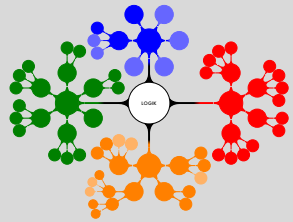

Lecture 8

Numerical Techniques: Differential Equations - Eigenvalue Problems

Wave Motion Along a Spring, Hydrogen Atom

IKC-MH.55 *Scientific Computing with Python* at December 15, 2023

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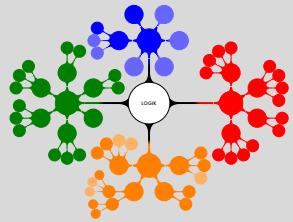

Differential Equations

1 Initial Value Problems.

2 Boundary Value Problems.

3 Eigenvalue (characteristic-value) Problems:

Even if the boundary conditions of the differential equation are available, the solutions can only exist for some *specific values* of a parameter in the system. For example,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)$$

- In Schrödinger equation, there are solutions that $\psi(x)$ goes to zero at infinity for certain values of the energy E.
- These E_n values satisfying this condition are the **eigenvalues** of the differential equation.

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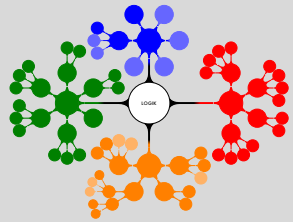

Boundary/Eigen Value Problems

- See the following 2nd degree differential equation:

$$y'' = f(x, y, y' : \lambda)$$

- Again, let the boundary conditions of this equation to be given at both ends.
- If these conditions can only be satisfied for *certain* λ *values*, we call it the *eigenvalue problem*.
  - e.g.: Vibrations of a wire with both ends fixed give stable solution only for *certain wavelengths*.
  - e.g.: Solutions of the Schrödinger equation that are zero at infinity exist only for *certain energy eigenvalues*.
- Some boundary value problems in physics/engineering have a solution based on an eigenvalue.
- **In terms of numerical solution, boundary value and eigenvalue problems are solved by the same method.**

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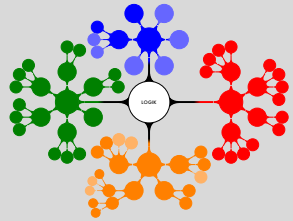


Eigenvalue Problems I

1 For example, standing waves are the solutions of the following differential equation for a string fixed at both ends:

$$\frac{d^2y(x)}{dx^2} + k^2 y(x) = 0$$

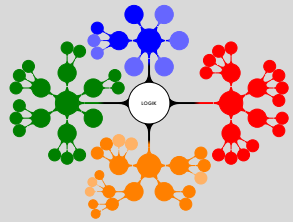
Here $k = 2\pi/\lambda$ represents the wavenumber.

- If the two ends of the L-length string are fixed, then corresponding boundary values are:

$$y(0) = y(L) = 0$$

- Although there are sufficient boundary conditions, there are only solutions for *certain k* values.
- It is impossible to satisfy these boundary conditions for other k values.
- The standing wave solution in the string:

$$y(x) = Asinkx + Bcoskx$$



Eigenvalue Problems II

- Boundary conditions to find the coefficients A, B;

$$y(0) = 0 \rightarrow \quad A * 0 + B * 1 = 0 \quad \rightarrow B = 0$$
$$y(L) = 0 \rightarrow \quad A \sin kL = 0 \quad \rightarrow kL = n\pi \ (n = 1, 2, \ldots)$$

- According to these results, there is only one set of solution as $k = \pi/L, 2\pi/L, \ldots$ values. ($k_n = n\pi/L \rightarrow$ *eigenvalue(s)*.)

2 Another example is the Schrödinger equation in quantum mechanics. If we write it in one-dimensional space,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

Here $V(x)$ is the potential energy function of the particle, and E is its total energy.

- Boundary conditions for the wave function are given for $x = \pm\infty$:

$$\psi(\pm\infty) \rightarrow 0$$

- Again, this differential equation has solutions satisfying the boundary conditions only for *certain E* eigenvalues.

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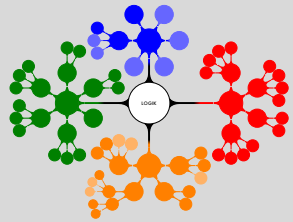

Eigenvalue Problems III

For eigenvalue problems, the trial-and-error (shooting) method is also used.

