system has the form $\psi_4(x) = A_4 \sin\left(\frac{4\pi x}{L}\right)$, where A_4 is the normalization constant. Plot $\psi_4(x)$, labeling the x-values where $\psi_4(x)$ vanishes, and where it has extrema (maxima and minima).

$\psi_4(x) = A_4 \sin \frac{4\pi x}{L}$



(c) (5 pts) Plot $(\psi_4(x))^2$, labeling the x-values where it vanishes, and where it has extrema.

$(\psi_4(x))^2 \equiv P_4(x) = A_4^2 \sin^2 \frac{4\pi x}{L}$



(d) (5 pts) What are the most probable positions? And the least probable?

where $P_4(x) = \max = A_4^2$

where $P_4(x) = \min = 0$

Thus $x = -\frac{3L}{8}, -\frac{L}{8}, +\frac{L}{8}$ & $+\frac{3L}{8}$

Thus $x = -\frac{L}{2}, -\frac{L}{4}, 0, +\frac{L}{4}$ & $+\frac{L}{2}$

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2. (20 points) Consider an electron in the $2py$ state of He^{+}. Calculate the probability of finding it in a small volume $(10^{-14}\text{m})^3 \equiv v$ centered at the point $r, \theta, \varphi = a_o, \pi/2, \pi/2$, ***relative to*** the probability of finding it in a small volume $v = (10^{-14}\text{m})^3$ centered at the point $r, \theta, \varphi = a_o/4, \pi/4, \pi/4$.

$$P_{\nu,\,\text{at }\vec{r}} = \int_{\nu,\,\text{at }\vec{r}} \left(\psi_{2p_y}(\vec{r})\right)^2 dV \approx \underbrace{\left(\psi_{2p_y}(\vec{r})\right)^2}_{Y_{py}^2\, R_{2p}^2} \nu$$

$$= \frac{\cancel{3}}{\cancel{4}\pi} \sin^2\theta \sin^2\varphi \, \frac{1}{\cancel{24}} \frac{\cancel{2}^{3}}{a_o^3} \left(\frac{\cancel{2}r}{a_o}\right)^2 e^{-2r/a_o}$$

Thus

$$\frac{P_{\nu,\,\text{at } a_o, \frac{\pi}{2}, \frac{\pi}{2}}}{P_{\nu,\,\text{at } \frac{a_o}{4}, \frac{\pi}{4}, \frac{\pi}{4}}} = \frac{\frac{1}{\cancel{\pi}}\, 1^2\, 1^2\, \cancel{\frac{1}{a_o^3}}\, 1^2\, e^{-2}}{\frac{1}{\cancel{\pi}} \left(\frac{1}{\sqrt{2}}\right)^2 \left(\frac{1}{\sqrt{2}}\right)^2 \cancel{\frac{1}{a_o^3}} \left(\frac{1}{4}\right)^2 e^{-1/2}} = \frac{e^{-2}}{\frac{1}{64} e^{-0.5}} = 14$$

3. (20 points) What is (i.e., *derive*) the most probable distance for the 1s electron in the Li^{2+} ion?

$Z = 3$

$$\psi_{1s}^{Li^{2+}}(\vec{r}) = \left(\frac{1}{4\pi}\right)^{1/2} 2 \left(\frac{3}{a_o}\right)^{3/2} e^{-3r/a_o}$$

$$\left(\psi_{1s}(\vec{r})\right)^2 = \frac{1}{\cancel{4}\pi} \cancel{4} \frac{27}{a_o^3} e^{-6r/a_o}$$

$$P_{1s}(r)\,dr = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} \left(\psi_{1s}(\vec{r})\right)^2 r^2\,dr\,\sin\theta\,d\theta\,d\varphi$$

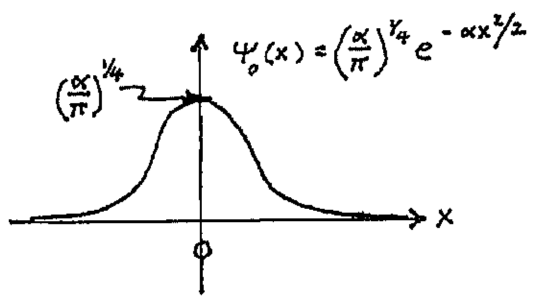
$$= \frac{1}{\cancel{\pi}}\frac{27}{a_0^3} e^{-6r/a_0} r^2\,dr \underbrace{\int_0^{\pi} \underbrace{\sin\theta\,d\theta}_{d(-\cos\theta)}}_{-\cos\theta\big|_0^{\pi} = 2} \underbrace{\int_0^{2\pi} d\varphi}_{2\cancel{\pi}}$$

$$= \underbrace{\frac{108}{a_0^3} r^2 e^{-6r/a_0}}_{P_{1s}(r)} dr$$

$$\frac{dP}{dr} = \frac{108}{a_0^3}\left[2\cancel{r}\,\cancel{e^{-6r/a_0}} + r\cancel{r}\,\cancel{e^{-6r/a_0}}\left(-\frac{6}{a_0}\right)\right] = 0$$

Thus $\boxed{r_{mp} = \frac{a_0}{3}}$

4. (30 points) The figure below is a plot of the lowest-energy, normalized, allowed wavefunction, $\psi_o(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$, of a mass m moving in one dimension (x) under the influence of a force F=-kx. Here x is the displacement of the particle from the origin, and $\alpha = \frac{2\pi}{h}(km)^{1/2}$. Note that the *force F=-kx* corresponds to the *potential energy* $\frac{1}{2}kx^2$.



