PHY 711 Classical Mechanics and Mathematical Methods
10-10:50 AM MWF in Olin 103

Notes on Lecture 22 – Chap. 7 (F&W)

Sturm-Liouville equations

1. Eigenvalues and eigenfunctions
2. Rayleigh-Ritz approximation method
3. Green's function solution methods based on eigenfunction expansions
4. Green's function solution methods based on solutions of the homogeneous equations

Physics and Chemistry Joint Colloquium

Thursday

.

October 19th, 2023

Molecular Photovoltaics and the Advent of Perovskite Solar Cells

Photovoltaic cells using molecular dyes, semiconductor quantum dots or perovskite pigments as light harvesters have emerged as credible contenders to conventional devices. Dye sensitized solar cells (DSCs) use a three-dimensional nanostructured junction for photovoltaic electricity production and currently reach a power conversion efficiency (PCE) of 15.2 % in full sunlight and over 30 % in ambient light. They possess unique practical advantages in terms of particularly high effective electricity production from ambient light, ease of manufacturing, flexibility and transparency, bifacial light harvesting, and aesthetic appeal, which have fostered large scale industrial production and commercial applications. They served as a launch pad for perovskite solar cells (PSCs) which are presently being intensively investigated as one of the most promising future PV technologies, the PCE of solution processed laboratory cells having currently reached 25.7%. Present research focuses on their scale up to as well as ascertaining their long-term operational stability. This lecture will cover the most recent findings in these revolutionary photovoltaic domains.

Michael Grätzel

EPFL

Switzerland

Note that lecture location is in Salem Hall ➔

4 pm - Salem 012

Refreshments served prior to seminar

10	Mon, 9/18/2023	Chap. 5	Dynamics of rigid bodies	#9
11	Wed, 9/20/2023	Chap. 5	Dynamics of rigid bodies	#10
12	Fri, 9/22/2023	Chap. 5	Dynamics of rigid bodies	#11
13	Mon, 9/25/2023	Chap. 1	Scattering analysis	#12
14	Wed, 9/27/2023	Chap. 1	Scattering analysis	#13
15	Fri, 9/29/2023	Chap. 1	Scattering analysis	#14
16	Mon, 10/2/2023	Chap. 4	Small oscillations near equilibrium	
17	Wed, 10/4/2023	Chap. 4	Normal mode analysis	Mid term start
18	Fri, 10/6/2023	Chap. 4	Normal mode analysis	
22	Mon, 10/9/2023	Chap. 7	Normal modes of continuous string	
20	Wed, 10/11/2023		Review and summary	Mid term due
	Fri, 10/13/2023	Fall Break		
21	Mon, 10/16/2023	Chap. 7	The wave and other partial differential equations	#15
22	Wed, 10/18/2023	Chap. 7	Sturm-Liouville equations	#16
23	Fri, 10/20/2023			
24	Mon, 10/23/2023			
25	Wed, 10/25/2023			
26	Fri, 10/27/2023			
27	Mon, 10/30/2023			
28	Wed, 11/01/2023			

PHY 711 – Assignment #16

Assigned: 10/18/2023 Due: 10/23/2023

Continue reading Chapter 7 in **Fetter and Walecka**.

1. Consider the differential eigenvalue problem

$$-\frac{d^2}{dx^2} f_n(x) = \lambda_n f_n(x),$$

with boundary values $f_n(x=0) = 0 = f_n(x=a)$.

(a) Find the first few eigenvalues λ_n and eigenfunctions $f_n(x)$.

(b) Consider a trial function

$$f_{trial}(x) \equiv x(a^2 - x^2)$$

to estimate the lowest eigenvalue of this system using the Rayleigh-Ritz method. How well does it do?

Review – Sturm-Liouville equations defined over a range of x.

Homogenous problem: $$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)\varphi_0(x)=0$$

Inhomogenous problem: $$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)\varphi(x)=F(x)$$

Eigenfunctions:

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)\right)f_n(x)=\lambda_n\sigma(x)f_n(x)$$

Note that, because Sturm-Liouville operator is Hermitian, the eigenvalues are real and the eigenfunctions are orthogonal. In the last lecture, we argued that the eigenfunctions form a "complete" set over the range of x defined for the particular system.

