Chemistry 60649 Fall 2008
Professor J. Daniel Gezelter Due Wed. 9/17/2008

Problem Set 2

1. The Classical Wave Equation

   a) Use the method of separation of variables to show that the solution to the wave equation

   $$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}$$

   for electromagnetic waves in a cubic box of side L is given by:

   $$\psi(x,y,z,t) = Ae^{-i\omega t}\sin\frac{l\pi x}{L}\sin\frac{m\pi y}{L}\sin\frac{n\pi z}{L}$$

   with l, m, n integers. The boundary conditions are that $\psi = 0$ at $x, y, z = 0$ and at $x, y, z = L$.

   b) Show that the relation between the values of l, m, n and ω is given by

   $$\frac{\omega^2}{c^2} = \frac{\pi^2}{L^2}(l^2 + m^2 + n^2)$$

   c) We are often interested in a quantity called the density of states which is the distribution of eigenvalues. To find this quantity, we define

   $$r^2 = l^2 + m^2 + n^2$$

   and calculate the number of modes (eigenfunctions) $n(r)$ in the range from r to $r + dr$. For large r this is given by the increment in volume of one octant of a sphere going from radius r to $r + dr$ (when $l, m, n > 0$). Liboff shows this graphically in Figure 2.17. Use this and the relation between r and ω to show that

   $$n(r)dr = \frac{L^3\omega^2}{2\pi^2c^3}d\omega$$

   d) Use the relationship between linear and angular frequency, $\omega = 2\pi\nu$, to find the energy density of electromagnetic radiation in the box, $u(\nu)$, given in Eq. (1).

   $$En(r)dr = L^3u(\nu)d\nu$$

   $$u(\nu) = \frac{8\pi\nu^2}{2c^3}E \tag{1}$$

e) When multiplied by a factor of 2 to account for the two independent modes of polarization for each set of quantum numbers, and using equipartition of energy to set $E = kT$, Rayleigh obtained his and Jeans' law for black body radiation with the "ultraviolet catastrophe"

$$u(\nu) = \frac{8\pi kT}{c^3}\nu^2$$

Describe physically why this is a "catastrophe".

What was the fatal flaw in the derivation in parts a)-e)?

2. Determine $\langle E \rangle$ for the wavefunction

$$\psi(x,t) = c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar}, \text{ with } E_1 \neq E_2$$

Assume the Hamiltonian is time-independent and that ψ_1 and ψ_2 are normalized eigenfunctions of the Hamiltonian. Give the answer in the case when you also know that

$$\int \psi_1^*(x)\psi_2(x)dx = \int \psi_2^*(x)\psi_1(x)dx = 0$$

(i.e. ψ_1 and ψ_2 are orthogonal). What happens if this is not true?

3. Determine the energy levels and eigenfunctions for the following problem:

$$V(x) = 0 \qquad -\tfrac{a}{2} \leq x \leq \tfrac{a}{2}$$

$$V(x) = \infty \qquad |x| > \tfrac{a}{2}$$

4. The uncertainty principle

In this problem, we will see an example of how the relation $\Delta k \Delta x \sim 1$ arises for an electromagnetic wave. Consider a wave of the form:

$$E(x) = E_x \exp(-\frac{x^2}{2a^2} + ik_o x)$$

a) Determine $|E(x)|^2 = E(x)E^*(x)$ and draw a rough plot of $|E(x)|^2$ vs. x to show that the spatial extent of this wave is $\sim a$.

b) Next, we will decompose $E(x)$ into plane waves of the form e^{ikx}. $E(x)$ can be expressed as a superposition of plane waves, i.e.,

$$E(x) = \int_{-\infty}^{\infty} dk f(k) e^{ikx}$$

where $f(k)$ is the contribution (Fourier component) of the plane wave with wavenumber k. We can determine $f(k)$ by,

$$
\begin{aligned}
f(k) &= \tfrac{1}{2\pi}\int_{-\infty}^{\infty} dx E(x) e^{-ikx} \\
&= \tfrac{E_x}{2\pi}\int_{-\infty}^{\infty} dx \exp(-\tfrac{x^2}{2a^2} + i(k-k_o)x)
\end{aligned}
$$

Work out this integral (you've seen it before) and draw a rough plot of $|f(k)|^2$ vs. k. Show that the width of this distribution is $\Delta k \sim 1/a$.
Hence, $\Delta k \Delta x \sim 1$.

5. Show that
$$\sigma_x = \sqrt{< x^2 > - < x >^2}$$
for a particle in a box is less than a, the width of the box, for any value of n. If σ_x is the uncertainty in the position of the particle, could σ_x ever be larger than a? What does this tell us about the uncertainty in momentum, σ_p?