CHEM 3PA3, Fall 2016 – Assignment #1 Solutions

1. Given the lowest four eigenfunctions for an electron in a one-dimensional box of length $L = 1$, in natural units:

$$\begin{aligned}\psi_1(x) &= \sqrt{2}\sin(\pi x)\\ \psi_2(x) &= \sqrt{2}\sin(2\pi x)\\ \psi_3(x) &= \sqrt{2}\sin(3\pi x)\\ \psi_4(x) &= \sqrt{2}\sin(4\pi x)\end{aligned} \qquad \textbf{1.1}$$

with corresponding eigenvalues $E_1 = \pi^2/2,\ E_2 = 2\pi^2,\ E_3 = 9\pi^2/2,\ E_4 = 8\pi^2$. The initial state at time $t = 0$ is:

$$\Psi(x,0) = \frac{1}{\sqrt{2}}\big(\psi_1(x) + \psi_2(x)\big) \qquad \textbf{1.2}$$

a) To evaluate the probability distribution, we need the time-evolution of the initial state. Since it is a superposition of eigenstates of the time-independent problem, and the Hamiltonian does not explicitly contain time, we can use the general solution of the time-dependent Schrödinger equation:

$$\Psi(x,t) = \sum_n c_n e^{-i\hat{H}t}\psi_n = \sum_n c_n e^{-iE_n t}\psi_n \qquad \textbf{1.3}$$

The coefficients c_n are just the overlap integrals $\langle\psi_n|\Psi(x,0)\rangle$, which we can read off from **1.2** as both being $1/\sqrt{2}$. Thus:

$$\Psi(x,t) = e^{-i\frac{\pi^2}{2}t}\sin(\pi x) + e^{-2i\pi^2 t}\sin(2\pi x), \qquad \textbf{1.4}$$

after cancelling $\sqrt{2}$ factors and substituting in energy eigenvalues.

The probability density is then found by forming the square-norm of **1.4** (note the complex conjugation in the first parenthesis):

$$\begin{aligned}|\Psi(x,t)|^2 &= \left(e^{i\frac{\pi^2}{2}t}\sin(\pi x) + e^{2i\pi^2 t}\sin(2\pi x)\right)\left(e^{-i\frac{\pi^2}{2}t}\sin(\pi x) + e^{-2i\pi^2 t}\sin(2\pi x)\right)\\ &= \sin^2(\pi x) + e^{-\frac{3}{2}i\pi^2 t}\sin(\pi x)\sin(2\pi x) + e^{\frac{3}{2}i\pi^2 t}\sin(\pi x)\sin(2\pi x) + \sin^2(2\pi x)\\ &= \sin^2(\pi x) + 2\cos\left(\frac{3}{2}\pi^2 t\right)\sin(\pi x)\sin(2\pi x) + \sin^2(2\pi x)\end{aligned} \qquad \textbf{1.5}$$

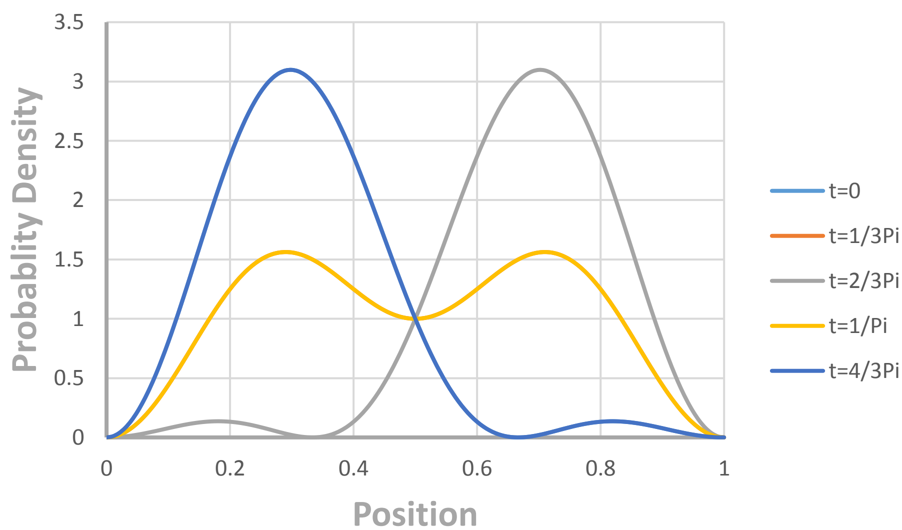
where the Euler formula has been applied in going to the final step in **1.5**. To plot the probability density at each given time step, we need to evaluate **1.5** over a series of points spanning the length of the box. Using an increment of $L/N = 0.01$, in, for example, Microsoft Excel, the first several rows of the workbook would appear as follows:

	t=0	t=1/3Pi	t=2/3Pi	t=1/Pi	t=4/3Pi
0	0	0	0	0	0
0.01	0.008874	0.004929	0.000985	0.004929	0.008874
0.02	0.035391	0.019651	0.003912	0.019651	0.035391
0.03	0.079236	0.043968	0.0087	0.043968	0.079236
⋮	⋮	⋮	⋮	⋮	⋮