- However, an estimated value is given to the eigenvalue instead of giving to the derivatives at the boundary.
- Then, a trial solution is obtained.
- By comparing this trial solution with the value at the boundary condition, the eigenvalue is readjusted and another trial is performed.
- Finally, the solution is to be found when the true eigenvalue is approached within a certain margin of error.

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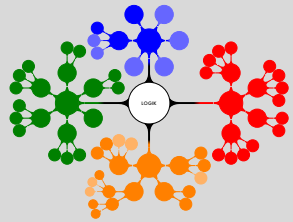

Standing Waves on a String I

- The wave equation and boundary conditions in a string of length $L = 1\ m$ with both fixed ends are as follows:

$$\frac{d^2y(x)}{dx^2} + k^2 y(x) = 0 \quad \& \quad y(0) = y(1) = 0$$

Firstly, transform this quadratic equation into a system of linear (first degree) equations:

$$y \rightarrow y_1$$
$$\frac{dy}{dx} \rightarrow y_2$$

with these values (y_1 *and* y_2), the system of equations to be solved: (**Now, we have a set of equations.**)

$$\frac{dy_1}{dr} = y_2$$
$$\frac{dy_2}{dr} = -k^2 y_1$$

and the boundary conditions are:

$$y(0) = 0$$
$$y(1) = 0$$

- Here, the trial-and-error approach differs from the previously discussed boundary value problem.
- Different estimates for $y_2(0)$ values do not make it zero at the other boundary.

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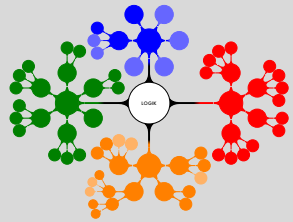
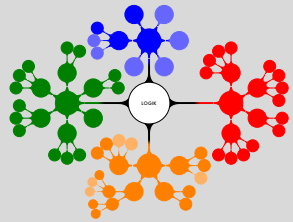


Standing Waves on a String II

- Instead, an **estimated value for the k eigenvalue** is taken and a solution search is initiated.
- Searching continues by increasing the value of k until the boundary condition (here $y(1) = 0$) at the other end is satisfied.
- For example, the solution at the other boundary is $y_{1k}(1)$ for a given value of k.
- Accordingly, the next step is find the root of the following equation:

$$F(k) = y_{1k}(1) - y(1) = 0$$

  When we encountered an eigenvalue k, then $F(k)$ will change sign as indicating the root.
- (**Example py-file:** The program to find the 5 smallest of the k eigenvalues in a string: standingwawes.py)
- The program can find the eigenvalues $k = n\pi/L = \pi, 2\pi, 3\pi, \ldots$ on a string of length L=1 m.
- However, the error margin is to be increased by increasing eigenvalues (see k_n/π values).



Standing Waves on a String III

```
n =  1 kn = 3.1415926814 kn/pi=1.00000001
n =  2 kn = 6.2831861228 kn/pi=2.00000026
n =  3 kn = 9.4247841388 kn/pi=3.00000197
n =  4 kn = 12.5663965940 kn/pi=4.00000827
n =  5 kn = 15.7080422640 kn/pi=5.00002515
```

