**NAME:** SLEEPY **CHEMISTRY 444, SPRING, 2007 (07S)**

**Circle Section Number: 10 11 80** **Examination 2, April 14, 2007**

*Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.*

| DO NOT WRITE IN THIS SPACE | |
|---|---|
| p. 1 | /10 |
| p. 2 | /15 |
| p. 3 | /10 |
| p. 4 | /15 |
| p. 5 | /15 |
| p. 6 | /10 |
| p. 7 | /10 |
| p. 8 | /15 |
| ============= | |
| p. 9 | /5 |
| (Extra credit) | |
| ============= | |
| TOTAL PTS | |
| | /100 |

**1. (10 points)** The ground state wave function for the one-dimensional harmonic oscillator is

$$\Psi_0(x) = A\exp\left[-\frac{x^2}{2\alpha^2}\right]$$

where *x* is the deviation from the equilibrium position. Normalize this wave function.

**The normalization is the requirement that the following integral be equal to 1.**

$$\int_{-\infty}^{+\infty}\Psi_0^*(x)\Psi_0(x)dx = 1$$

**Substituting the function into this equation gives**

$$\int_{-\infty}^{+\infty}A^*\exp\left(-\frac{x^2}{2\alpha^2}\right)A\exp\left(-\frac{x^2}{2\alpha^2}\right)dx = 1$$

$$|A|^2\int_{-\infty}^{+\infty}\exp\left(-\frac{x^2}{\alpha^2}\right)dx = 1$$

**Since this is an even function, one may replace the integral in the following manner**

$$|A|^2\,2\int_{0}^{+\infty}\exp\left(-\frac{x^2}{\alpha^2}\right)dx = 1$$

**This integral is given in the Handbook.**

$$|A|^2\left(\frac{2}{2}\sqrt{\pi\alpha^2}\right) = 1$$

**Assuming that A is a real number, this gives**

$$A = \frac{1}{\pi^{1/4}\alpha^{1/2}}$$

**So, the normalized function is**

$$\Psi_0(x) = \left(\frac{1}{\pi^{1/4}\alpha^{1/2}}\right)\exp\left[-\frac{x^2}{2\alpha^2}\right]$$

**2. (15 points)** Determine $<x^2> - <x>^2$ for a particle in a one-dimensional box of length *a* when the system is in a state with the quantum number *n*.

**The normalized wave function for the particle in a box is**

$$\Psi_n(x) \quad = \quad \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

**One needs to calculate the two expectation values:**

$$< x > \quad = \quad \int_0^a \Psi_n(x)x\Psi(x)dx \quad = \quad \frac{2}{a}\int_0^a x\sin^2\left(\frac{n\pi x}{a}\right)dx$$

**A change of variable helps to get this integral into the proper form. Letting** $y \quad = \quad \frac{n\pi x}{a}$**, the integral becomes**

$$< x > \quad = \quad \frac{2}{a}\left(\frac{a}{n\pi}\right)^2 \int_0^{n\pi} y\sin^2 y\, dy$$

**This integral is found in the Handbook, and the result is**

$$< x > \quad = \quad \frac{2}{a}\left(\frac{a}{n\pi}\right)^2\left[\frac{n^2\pi^2}{4} - \frac{n\pi}{4}\sin(2n\pi) - \frac{\cos(2n\pi)}{8} + \frac{\cos(0)}{8}\right]$$

$$= \quad \frac{2a}{n^2\pi^2}\left[\frac{n^2\pi^2}{4}\right] \quad = \quad \frac{a}{2}$$

**Similarly, one can calculate the other expectation value:**

$$< x^2 > \quad = \quad \frac{2}{a}\left(\frac{a}{n\pi}\right)^3 \int_0^{n\pi} y^2 \sin^2 y\, dy$$

**Once again, this integral is found in the integral table:**

$$< x^2 > \quad = \quad \frac{2}{a}\left(\frac{a}{n\pi}\right)^3\left[\frac{n^3\pi^3}{6} - \left(\frac{n^2\pi^2}{4} - \frac{1}{8}\right)\sin 2n\pi - \frac{n\pi}{4}\cos 2n\pi\right]$$

$$= \quad \frac{2a^2}{n^3\pi^3}\left[\frac{n^3\pi^3}{6} - \frac{n\pi}{4}\right] \quad = \quad a^2\left[\frac{1}{3} - \frac{1}{2n^2\pi^2}\right]$$

