Lecture #19: Variation Method and Partial Differential Equations

I. Variation Method

A. Finding Approximate Eigenvalues and Eigenfunctions

1. Recall, for a normalized function $\psi = \sum_i a_i |\phi_i\rangle$, the expectation value is a weighted function of eigenvalues,

$$\langle H \rangle = \langle \psi | H | \psi \rangle = \sum_i |a_i|^2 \lambda_i$$

2. This holds true, even if we don't know λ_i and $|\phi_i\rangle$.

3. $\langle H \rangle$ is an upper limit to the smallest eigenvalue.

4. Variation Method: To estimate $|\phi_i\rangle$ and λ_i,
   (1) Assume a functional form ψ that contains parameters
   (2) Minimize $\langle H \rangle$ with respect to the parameters.

B. Example: Electron wave functions

1. Single-electron wave function $\psi = \left(\frac{\zeta^3}{\pi}\right)^{\frac{1}{2}} e^{-\zeta r}$ where ζ is parameter.

   a. Hartree Atomic Units: $m_e = e = \hbar = 1$.

2a. Kinetic energy operator: $\langle T \rangle = \langle \psi | T | \psi \rangle = \zeta^2/2$

b. Potential energy $\langle V \rangle = -Z\zeta$ Z - atomic number of nucleus.

3. Thus $\langle H \rangle = \langle T + V \rangle = \zeta^2/2 - Z\zeta$

4. Minimize w.r.t. ζ: $\frac{d}{d\zeta}\left[\frac{\zeta^2}{2} - Z\zeta\right] = \zeta - Z = 0 \Rightarrow \boxed{\zeta = Z}$

5. Thus $\psi = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr}$ and $\langle H \rangle = \frac{Z^2}{2} - Z^2 = -\frac{Z^2}{2}$

6. Two-electron Atom a. Take $\Psi = \psi(1)\psi(2)$ with same ζ.

   b. $H = T(1) + T(2) + V(1) + V(2) + U(1,2)$ where $U(1,2) = \frac{1}{|r_1 - r_2|}$

I. B. (Continued) Hawes (2)

7. $\langle H \rangle = \frac{\zeta^2}{2} + \frac{\zeta^2}{2} - Z\zeta - Z\zeta + \frac{5\zeta}{8} \underset{\uparrow}{=} \zeta^2 - \frac{27\zeta}{8}$

Z = 2 for Helium

8. Minimize: Taking $\frac{d}{d\zeta}\langle H \rangle = 0$ yields $\boxed{\zeta = \frac{27}{16}}$

9. a. Thus $\langle H \rangle = -\left(\frac{27}{16}\right)^2 = -2.8477$ hartree

b. Best numerical value is $\langle H \rangle = -2.9037$ hartree, 2% higher.

c. NOTE: Even a very rough guess for two wave eigenfunction yields a relatively good answer!

II. Partial Differential Equations (PDEs)

A. Introduction:

1. Differential equations with derivatives of more than 1 independent variable, $\phi(x,y)$ $\left(\frac{\partial^2 \phi}{\partial x^2}\right)_y$, $\frac{\partial^2 \phi}{\partial x \partial y}$, $\left(\frac{\partial^2 \phi}{\partial y^2}\right)_x$, etc.

2. Linear operator: $\frac{\partial\left[a\phi(x,y) + b\phi(x,y)\right]}{\partial x} = a\frac{\partial \phi(x,y)}{\partial x} + b\frac{\partial \phi(x,y)}{\partial x}$

3. General form: $\mathcal{L}\,\phi(x,y) = F(x,y)$

   a. Homogeneous if $F(x,y) = 0$, inhomogeneous if $F(x,y) \neq 0$.

4. Superposition Principle: Any linear combination of solutions is a solution for homogeneous PDEs

5. Types of PDEs:

   a. Linear, Homogeneous $\nabla^2\psi = 0$ Laplace's Eq.

   b. Linear, Inhomogeneous $\nabla^2\psi = f(\underset{\sim}{r})$ Poisson's Eq.

   c. Nonlinear, Inhomogeneous $\frac{\partial \underset{\sim}{u}}{\partial t} + \underset{\sim}{u}\cdot\nabla\underset{\sim}{u} = -\frac{\nabla p}{\rho}$ Euler's Eq. (Hydrodynamics

6. Examples:

a. Laplace's Equation $\nabla^2 \psi = 0$

b. Poisson's Equation $\nabla^2 \psi = -\frac{\rho}{\varepsilon_0}$

c. Diffusion Equation $\nabla^2 \psi = \frac{1}{a^2} \frac{\partial \psi}{\partial t}$

d. Wave Equation $\nabla^2 \psi = \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2}$

e. Schrödinger's Equation $-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t}$

f. Maxwell's Equations (Coupled, first-order equations)

III. First-Order PDEs

A. Method of Characteristics:

1. Consider $\mathcal{L}\phi = a\frac{\partial \phi}{\partial x} + b\frac{\partial \phi}{\partial y} = 0$ where $\phi(x,y)$ and a, b are constants.

