Chem. 562
Fall 2009

Name ________________________

Please put your name on all pages.

# Exam 1

1. This exam contains 6 pages of questions and instructions, two pages of equations and integrals, a page of tables, a periodic table, and a set of constants and conversion factors.
2. Show your work and make your reasoning clear.
3. You have 1.5 hours to work on the exam.

1.________/25

2.________/25

3.________/25

4.________/25

Total ______/100

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1a. (13 pts.) Evaluate the commutator $[\hat{A}, \hat{B}]\psi$ for the two operators

$$\hat{A} = \frac{d}{dx} + x \text{ and } \hat{B} = \frac{d}{dx} - x .$$

$$[\hat{A},\hat{B}]\psi = (\hat{A}\hat{B} - \hat{B}\hat{A})\psi$$

$$\hat{A}\hat{B}\psi = \left(\frac{d}{dx} + x\right)\left(\frac{d}{dx} - x\right)\psi$$

$$= \left(\frac{d}{dx} + x\right)(\psi' - x\psi)$$

$$= \psi'' + x\psi' - \frac{d}{dx}(x\psi) - x^2\psi$$

$$= \psi'' + \cancel{x\psi'} - \psi - \cancel{x\psi'} - x^2\psi$$

$$\hat{B}\hat{A}\psi = \left(\frac{d}{dx} \mp x\right)\left(\frac{d}{dx} \pm x\right)\psi$$

$$= \left(\frac{d}{dx} - x\right)(\psi' + x\psi)$$

$$= \psi'' - x\psi' + \frac{d}{dx}(x\psi) - x^2\psi$$

$$= \psi'' - \cancel{x\psi'} + \psi + \cancel{x\psi'} - x^2\psi$$

$$[\hat{A},\hat{B}]\psi = \psi'' - \psi - x^2\psi - (\psi'' + \psi - x^2\psi)$$

$$= -2\psi$$

1b. (12 pts) Use your result from above to determine the uncertainty principle for these two operators using $\Delta\hat{A}\Delta\hat{B} \geq \frac{1}{2}\left|\left\langle\left[\hat{A},\hat{B}\right]\right\rangle\right|$.

$$\Delta\hat{A}\Delta\hat{B} \geq \frac{1}{2}\left| \int \psi^* \underbrace{[\hat{A},\hat{B}]}_{-2} \psi \, dx \right|$$

$$\geq \frac{1}{2}|-2|$$

$$\geq 1$$

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2a. (5 pts.) Using the two eigenfuctions $\psi_m$ and $\psi_n$, mathematically define orthonormal.

$$\int \psi_m^* \psi_n \, dx = \delta_{nm} \qquad \delta_{nm} = \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases}$$

2b. (10 pts.) Prove that the wavefunctions of a Hermetian operator $\hat{A}$ are orthogonal. The definition of a Hermitian operator is

$$\int \psi_m^* \hat{A} \psi_n dx = \int \psi_n \hat{A}^* \psi_m^* dx .$$

Start by using the equations

$$\hat{A}\psi_n = a_n \psi_n \quad \text{and} \quad \hat{A}\psi_m = a_m \psi_m .$$

$\times \int \psi_m^*$ $\qquad\qquad$ $^* \times \int \psi_n$

$$\int \psi_m^* \hat{A} \psi_n = a_n \int \psi_m^* \psi_n \qquad \int \psi_n \hat{A}^* \psi_m^* = a_m^* \int \psi_n \psi_m^*$$

subtract

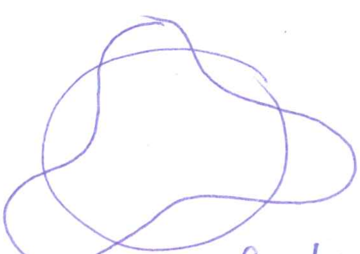
$$\underbrace{\int \psi_m^* \hat{A} \psi_n - \int \psi_n \hat{A}^* \psi_m^*}_{=0 \text{ because Hermetian}} = (a_n - a_m^*) \int \psi_n \psi_m^*$$

$$(a_n - \cancel{a_m}\, a_m^*) \int \psi_n \psi_m^* = 0$$

if non-degenerate, divide by $(a_n - a_m^*)$

$$\therefore \int \psi_n \psi_m^* = 0 \quad \text{e.g. orthogonal.}$$

2c. (10 pts.) Use the boundary conditions for the particle-on-a-ring wavefunction $\psi(\varphi)$ to derive the allowed quantum numbers $m_l = 0, \pm 1, \pm 2, \ldots$



wavefunction must repeat every $2\pi$.

$$\psi(\phi) = \psi(\phi + 2\pi) \qquad 1 = e^{im2\pi}$$

$$e^{im\phi} = e^{im(\phi + 2\pi)} \qquad \therefore m = 0, \pm 1, \pm 2 \ldots$$

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3. (25 pts.) Consider the particle-in-a-box for a box from x = 0 to x = L that has the eigenfunctions.

