# CHEM 452/452G HW #1 — Hand-in Concept Solutions

**Q1.4:** There will be a transition, but it will not be sharp! When $\lambda > a$, diffraction effects dominate. If a remains constant, but $\lambda$ begins to decrease, the fringe spacing in the diffraction pattern (see Fig. 12.5) will begin to decrease, consistent with Eq. 12.12:

$$\sin\theta = \frac{n\lambda}{a}, n = \pm1, \pm2, \pm3\ldots$$

We see that as $\lambda$ decreases, $\theta$ decreases, until there is effectively a negligible gap between fringes, and the "ray optics" picture is observed. The transfer from quantum to classical regimes must function in the same sort of gradual way. This is called the "correspondence principle."

**Q1.5:** The fact that increasing the light intensity changed the number, but not the velocity of the electrons emitted is interpreted to mean that the frequency of a photon contains the information about its energy, and that increasing intensity increased the number of photons, not the energy per photon. Another way to say that is that the energy comes in discrete packets (i.e., photons).

**Q2.1:** Plane waves have effectively no curvature, which means that they do not decay in power density (the intensity per square meter) as they propogate. Spherical waves, however, will decay because the further from the point source you are, the larger the sphere over which the total intensity emitted by the source becomes (surface area goes as $r^2$, where r is the distance from the source to the detector).

**1. Definitions**

a. <u>Wavefunction</u> – the quantum mechanical description of state. The conjugate square of the wavefunction ($\psi(x)^*\psi(x)dx$) gives the probability of finding the particle in the infinitesimal range dx.

b. <u>Operator</u> – a mathematical device which, when enacted on a function, produces a new function which may or may not be different from the original. Examples include differentiation, square root, and exponentiation.

c. <u>Eigenvalue</u> – the constant by which an eigenfunction is multiplied when an operator acts on that eigenfunction. Only a valid concept when a wavefunction is a true eigenvalue of the operator.

d. <u>Eigenfunction</u> – a function which, when operated on by a particular operator, is changed by a multiplicative factor (its eigenvalue).

e. <u>Hamiltonian</u> – the operator corresponding to the observable total energy, and comprised of kinetic and potential energy terms.

**2.** The Hamiltonian, $\hat{H}$, is an operator, not a scalar. Only numbers can be divided off of one another. If you prefer, think of E as an operator also: $\hat{E}$ means "multiply by E", so it is not true that "multiply by E" is the same thing as the "perform the Hamiltonian operation".