**Then, by subtracting these, one has the result:**

$$< x^2 > - < x >^2 \quad = \quad a^2\left[\frac{1}{3} - \frac{1}{2n^2\pi^2} - \frac{1}{4}\right] \quad = \quad \frac{a^2}{2}\left[\frac{1}{6} - \frac{1}{n^2\pi^2}\right]$$

Score for Page

**3. (10 points)** Give the simplest form of each of the following commutators (where x, y, and z are the co-ordinates of a particle relative to some origin, and r is the distance of the particle from the origin):

(a) $$\left[x, \frac{d}{dx}\right] f \quad = \quad x\frac{df}{dx} - \frac{d}{dx}(xf) \quad = \quad x\frac{df}{dx} - x\frac{df}{dx} - f \quad = \quad -f$$

**Therefore,** $$\left[x, \frac{d}{dx}\right] \quad = \quad -1$$

(b) $$\left[x, \frac{d}{dy}\right] f \quad = \quad x\frac{df}{dy} - \frac{d}{dy}(xf) \quad = \quad x\frac{df}{dy} - \left(\frac{dx}{dy}\right) f - x\left(\frac{df}{dy}\right) \quad = \quad 0$$

**Therefore,** $$\left[x, \frac{d}{dy}\right] \quad = \quad 0$$

(c) $$\left[\frac{d}{dy}, xy\right] f \quad = \quad \frac{d}{dy}(xyf) - xy\frac{df}{dy} \quad = \quad xy\frac{df}{dy} + xf\frac{dy}{dy} - xy\frac{df}{dy} \quad = \quad xf$$

**Therefore,** $$\left[\frac{d}{dy}, xy\right] \quad = \quad x$$

(d) $$\left[\frac{d}{dx}, r\right] f \quad = \quad \frac{d}{dx}(rf) \quad - \quad r\frac{df}{dx} \quad = \quad f\frac{dr}{dx} \quad + \quad r\frac{df}{dx} \quad - \quad r\frac{df}{dx}$$

$$= \quad f\frac{dr}{dx} \quad = \quad f\frac{d}{dx}\left(x^2 + y^2 + z^2\right)^{1/2} \quad = \quad f\left(\frac{1}{2}\right)\frac{1}{\left(x^2 + y^2 + z^2\right)^{1/2}}\left(2x\right) \quad = \quad \frac{x}{r} f$$

**Therefore,** $$\left[\frac{d}{dx}, r\right] \quad = \quad \frac{x}{r}$$

Score for Page

**4. (15 points)** For the following functions and operators, determine whether the function is an eigenfunction of the operator. If it is, indicate the eigenvalue. Show your work below the box.

| **Operator** | **Function** | **Eigenfunction?** | **Eigenvalue, if there is one.** |
|---|---|---|---|
| $\frac{d}{dx}$ | $\exp(ikx)$ | ☑ Yes ☐ No | $ik$ |
| $\frac{d}{dy}$ | $\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi y}{a}\right)$ | ☐ Yes ☑ No | |
| $L^2$ | $\frac{1}{\sqrt{3}}Y_{21}(\theta,\phi)+\sqrt{\frac{2}{3}}Y_{20}(\theta,\phi)$ | ☑ Yes ☐ No | $2(2+1)\hbar^2 \quad = \quad 6\hbar^2$ |
| $-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$ | $A\exp\left(-\frac{r}{a_0}\right)$ | ☐ Yes ☑ No | |
| $\frac{d}{dx}$ | $\exp(-iky)$ | ☑ Yes ☐ No | 0 |

$$\frac{d}{dx}\exp(ikx) \quad = \quad ik\exp(ikx)$$

$$\frac{d}{dy}\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi y}{a}\right) \quad = \quad \frac{n\pi}{a}\sqrt{\frac{2}{a}}\cos\left(\frac{n\pi y}{a}\right)$$

$$L^2\left\{\frac{1}{\sqrt{3}}Y_{21}(\theta,\phi)+\sqrt{\frac{2}{3}}Y_{20}(\theta,\phi)\right\} \quad = \quad L^2\frac{1}{\sqrt{3}}Y_{21}(\theta,\phi)+L^2\sqrt{\frac{2}{3}}Y_{20}(\theta,\phi)$$