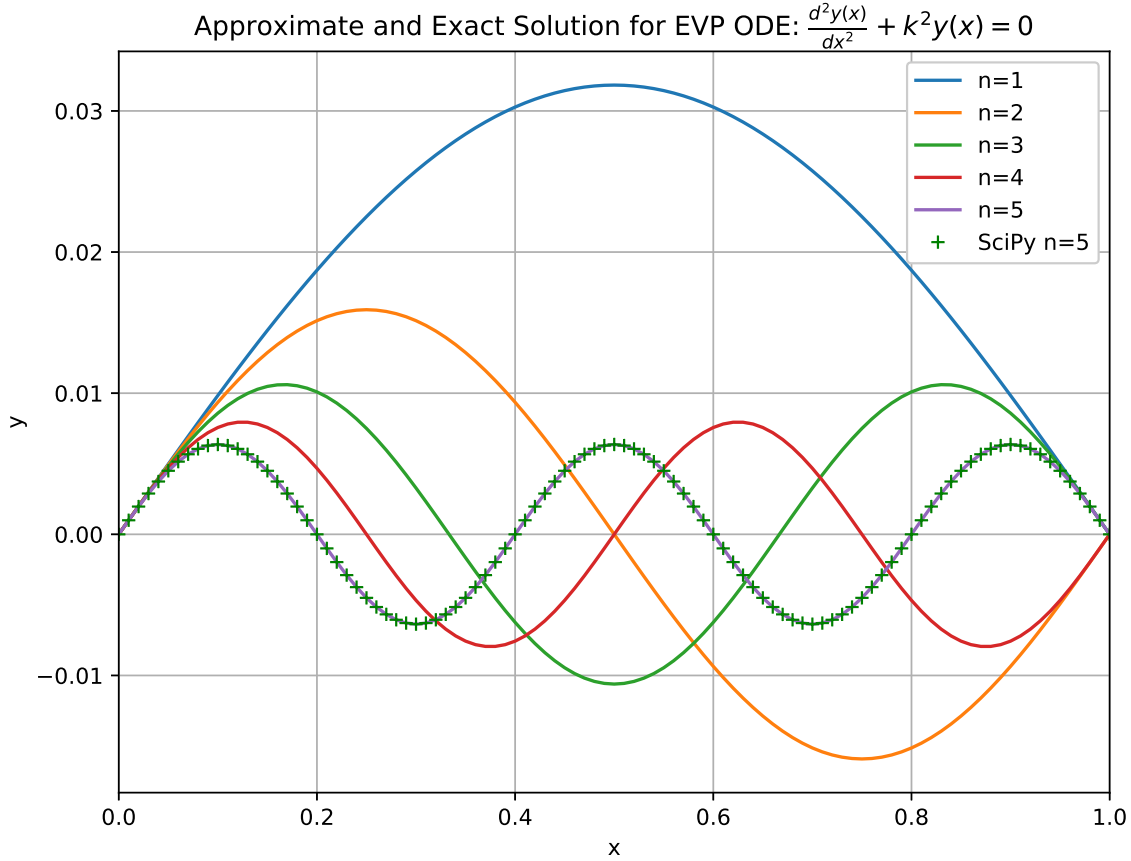


Figure: Solution for the Eigenvalue Problem for the ODE: $\frac{dy_2}{dx} = -k^2 y_1$.

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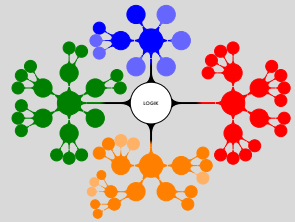
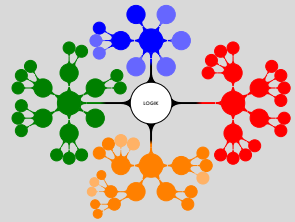


Numerical Solutions of Schrödinger Equation I

- In quantum mechanics, the Schrödinger equation is used to find the eigenvalues and eigenfunctions of the particle moving in one dimension at the potential $V(x)$:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

- An **analytical solution** to this equation is available for only very few potential functions such as harmonic oscillator, infinite well, hydrogen atom, ...
- Therefore, **numerical solutions** of the Schrödinger equation is an indispensable tool in physics research.
- The numerical solution of the Schrödinger equation is complicated for general solutions of the problem.
- However, if we assume the potential function to be as symmetric, the problem can be solved in a much easier way.



Numerical Solutions of Schrödinger Equation II

- For a symmetric potential,

$$V(-x) = V(x)$$

- Therefore, the solutions of the Schrödinger equation also fall into two groups:

  Symmetrical wave functions: $\psi(-x) = \psi(x)$
  Antisymmetric wave functions: $\psi(-x) = -\psi(x)$

- This property allows us to determine exactly the initial conditions necessary to start the eigenvalue problem.

Symmetric (even) wave functions: $\psi(0) = 1 \quad \& \quad \psi'(0) = 0$
Antisymmetric (odd) wave functions: $\psi(0) = 0 \quad \& \quad \psi'(0) = 1$

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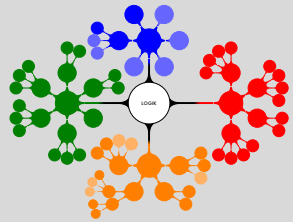

Hydrogen Atom I

- In quantum mechanics, the hydrogen atom is considered as a system of electrons with a charge of $-e$ around a proton with a charge of $+e$.
- If the electrostatic potential energy between the electron-proton is substituted in the Schrödinger equation as $V(r) = -e^2/r$,

$$-\frac{\hbar^2}{2m_r}\nabla^2\psi(\vec{r}) - \frac{e^2}{r}\psi(\vec{r}) = E\psi(\vec{r})$$