2. We want to find a variable transformation $(x,y) \to (s,t)$ such that the PDE is transformed to an ODE.

a. Choose $x(s,t)$ and $y(s,t)$. Thus $\phi(x,y) = \phi[x(s,t), y(s,t)] = \hat{\phi}(s,t)$

b. And $\frac{\partial \phi}{\partial x} = \frac{\partial \hat{\phi}}{\partial s}\frac{\partial s}{\partial x} + \frac{\partial \hat{\phi}}{\partial t}\frac{\partial t}{\partial x}$

$\frac{\partial \phi}{\partial y} = \frac{\partial \hat{\phi}}{\partial s}\frac{\partial s}{\partial y} + \frac{\partial \hat{\phi}}{\partial t}\frac{\partial t}{\partial y}$

c. Collecting $\frac{\partial \hat{\phi}}{\partial s}$ and $\frac{\partial \hat{\phi}}{\partial t}$, $\mathcal{L}\phi = \frac{\partial \hat{\phi}}{\partial s}\left[a\frac{\partial s}{\partial x} + b\frac{\partial s}{\partial y}\right] + \frac{\partial \hat{\phi}}{\partial t}\underbrace{\left[a\frac{\partial t}{\partial x} + b\frac{\partial t}{\partial y}\right]}_{\text{Set} = 0.} =$

d. Want $a\underbrace{\left(\frac{\partial t}{\partial x}\right)_y}_{=b} + b\underbrace{\left(\frac{\partial t}{\partial y}\right)_x}_{=-a} = 0$

$\Rightarrow \left(\frac{\partial t}{\partial x}\right)_y = b \Rightarrow t = bx + C_1(y)$

$\Rightarrow \left(\frac{\partial t}{\partial y}\right)_x = -a \Rightarrow t = -ay + C_2(x)$

e. Thus $\boxed{t = bx - ay}$

3. To find $s(x,y)$, we want coordinates s & t to be orthogonal.

a. $dt = 0 = b\,dx - a\,dy$ (Line of constant t) $\Rightarrow \frac{dy}{dx} = \frac{b}{a}$

b. Orthogonal lines on (x,y) plane have $\frac{dy}{dx} = \frac{-a}{b}$ $\Rightarrow a\,dx + b\,dy = 0 = ds$

$\Rightarrow \boxed{s = ax + by}$

c. NOTE: $\underset{\sim}{\hat{e}}_t \cdot \underset{\sim}{\hat{e}}_s = 0 \Rightarrow$ orthogonal

III. A. Continued

4\. a. Thus $\mathcal{L}\phi = a\dfrac{\partial\phi}{\partial x} + b\dfrac{\partial\phi}{\partial y} = \boxed{(a^2+b^2)\dfrac{\partial\hat{\phi}}{\partial s} = 0}$ where $\hat{\phi}(s,t)$.

b. General Solution $\boxed{\hat{\phi}(s,t) = f(t)}$ where $f(t)$ is arbitrary

c. In terms of original variables, $\boxed{\phi(x,y) = f(bx-ay)}$

d. Check: $\mathcal{L}\phi = a\dfrac{\partial f(bx-ay)}{\partial x} + b\dfrac{\partial f(bx-ay)}{\partial y} = [a(b)+b(-a)]\dfrac{\partial f}{\partial t} = 0.$

5\. Characteristic Curves:

a. Curves of constant t are the characteristics of the PDE.

b. The solution ϕ is constant along the characteristics, (t=const.)

