CHEM 452/452G HW #3 — Hand-In Concept Solutions

Q6.2

If you decrease Δk for constant m, what it means is that you are keeping the same number of waves, but not covering as much difference in the wavevector. Thus, the same number of waves would be present in the upper part, but their wavelengths would be more similar. This would manifest in the interference pattern by providing a larger envelope, but with the same fringe spacing (you can show this empirically in Mathematica). Effectively, the reduction in the range of k values included is a *decrease* the uncertainty in the momentum, so it must be compensated by an *increase* in the uncertainty of the position (the widening envelope).

Q6.4

Experiments always measure observables. By the postulates, the only values for a particular observable which can be observed are the eigenvalues of the corresponding operator. Thus, every time an experiment is performed on a superposition state, $\psi(x)$, composed of eigenfunctions, $\varphi(x)$,

$$\psi(x) = \sum_n b_n \varphi_n \ ,$$

you will always measure one of the eigenvalues of whatever operator your experiment measures (i.e., you will collapse the wavefunction to one of the φ_n, and your experiment will give the eigenvalue for that state). While you can get a sense of the relative weights by performing many, many experiments, you are always sampling from a probability distribution. In the limit of large numbers, your values for the expansion coefficients, b_n, will approach the correct values, but you cannot be truly certain that the values are correct.

Q9.11

We would expect that they might be unitless, no? When you square them, you get the probability, which is just a number, right? Not quite: you have to integrate in all three dimensions, and since we used r, that means we have to include r^2 in our integration. This is accounted for, fortunately, in the values seen in the unlabeled table in Section 20.3: they all have a factor of $\left(\frac{1}{a_0}\right)^{\frac{3}{2}}$ included in them. All other occurrences of units are scaled: we see lots of r/a_0 terms, but they will be unitless. Thus, the units are in $m^{-3/2}$. This is, conveniently, the answer to the second part of the question. By multiplying by $a_0^{3/2}$, we plot something which is unitless.

Q9.13

As the length of the box increases, the energy levels are spaced more closely. This is what happens to the Coulomb potential as we approach the ionization limit: the length of the box gets larger. Thus, as the energy of a state approaches that for $n = \infty$, the levels get closer and closer to one another.