Eigenvalues and eigenfunctions of Sturm-Liouville equations

In the domain $a \le x \le b$:

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)\right)f_n(x)=\lambda_n\sigma(x)f_n(x)$$

Alternative boundary conditions; 1. $f_m(a)=f_m(b)=0$

or 2. $\tau(x)\left.\frac{df_m(x)}{dx}\right|_a=\tau(x)\left.\frac{df_m(x)}{dx}\right|_b=0$

or 3. $f_m(a)=f_m(b)$ and $\frac{df_m(a)}{dx}=\frac{df_m(b)}{dx}$

Properties:

Eigenvalues λ_n are real

Eigenfunctions are orthogonal: $\int_a^b \sigma(x)f_n(x)f_m(x)dx=\delta_{nm}N_n,$

where $N_n \equiv \int_a^b \sigma(x)(f_n(x))^2 dx.$

Variation approximation to lowest eigenvalue

In general, there are several techniques to determine the eigenvalues λ_n and eigenfunctions $f_n(x)$. When it is not possible to find the ``exact'' functions, there are several powerful approximation techniques. For example, the lowest eigenvalue can be approximated by minimizing the function

$$\lambda_0 \leq \frac{\left\langle \tilde{h} \middle| S \middle| \tilde{h} \right\rangle}{\left\langle \tilde{h} \middle| \sigma \middle| \tilde{h} \right\rangle}, \qquad S(x) \equiv -\frac{d}{dx}\tau(x)\frac{d}{dx} + v(x)$$

where $\tilde{h}(x)$ is a variable function which satisfies the correct boundary values. The ``proof'' of this inequality is based on the notion that $\tilde{h}(x)$ can in principle be expanded in terms of the (unknown) exact eigenfunctions $f_n(x)$:

$\tilde{h}(x) = \sum_n C_n f_n(x),$ where the coefficients C_n can be assumed to be real.

Estimation of the lowest eigenvalue – continued:

From the eigenfunction equation, we know that

$$S(x)\tilde{h}(x) = S(x)\sum_n C_n f_n(x) = \sum_n C_n \lambda_n \sigma(x) f_n(x).$$

It follows that:

$$\left\langle \tilde{h} \middle| S \middle| \tilde{h} \right\rangle = \int_a^b \tilde{h}(x) S(x) \tilde{h}(x) dx = \sum_n |C_n|^2 N_n \lambda_n.$$

It also follows that:

$$\left\langle \tilde{h} \middle| \sigma \middle| \tilde{h} \right\rangle = \int_a^b \tilde{h}(x) \sigma(x) \tilde{h}(x) dx = \sum_n |C_n|^2 N_n,$$

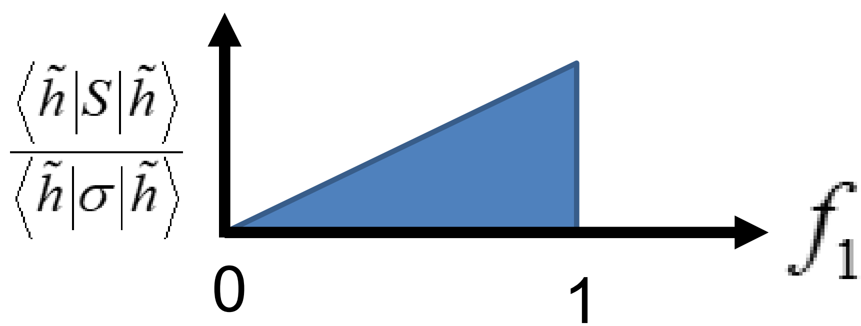
Therefore $$\frac{\left\langle \tilde{h} \middle| S \middle| \tilde{h} \right\rangle}{\left\langle \tilde{h} \middle| \sigma \middle| \tilde{h} \right\rangle} = \frac{\sum_n |C_n|^2 N_n \lambda_n}{\sum_n |C_n|^2 N_n} \geq \lambda_0.$$

Some additional comments -- $\dfrac{\langle \tilde{h}|S|\tilde{h}\rangle}{\langle \tilde{h}|\sigma|\tilde{h}\rangle} = \dfrac{\sum_n |C_n|^2 N_n \lambda_n}{\sum_n |C_n|^2 N_n} \geq \lambda_0.$

$$\frac{\langle \tilde{h}|S|\tilde{h}\rangle}{\langle \tilde{h}|\sigma|\tilde{h}\rangle} = \sum_{n=0}^{\infty} f_n \lambda_n \quad \text{where } f_n \equiv \frac{|C_n|^2 N_n}{\sum_m |C_m|^2 N_m} \text{ and } \sum_{n=0}^{\infty} f_n = 1$$

