Chem 1410 – Exam #1
September 29, 2008

The exam is open book (Engel only) and open notes (class notes only).

Question 1: 20 points

Question 2: 20 points

Question 3: 20 points

Question 4: 20 points

Question 5: 20 points

1. Do either of the following operators commute? [Circle either Y (yes) or N (no).]

a. $\dfrac{d}{dx}$, H for the particle-in-the-box problem. — Y N

Recall H is not constant over $-\infty < x < \infty$

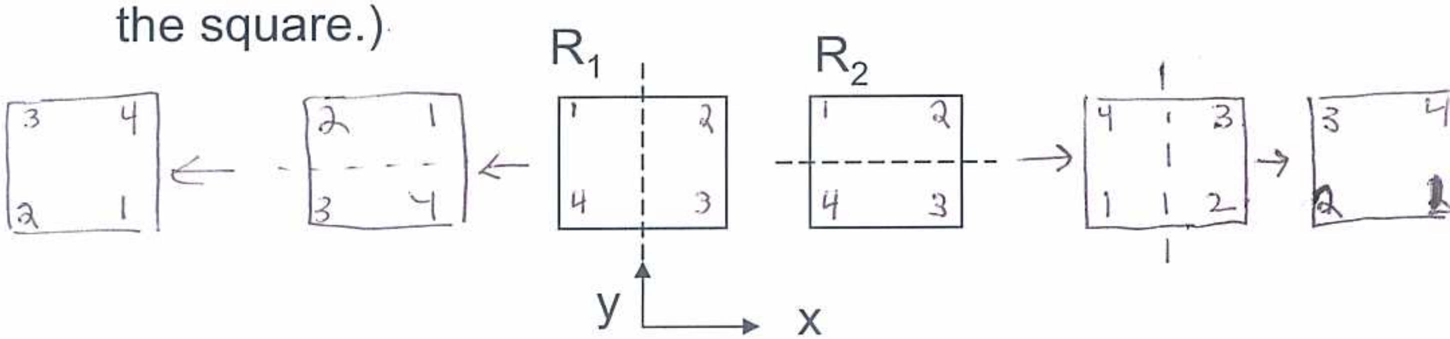
b. H and H^2 for the harmonic oscillator (for which $V = \dfrac{1}{2}kx^2$) — Y N

Actually this is true for any V.

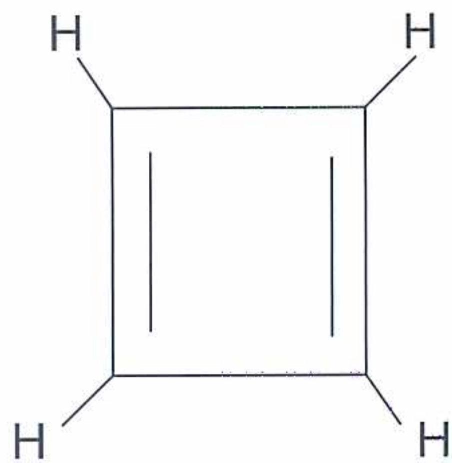
c. y and x for a two-dimensional harmonic oscillator with $V(x,y) = \dfrac{1}{2}k(x^2 + y^2)$ — Y N

x and y will commute for any potential

d. reflection of a square in the xy plane through the yz and xz planes. The two reflection operators are R_1 and R_2 and are shown below. (Hint: You may find it useful to number the four corners of the square.) — Y N



2. Consider the organic molecule cyclobutadiene.



a. Describe how you would model the orbitals of cyclobutadiene using a particle-in-the-box model.

Use the 2D particle in the box

$$\psi_{nx,ny} = \frac{2}{a} \sin(n_x \pi a) \sin(n_y \pi a)$$

where a is the length of the side of the box.

$$a \approx R_{cc} + 2(0.5)\ \text{Å} \approx 2.5\ \text{Å}$$

b. Provide an estimate of the first excitation energy. Show your work.

$$E_{nx,ny} = \frac{h^2}{8ma^2}\left[n_x^2 + n_y^2\right]$$

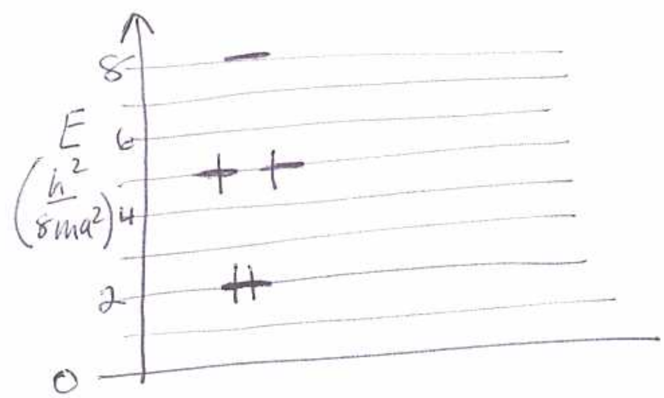
$$E_{11} = 2\left(\frac{h^2}{8ma^2}\right)$$

