Chem237: Lecture 18

Shane Flynn

5/16/18

1 Note

I have just transcribed the lecture notes, no thought has gone in yet. We need to sit down and analyze this. 9-17-19

2 PDEs

Partial Differential Equations (PDEs) can have ∞ dimensionality, the problems usually involve boundry conditions with an arbitrary function. So you usually need to know the funciton and its derivative, and the value of the funciton and the vaue of the functions derivative at the boundry to solve.

Consider a second order PDE (the wave equation with constant coefficient c)

$$\frac{\partial^2}{\partial t^2}U - c^2\frac{\partial^2}{\partial x^2}U = 0 \tag{1}$$

We can give some initial conditions like

$$\begin{aligned} U(x, t = 0) &= \phi x \\ \frac{\partial}{\partial t}U(x, t = 0) &= \psi(x) \end{aligned} \tag{2}$$

This PDE is linear and seperable, it is the easiest case to solve. As we will see, given a certain set of boundry conditions we may not actually get a yseful solution (for example: could get a solution being an infinite sum we can't solve).

One way to approach this problem is to guess a solution (standard approach in PDEs). If we assume the

$$U(x, t) = [f(x - ct) + g(x + ct)] \tag{3}$$

We need to satify the initial conditions

$$\frac{\partial}{\partial x}U = -cf'(x) + cg'(x) = \psi(x) \tag{4}$$

$$\int dx\frac{dU}{dx} \Rightarrow f(x) - g(x) = \frac{-1}{c}\int^x dy\ \psi(y) \tag{5}$$

Where the lower boundis undefined, because f(x) and g(x) are defined up to a constant we do not know the lower bound.

So second order PDE, infinte solutioon space, need to specify boundry conditions.

$$\begin{aligned} \int f(x) - g(x) &= -\frac{1}{2}\int^x dy\ \psi(y) \\ -cf'(x) + cg'(x) &= \psi(x) \end{aligned} \tag{6}$$

Solving these two equations simultansously gives the general solution to the 2D problem.

$$U(x, t) = \frac{1}{2}\left[\phi(x - ct) + \phi(x + ct)\right] + \frac{1}{2c}\int_{x+t}^{x+ct} dy\ \psi(y) \tag{7}$$

This can be easily generalized to the 3D case, U(x,y,z,t)

$$\frac{\partial^2}{\partial t^2}U - c^2\Delta U = 0 \tag{8}$$

3 Diffusion Equation

Fick's law is a well known linear response expression of teh form

$$J = -\frac{\sigma^2}{2}\frac{\partial}{\partial x}\rho \tag{9}$$

Here we will derive the diffusion equaiton

COnsider an interval J(x) to J(x + Δx). Assuming ρ=constant within our interval Δx then

$$\frac{\partial}{\partial x}\rho \; \Delta x = J(x) - J(x + \Delta x) \tag{10}$$

$$\frac{\partial}{\partial t}\rho = \frac{J(x) - J(x+\Delta x)}{\Delta x} \xrightarrow{\Delta \text{x}=0} \frac{\partial}{\partial t}\rho = -\frac{\partial}{\partial x}J \tag{11}$$

$$\begin{gathered} J = -\frac{\sigma^2}{2}\frac{\partial}{\partial x}\rho, \quad \frac{\partial}{\partial t}\rho = -\frac{\partial}{\partial x}J \Rightarrow \\ \frac{\partial}{\partial t}\rho = \frac{\sigma^2}{2}\frac{\partial^2}{\partial x^2}\rho \end{gathered} \tag{12}$$

3.1 Solving This Equaiton

$\rho_t(x) = \rho(x,t)$ with initial conditions $\rho_{t=0}(x) = \rho_0(x)$.