For the case of only two non-trivial eigenvalues:

$$\frac{\langle \tilde{h}|S|\tilde{h}\rangle}{\langle \tilde{h}|\sigma|\tilde{h}\rangle} = f_0\lambda_0 + f_1\lambda_1 = \lambda_0 + (\lambda_1 - \lambda_0) f_1$$



Rayleigh-Ritz method of estimating the lowest eigenvalue

$$\lambda_0 \le \frac{\langle \tilde{h} | S | \tilde{h} \rangle}{\langle \tilde{h} | \sigma | \tilde{h} \rangle},$$

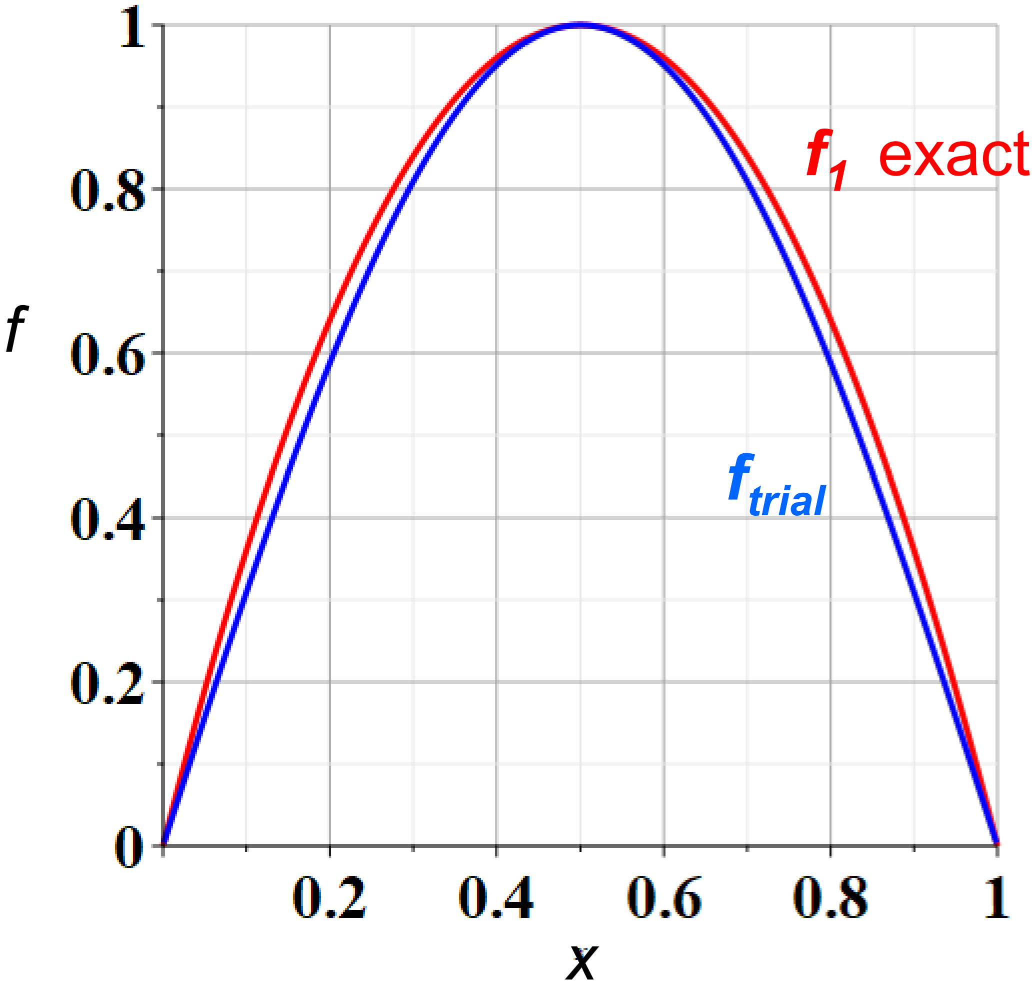
Example: $$-\frac{d^2}{dx^2} f_n(x) = \lambda_n f_n(x) \qquad \text{with } f_n(0) = f_n(a) = 0$$

Exact eigenfunctions: $$f_n(x) = \sin\left(\frac{n\pi x}{a}\right) \qquad n = 1, 2, 3....$$

