Chem 2430: Answers HW #2

1. $$E = \frac{\pi^2\hbar^2}{2m}\left[\frac{n_x{}^2}{\ell_x{}^2} + \frac{n_y{}^2}{\ell_y{}^2}\right]$$

Let $\ell_x = a + \delta$, $\ell_y = a - \delta$

$$E = \frac{\pi^2\hbar^2}{2m}\left[\frac{n_x{}^2}{(a+\delta)^2} + \frac{n_y{}^2}{(a-\delta)^2}\right]$$

$$= \frac{\pi^2\hbar^2}{2ma^2}\left\{n_x{}^2\left(1 - \frac{2\delta}{a} + \frac{3\delta^2}{a^2} + \ldots\right) + n_y{}^2\left(1 + \frac{2\delta}{a} + \frac{3\delta^2}{a^2} + \ldots\right)\right\}$$

Consider $n_x = n_y = 1$

$$E_{1,1} \approx \frac{\pi^2\hbar^2}{2ma^2}\left(2 + \frac{6\delta^2}{a^2}\right)$$

a) For the (1,1) level E does not depend linearly on δ

b) However there is a quadratic dependence.

The energy goes up as $\dfrac{\delta\pi^2\hbar^2 6^2}{2a^4}$

The area of the box is $a^2 - \delta^2$. So the particle is more confined in the distorted box which causes the energy to be higher.

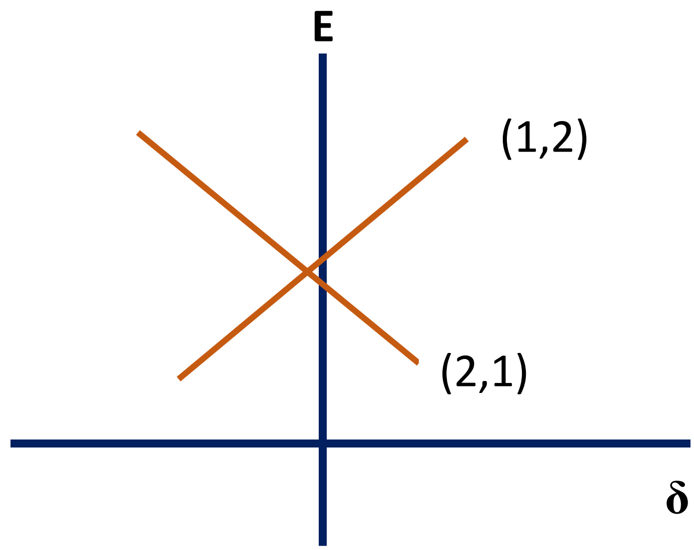
c) Now consider the (2,1) and (1,2) levels

$$E_{1,2} = \frac{\pi^2\hbar^2}{2ma^2}\left\{1\left(1 - \frac{2\delta}{a} + \ldots\right) + 4\left(1 + \frac{2\delta}{a} + \ldots\right)\right\}$$

$$= \frac{\pi^2\hbar^2}{2ma^2}\left\{5 + \frac{6\delta}{a}\right\}$$

$$E_{2,1} = \frac{\pi^2\hbar^2}{2ma^2}\left\{4\left(1-\frac{2\delta}{a}+-\right)+1\left(1+\frac{2\delta}{a}+-\right)\right\}$$

$$= \frac{\pi^2\hbar^2}{2ma^2}\left\{5-\frac{6\delta}{a}\right\}$$



So one level goes down and the other level goes up in energy.

2. Evaluate $\langle 1|\hat{x}^2|1\rangle$ and $\langle 2|\hat{x}^2|2\rangle$ for the particle in the box problem

$$\langle 1|\hat{x}^2|1\rangle = \frac{2}{L}\int_0^L\left(\sin\frac{\pi x}{L}\right)^2 x^2dx = \frac{L^2}{3}-\frac{L^2}{2\pi^2}$$

so $\sqrt{\langle 1|\hat{x}^2|1\rangle} = \frac{L}{\sqrt{3}}$

$$\langle 2|\hat{x}^2|2\rangle = \frac{2}{L}\int_0^L\left(\sin\frac{2\pi x}{L}\right)^2 x^2dx = \frac{L^2}{3}-\frac{L^2}{8\pi^2}$$

3.b

region I $\quad 0 \le x \le a$

region II $\quad a \le x \le b$

region III $\quad x \ge b$

$$\psi_I = A\sin kx, k = \sqrt{2mE/\hbar^2}$$

$$\psi_{II} = Be^{Kx} + Ce^{-Kx}, K = \sqrt{2m(V-E)/\hbar^2}$$

$$\psi_{III} = De^{-ikx} + Fe^{ikx}$$

At $x = a : A\sin(ka) = Be^{Ka} + Ce^{-Ka}$

$$kA\cos(ka) = BKe^{Ka} - CKe^{-Ka}$$

$$A\left(K\sin(ka) + k\cos(ka)\right) = 2BKe^{Ka}$$

$$A\left(K\sin(ka) - k\cos(ka)\right) = 2CKe^{Ka}$$

So we now have B and C in terms of A

At $x = b : Be^{Kb} + Ce^{-Kb} = De^{-ikb} + Fe^{ikb}$

$$BKe^{Kb} - CKe^{-Kb} = -iDke^{-ikb} + iFke^{ikb}$$

So you can get D and F in terms of B, and thus in terms of A.

The solution is somewhat easier if we write

$$\psi_{III} = D\sin\left(kx + \delta\right)$$

Then at x = b

$$Be^{Kb} + Ce^{-Kb} = D\sin\left(kb+\delta\right)$$

$$BKe^{Kb} - CKe^{-Kb} = Dk\cos\left(kb+\delta\right)$$

$$\frac{Be^{Kb} + Ce^{-Kb}}{BKe^{Kb} - CKe^{-Kb}} = \frac{\tan\left(kb+\delta\right)}{k}$$

$$\frac{k\left(Be^{Kb} + Ce^{-Kb}\right)}{K\left(Be^{Kb} - Ce^{-Kb}\right)} = \tan\left(kb+\delta\right)$$

Now substitute our expression for B and C one can then find δ vs k, and thus δ vs E

c) $\psi_I = A\sin kx$

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

At $x = a : \psi_I(a) = A\sin(ka)$

$$\psi_{II}(a) = Be^{-Ka}$$

$$\psi_I'(a) = Ak\cos(ka)$$

$$\psi_{II}' = -BKe^{-KA}$$

$$\left.\begin{array}{l} A\sin(ka) = Be^{-Ka} \\ Ak\cos(ka) = -BKe^{-Ka} \end{array}\right| \qquad B = Ae^{Ka}\sin\left(ka\right)$$

$$\psi_I''(a) = -Ak^2 \sin(ka)$$

$$\psi_{II}''(a) = BK^2 e^{-Ka} = AK^2 \sin(ka)$$

So the second derivative change is $\left(K^2 + k^2\right)\sin\left(ka\right)$