$$= \quad \frac{1}{\sqrt{3}}L^2Y_{21} \quad + \quad \sqrt{\frac{2}{3}}L^2Y_{20} \quad = \quad \frac{1}{\sqrt{3}}(2)(2+1)\hbar^2Y_{21} \quad + \quad \sqrt{\frac{2}{3}}(2)(2+1)\hbar^2Y_{20} \quad =$$

$$= \quad (2)(2+1)\hbar^2\left\{\frac{1}{\sqrt{3}}Y_{21}(\theta,\phi)+\sqrt{\frac{2}{3}}Y_{20}(\theta,\phi)\right\}$$

$$-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\left(A\exp\left(-\frac{r}{a_0}\right)\right) \quad \neq \quad constant\times A\exp\left(-\frac{r}{a_0}\right)$$

$$\frac{d}{dx}\exp(-iky) \quad = \quad 0 \quad = \quad 0\times\exp(-iky)$$

| Score for Page |
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**5. (15 points)** (a) What is the energy of the lowest-energy state of the particle having the mass of an electron in a one-dimensional box that is exactly 1 micron ($10^{-6}$ m) in width?

**This is a particle in a one-dimensional box. The energy of this particle is given by the following formula:**

$E_n = \frac{h^2}{8ma^2} n^2$, **where the lowest-energy state has the quantum number 1. Using the mass of the electron, the size of the box and the value of Planck's constant, one gets the result:**

$$E_1 = \frac{\left(6.6260755 \times 10^{-34}\ J\ s\right)^2 1^2}{8(9.1093897 \times 10^{-31}\ kg)(10^{-6}\ m)^2} = 6.025 \times 10^{-26}\ J$$

(b) Suppose there was a transition from the state of part (a) to the next-highest energy state. Calculation the energy absorbed in this transition? What is the wavelength of radiation corresponding to this transition?

**This is a calculation of the energy difference. The next-highest energy state has n = 2.**

$$\Delta E = E_2 - E_1 = \frac{h^2}{8ma^2}\left(2^2 - 1^2\right) = \frac{3h^2}{8ma^2} = \frac{3(6.6260755 \times 10^{-34}\ J\ s)^2}{8(9.1093897 \times 10^{-31}\ kg)(10^{-6}\ m)^2}$$

$$= 1.807 \times 10^{-25}\ J$$

**This must be converted to a wavelength, using Planck's constant and the speed of light:**

$\Delta E = h\nu = \frac{hc}{\lambda}$, **which gives**

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.6260755 \times 10^{-34}\ J\ s)(2.99792458 \times 10^{8}\ m\ s^{-1})}{1.807 \times 10^{-25}\ J} = 1.10\ m$$

Score for Page

**6. (10 points)** For the phrases in column A indicate the appropriate definition from column B by placing the number in the blank to the left of the phrase:

| A | B |
|---|---|
| _9_ **Blackbody radiation** | **1.** $\delta x \delta p_x \geq \frac{\hbar}{2}$ |
| _1_ **Heisenberg's uncertainty principle** | **2.** $\frac{h}{mv}$ |
| _4_ **Hermite polynomials** | **3.** Eigenfunctions of the square of the angular momentum |
| _5_ **Laguerre polynomials** | **4.** Included in the harmonic-oscillator wave functions |
| _8_ **Wave-particle duality** | **5.** Included in the hydrogen-atom wave functions |
| | **6.** Ejection of electrons |
| | **7.** The linear momentum of an electron in an orbit is quantized. |
| | **8.** The characteristic demonstrated by the experiments of Davisson and Germer |
| | **9.** Emission spectrum by a body that is in equilibrium with a radiation field specified by a temperature T |
| | **10.** Translational wave functions |

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**7. (10 points)** For the quantum mechanical 1-D harmonic oscillator, the virial theorem says that

$$<T> \;=\; <V>,$$

where $T$ is the kinetic-energy operator and $V$ is the potential-energy operator. Knowing that the expectation values of the linear momentum and the position are zero, use this result to find the product of the standard deviations, $\sigma_p \sigma_x$, for a harmonic oscillator in the $n$ = 3 state. [HINT: $E \;=\; <T> \;+\; <V> \;=\; \frac{<p^2>}{2m} \;+\; \frac{k}{2}<x^2>$, where $k$ is the force constant and $m$ is the particle's mass. $\sigma_A \;=\; \sqrt{<A^2> - <A>^2}$ ]