$$E_{12} = E_{21} = 5\left(\frac{h^2}{8ma^2}\right)$$

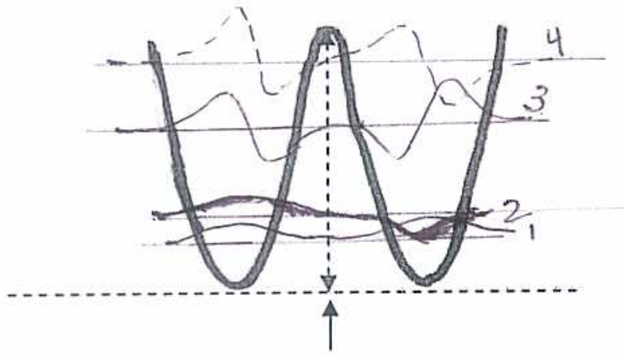
$$E_{22} = 8\left(\frac{h^2}{8ma^2}\right)$$

$$\Delta E = (8-5)\frac{h^2}{8ma^2} = \frac{3h^2}{8ma^2}$$

$$\approx 17\ \text{eV}$$



3. Sketch the first four energy eigenfunctions associated with the potential drawn to the right; assume that all four of these have energies below V_0. In each case, sketch a horizontal line indicating your qualitative estimate of the energy of the eigenfunction.

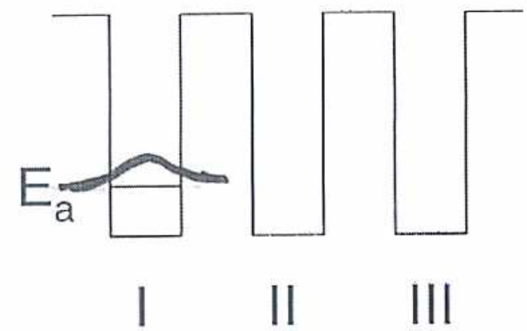


V_o = height of barrier

The energy splitting between levels 3 and 4 will exceed that between levels 1 and 2.

1 has ∅ nodes.
2 has 1 node in the "middle"
3 has 2 nodes, one in each well
4 has 3 nodes, one in each well, and one in the middle.

4. Consider the three-well potential shown to the right. Suppose a clever experimentalist prepares the system so that its wave function is initially localized in potential well I, as shown in the figure.



a. Suppose you do repeated measurements of the energy. Will all measurements give the same energy? Why or why not?

If you are making measurements on different replicas, then different measurements can give different energies. If you instead, do multiple measurements on the same system, all measurements will give the same energy

b. Describe how you would expect the system to evolve in time.

The wavefunction will delocalize from well I to II to III.

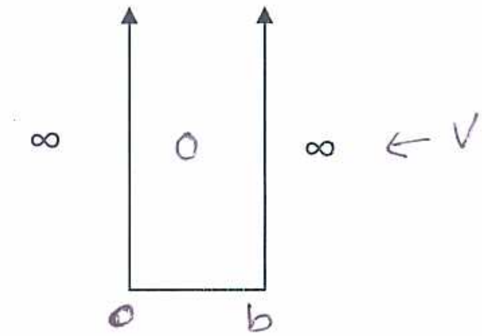
c. Give a qualitative description of the initial wave function of the system in terms of the energy eigenfunction. (Hint: How many different eigenfunctions do you expect to be important?

One anticipates that the initial wavefunction, depicted above, is a linear combination of the three lowest energy eigenfunctions of the system.

5. Consider the wavefunction

$\psi = x(b-x)$ for the

potential shown to the right.



a. What is the average of x?

$\langle x \rangle = \frac{b}{2}$ from the symmetry of the problem.

b. What is the average of x^2?

$$\langle x^2 \rangle = \frac{\int_0^b x^4 (b-x)^2 \, dx}{\int_0^b x^2 (b-x)^2 \, dx} = \frac{\left(b^2 \frac{x^5}{5} - 2b\frac{x^6}{6} + \frac{x^7}{7}\right)\Big|_0^b}{\left(b^2 \frac{x^3}{3} - 2b\frac{x^4}{4} + \frac{x^5}{5}\right)\Big|_0^b} = \frac{2}{7} b^2$$

c. What is the average of p_x^2?

$$\langle p_x^2 \rangle = \frac{-\hbar^2 \int_0^b x(b-x) \frac{d^2}{dx^2} x(b-x)}{b^5\left(\frac{1}{3} - \frac{1}{2} + \frac{1}{5}\right)} = \frac{\int_0^b x(b-x)[-2](-\hbar^2)}{b^5\left(\frac{1}{3} - \frac{1}{2} + \frac{1}{5}\right)} = \frac{10\hbar^2}{b^2}$$

d. What is the energy associated with this wavefunction?

$$\langle \hat{H} \rangle = \left\langle \frac{p_x^2}{2m} \right\rangle = \frac{5\hbar^2}{mb^2}$$