Chemistry 562 **Spring 2012**

Problem Set 4

Due beginning of class on Friday, February 17

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

1. (a) Confirm that a function of the form $e^{-\frac{x^2}{2\alpha^2}}$ is a solution of the Schrödinger equation for the ground state of a harmonic oscillator.

   (b) Find an expression for α in terms of the mass and force constant of the oscillator.

2. The two degenerate bend vibrations of carbon dioxide can be represented by a 2-D quantum harmonic oscillator with $k=k_x=k_y$.

   (a) Sketch the potential energy as a function of x and y.

   (b) Write the equation for the energy and the wave function of this 2-D harmonic oscillator by analogy with the same relationships for the 1-D and 2-D particle in a box.

   (c) Which of the three wavefunctions, $\{\upsilon_x,\upsilon_y\}=\{0,0\},\{5,5\}$, and $\{10,10\}$, has a probability distribution that is most similar to a classical oscillator. Order the three wavefunctions from lowest to highest probability of finding the oscillator in the classically forbidden region. Explain your reasoning.

3. Imagine that you have two free particles. One that is traveling to the left and the other to the right, both with momentum k.

   (a) Derive an equation for their interference as a function of the position x.

   (b) Are there any positions where one cannot observe either particle? What are they?

4. *Problem* 8.35 (For part b, also calculate the wavelength of the radiation. Is this result consistent with what you know about the spectral characteristics of chlorophyll?)

835

1) $\hat{H}\psi = E\psi$ for SHO:

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx}\psi + \frac{1}{2}kx^2\psi = E\psi$$

use $\psi = e^{-x^2/2\alpha^2}$ and confirm

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\left(e^{-x^2/2\alpha^2}\right) + \frac{1}{2}kx^2 e^{-x^2/2\alpha^2} \stackrel{?}{=} E\, e^{-\frac{x^2}{2\alpha^2}}$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\left(e^{-x^2/2\alpha^2}\right) + \frac{1}{2}kx^2 e^{-x^2/2\alpha^2} \stackrel{?}{=} E\, e^{-x^2/2\alpha^2}$$

$$\frac{\hbar^2}{2m}\frac{d}{dx}\left(\frac{-x}{\alpha^2}e^{-x^2/2\alpha^2}\right) \pm\frac{1}{2}kx^2 e^{-x^2/2\alpha^2} + \frac{1}{2}kx^2 e^{-x^2/2\alpha^2} \stackrel{?}{=} E\, e^{-x^2/2\alpha^2}$$

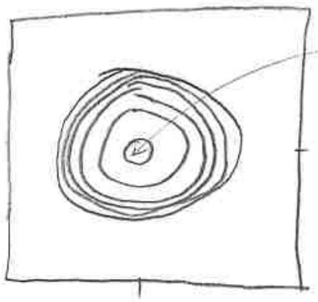
$$\frac{-\hbar^2}{2m}\left(\frac{-1}{\alpha^2}e^{-\frac{x^2}{2\alpha^2}} + \frac{-x}{\alpha^2}\frac{(-x)}{\alpha^2}e^{-\frac{x^2}{2\alpha^2}}\right)$$

$$\frac{\hbar^2}{2m\alpha^2}e^{-x^2/2\alpha^2} - \frac{\hbar^2 x^2 e^{-\frac{x^2}{2\alpha^2}}}{2m\alpha^4} + \frac{1}{2}k\,x^2 e^{-\frac{x^2}{2\alpha^2}} \stackrel{?}{=} E e^{-x^2/2\alpha^2}$$

$$\frac{\hbar^2}{2m\alpha^4} = \frac{1}{2}k \quad \text{and} \quad \frac{\hbar^2}{2m\alpha^2} = E$$

$$\alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4} \qquad \therefore \quad E = \frac{\hbar^2}{2m\hbar}\sqrt{mk} = \frac{1}{2}\hbar\sqrt{\frac{k}{m}} = \frac{1}{2}\hbar\omega$$

2) a). Potential, V as fxn of x & y



Potential is parabolic in both x and y, with graduations getting closer together as x and y increase.