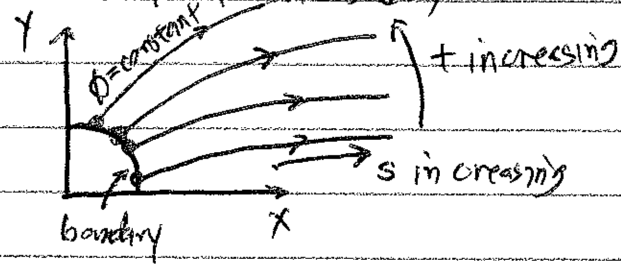
c. The variable s increases along the characteristics.

d. Characteristics are stream lines of s

6\. Boundary Conditions and Inconsistency

a. If we know ϕ at some point on a boundary, we know it all along the characteristic.

b. If a boundary condition is specified along a characteristic or a if characteristic intersects a boundary twice, it will generally lead to an inconsistency.



B. General First-Order PDE

1\. $\mathcal{L}\phi = a\dfrac{\partial\phi}{\partial x} + b\dfrac{\partial\phi}{\partial y} + q(x,y)\,\phi = F(x,y)$

2. Same characteristic transformation: $s = ax + by$, $t = bx - ay$

a. $(a^2+b^2)\frac{\partial \hat{\phi}}{\partial s} + \hat{q}(s,t)\hat{\phi} = \hat{F}(s,t)$ where $\hat{q}(s,t) = q[x(s,t), y(s,t)]$, etc.

b. NOTE: $x(s,t) = \frac{as+bt}{a^2+b^2}$, $y(s,t) = \frac{bs-at}{a^2+b^2}$

c. Result is an ODE in variable s with a parameter t.

3. Ex: $\frac{\partial \phi}{\partial x} + \frac{\partial \phi}{\partial y} + (x+y)\phi = 0$

a. Transform to characteristic variables: $t = x-y$, $s = x+y$

b. Thus $2\frac{\partial \hat{\phi}}{\partial s} + s\hat{\phi} = 0$

c. Using separation of variables: $\frac{d\phi}{\phi} = -\frac{1}{2}s\,ds \Rightarrow \ln\phi = -\frac{s^2}{4} + C(t)$

$\Rightarrow \hat{\phi}(s,t) = e^{-s^2/4} f(t)$

d. Using $\frac{s^2}{4} = \frac{t^2}{4} + xy$, $e^{-s^2/4}f(t) = e^{-xy}\left[e^{-t^2/4}f(t)\right] = e^{-xy}g(t)$, so

$\boxed{\phi(x,y) = e^{-xy}g(x-y)}$ where $g(t)$ is arbitrary.

C. 3D PDEs

1. Consider $a\frac{\partial \phi}{\partial x} + b\frac{\partial \phi}{\partial y} + c\frac{\partial \phi}{\partial z} = 0$ where $\phi(x,y,z)$ & a,b,c constants.

2. Determine $s(x,y,z)$, $t(x,y,z)$ and $u(x,y,z)$ such that

a. $\frac{\partial \hat{\phi}}{\partial t} = 0$ and $\frac{\partial \hat{\phi}}{\partial u} = 0$ where $\hat{\phi}(s,t,u)$

b. Choose transformation maintaining (s,t,u) as orthogonal coordinates.

c. Yields $(a^2+b^2+c^2)\frac{\partial \hat{\phi}}{\partial s} = 0$

d. General Solution: $\hat{\phi} = f(t,u)$ $f(t,u)$ is arbitrary function.

i. $t = \text{const}$, $u = \text{const}$ are characteristics $\Rightarrow \hat{\phi} = \text{constant}$

ii. A given (t,u) chooses characteristic, along which s increases.

3. Boundary Conditions and Inconsistency

a. A boundary condition along a surface cannot contain a characteristic, nor can a characteristic intersect the boundary surface twice, or an inconsistency may arise.

IV Second-Order PDEs

A. Method of Characteristics and Classes of PDEs

1. Hyperbolic PDE $a^2\frac{\partial^2\phi}{\partial x^2} - c^2\frac{\partial^2\phi}{\partial y^2} = 0 \qquad \phi(x,y)$

a. Factor: $\underbrace{\left[a\frac{\partial}{\partial x} + c\frac{\partial}{\partial y}\right]}_{=0}\underbrace{\left[a\frac{\partial}{\partial x} - c\frac{\partial}{\partial y}\right]}_{=0}\phi = 0$ Note: Linear differential operators commute here.

b. Solutions: $\phi_1(x,y) = f(cx - ay) \quad \phi_2(x,y) = g(cx + ay)$ ← Characteristic Solutions, f & g are arbitrary.

