Chemistry 562 **Spring 2012**

Problem Set 3

Due beginning of class on Friday, February 10

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

5 1. Recall the normalized first excited (υ=1) wave function for the quantum harmonic oscillator from the last problem set,

$$\psi_1(x) = \sqrt{\frac{1}{2\alpha\sqrt{\pi}}}\,\frac{2x}{\alpha}\cdot e^{\frac{-x^2}{2\alpha^2}}$$

1 (a.) Find $\langle x \rangle$

2 (b.) Find $\langle p^2 \rangle$

1 (c.) Using (a.) and (b.) and the results from Problem Set 2, Problem 2, calculate

(i.) $(\Delta x)^2$

(ii.) $(\Delta p)^2$

1 (d.) Find $\Delta x \Delta p$ for $\alpha = \left(\frac{\hbar^2}{mk}\right)^{\frac{1}{4}}$. Does this result satisfy the Heisenberg Uncertainly Principle?

2 2. *Problem* 8.32 (Make life simple by assuming κ and L are large enough that you can treat the barrier as being "high and wide.")

3 3. For a normalized wave function

$$\psi(x) = c_1\psi_1(x) + \frac{1}{\sqrt{8}}\psi_2(x) + \frac{1}{\sqrt{2}}\psi_3(x)$$

where ψ_1(x), ψ_2(x), and ψ_3(x) are the normalized eigenfunctions of $\hat{H}$.

1 (a.) Solve for c_1.

1 (b.) Calculate $\langle E \rangle$ in terms of E_1, E_2, and E_3. Show all your work.

1 (c.) If we measure the energy of a single system, what is the probability that we will obtain E_1?

(over)

1) a) $\langle x \rangle = \frac{1}{2\alpha\sqrt{\pi}} \frac{2^2}{\alpha^2} \int_{-\infty}^{\infty} x^3 e^{-x^2/\alpha^2} dx = 0$

odd · even

$$\langle p^2 \rangle = \frac{1}{2\alpha\sqrt{\pi}} \frac{2^2}{\alpha^2} \int_{-\infty}^{\infty} x e^{-x^2/2\alpha^2} \left(\frac{\hbar}{i}\right)^2 \frac{d^2}{dx^2} \left(x \cdot e^{-x^2/2\alpha^2} \right) dx$$

$$\frac{d^2}{dx^2} x e^{-x^2/2\alpha^2} = \frac{d}{dx}\left(x \left(-\cancel{2}x/\cancel{2}\alpha^2\right) e^{-x^2/2\alpha^2} + e^{-x^2/2\alpha^2} \right)$$

$$= \frac{-2x}{\alpha^2} e^{-x^2/2\alpha^2} + \frac{-x^2}{\alpha^2}\left(\frac{-2x}{2\alpha^2}\right) e^{-x^2/2\alpha^2} - \frac{\cancel{2}x}{\cancel{2}\alpha^2} e^{-x^2/2\alpha^2}$$

$$= \left(\frac{x^3}{\alpha^4} - \frac{3x}{\alpha^2}\right) e^{-x^2/2\alpha^2}$$

b) $\langle p^2 \rangle = \frac{-2\hbar^2}{\alpha^3\sqrt{\pi}} \int_{-\infty}^{\infty} x e^{-x^2/2\alpha^2} \left(\frac{x^3}{\alpha^4} - \frac{3x}{\alpha^2}\right) e^{-x^2/2\alpha^2} dx$

$$= \frac{-2\hbar^2}{\alpha^3\sqrt{\pi}} \cdot \int_{-\infty}^{\infty} \left[\frac{x^4}{\alpha^4} e^{-x^2/\alpha^2} - \frac{3x^2}{\alpha^2} e^{-x^2/\alpha^2} \right] dx$$

$$= \frac{-2\hbar^2}{\alpha^3\sqrt{\pi}} \left(\frac{2}{\alpha^4} \frac{(2\cdot 2)!}{2!\,2^5} \sqrt{\frac{\pi}{\left(\frac{1}{\alpha^2}\right)^5}} - \frac{3\cdot 2}{\alpha^2} \frac{1}{4} \sqrt{\frac{\pi}{\left(\frac{1}{\alpha^2}\right)^3}} \right)$$

$$= \frac{-2\hbar^2}{\cancel{\alpha^3}\cancel{\sqrt{\pi}}} \left(\frac{3\cancel{\alpha}}{4\cancel{\alpha^4}} \cdot \cancel{\alpha^5}\cancel{\sqrt{\pi}} - \frac{3}{2\cancel{\alpha^2}}\cancel{\alpha} \cdot \cancel{\alpha^3}\cancel{\sqrt{\pi}} \right) = \frac{-2\hbar^2}{\alpha^2}\left(\frac{-3}{4}\right) = \frac{3\hbar^2}{2\alpha^2}$$

