Chem 3322 homework #2 solutions

Problem 1, 10 marks – **separation of variables**

The heat equation is:

$$\frac{\partial u}{\partial t} = \alpha \nabla^2 u \tag{1}$$

where α is the thermal diffusivity of a substance, and $u(x, y, z, t)$ describes the temperature of a substance as a function of space and time. Show that the separation of variables procedure can be successfully applied to this partial differential equation to separate the space and time variables into separate differential equations. You can leave the spatial variables together for this question. We will see, later in the course, how to separate the three spatial variables into three separate equations, but don't do that here.

Solution:

We postulate that we can write

$$u(x, y, z, t) = S(x, y, z)\theta(t) \tag{2}$$

Substituting this into Eq. (1) yields, on the left hand side

$$S(x, y, z)\frac{d\theta(t)}{dt} \tag{3}$$

and on the right hand side,

$$\alpha\theta(t)\nabla^2 S(x, y, z) \tag{4}$$

Dividing both sides by u yields, on the left hand side,

$$\frac{1}{\theta(t)}\frac{d\theta(t)}{dt} \tag{5}$$

and on the right hand side,

$$\alpha\frac{1}{S(x, y, z)}\nabla^2 S(x, y, z) \tag{6}$$

For the equality of Eq. (1) to hold (and we didn't change the nature of the equality by dividing both sides by u), the left hand side (Eq. 5) cannot depend on time and the right hand side (Eq. 6) cannot depend on space. Also, clearly the left hand side doesn't depend on space (and clearly the right hand side doesn't depend on time), so we must conclude that each side, separately, must be a constant. But then the equality demands that this constant be the same for both sides. Let us call the constant c.

This generate a pair of equations, one involving the spatial variables and one involving the time variable, which completes the question:

$$\alpha \nabla^2 S(x, y, z) = cS(x, y, z) \tag{7}$$

$$\frac{d\theta(t)}{dt} = c\theta(t) \tag{8}$$

Problem 2, 10 marks – **Schrödinger Equation**

a) For a particle in free space ($V = 0$), the angular frequency ω and the wave number k of its associated wave function are related by

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \tag{9}$$

a) Verify that, if a monochromatic wave of the form $\psi = e^{i(kx-\omega t)}$ is substituted into the Schrödinger time dependent equation (also called the Schrödinger wave equation), the above relation is reproduced.

Solution:

Taking partial derivatives gives

$$\frac{\partial \psi}{\partial t} = -i\omega\psi \tag{10}$$

and

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2\psi \tag{11}$$

Substituting into Schoedinger's Equation and canceling ψ from both sides and rearranging gives the desired relationship between k and ω.

b) Show that $\psi = \cos(kx - \omega t)$ fails to satisfy the Schrödinger time dependent equation.

Solution:

In this case,

$$\frac{\partial \psi}{\partial t} = \omega \sin(kx - \omega t) \tag{12}$$

and

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2 \psi = -k^2 \cos(kx - \omega t) \tag{13}$$

If we substitute into the Schrödinger equation, we see that the two sides are not equal (for an arbitrary choice of the independent variables x and t), for example at $x = 0$, $t = 0$.

Problem 3 – Schrödinger Equation with a step potential, 10 marks

For the step potential we discussed in class, we decided that we could have different wavelengths on either side of the step but a single frequency. In this problem we will examine this observation in a little more detail. As we discussed, such a wavefunction must be continuous, and its first derivative with respect to position must also be continuous, since the Schrödinger equation includes a second derivative with respect to position (a twice-differentiable function must be continuous and must have a continuous first derivative.) With the potential energy defined as

$$V(x) = \begin{cases} 0 & \text{for } x < 0 \\ 1 & \text{for } x \geq 0 \end{cases} \tag{14}$$

we will consider the following wavefunction

$$\psi(x,t) = \begin{cases} Ae^{i(k_1 x - \omega t)} + Be^{-i(k_1 x + \omega t)} & \text{for } x < 0 \\ Ce^{i(k_2 x - \omega t)} & \text{for } x \geq 0 \end{cases} \tag{15}$$

The interpretation of this wavefunction is that we are considering a particle, initially in the $x < 0$ region of space, traveling to the right. As such, the A coefficient represents the particle traveling to the right in the $x < 0$ region of space. The B coefficient represents the particle traveling to the left in the $x < 0$ region of space, meaning that it has been reflected from the step. The C coefficient represents the particle traveling to the right in the $x > 0$ region of space, meaning that it has been transmitted through the step.

Show that this wavefunction solves the Schrödinger equation as long as

$$\hbar\omega = \frac{\hbar^2 k_1^2}{2m} = \frac{\hbar^2 k_2^2}{2m} + 1 \tag{16}$$

Also, work out the relationships between the coefficients A, B, and C such that the wavefunction is continuous and has a continuous first derivative over all of space (with $k_1 \neq k_2$).

Solution:

For $x < 0$, when we substitute ψ into the TDSE with $V(x) = 0$ we get

$$-i^2 \hbar \omega \psi = -\frac{\hbar^2}{2m} i^2 k_1^2 \psi \tag{17}$$

or

$$\hbar \omega = \frac{\hbar^2}{2m} k_1^2 \tag{18}$$

For $x > 0$, when we substitute ψ into the TDSE with $V(x) = 1$ we get

$$\hbar \omega = \frac{\hbar^2}{2m} k_2^2 + 1 \tag{19}$$

Now we need to apply the boundary conditions. First, we need $\psi_1(x = 0) = \psi_2(x = 0)$ where ψ_1 is the $x < 0$ wavefunction and ψ_2 is the $x > 0$ wavefunction. The time variable cancels from both sides, yielding the equation

$$A + B = C \tag{20}$$

Second, we need

$$\frac{\partial \psi_1}{\partial x} = \frac{\partial \psi_2}{\partial x} \tag{21}$$

at $x = 0$. The time variable cancels from both sides, yielding the equation

$$k_1(A - B) = k_2 C \tag{22}$$

If we want, we can use these two equations to express B and C in terms of A:

$$B = \frac{A(k_1 - k_2)}{(k_1 + k_2)} \tag{23}$$

$$C = \frac{2k_1 A}{(k_1 + k_2)} \tag{24}$$