  Here $m_r = m_e m_p/(m_e + m_p)$ is the reduced mass of the electron-proton system.
- Since the potential energy depends only on the distance r, the solution is defined with the spherical coordinates (r, θ, ϕ) in three-dimensional space:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

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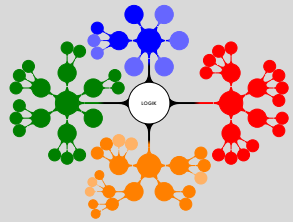

Hydrogen Atom II

- The solutions of the equation provided by the angular variables (θ, ϕ) are independent of the $V(r)$ potential and consist of functions called *spherical harmonics* $Y(\theta, \phi)$.
- The equation provided by the $R(r)$ function is called *radial Schrödinger equation*.

$$-\frac{\hbar^2}{2m_r}\left[\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right]+\left[\frac{l(l+1)\hbar^2}{2m_r r^2}-\frac{e^2}{r}\right]R(r)=-|E|R(r)$$

- Attempt to find the bound energy (eigen)values and wave (eigen)functions of the radial Schrödinger equation numerically :
- First, it is necessary to make the radial equation dimensionless bu defining a new wavefunction:

$$u(r)=rR(r)$$

- The radial equation in terms of this new function $u(r)$ becomes simpler:

$$\frac{d^2u}{dr^2}-\left[\frac{l(l+1)}{r^2}-\frac{2m_re^2}{\hbar^2 r}\right]u(r)=-\frac{2m_r|E|}{\hbar^2}u(r)$$

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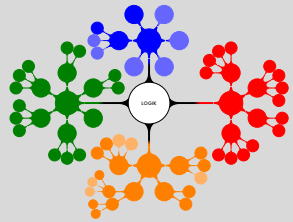

Hydrogen Atom III

- Now, a variable change is made as the following:

$$k = \frac{\sqrt{2m_r|E|}}{\hbar}, \quad \rho = 2kr, \quad \lambda^2 = \frac{1}{ka_0} = \frac{\Re}{|E|}$$

Here, the Rydberg constant $\Re$ and the Bohr radius a_0 are defined as:

$$a_0 = \frac{\hbar^2}{m_r e^2}, \quad \Re = \frac{\hbar^2}{2m_r a_0^2}$$

- As a result of these changes, the dimensionless radial equation becomes:

$$\boxed{\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)u = 0} \qquad (1)$$

where l is *orbital quantum number* and λ is *principal quantum number*.

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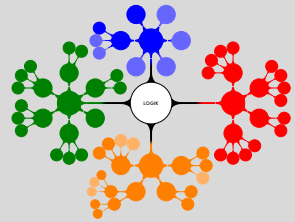


Hydrogen Atom IV

Numerical Solution. Firstly, transform this quadratic Equation 1 into a system of linear (first degree) equations:

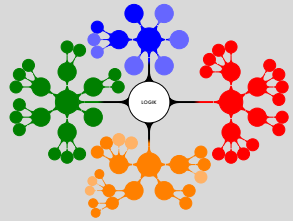
$$u \rightarrow y_1$$
$$\frac{du}{d\rho} \rightarrow y_2$$

with these values (y_1 *and* y_2), the system of equations to be solved: (**Now, we have a set of equations.**)

$$\frac{dy_1}{d\rho} = y_2$$
$$\frac{dy_2}{d\rho} = \left[\frac{l(l+1)}{\rho^2} - \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)\right] y_1$$

- For the initial conditions:
  - $u(0) \sim 0$
  - Since the absolute magnitude of the wave function has no physical meaning, the arbitrary value $u'(0) = 1$ can be taken.
- Then;

$$y_1(0) = 0 \quad \text{and} \quad y_2(0) = 1$$



Hydrogen Atom V

(**Example py-file:** Program that solves the radial Schrödinger equation for the hydrogen atom: hydrogenatom.py)

- Program does not graph the $u(r)$ functions, but the $|u|^2$ probability densities, which is physically meaningful.
- It calculates according to the l quantum number which is supplied by the user.
- The error margin is to be increased by increasing n quantum number.

```
Enter Orbital Quantum Number l (0,1,2,3 as s,p,d,f) =0
n =  1 Eigenvalue (lambda) = 1.0000014120
n =  2 Eigenvalue (lambda) = 2.0001120977
n =  3 Eigenvalue (lambda) = 3.0035437774
```

Figure: Solution for the Eigenvalue Problem for the ODE: $\frac{dy_2}{d\rho} = \left[\frac{l(l+1)}{\rho^2} - \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)\right] y_1$.