The Excel formulas to generate columns 2-6 are as follows:

=(SIN(PI()*A2))^2+2*SIN(PI()*A2)*SIN(2*PI()*A2)+(SIN(2*PI()*A2))^2
=(SIN(PI()*A2))^2+(SIN(2*PI()*A2))^2
=(SIN(PI()*A2))^2-2*SIN(PI()*A2)*SIN(2*PI()*A2)+(SIN(2*PI()*A2))^2
=(SIN(PI()*A2))^2+(SIN(2*PI()*A2))^2
=(SIN(PI()*A2))^2+2*SIN(PI()*A2)*SIN(2*PI()*A2)+(SIN(2*PI()*A2))^2

Note that the spatial dependence of the wavefunction at times $t = 0$ and $t = 4/3\pi$ is equivalent, and similarly, for times $t = 1/3\pi$ and $t = 1/\pi$ (overlayed in the figure below). This is because the particle evolves back to its original distribution, owing to the fact that all of the time-dependence in **1.5** stems from the cosine function, which is periodic.



b) To evaluate the probability that the particle is in a particular region of the box, we can use the composite trapezoidal rule to numerically approximate the necessary integral of the probability density **1.5** for each of the given time steps:

$$\int_a^b dx\, f(x) \cong \frac{b-a}{N}\left[\frac{f(a)}{2} + \sum_{k=1}^{N-1} f\left(a + k\frac{(b-a)}{N}\right) + \frac{f(b)}{2}\right] \tag{1.6}$$

Here, $b - a = L = 1$, and so $(b-a)/N = 0.01$, the increment we used in part **a)**, with $f(x) = |\Psi(x,t)|^2$. We then obtain:

$$\begin{aligned} P\left(x < \frac{L}{2}, t = 0\right) &\cong 0.92 \\ P\left(x < \frac{L}{2}, t = \frac{1}{3\pi}\right) &\cong 0.50 \\ P\left(x < \frac{L}{2}, t = \frac{2}{3\pi}\right) &\cong 0.08 \\ P\left(x < \frac{L}{2}, t = \frac{1}{\pi}\right) &\cong 0.50 \\ P\left(x < \frac{L}{2}, t = \frac{4}{3\pi}\right) &\cong 0.92 \end{aligned} \tag{1.7}$$

The Excel formula to calculate, for example, the $t = 0$ probability would be `=0.01*(SUM(B2:B52)-0.5*(B2+B52))', where the columns are referenced as defined in part **a)**.

2. The transition probability between states under the influence of an electromagnetic field (i.e. light) is proportional to the square-norm of the dipole moment (which is itself proportional to the expectation value for the overlap of the initial state and the position operator acting on the final state):

$$P_{n' \leftarrow n} \propto |\langle \psi_n | x | \psi_{n'} \rangle|^2 \tag{2.1}$$

These integrals can be evaluated for the required transitions by again applying the trapezoidal rule (**1.6**) with a grid of points. The first step is to evaluate the bracket $\langle \psi_n | x | \psi_{n'} \rangle$. The first few rows of an Excel spreadsheet with these calculations would appear as follows:

	1->2	1->3	1->4	2->3	2->4
0	0	0	0	0	0
0.01	3.94E-05	5.91E-05	7.87E-05	0.000118	0.000157
0.02	0.000315	0.000471	0.000625	0.000939	0.001247
0.03	0.001058	0.001575	0.002079	0.003137	0.004139
⋮	⋮	⋮	⋮	⋮	⋮

which are tabulated using the following Excel formulas for columns 2-6:

=2*SIN(PI()*A2)*SIN(2*PI()*A2)*A2
=2*SIN(PI()*A2)*SIN(3*PI()*A2)*A2
=2*SIN(PI()*A2)*SIN(4*PI()*A2)*A2
=2*SIN(2*PI()*A2)*SIN(3*PI()*A2)*A2
=2*SIN(2*PI()*A2)*SIN(4*PI()*A2)*A2

Summing the columns in accord with **1.6** (e.g. `=0.01*(SUM(B3:B101)+0.5*(B2+B102))' for the 1->2 transition) gives:

$$\langle\psi_1|x|\psi_2\rangle \cong -0.18 \;\Longrightarrow\; P_{2\leftarrow1} \cong 0.032$$
$$\langle\psi_1|x|\psi_3\rangle \cong 2.4\times10^{-17} \;\Longrightarrow\; P_{3\leftarrow1} \cong 5.5\times10^{-34}$$
$$\langle\psi_1|x|\psi_4\rangle \cong -0.014 \;\Longrightarrow\; P_{4\leftarrow1} \cong 2.1\times10^{-4}$$ 2.2
$$\langle\psi_2|x|\psi_3\rangle \cong -0.19 \;\Longrightarrow\; P_{3\leftarrow2} \cong 0.032$$
$$\langle\psi_2|x|\psi_4\rangle \cong -3\times10^{-17} \;\Longrightarrow\; P_{4\leftarrow2} \cong 9\times10^{-34}$$

Here the effect of the selection rules in the particle in a box problem is strongly pronounced. The odd-to-odd and even-to-even transitions are, within numerical error, identically zero. The $1\rightarrow4$ transition is much weaker than the allowed transitions because, while not explicitly forbidden by the selection rules, the overlap between a wavefunction with no nodes within the box and one with three is not terribly high, so the relative incompatibility of the participating states is reflected in the lower transition likelihood.