(a) (5 pts) What are the dimensions (or, if you prefer, the SI units) of k?

$$[k] = \left[\frac{F}{x}\right] = \frac{kg\,m\,s^{-2}}{m} = kg\,s^{-2} \left(\leftrightarrow \frac{N}{m} \leftrightarrow \frac{J}{m^2}\right)$$

dimensions of

(b) (5 pts) What are the dimensions (units) of α?

$$[\alpha] = \left[\frac{(km)^{1/2}}{h}\right] = \frac{(kg\, s^{-2}\, kg)^{1/2}}{\underbrace{J \cdot s}_{kg\, m^2 s^{-1}}} = \frac{kg\, s^{-1}}{kg\, m^2 s^{-1}} = \frac{1}{m^2}$$

CHECK: αx^2 dimensionless $\Rightarrow [\alpha] = \left[\frac{1}{x^2}\right] = \frac{1}{m^2}$ ✓

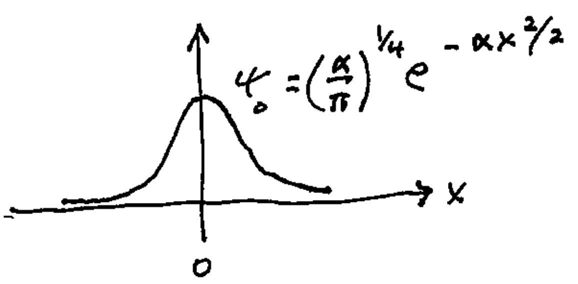
(c) (5 pts) What are the dimensions of $\psi_o(x)$? And of $(\psi_o(x))^2$? And of $(\psi_o(x))^2 dx$?

$$[\psi_0(x)] = [\alpha^{1/4}] = (m^{-2})^{1/4} = \frac{1}{m^{1/2}}$$

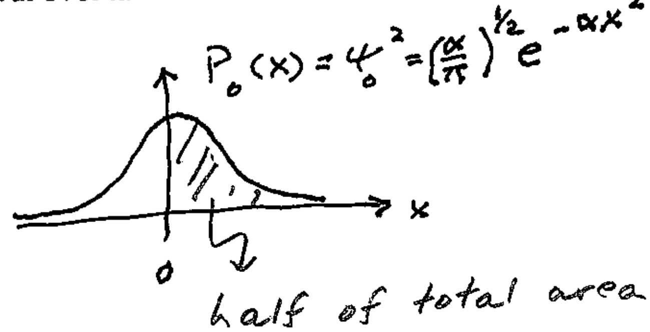
$$[\psi_0^2(x)] = \frac{1}{m}$$

$$[\underbrace{(\psi_0(x))^2 dx}_{\text{probability}}] = \text{dimensionless}$$

(d) (5 pts) What is the probability of finding a positive value for x? Write an explicit expression for this probability as a definite integral over x.



$\Longrightarrow$



$P_{x>0} = \int_0^{\infty} P_0(x)\, dx = \frac{1}{2}$, because, from symmetry and normalization,

$$\int_{-\infty}^{+\infty} P_0(x) = \int_{-\infty}^{+\infty} (\psi_0(x))^2 dx = 1 = 2\int_{0}^{\infty} P_0(x)\, dx$$

(e) (10pts) Using the fact that $\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{2} \cdot \frac{1}{\alpha^{3/2}}$, calculate the average potential energy in the lowest allowed state, $\left(\frac{1}{2}kx^2\right)_{average,\, in\, ground\, state} = \int_{-\infty}^{+\infty}\left(\frac{1}{2}kx^2\right)\psi_o^2(x)dx$, and compare it the total energy, $\frac{1}{2}h\nu = \frac{1}{2}h(\frac{1}{2\pi}\sqrt{\frac{k}{m}})$.

$$\overline{PE} = \int_{-\infty}^{+\infty}\left(\frac{1}{2}kx^2\right)\underbrace{\left(\psi_o(x)\right)^2}_{\left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha x^2}} dx$$

$$= \frac{1}{2}k\left(\frac{\cancel{\alpha}}{\cancel{\pi}}\right)^{1/2} \underbrace{\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx}_{\frac{\cancel{\sqrt{\pi}}}{2}\frac{1}{\alpha}\frac{1}{\cancel{\alpha^{1/2}}}} = \frac{1}{4}\frac{k}{\alpha} = \frac{h}{8\pi}\sqrt{\frac{k}{m}}$$

$$\alpha = \frac{2\pi}{h}(km)^{1/2}$$

Thus

$$\overline{PE} = \frac{1}{4}h\underbrace{\left(\frac{1}{2\pi}\sqrt{\frac{k}{m}}\right)}_{\nu} = \frac{1}{2}\left[\underbrace{\frac{1}{2}h\nu}_{\text{total energy}}\right]$$

$$\overline{PE} = \frac{1}{2}\overline{E}$$