HW #5 Chem. 1410 Spring 2001

1. a) What is the energy of the particle-in-a-box with a sloped bottom for the trial function $\psi = \sin\frac{\pi x}{a}$?

$$E = \frac{\int_0^a \psi H \psi \, dx}{\int_0^a \psi \psi \, dx} = \frac{\int_0^a \sin\frac{\pi x}{a}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + x\right]\sin\frac{\pi x}{a}\, dx}{\int_0^a \left(\sin\frac{\pi x}{a}\right)^2 dx}$$

$$= \frac{\frac{a}{2}E_1 + \int_0^a x\left(\sin\frac{\pi x}{a}\right)^2 dx}{\frac{a}{2}} = E_1 + \frac{a^2/4}{a/2}$$

$$E = E_1 + \frac{a}{2} = \frac{h^2}{8ma^2} + \frac{a}{2}$$

so the sloped bottom causes an $a/2$ shift in the energy.

b) Now consider the trial wavefunction

$$\psi = c_1 \sin\frac{\pi x}{a} + c_2 \sin\frac{2\pi x}{a}$$

The Hamiltonian matrix is:

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix}$$

$$H_{11} = E_1 \frac{a}{2} + \frac{a^2}{4}, \quad H_{22} = E_2 \frac{a}{2} + \frac{a^2}{4}$$

$$S_{11} = \frac{a}{2}, \quad S_{22} = \frac{a}{2}, \quad S_{12} = 0$$

$$H_{12} = \int_0^a \sin\frac{\pi x}{a}\; x \;\sin\frac{2\pi x}{a}\, dx = -\frac{8}{9}\left(\frac{a}{\pi}\right)^2$$

↑ from either Mathcad or an integral table

Taking the determinant of the matrix:

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{12} - ES_{12})^2 = 0$$

$$\Rightarrow \left(E_1 \frac{a}{2} + \frac{a^2}{4} - E\frac{a}{2}\right)\left(E_2 \frac{a}{2} + \frac{a^2}{4} - E\frac{a}{2}\right) - \left(\frac{8}{9}\left(\frac{a}{\pi}\right)^2\right)^2 = 0$$

$$\Rightarrow \left(E_1 + \frac{a}{2} - E\right)\left(E_2 + \frac{a}{2} - E\right) - \left(\frac{16a}{9\pi^2}\right)^2 = 0$$

$$E = \frac{E_1 + E_2 + a}{2} \pm \frac{1}{2}\sqrt{(E_1 - E_2)^2 + 4\left(\frac{16a}{9\pi^2}\right)^2}$$

$$E_+ \approx \frac{E_1 + E_2}{2} + \frac{a}{2} + \frac{(E_1 - E_2)}{2}\sqrt{1 + \frac{4}{(E_1 - E_2)^2}\left(\frac{16a}{9\pi^2}\right)^2}$$

$$E_+ \approx \frac{E_1 + E_2}{2} + \frac{a}{2} + \frac{(E_1 - E_2)}{2}\left[1 + \frac{2\left(\frac{16a}{9\pi^2}\right)^2}{(E_1 - E_2)^2} + \cdots\right]$$

$$E_+ = E_1 \cancel{E_2} + \frac{a}{2} + \frac{\left(\frac{16a}{9\pi^2}\right)^2}{E_1 - E_2}$$ ← this term is negative

$$E_+ = \frac{h^2}{8ma^2} + \frac{a}{2} + \frac{256\, a^4\,(8m)}{-3 \cdot h^2\; 81\, \pi^4} = \frac{h^2}{8ma^2} + \frac{a}{2} - \frac{2048\, m a^4}{243\, \pi^4 h^2}$$

There really should be a parameter in front of the perturbation a so that the units turn out right

2. Consider a Harmonic Oscillator in the presence of an electric field.

$$H^{0} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \quad , \quad H^{(1)} = V = e\mathcal{E}x$$

$$E^{(1)} = e\mathcal{E}\langle \psi_0^{(0)} | x | \psi_0^{(0)} \rangle = 0$$ by properties of even/odd functions.

$$E^{(2)} = \sum_{i \neq 0} \frac{|\langle \psi_0^{(0)} | e\mathcal{E}x | \psi_i^{(0)} \rangle|^2}{E_0^{(0)} - E_i^{(0)}}$$

$$E^{(2)} = \frac{e^2\mathcal{E}^2 |\langle \psi_0^{(0)} | x | \psi_1^{(0)} \rangle|^2}{-\hbar\omega}$$

We know from our discussion of selection rules that the only non-zero contribution comes from $i = 1$.

$$\langle \psi_0 | x | \psi_1 \rangle = N_0 N_1 \int_{-\infty}^{\infty} e^{-\alpha x^2/2} x (2\sqrt{\alpha}\, x) e^{-\alpha x^2/2} dx$$

$$= \frac{N_0 N_1}{2\sqrt{\alpha}} \int_{-\infty}^{\infty} \left(2\sqrt{\alpha}\, x e^{-\alpha x^2/2}\right)^2 dx = \frac{N_0}{N_1 2\sqrt{\alpha}} \int_{-\infty}^{\infty} \psi_1^2 \, dx$$

$$= \frac{N_0}{2\sqrt{\alpha} N_1} = \frac{1}{\frac{2\sqrt{\alpha}}{\sqrt{2}}} = \frac{1}{\sqrt{2\alpha}}$$

$$E^{(2)} = -\frac{e^2\mathcal{E}^2}{\hbar\omega}\left(\frac{1}{2\alpha}\right) = -\frac{e^2\mathcal{E}^2}{2\hbar\omega}\frac{\hbar}{\sqrt{k\mu}} = -\frac{e^2\mathcal{E}^2}{2\sqrt{\frac{k}{\mu}}\sqrt{k\mu}}$$

$$E^{(2)} = -\frac{e^2\mathcal{E}^2}{2k}$$