b) $E_{2D} = E_{vx} + E_{vy} = (v_x + \frac{1}{2})\hbar\omega_x + (v_y + \frac{1}{2})\hbar\omega_y = (v_x + v_y + 1)\hbar\omega \qquad \omega_x = \omega_y \equiv \omega$

$\psi_{2D} = \psi_x \psi_y = N_{vx} H_{vx}(z_x) e^{-z_x^2/2} \cdot N_{vy} H_{vy}(z_y) e^{-z_y^2/2}$

$z_x(x) = \frac{x}{\alpha_x} \qquad z_y(y) = \frac{y}{\alpha_y} \qquad \alpha_i = \left(\frac{\hbar^2}{\mu_i k_i}\right)^{1/4} \qquad \mu_i = \mu_x \mu_y$

$k_i = k_x k_y$

$\therefore \alpha_i = \alpha_x = \alpha_y \equiv \alpha$

c) The Hermite polynomials drive the ψ amplitude to the edge of the potential with increasing quantum number, so that it becomes more like the classical solution (more probability at turning points) at high q.n..

→ more classical, less tunnelling

$\{0,0\}, \{5,5\}, \{10,10\}$

← more q.n. more tunnelling

We don't see tunnelling in classical problems, so it must turn off as $v \to \infty$

3) a) $\psi_1 = e^{ikx}$

$\psi_2 = e^{-ikx}$

$$I(x) = |(\psi_1(x) + \psi_2(x))|^2 = \psi_1^* \psi_1 + \psi_2^* \psi_2 + \psi_1^* \psi_2 + \psi_2^* \psi_1$$

$$= e^{-ikx} e^{ikx} + e^{ikx} e^{-ikx} + e^{-ikx} e^{-ikx} + e^{ikx} e^{ikx}$$

$$= 2 + e^{-2ikx} + e^{2ikx}$$

$$= 2 + 2\cos^2 kx - 1 - 2i \sin kx \cos kx + 2\cos^2 kx - 1 + 2i \sin kx \cos kx$$

$$I(x) = 4\cos^2 kx$$

b) $I(x) = 0$

$4\cos^2 kx = 0$ $\qquad x_n = \frac{(2n-1)}{2k}\pi$

4) Problem 2.35

$r = 440 \text{ pm}$

$22e^-$, $2e^-$ fill one orbital

m_ℓ	E_n
0	1
-1, 1	2, 3
-2, 2	4, 5
-3, 3	6, 7
-4, 4	8, 9
-5, 5	10, (11) ← HOMO
-6, 6	12, (13) ← LUMO

HOMO: $E_{11} = \dfrac{m_\ell^2 \hbar^2}{2I}$ $m_\ell = 5$

$I = m_e r^2$

$I = 9.1 \times 10^{-31} \text{ kg} \cdot (440 \times 10^{-12} \text{ m})^2$
$= 1.76 \times 10^{-49} \text{ kg m}^2$

$$E_{11} = \frac{5^2 \cdot (6.626 \times 10^{-34} \text{ kg m}^2/\text{s}^2 \cdot \text{s})^2}{(2\pi)^2 2 \cdot 1.76 \times 10^{-49} \text{ kg m}^2} = 7.89 \times 10^{-19} \frac{\text{kg m}^2}{\text{s}^2} = 7.89 \times 10^{-17} \text{ J}$$

$$J_z = \frac{m_\ell h}{2\pi} = \frac{5 \cdot 6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{2\pi} = 5.27 \times 10^{-34} \text{ J} \cdot \text{s}$$

↑ units of ang momentum

$$E_{12} - E_{11} = \frac{6^2 \hbar^2}{2I} - \frac{5^2 \hbar^2}{2I} = (36 - 25)\frac{\hbar^2}{2I} = \frac{11\hbar^2}{2I} = 3.47 \times 10^{-19} \text{ J}$$

$$\nu = \frac{E}{h} = \frac{3.47 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 5.23 \times 10^{14} \text{ Hz} \Rightarrow 573 \text{ nm}$$