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right).$$

3a. (5 pts) Normalize the wavefunction $\Psi(x) = c\psi_1(x) + c\psi_2(x)$, which is a particle with equal probability of being in n=1 and n=2.

$$\int \Psi^* \Psi \, dx = 1 = \int (c\psi_1^* + c\psi_2^*)(c\psi_1 + c\psi_2)\, dx$$

$$= c^2 \left[ \underbrace{\int \psi_1^* \psi_1}_{1} + \underbrace{\int \psi_1^* \psi_2}_{0} + \underbrace{\int \psi_2^* \psi_1}_{0} + \underbrace{\int \psi_2^* \psi_2}_{1} \right]$$

$$= 2c^2 \qquad \therefore \; c^2 = \frac{1}{\sqrt{2}}$$

3b. (10 pts) Calculate <p$^2$> for $\psi_1(x)$.

$$\sqrt{\frac{2}{L}}$$

$$\langle p^2 \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)\left(-i\hbar \frac{d}{dx}\right)\left(-i\hbar \frac{d}{dx}\right) \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2}{L}(-\hbar^2) \int_0^L \sin\left(\frac{n\pi x}{L}\right) \frac{d^2}{dx^2} \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2}{L}(-\hbar^2) \int_0^L \sin\left(\frac{n\pi x}{L}\right)\left(-\frac{n^2\pi^2}{L^2}\right) \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2n^2\pi^2\hbar^2}{L^3} \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{2n^2\pi^2\hbar^2}{L^3}\left[\frac{x}{2} - \frac{L^2}{4n^2\pi^2}\sin\left(\frac{2n\pi x}{L}\right)\right]_0^L$$

$$= \frac{\cancel{2} n^2\pi^2\hbar^2}{L^{\cancel{3}2}}\left[\frac{\cancel{L}}{\cancel{2}}\right] = \frac{n^2\pi^2\hbar^2}{L^2}$$

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3c. (5 pts) Consider a box that instead has walls at x = –L and x = +L. Draw the two lowest eigenstates $\psi_1(x)$ and $\psi_2(x)$.

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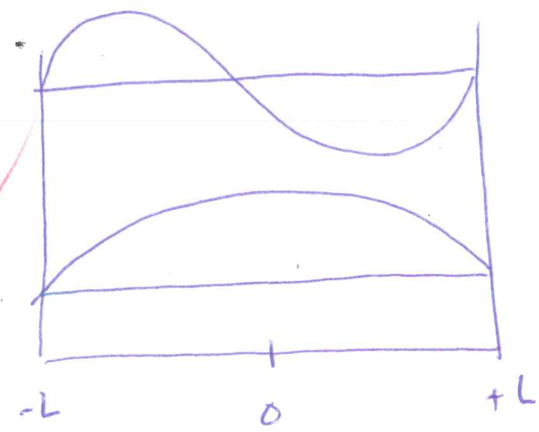


3d. (5 pts) Derive or write the eigenfunction $\psi_1(x)$ that you drew in question 3c above.

since the origin has shifted + box is twice as large.

$$\psi_1(x) = \sqrt{\frac{2}{2L}} \cos\left(\frac{n\pi x}{2L}\right)$$

4. (25 pts) A particle exists in a rectangular box with infinitely high potentials on all sides. Along the x-dimension the box has straight walls separated by a distance L. Along the y-dimension, the box has curved walls with a potential $V(y)=ky^2/2$.

4a. (5 pts) Write down the 2D Hamiltonian for this system.

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} + \frac{d}{dy^2}\right) + \frac{1}{2}ky^2$$

4b. (10 pts) Write down the 2D eigenfunctions, eigenenergies, and quantum numbers for this particle.

Because the $\hat{H}$ is seperable.

$$\psi_{n,v}(x,y) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right) N_v H_v\left(\frac{y}{\alpha}\right) e^{-\left(\frac{y}{\alpha}\right)^2/2}$$

4c. (10 pts) Draw the wavefunction as a contour plot for the particle that has been excited by <u>one</u> quantum along x but is in its <u>ground</u> state along y. Also draw the projections of the wavefunction along the x and y axes.