2. Elliptic PDE: $a^2\frac{\partial^2\phi}{\partial x^2} + c^2\frac{\partial^2\phi}{\partial y^2} = 0$

a. Factor: $\left[a\frac{\partial}{\partial x} + ic\frac{\partial}{\partial y}\right]\left[a\frac{\partial}{\partial x} - ic\frac{\partial}{\partial y}\right]\phi = 0$

b. Leads to complex characteristics that do not yield physically relevant solutions.

3. More General Case: $\mathcal{L}\phi = a\frac{\partial^2\phi}{\partial x^2} + 2b\frac{\partial^2\phi}{\partial x\partial y} + c^2\frac{\partial\phi}{\partial y^2} = 0$

a. Factor: $\mathcal{L} = \left(\frac{b + \sqrt{b^2-ac}}{c^{\frac{1}{2}}}\frac{\partial}{\partial x} + c^{\frac{1}{2}}\frac{\partial}{\partial y}\right)\left(\frac{b - \sqrt{b^2-ac}}{c^{\frac{1}{2}}}\frac{\partial}{\partial x} + c^{\frac{1}{2}}\frac{\partial}{\partial y}\right)$

b. Classes: i. $b^2 - ac > 0$ Hyperbolic, two real characteristics

ii. $b^2 - ac < 0$ Elliptic, two complex conjugate characteristics

iii. $b^2 - ac = 0$ Parabolic, one real characteristic, $a\frac{\partial\phi}{\partial x} - \frac{\partial^2\phi}{\partial y^2}$.

c. General Characteristic transformation: i. $\xi = c^{\frac{1}{2}}x - c^{-\frac{1}{2}}by$, $\eta = c^{-\frac{1}{2}}y$

ii. $\mathcal{L}\phi = (ac - b^2)\frac{\partial^2\phi}{\partial\xi^2} + \frac{\partial^2\phi}{\partial\eta^2}$

iii. Characteristic slopes: $\frac{dy}{dx} = \frac{c}{b \pm \sqrt{b^2-ac}}$

B. Derivatives in Time and Space

1. The elliptic, hyperbolic, and parabolic classifications are most frequently used in common physics problems involving time & space derivatives.

IV B. (Continued)

2. Classifications: a. Laplace Eq. $\nabla^2\psi = 0$ elliptic

b. Poisson Eq. $\nabla^2\psi = -\frac{\rho}{\epsilon_0}$ elliptic

c. Wave Eq. $\nabla^2\psi = \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}$ hyperbolic

d. Diffusion Eq. $\nabla^2\psi = a\frac{\partial\psi}{\partial t}$ parabolic

3. Note: If coefficients are spatially dependent, classification is only local.

4. Boundary Conditions (often initial conditions — boundary in time)

a. Cauchy BCs: ϕ, $\frac{\partial\phi}{\partial t}$ at $t=0$

b. Dirichlet BCs: ϕ specified on boundary

c. Neumann BCs: $\frac{\partial\phi}{\partial t}$ specified on boundary

C. Nonlinear PDEs

1a. Linear Wave Eq: $\frac{\partial\psi}{\partial t} + c\frac{\partial\psi}{\partial x} = 0$ b. Nonlinear Wave Eq: $\frac{\partial\psi}{\partial t} + c(\psi)\frac{\partial\psi}{\partial x} = 0$

Speed depends on wave ψ.

2. Dispersive Waves: Solution $\psi(x,t) = A\cos[kx - \omega(k)t]$ where $\omega''(k) \neq 0$.

3. Korteweg-deVries Equation: $\boxed{\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi}{\partial x} + \frac{\partial^3\psi}{\partial x^3} = 0}$

NL term

a. Solutions: Solitons

i. Wave steepening (NL) balanced by wave dispersion

$\Rightarrow$ Wave packet shape remains in steady state.

ii. Example: River Bore (Severn Bore in England).

4. Solution Method: a. Characteristic $\psi(\xi = x - ct)$

b. Thus $(\psi - c)\frac{d\psi}{d\xi} + \frac{d^3\psi}{d\xi^3} = 0$ $\leftarrow$ ODE.

c. Integrate: $\frac{d^2\psi}{d\xi^2} = c\psi - \frac{\psi^2}{2}$

d. Multiply by $\frac{d\psi}{d\xi}$ and integrate $\Rightarrow \left(\frac{d\psi}{d\xi}\right)^2 = c\psi^2 - \frac{\psi^3}{3}$

e. Square root and integrate $\Rightarrow$ $\boxed{\psi(x-ct) = \frac{3c}{\cosh^2\left[\frac{1}{2}c^{1/2}(x-ct)\right]}}$