Chemistry 3PA3

Assignment 1

due Oct. 7, 2016

This assignment can be done using Excel, or any other numerical platform.

1. The lowest four energy eigenfunctions for an electron in a one dimensional box of width, L = 1, are given as follows:

$$\psi_1(x) = \sqrt{2}\sin(\pi x),$$

$$\psi_2(x) = \sqrt{2}\sin(2\pi x),$$
$$\psi_3(x) = \sqrt{2}\sin(3\pi x)$$

and

$$\psi_4(x) = \sqrt{2}\sin(4\pi x).$$

The associated energy eigenvalues – in atomic units, wherein $\hbar$ = 1 and the mass of the electron equals 1 – are $\pi^2/2$, $2\pi^2$, $9\pi^2/2$ and $8\pi^2$, respectively.

(a) Suppose the electron is initially (i.e., at time = 0) in the state,

$$\Psi(x,0) = \psi(x) = \frac{1}{\sqrt{2}}(\psi_1(x) + \psi_2(x)).$$

Plot the probability distribution, $|\Psi(x,t)|^2$, for the outcome of electron position measurement, at t = 0, $1/(3\pi)$, $2/(3\pi)$, $1/\pi$ and $4/(3\pi)$. To do this, evaluate the mod-squared wavefunction for x from 0 to 1 with an increment of 0.01.

(b) Determine the probability that the electron is on the left side of the box (i.e., $x < ½$) for each of the times in part (a). To do this, approximate the required integral as the product of the x increment and a sum over the discrete set of x values used in part (a). To do this more accurately, the integrand associated with the first and last x values should be multiplied by ½.

2. The interaction of the electron with light can induce transitions between the states of the electron in a box. The probability of a transition between two states, $\psi_n(x)$ and $\psi_{n'}(x)$, is proportional to

$$\langle \psi_n | x \psi_{n'} \rangle.$$

Determine the relative probabilities of the transitions from n = 1 to n' = 2, 3 and 4, and from n = 2 to n' = 3 and 4. Use a grid of x values to approximate the integrals, as in question 1.

3. The energy eigenfunctions of an electron in a two dimensional box (a 1 × 1 box) are labeled by two quantum numbers, n_x and n_y. For example,

$$\psi_{2,3}(x,y) = 2\sin(2\pi x)\sin(3\pi y).$$

(a) Evaluate $\psi_{2,3}(x)$ on a 11 × 11 grid of x and y values. Multiply these values by 10/max($\psi_{2,3}(x)$), and show only a single digit to give a visual representation of the wavefunction. [Option: Make a contour plot.]

(b) Determine the probability that electron is in the bottom left (i.e., $x < \frac{1}{2}$ and $y < \frac{1}{2}$) of the box by estimating the required integral as the product of x and y increments and a sum over $\left|\psi_{2,3}(x,y)\right|^2$ values. First and last x and y values should be multiplied by ½.