Chem 3322 homework #3, due February 9, 2024

Problem 1

The function $\psi = e^{i(kx-\omega t)}$ represents a monochromatic wave travelling in the positive x direction with velocity

$$v_{\text{phase}} = \frac{\omega}{k} \tag{1}$$

where we use the term "phase" velocity to distinguish this velocity from others that will appear in this problem.

a) Show, using $E = \hbar\omega$ and $p = \hbar k$, that the phase velocity of this monochromatic ψ is *not* equal to the classical velocity v of the particle it represents! Assume that $V = 0$ (free particle).

b) At first sight, the result of part (a) seems counter-intuitive and is distressing. Note, however, that ψ itself does not have a physical interpretation: it is $|\psi|^2$ that we interpret physically as a probability density. What is $|\psi|^2$ for this wavefunction? Do we still have a contradiction?

c) Now, suppose we *add* to the above wave a second wave with slightly different k and ω values: say, $k + \Delta k$ and $\omega + \Delta\omega$. Then,

$$\psi_{\text{sum}} = e^{i(kx-\omega t)} + e^{i[(k+\Delta k)x-(\omega+\Delta\omega)t]} \tag{2}$$

Find an expression for $|\psi_{\text{sum}}|^2$, reducing it to an explicitly real form containing only trigonometric functions (*i.e.* get rid of all i's).

d) Show that $|\psi_{\text{sum}}|^2$ represents a wave travelling in the positive x direction with a so-called "group" velocity of

$$v_{\text{group}} = \frac{\Delta\omega}{\Delta k} \tag{3}$$

This velocity is characteristic of *any* superposition of a group of waves with closely spaced k and ω values. Hence the name "group" velocity.

e) Finally, notice that the ratio $\frac{\Delta\omega}{\Delta k}$ is essentially the *derivative* $\frac{d\omega}{dk}$ of ω with respect to k. Take the derivative of the quantum mechanical relation between ω and k, and show that the group velocity *is* equal to the classical velocity of the particle. In other words, interfering wave *groups* travel with the expected classical velocity.

Problem 2

Classical physics predicts that there is no stable orbit for an electron moving around a proton. What criterion did Niels Bohr and/or Louis de Broglie use to define special orbits that he/they assumed were stable? (it may help to read a general chemistry book)