3. Given the following eigenfunction of the two-dimensional box, with unit side lengths:

$$\psi_{2,3}(x,y) = 2\sin(2\pi x)\sin(3\pi y)$$ 3.1

To plot this wavefunction and get an idea of its nodal lines, we can set up a series of eleven points in $[0,1]$ (i.e including the endpoints) in both a row and a column in Excel, intersecting in a blank cell. To fill out all of the points in the 11x11 grid, we can use the Excel formula `=2*SIN(2*PI()*B$12)*SIN(3*PI()*$A11)', entered into the cell directly diagonally up from the blank one at the intersection of the rows and columns (i.e. entered at the origin). This will hold the value in the same row at the edge of the grid constant when it is filled across columns, and hold the value in the same column at the edge of the grid constant when it is filled up rows. The output will appear similar to what follows:

1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.90	0.00	0.95	1.54	1.54	0.95	0.00	-0.95	-1.54	-1.54	-0.95	0.00
0.80	0.00	1.12	1.81	1.81	1.12	0.00	-1.12	-1.81	-1.81	-1.12	0.00
0.70	0.00	0.36	0.59	0.59	0.36	0.00	-0.36	-0.59	-0.59	-0.36	0.00
0.60	0.00	-0.69	-1.12	-1.12	-0.69	0.00	0.69	1.12	1.12	0.69	0.00
0.50	0.00	-1.18	-1.90	-1.90	-1.18	0.00	1.18	1.90	1.90	1.18	0.00
0.40	0.00	-0.69	-1.12	-1.12	-0.69	0.00	0.69	1.12	1.12	0.69	0.00
0.30	0.00	0.36	0.59	0.59	0.36	0.00	-0.36	-0.59	-0.59	-0.36	0.00
0.20	0.00	1.12	1.81	1.81	1.12	0.00	-1.12	-1.81	-1.81	-1.12	0.00
0.10	0.00	0.95	1.54	1.54	0.95	0.00	-0.95	-1.54	-1.54	-0.95	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00

Since Excel does not allow self-referential formulas, to perform the scaling necessary to make the rudimentary contour plot, it is necessary to copy out the grid above and divide in the maximum value taken over the original grid (and multiply by the factor of 10, prior to reducing the displayed digits to 1). In common programming languages like MATLAB and Fortran, the original array can just be re-stored with its max() divided out, i.e. Psi23 = Psi23/max(Psi23), or equivalent. The objective, in either case, is to obtain a contour plot which illustrates the nodal lines across the wavefunction (your values may have been normalized differently; the factor in the bottom-left cell is Max(B1:L11), which corresponds to the maximum over the grid):

1.00	0	0	0	0	0	0	0	0	0	0	0
0.90	0	5	8	8	5	0	-5	-8	-8	-5	0
0.80	0	6	10	10	6	0	-6	-10	-10	-6	0
0.70	0	2	3	3	2	0	-2	-3	-3	-2	0
0.60	0	-4	-6	-6	-4	0	4	6	6	4	0
0.50	0	-6	-10	-10	-6	0	6	10	10	6	0
0.40	0	-4	-6	-6	-4	0	4	6	6	4	0
0.30	0	2	3	3	2	0	-2	-3	-3	-2	0
0.20	0	6	10	10	6	0	-6	-10	-10	-6	0
0.10	0	5	8	8	5	0	-5	-8	-8	-5	0
0.00	0	0	0	0	0	0	0	0	0	0	0
1.90	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00

Note the transition between positive and negative values at the fourth and seventh rows; the nodal lines along the x-direction (i.e. the zeroes of the y part of the wavefunction) are located here.

b) In order to estimate the probability, we first require the probability density, which in Excel requires making another duplicate of the grid with the squared values of the (unscaled) wavefunction in **a)**. It is easiest to integrate row-by-row (or equivalently, column-by-column), and then sum up the partial integrals. Using a syntax like `=0.01*(SUM(B11:G11)-0.5*(B11+G11))' to do the first row according to the trapezoidal rule (**1.6**), we can build up a list of the partial sums for each of the rows from $y = 0$ to $y = 0.5$, which cover from $x = 0$ to $x = 0.5$ (column G corresponds to $x = 0.5$ in the above reference scheme, and $y = 0.5$ is row 6). Summing all of these values (and then subtracting off half of the first and last values in this second list) gives a numerical integration of the $x < L/2,\ y < L/2$ quadrant of the box. By examining the symmetry in the contour plot from **a)**, we would expect to obtain

$$P\left(x < \frac{L}{2}, y < \frac{L}{2}\right) = \frac{1}{4},$$

which the numerical integration should bear out.