Problems in Chapter 15 (or 4) Chemistry 455A

Comments and hints about thinking about the problems:

Questions 1-9 are very good. My comments on these questions and hints for thinking about the answers.

Q15.1 Why are standing waves not compatible with the classic result? Hint: The nodes to not move with time and they are spread from negative infinity to positive infinity

Q15.2 Why can't you normalize the wave function for the free particle: It has unit amplitude so the integral is not finite, over an infinite interval. This sort of violates postulate one. People do like this problem for that reason, and modify wave functions to get around this conundrum.

Q15.3 Show the function of the P.I.B. (particle in a box) is continuous. How about the first derivative? How about the second derivative? First is discontinuous which might imply disaster when taking the next derivative, but then it all seems to work OK anyway.

Q15.4 Are energy levels degenerate for the 1D case? Look at the energies, are any two the same for different quantum numbers? In fact there is a very general theorem that no one D system can have two energy levels the same with different integer counters. But in 2 and 3 D if the dimensions of the box are square and cubical then you can have energies the same (degenerate) for different quantum numbers. More types of degeneracies happen in 3D.

Q15.5 Are we computing an absolute energy for the Kinetic energy, you bet.

Q15.6 Why are traveling waves not compatible with the boundary conditions? Follow the nodes with time, they move for traveling waves. For the standing wave solutions the time dependence on the wave function is the same as a phase factor, so the probability does not change in time even though the wave function does. The type of time dependence cannot contribute to anything physical as long as the wave function is in a single definite eigenstate.

Q15.7 What is the zero point energy for an electron or a He atom? Use the equation for the PIB and change the mass, and the zero point applies to the ground state or n=1 state.

Q15.8 How does the particle get from one side of the box to the other? Think of a guitar string moving, when it is up an octave: both sides are oscillating but it is stationary in the middle. This is done by touching the string half way and plucking.

Q15.9 Probability and Probability density. The density is the probability per unit distance (or volume for 3 D case). As the term density implies. So psi-stared times psi is the density and when you multiply by dx or dv (for 3 D) , the product is the probability over that interval dx. Of course to get the probability over some finite interval you should integrate the probability density.

Problems 1- 4 are for the Free Particle or particle in Free Space. V=0 everywhere.

P 15.1 Think about where the node is as a function of time. Re means take the real part of the exp term. Use Euler's identity here (this comes in real handy). To keep a node stationary the x must change as t changes. So this shows how x moves with t and so you can see whether x is increasing or decreasing with time.

P15.2 deBroglie's idea here.

P15.3 Operate on these functions with the momentum operator and see what you get. Use the relations of 15.2 to help identify the momentum.

P15.4 Good problem, again Euler's identity (run the other way) is very useful to see the result. Just operate with the Momentum operator and see whether the total of the two parts stays together as the wave function or if something messes up the summation.

Problems 15.5 – 15.15 These are all good PIB problems

P15.5 just identify whether an eigenfunctions or not. A) is a bit trickier because it does not obey boundary conditions. Make sure you can see that.

P15.6 Do some math. Not a great question, but the trick makes the integral easier. Nice to verify the functions are normalized. When they are it saves time later when evaluating properties.

P15.7 You can just equate the wave function to be zero at the two boundaries. You might compare with Problem 21 in chapter 13 (or 2) and use Euler's identity again, here we have it again.
I'm not sure what part b is about. I would have thought we could normalize everything so we get proper values of A and B. Maybe the problem means what does the probability density look like as a function of x and do you get the same result with either way to write it. Well, it had better come out that way because it is supposed to be another way to write the same eigenfunctions, and it must be normalized.

P 15.8 This is kind of a dog of a problem. I like P15.14 better for this. Do it instead. But make sure you understand the question by setting up the integral you have to do. You can use the rule in P15.4 to evaluate the integral in this and P15.14 as well. Also just do the general case of n, then substitute n=1 and n=3 for the two cases of interest here. It might be useful to do because the answer is given for this one.

P15.9 Are the eigenfunctions also eigenfunctions of the x operator. Well all you have to do is multiply x by the eigenfunctions. What do you make of it? Can that be just proportional to the original eigenfunctions times a constant? Also, to calculate the average position, do it for the general case (don't use n=3). By symmetry you can show that you have to find the particle is in the middle of the box. The best way to do this is draw a picture. The wave function squared is positive everywhere and just repeating

lumps. The probability must be an even function about the center and always positive. But (x-a/2) is an odd function about the center and so the integral must vanish because the integrand (being the product of the x part and the probability) is odd about the range of integration. So the answer must be the particle is on average always in the middle. What else would you expect? QM can be strange but it can't do that, can it?
If you really want to check it out, I found the following integral in a book that helps you do this problem. This does not take advantage of the symmetry I argued for, and so you can just do the problem from:

$$\int x \sin^2 x dx = \frac{x^2}{4} - \frac{x}{2}\sin 2x - \frac{1}{8}\cos 2x$$

as an indefinite integral. When you evaluate it at the limits on the first term will contribute to your answer. The answer should be independent of n.

P15.10 This is a very important problem. Be sure you know why the functions are not eigenfunctions of momentum. Also the average momentum again by symmetry should be clear, as the particle is going in one direction and then in another later and it has to bounce back and forth so on net it doesn't go anywhere because it is in the box. So you should be able to see by the symmetry of the integrand how the average momentum for any n should come out.

P15.11 This is an OK problem, and should be pretty straightforward, just comparing changes in m, n, and a. One sort of surprise is the energy gets smaller as the mass goes up. This is surprising because E = (1/2) mv^2 says that energy goes up as mass goes up. So what does this say about velocity? What does it say about momentum of the PIB as m changes?

P15.12 Here you should recognize this as the sum of two eigenfunctions with different energy. So this is one of those cases where it can't be an eigenfunctions just because the superposition or sum of two eigenfunctions with different energies can never be another eigenfunctions.

P15.13 This function is acceptable in the sense that any trial function is probably acceptable, but it is not an eigenfunction. But it is a nice trial function and fun to compare with the real eigenfunctions. By symmetry you should find the particle is in the middle. The fun part comes in looking at the width or variance after getting the square of it. The integral can be done because the integrand in all cases is a polynomial in x. So this is good practice. You should compare with the variance due to the eigenfunctions. As this trial function has no nodes it is much like an approximation to the ground state. Remember this function is just the wave function so even evaluating the norm will give you a 4^{th} order polynomial in the integrand. One way to simplify you life is define a new variable y=x/a in the integrand. That way the integral runs over zero to one. Much simpler.

P15.14 So here you can use the integral mentioned above in P15.6 to evaluate the density in the first ¼ of the box. Hopefully, as the n gets larger we have the classical result which of course says uniform positions because the reversal of direction is instantaneous for a classical particle as it hits the wall. A QM particle in a low energy state is aware of the wall all the time (sorry, no time in the problem) and so is not as often near the wall. You can tell that just from looking at the wave function (or the wave function squared, which is the probability density) in the ground state (they look pretty much alike). And the particle is definitely not near the wall.

P15.15 This is fundamental as it connects Schrodinger's time dependent equation with the time independent equation and relates the time dependent solution to the time independent solutions. This point is not strongly covered in the text and you should verify that you can start with Postulate 5 and get the time independent equation from it, and that implies you are going after the eigenfunctions. Realize postulate 5 does not require the wave function to be an eigenfunction of anything. So there is a special process done to get eigenfunctions. So why do we go through this, at all?