Turns out the solution is a Gaussian

$$\rho_t(x) = \frac{1}{\sqrt{2\pi\sigma^2 t}} \exp\left[-\frac{x^2}{2\sigma^2 t}\right] \tag{13}$$

In the limit of t=0, the Gaussian becomes a Delta function.

$$\int_{-\infty}^{\infty} dx \; \delta(x) f(x) = f(0) \tag{14}$$

The Delta function can also be defined as

$$\int_{-\epsilon}^{\epsilon} dx \; \delta(x) f(x) = f(0) \xrightarrow{\epsilon\, =\, 0} f(0)\int_{-\epsilon}^{\epsilon} dx \; \delta(x) = 1 \tag{15}$$

In the limit of ϵ going to 0 we have $\epsilon >> \sqrt{2\sigma^2 t}$, therefore

$$\int_{-\epsilon}^{\epsilon} dx \; \rho_t(x) \to 1 \tag{16}$$

Let g define a Gaussian $g_t(x)$ (is a distribution).

$$\int_{-\infty}^{\infty} dx \; g_t(x) = \int_{-\infty}^{\infty} dx \; g_0(x) \tag{17}$$

This is conservation of mass, integrals over space must be constant.

$$\int_{-\infty}^{\infty} dx \; x \; g_t(x) = 0 \tag{18}$$

Due to symmetry gaussian integral is 0 for the first moment.

$$\int_{-\infty}^{\infty} dx \; x^2 \; g_t(x) = \sigma^2 t \tag{19}$$

The second moment gives a broader gaussian (grows linear wrt t). Therefore the rmsd is $\sqrt{t}$ this is due to the diffusion process.

So for a delta function initial condiiton you get a simple solution of a Gaussian.

What about a general initial condition?

Theorem: This differential equation is a special case if $\rho_0(x) = \phi(x)$, then

$$\rho_t(x) = \int_{-\infty}^{\infty} dy\ \phi(y) g_t(x-y) \tag{20}$$

Apply the operator (in parenthesis) to the function $\rho_t(x)$

$$\left(\frac{\partial}{\partial t} - \frac{\sigma^2}{2}\frac{\partial^2}{\partial x^2}\right)\rho_t(x) = \int_{-\infty}^{\infty} dy\ \left[\frac{\partial}{\partial t} - \frac{\sigma^2}{dx^2} g_t(x-y)\right]\phi(y) \tag{21}$$

The RHS is a soln. to a differential equation with initial condiiton $\delta(x-y)$. At t=0, delta function is 0 or 1 therefore

$$\int_{-\infty}^{\infty}\left(\frac{\partial}{\partial t} - \frac{\sigma^2}{dy^2} g_t(x-y)\right)\phi(y)dy \xrightarrow{\text{t=0}} \phi(x) \tag{22}$$

3.2 Schrodinger

TISE

$$\left(\widehat{H} - E_k\right)\psi_k = 0 \Rightarrow \widehat{H}\psi = E\psi \tag{23}$$

Where $\widehat{H} = -\nabla^2 + U(r)$.

The TDSE is given by

$$i\frac{\partial}{\partial t}\psi = \widehat{H}\psi \tag{24}$$

If H is not a function of t then it is seperable.

$$\psi(r,t) = \exp\left[i\widehat{H}t\right]\psi(r,0) \tag{25}$$

This is informative but it is not a solution. If H is not a function of t then $e^{i\widehat{H}T}$ is equivalent to the eigenvalue problem of TISE $\widehat{H}\psi = E\psi$.

If this is the case we can do eigendecomposition.

$$\begin{aligned} e^{i\widehat{H}t} &= \sum_k c^{iE_k t}\left|\psi_k\right\rangle\left\langle\psi_k\right| \\ \psi)r,t) &= e^{i\widehat{H}t}\psi(r,0) \\ &= \sum_{k=1}^{\infty} e^{iE_k t}\left\langle\psi_k|\psi_0\right\rangle\psi_k(r) \end{aligned} \tag{26}$$

In the gevinning of class we did not use seperability the wave equation was simple and we guessed a solution. Now we have a seperabel pde (second order) not simple, so we use seperability and just get an infinite sum to solve.