Chem 3322 homework #3 solutions

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).

Solution:

$$v_{\text{phase}} = \frac{\omega}{k} = \frac{E}{p} = \frac{\frac{1}{2}mv^2}{mv} = \frac{v}{2} \tag{2}$$

so that the phase velocity is half of the classical velocity v.

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?

Solution:

$|\psi|^2 = 1$ so that there is no time dependence any more. Therefore the velocity would seem to be zero (stationary state). Since half of zero is still zero, it would appear we have removed the contradiction from part (a), although in reality things aren't that simple...

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,

$$\psi_{\text{sum}} = e^{i(kx-\omega t)} + e^{i[(k+\Delta k)x-(\omega+\Delta\omega)t]} \tag{3}$$

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).

Solution:

$$|\psi_{\text{sum}}|^2 = 1 + 1 + e^{i[(k+\Delta k)x-(\omega+\Delta\omega)t]}e^{-i(kx-\omega t)} + e^{-i[(k+\Delta k)x-(\omega+\Delta\omega)t]}e^{i(kx-\omega t)} \tag{4}$$

$$= 2 + 2\cos(\Delta kx - \Delta\omega t) \tag{5}$$

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

$$v_{\text{group}} = \frac{\Delta\omega}{\Delta k} \tag{6}$$

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

Solution: compare our answer to (d) with part (a) to see that $v_{\text{group}} = \Delta\omega/\Delta k$

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.

Solution:

For a free particle, the quantum mechanical relation between ω and k is

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \tag{7}$$

Thus $\omega = (\hbar k^2)/(2m)$, giving

$$\frac{d\omega}{dk} = \frac{d}{dk}\left(\frac{\hbar k^2}{2m}\right) = \frac{\hbar k}{m} = \frac{p}{m} = \frac{mv}{m} = v \tag{8}$$

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)

Solution: Bohr postulated that the angular momentum of the electron, in its orbit around the nucleus, is quantized.