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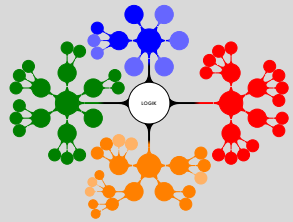

Hydrogen Atom VI

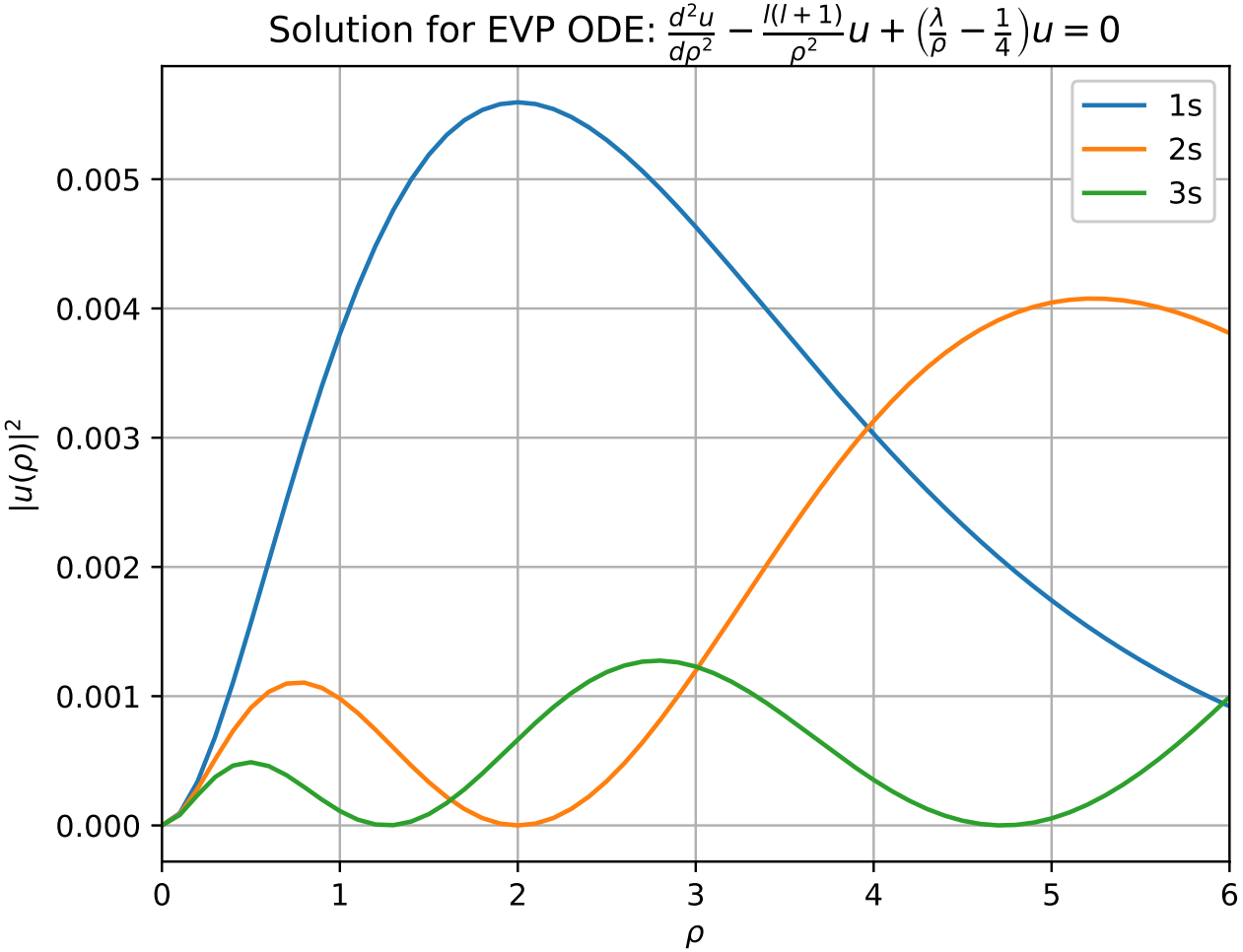

Figure: Solution for the Eigenvalue Problem for the ODE:
$\frac{dy_2}{d\rho} = \left[\frac{l(l+1)}{\rho^2} - \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)\right] y_1.$

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