Chem 2430 Exam #1

(1) $\psi = \frac{1}{\sqrt{3}}\psi_1 + \sqrt{\frac{2}{3}}\,\psi_2 \Rightarrow$ (a) $E = \frac{1}{3}E_1 + \frac{2}{3}E_2 = \frac{3}{2}\frac{\pi^2\hbar^2}{2mL^2}$

(b) $\langle\psi|x|\psi\rangle = \frac{1}{3}\langle\psi_1|x|\psi_1\rangle + \frac{2}{3}\langle\psi_2|x|\psi_2\rangle + \frac{2\sqrt{2}}{3}\langle\psi_1|x|\psi_2\rangle$

$= \frac{1}{3}\frac{L}{2} + \frac{2}{3}\frac{L}{2} + \frac{2\sqrt{2}}{3}\frac{2}{L}\int_0^L \sin\left(\frac{\pi x}{L}\right) x \sin\left(\frac{2\pi x}{L}\right) dx$

$= 0.50L - \frac{32}{27}\frac{\sqrt{2}L}{\pi^2} = 0.50L - 0.17L = 0.33L$

(2) This is a stationary state as it is an eigenfunction of H.

(3) (a) $\langle 0|(a^+ + a)(a^+ - a)|0\rangle = \langle 0|aa^+|0\rangle = 1$

(b) $\langle 1|(a^+ - a)(a^+ + a)|1\rangle = \langle 1|a^+a - aa^+|1\rangle = 1 - 2 = -1$

(4) I will stick with atomic units.

(a) $m_p = 1836$ so $\mu_p = 918$ a.u.

$\omega = \sqrt{\frac{k}{\mu}} = \sqrt{\frac{0.32}{918}} = 0.0187$ a.u

$ZPE = \frac{1}{2}\omega = 0.00935$ a.u. $(2052\ \text{cm}^{-1})$

(b) To find the classical turning points

$\frac{1}{2}kx^2 = 0.00935 \Rightarrow x = \pm 0.241$ a.u

$\alpha = \sqrt{k\mu} = 17.14$

Prob of being in classical region $= 2\sqrt{\frac{\alpha}{\pi}}\int_0^{0.241} e^{-17.14x^2}\,dx$
$= 0.85$. So 15% probability in forbidden region.

(5) Electron on ring to model π electrons of benzene

radius of benzene ~ 3 a.u.

Allow for "size" of atomic orbitals so take $r_0 = 4$ a.u.

$E = \frac{m^2}{2r_0^2}$ (in a.u.)

— — $m = \pm 2$
— — $m = \pm 1$
— $m = 0$

Since benzene has six π electrons, the transition is $m=1 \to m=2$

Excitation energy $= \frac{4-1}{2} \frac{1}{r_0^2} \sim .094$ a.u. $= 2.4$ eV

(6) $V = \frac{1}{2} k x^2 + \frac{1}{2} k y^2$

(a) $E = \hbar\omega(n_x + n_y + 1)$

$ZPE = \hbar\omega$

The degeneracy grows as $n_x + n_y + 1$

E.g. (2,0), (1,1), and (0,2) are degenerate

(b) $k_x = k + \delta$, $k_y = k - \delta$

$$\omega_x = \sqrt{\frac{k_x}{\mu}} = \sqrt{\frac{k+\delta}{\mu}} = \sqrt{k/\mu}\sqrt{1 + \delta/k}$$
$$= \omega\left(1 + \delta/2k - 1/8\left(\frac{\delta}{k}\right)^2 + \cdots\right)$$

$$\omega_y = \sqrt{\frac{k_y}{\mu}} = \sqrt{\frac{k-\delta}{\mu}} = \sqrt{k/\mu}\sqrt{1 - \delta/k}$$
$$= \omega\left(1 - \delta/2k - 1/8\left(\frac{\delta}{k}\right)^2 - \cdots\right)$$

$$\omega_x + \omega_y = 2\omega - (1/4)\left(\frac{\delta}{k}\right)^2 \omega$$

Change in $ZPE = -\frac{\omega}{8}\left(\frac{\delta}{k}\right)^2$

(7) $\psi_I = A \sin(kx)$

$\psi_{II} = Be^{Kx} + Ce^{-Kx}$

$\psi_{III} = D \sin[k(x-2a-b)]$

$k = \sqrt{\frac{2mE}{\hbar^2}}$

$K = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$

$\psi_I(a) = \psi_{II}(a)$ and $\psi_I'(a) = \psi_{II}'(a)$

$$A \sin(ka) = Be^{Ka} + Ce^{-Ka}$$
$$kA \cos(ka) = K(Be^{Ka} - Ce^{-Ka})$$

can get B and C in terms of A and the other quantities.

$\psi_{II}(a+b) = \psi_{III}(a+b)$, $\psi_{II}'(a+b) = \psi_{III}'(a+b)$

$$Be^{K(a+b)} + Ce^{-K(a+b)} = D \sin(-ka)$$
$$K(Be^{K(a+b)} - Ce^{-K(a+b)}) = Dk \cos(-ka)$$

Can get D in terms of B or C, and then in terms of A