Chemistry 3730 Fall 2002 Test 1 Solutions

1. First, define the wavefunction:

```
> psi := (nx,ny,x,y,Lx,Ly) ->
2/sqrt(Lx*Ly)*sin(nx*Pi*x/Lx)*sin(ny*Pi*y/Ly);
```

$$\psi := (nx, ny, x, y, Lx, Ly) \rightarrow \frac{2\sin(\frac{nx\,\pi\,x}{Lx})\sin(\frac{ny\,\pi\,y}{Ly})}{\sqrt{Lx\,Ly}}$$

In this case, $n_x = 2$ and $n_y = 1$. Also, $L_x = L_y = L$. We therefore want to evaluate the integral

$$\int_{y=0}^{L/8}\int_{x=L/5}^{L/3}\psi_{2,1}^2\,dx\,dy.$$

In Maple notation, this is

```
> int(int(psi(2,1,x,y,L,L)^2,x=L/5..L/3),y=0..L/8);
```

$$\frac{1}{960}(-120\cos(\frac{\pi}{8})\sin(\frac{\pi}{8})\sqrt{3} - 128\cos(\frac{\pi}{8})\sin(\frac{\pi}{8})\,\pi$$
$$-480\cos(\frac{\pi}{8})\sin(\frac{\pi}{8})\cos(\frac{2\pi}{5})\sin(\frac{2\pi}{5}) + 15\pi\sqrt{3} + 16\pi^2$$
$$+60\pi\cos(\frac{2\pi}{5})\sin(\frac{2\pi}{5}))\Big/\pi^2$$

This complicated result can be converted to a number using the `evalf()` function:

```
> evalf(%);
```

$$0.003102952577$$

2. (a) A normalized wavefunction is one for which

$$\int_{\text{all space}}\psi^*\psi\,dV = 1.$$

This is required because $\psi^*\psi$ is the probability density. The above integral is the probability that a particle will be found somewhere in space, which clearly must be 1.

(b) Again, we will start by defining the wavefunction:

```
> phi := (x,L) -> x*(L-x);
```

$$\phi := (x, L) \to x\,(L - x)$$

A normalized version of this function, ϕ_{norm}, can be made by multiplying ϕ by a constant:

$$\phi_{\mathrm{norm}} = A\phi.$$

The constant A must then satisfy

$$\int_0^L \phi_{\mathrm{norm}}^2\,dx = A^2 \int_0^L \phi^2\,dx = 1.$$

By elementary algebra, we find that

$$A = \frac{1}{\sqrt{\int_0^L \phi^2\,dx}}.$$

```
A := 1/sqrt(int(phi(x,L)^2,x=0..L));
```

$$A := \frac{\sqrt{30}}{\sqrt{L^5}}$$

(c) If ϕ is orthogonal to ψ_n, then

$$\int_0^L \phi^* \psi\,dx = 0.$$

```
> psi := (n,x,L) -> sqrt(2/L)*sin(n*Pi*x/L);
```

$$\psi := (n, x, L) \to \sqrt{\frac{2}{L}}\,\sin(\frac{n\pi x}{L})$$

We now check for orthogonality. Because the wavefunction is real-valued, the complex-conjugate operation doesn't do anything.

```
> assume(n,integer);
> int(phi(x,L)*psi(n,x,L),x=0..L);
```

$$-\frac{2\,L^3\,\sqrt{2}\,\sqrt{\frac{1}{L}}\,((-1)^{n\tilde{}} - 1)}{n\tilde{}^3\,\pi^3}$$

This is zero if the quantity in parentheses is zero, i.e. if $(-1)^n = 1$ which occurs if n is even. In other words, ϕ is orthogonal to all the even numbered exact wavefunctions ($n = 2, 4, 6, \ldots$).

3. First, define the wavefunction and let Maple know that n is an integer as above. The expectation value is

$$\langle x^2 \rangle = \int_0^L \psi_n^* x^2 \psi_n \, dx.$$

```
> int(psi(n,x,L)*x^2*psi(n,x,L),x=0..L);
```

$$\frac{(-6\,((-1)^{n\tilde{}})^2 + 2\,n\tilde{}^2\,\pi^2 + 3)\,L^2}{6\,n\tilde{}^2\,\pi^2}$$

```
> simplify(%);
```

$$\frac{(-3 + 2\,n\tilde{}^2\,\pi^2)\,L^2}{6\,n\tilde{}^2\,\pi^2}$$

The large n limit is also easy to get with Maple:

```
> limit(%,n=infinity);
```

$$\frac{L^2}{3}$$

4. (a) Two quantities are compatible if their operators commute. Recall that

$$\begin{aligned} \hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y. \\ \therefore [\hat{L}_x, \hat{x}] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{x}]. \end{aligned}$$

At this point, we can see that this commutator will only involve terms in $[\hat{y},\hat{x}]$, $[\hat{p}_z,\hat{x}]$, $[\hat{z},\hat{x}]$ and $[\hat{p}_y,\hat{x}]$, all of which are zero. Accordingly, $[\hat{L}_x,\hat{x}] = 0$ which means that L_x and x are compatible.

(b)

$$\begin{aligned} [\hat{L}_x, \hat{y}] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{y}] \\ &= [\hat{y}\hat{p}_z, \hat{y}] - [\hat{z}\hat{p}_y, \hat{y}] \\ &= \hat{y}\cancelto{0}{[\hat{p}_z, \hat{y}]} + \cancelto{0}{[\hat{y}, \hat{y}]}\hat{p}_z - \left\{ \hat{z}[\hat{p}_y, \hat{y}] + \cancelto{0}{[\hat{z}, \hat{y}]}\hat{p}_y \right\} \\ &= \hat{z}[\hat{y}, \hat{p}_y] = i\hbar\hat{z} \end{aligned}$$

Since this commutator is nonzero, L_x and y are *not* compatible.

5. False. Counterexample: $\hat{x}$ commutes with both $\hat{y}$ and $\hat{p}_y$, but $\hat{y}$ and $\hat{p}_y$ do not commute with each other.