# 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 $\lambda_i$ 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 $\lambda_i$,
(1) Assume a functional form $\psi$ 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 $\zeta$ 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. $\zeta$: $\frac{d}{d\zeta}\left[\frac{\zeta^2}{2} - Z\zeta\right] = \zeta - Z = 0 \Rightarrow \boxed{\zeta = Z}$

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 $\zeta$.

b. $H = T(1) + T(2) + V(1) + V(2) + U(1,2)$ where $U(1,2) = \frac{1}{|\vec{r}_1 - \vec{r}_2|}$

I. B. (Continued)

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

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

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 | $\nabla^2\phi = 0$ | Laplace's Eq. |
| b. Linear, Inhomogeneous | $\nabla^2\phi = f(\underline{r})$ | 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 |

II. A. (Continued)

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 $(x,y) \rightarrow (s,t)$ 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 coordinate $s$ & $t$ 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 $\mathcal{L}\phi = a\frac{\partial\phi}{\partial x} + b\frac{\partial\phi}{\partial y} = \boxed{(a^2+b^2)\frac{\partial\hat{\phi}}{\partial s} = 0}$ 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: $\mathcal{L}\phi = a\frac{\partial f(bx-ay)}{\partial x} + b\frac{\partial f(bx-ay)}{\partial y} = [a(b)+b(-a)]\frac{\partial f}{\partial t} = 0.$

5. Characteristic Curves:

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

b. The solution $\phi$ is constant along the characteristics, ($t$=const)

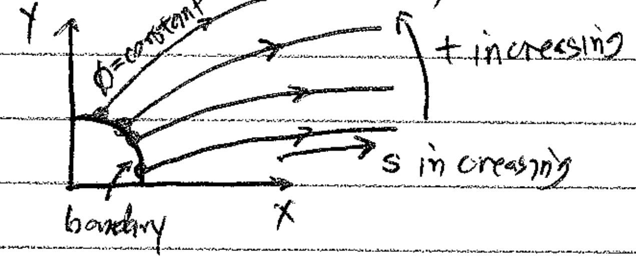
c. The variable s increases along the characteristics.

d. Characteristics are stream lines of s

6. Boundary Conditions and Inconsistency

a. If we know $\phi$ 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. $\mathcal{L}\phi = a\frac{\partial\phi}{\partial x} + b\frac{\partial\phi}{\partial y} + q(x,y)\,\phi = F(x,y)$

III B. (Continued)

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: $\frac{d\hat\phi}{\hat\phi}=-\frac{1}{2}s\,ds \Rightarrow \ln\hat\phi=-\frac{s^2}{4}+C(t)$

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

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. $t=$ const, $u=$ const are characteristics $\Rightarrow \hat\phi=$ 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 $a^2\frac{\partial^2\phi}{\partial x^2}-c^2\frac{\partial^2\phi}{\partial y^2}=0$ $\phi(x,y)$

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: $\phi_1(x,y)=f(cx-ay)$ $\phi_2(x,y)=g(cx+ay)$ ← 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: $\phi, \frac{\partial\phi}{\partial t}$ at $t=0$

b. Dirichlet BCs: $\phi$ 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: $\frac{\partial\psi}{\partial t} + \underset{\uparrow}{c(\psi)}\frac{\partial\psi}{\partial x} = 0$

Speed depends on wave $\psi$.

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

3. Korteweg-deVries Equation: $$\boxed{\frac{\partial\psi}{\partial t} + \underset{\substack{\uparrow \\ \text{NL term}}}{\psi}\frac{\partial\psi}{\partial x} + \frac{\partial^3\psi}{\partial x^3} = 0}$$

a. Solutions: Solitons

i. Wave steepening (NL) balanced by wave dispersion

⇒ 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 $(\psi - c)\frac{d\psi}{d\xi} + \frac{d^3\psi}{d\xi^3} = 0$ ← 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 ⇒ $\left(\frac{d\psi}{d\xi}\right)^2 = c\psi^2 - \frac{\psi^3}{3}$

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