**First, since the expectation value of the position and momentum are known to be zero, one has the following results:**

$$\sigma_x \;=\; \sqrt{<x^2>}$$

$$\sigma_p \;=\; \sqrt{<p^2>}$$

**By definition of the quantities, it is known that**

$$<p^2> \;=\; 2m<T>$$

$$<x^2> \;=\; \frac{2}{k}<V>$$

**Since the expectation values of the kinetic and potential energies are the same, one may substitute these into the definition of the product of the standard deviations to give**

$$\sigma_x \sigma_p \;=\; \sqrt{<x^2><p^2>} \;=\; \sqrt{4\frac{m}{k}<V><T>}.$$

**But one knows the sum of the energies:**

$$E \;=\; \left(3+\frac{1}{2}\right)\hbar\omega_0 \;=\; <T> \;+\; <V>.$$

**Since the problem states that the two expectation values are equal, one has the result that:**

$$<T> \;=\; <V> \;=\; \frac{1}{2}E \;=\; \frac{7}{4}\hbar\omega_0.$$

**This gives the following result**

$$\sigma_x \sigma_p \;=\; \sqrt{4\frac{m}{k}\left(\frac{7}{4}\hbar\omega_0\right)^2}.$$

**Using the definition of equation 11.36 in the Handbook, this reduces to:**

$$\sigma_x \sigma_p \;=\; \sqrt{\frac{49}{4}\hbar^2} \;=\; \frac{7}{2}\hbar.$$

Score for Page

**8. (15 points)** What is the likelihood that the electron resides in the region $0 \le r \le a_0$ for a 1s electron of a hydrogen atom?

**First, one needs the radial function. This is given by:**

$$R_{10}(r) \quad = \quad A\exp\left(-\frac{r}{a_0}\right)$$

**This function must be normalized, and that is done by the following requirement on the function:**

$$\int_0^{+\infty} R_{10}^2(r) r^2 dr \quad = \quad 1.$$

**Substitution gives a value for A.**

$$A^2 \int_0^{+\infty} \exp\left(-\frac{2r}{a_0}\right) r^2 dr \quad = \quad 1.$$

**The integral in this equation can be found on integral table in your Handbook.**

$$A^2 \left( \frac{2!}{\left(\frac{2}{a_0}\right)^3} \right) \quad = \quad 1.$$

**This gives the value for A:**

$$A \quad = \quad \frac{2}{a_0^{3/2}}.$$

**Then, the probability of finding the particle in that range is given by the integral:**

$$P(0, a_0) \quad = \quad \int_0^{a_0} R_{10}^2(r) r^2 dr \quad = \quad \frac{4}{a_0^3} \int_0^{a_0} \exp\left(-\frac{2r}{a_0}\right) r^2 dr$$

**Changing variables is convenient, so substitution gives**

$$P(0, a_0) \quad = \quad \frac{1}{2} \int_0^2 \exp(-\chi)\chi^2 d\chi,$$

**where**

$$\chi \quad = \quad \frac{2r}{a_0}.$$

**The integral can be evaluated by parts.**

$$\int \exp(-\chi)\chi^2 d\chi \quad = \quad -\left(\chi^2 + 2\chi + 2\right)\exp(-\chi)$$

**Substitution into the probability equation and evaluating the definite integral gives**

$$P(0, a_0) \quad = \quad \frac{1}{2}\left[-\left(2^2 + 2 \times 2 + 2\right)\exp(-2) \quad + \quad (0+) + 2)\exp(-0)\right]$$

$$= \quad 1 \quad - \quad 5\exp(-2) \quad = \quad 0.3233236$$

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**9. (5 points, extra credit)** The wave function for a particular particle is a sum of momentum eigenfunctions, where the $c_n$ and $k_n$ are constants:

$$\Psi(x) = \sum_{n=1}^{10} c_n \exp(ik_n x).$$

A measurement of the momentum give $k_5\hbar$. Give answers to the following question in terms of $\hbar$ and the constants in the above definition of the wave function.

(a) What was the probability of obtaining the $k_5\hbar$ result?

**The probability of obtaining the $k_5\hbar$ result is given by the square of the coefficient for that term:** $P_5 = c_5^* c_5$

(b) What is the wave function after the measurement?

**The measurement has put the system in the fifth state, so after measurement,** $\Psi_{after} = \exp(ik_5 x)$.

(c) What is wavelength of the particle after the measurement?

**The state of the system has the definite wavelength of the fifth state. The wavevector of this state is $k_5$, so the wavelength is simply** $\lambda = \dfrac{2\pi}{k_5}$.

Score for Page