1 c) i) $(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2$

$$= \frac{3}{2}\alpha^2 - 0 \quad = \frac{3}{2}\alpha^2$$

ii) $(\Delta p)^2 = \langle p^2 \rangle - \langle p \rangle^2$

$$= \frac{3}{2}\frac{\hbar^2}{\alpha^2} - 0 = \frac{3}{2}\frac{\hbar^2}{\alpha^2}$$

d) $\Delta x \Delta p = \sqrt{\frac{3}{2}\alpha^2}\sqrt{\frac{3}{2}\frac{\hbar^2}{\alpha^2}} = \frac{3}{2}\hbar \geq \frac{\hbar}{2}$

2) $T \approx 18\,\varepsilon(1-\varepsilon)e^{-2\kappa L}$

$\varepsilon = E/V$

$\kappa = \frac{\sqrt{2m(V-E)}}{\hbar}$

$\kappa = 7\ \text{nm}^{-1}$

8.3×10^{-7}

$$\frac{T_1}{T_2} = \frac{18\,\varepsilon(1-\varepsilon)e^{-2\cdot 7\text{nm}^{-1}\cdot 1\text{nm}}}{18\,\varepsilon(1-\varepsilon)e^{-2\cdot 7\text{nm}^{-1}\,2\text{nm}}} = \frac{e^{-14}}{e^{-28}} = e^{14} = 1.2\times10^6$$ times more likely at 1nm

3) a) $1 = |c_1|^2 + |c_2|^2 + |c_3|^2 = c_1^2 + \frac{1}{8} + \frac{1}{2} \qquad c_1 = \sqrt{\frac{3}{8}}$

b) $\langle E \rangle = \int \Psi \hat{H} \Psi = \int (c_1\psi_1 + c_2\psi_2 + c_3\psi_3)\hat{H}(c_1\psi_1 + c_2\psi_2 + c_3\psi_3)$

$$= \int (c_1\psi_1 + c_2\psi_2 + c_3\psi_3)(c_1E_1\psi_1 + c_2E_2\psi_2 + c_3E_3\psi_3)$$

$$= \int\Big[c_1^2E_1\cancel{\psi_1\psi_1}^{1} + c_1c_2E_2\cancel{\psi_1\psi_2}^{0} + c_1c_3E_3\cancel{\psi_1\psi_3}^{0} + c_2c_1E_1\cancel{\psi_2\psi_1}$$
$$+ c_2^2E_2\cancel{\psi_2\psi_2}^{1} + c_2c_3E_3\cancel{\psi_2\psi_3}^{0} + c_1c_3E_1\cancel{\psi_3\psi_1}^{1} + c_2c_3E_2\cancel{\psi_3\psi_2}^{0}$$
$$+ c_3^2E_3\cancel{\psi_3\psi_3}^{1}\Big] = c_1^2E_1 + c_2^2E_2 + c_3^2E_3 = \frac{3}{8}E_1 + \frac{1}{8}E_2 + \frac{1}{2}E_3$$

3) c) $P = c_1^2 = \frac{3}{4}$

4) a) More nodes ↔ Increasing n

nodes = $n-1$

Bigger Box → Smaller $|\Psi|$ → more spread-out particle → must remain normalized

$$E = \frac{n^2 h^2}{8mL^2} = \frac{1^2 h^2}{8 \cdot 1 \cdot 1} = 6 \times 10^{-22}\ \text{J}$$

ZPE prevents system from being in bottom of well

b) Degeneracy = 2 $\quad E_{2,1} = E_{1,2} = \left(\frac{1^2}{10_{nm}^2} + \frac{2^2}{10_{nm}^2}\right)\frac{h^2}{2m} = \left(\frac{2^2}{10_{nm}^2} \frac{1^2}{10_{nm}^2}\right)\frac{h^2}{2m}$

They are not degenerate if $L_1 = 10\,nm$, $L_2 = 15\,nm$

$$E_{2,1} \neq E_{1,2} \Rightarrow \left(\frac{2^2}{10_{nm}^2} + \frac{1^2}{15_{nm}^2}\right)\frac{h^2}{2m} \neq \left(\frac{1^2}{10_{nm}^2} + \frac{2^2}{15_{nm}^2}\right)\frac{h^2}{2m}$$

c) Nodes are now defined by lines rather than pts. There are still $n_i - 1$ nodes for $i = x$ or y. Increasing n_x has no effect on nodes in y.