Exact eigenvalues: $$\lambda_n = \left(\frac{n\pi}{a}\right)^2 \qquad n = 1, 2, 3.... \qquad \frac{\pi^2}{a^2} = \frac{9.869604404}{a^2}$$

Trial function $$f_{\text{trial}}(x) = x(x-a)$$

Raleigh-Ritz estimate: $$\frac{\left\langle x(a-x) \middle| -\frac{d^2}{dx^2} \middle| x(a-x) \right\rangle}{\left\langle x(a-x) \middle| x(a-x) \right\rangle} = \frac{10}{a^2}$$



1
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1
f
x
f1 exact
ftrial

Rayleigh-Ritz method of estimating the lowest eigenvalue

$$\lambda_0 \le \frac{\langle \tilde{h}|S|\tilde{h}\rangle}{\langle \tilde{h}|\sigma|\tilde{h}\rangle},$$

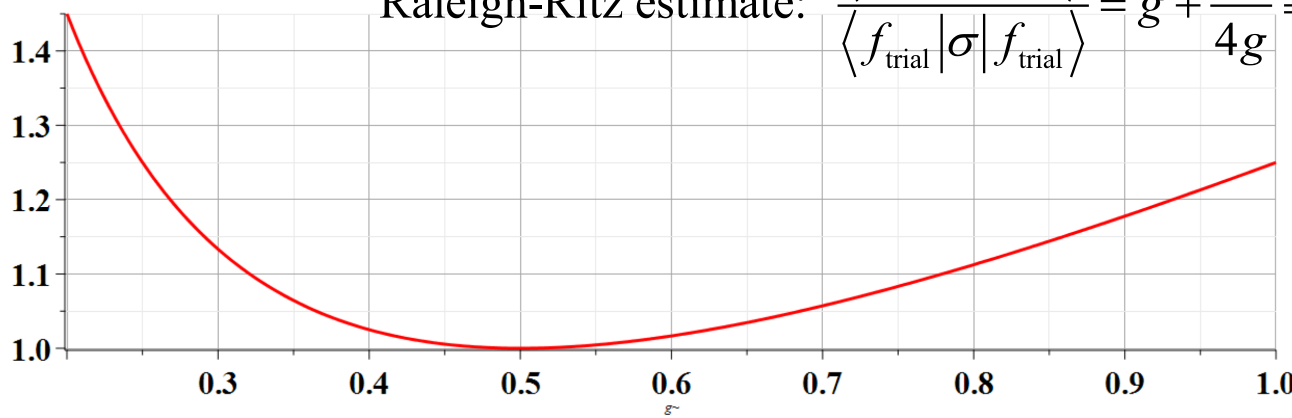
Another example – this time with a variable parameter

Example: $$-\frac{d^2 f_n(x)}{dx^2} + Gx^2 f_n(x) = \lambda_n f_n(x) \qquad \text{with } f_n(-\infty) = f_n(\infty) = 0$$

trial function $f_{\text{trial}}(x) = e^{-gx^2}$

Raleigh-Ritz estimate: $$\frac{\langle f_{\text{trial}}|S|f_{\text{trial}}\rangle}{\langle f_{\text{trial}}|\sigma|f_{\text{trial}}\rangle} = g + \frac{G}{4g} \equiv \lambda_{\text{trial}}(g)$$

$$\frac{\lambda_{\text{trial}}(g)}{\sqrt{G}}$$



$g/\sqrt{G}$

$$g_0 = \frac{1}{2}\sqrt{G} \qquad \lambda_{\text{trial}}(g_0) = \sqrt{G}$$

Note that for differential equation of the Schoedinger equation of the harmonic oscillator:

$$\sqrt{\mathrm{G}} = \frac{m\omega}{\hbar} \qquad \lambda_{\text{trial}} = \frac{2m}{\hbar^2}E_0 \qquad \Rightarrow E_0 = \frac{\hbar\omega}{2}$$

Recap -- Rayleigh-Ritz method of estimating the lowest eigenvalue

Example from Schroedinger equation for one-dimensional harmonic oscillator:

$$-\frac{\hbar^2}{2m}\frac{d^2 f_n(x)}{dx^2}+\frac{1}{2}m\omega^2 x^2 f_n(x)=E_n f_n(x) \qquad \text{with } f_n(-\infty)=f_n(\infty)=0$$

Trial function $\quad f_{\text{trial}}(x)=e^{-gx^2}$

Raleigh-Ritz estimate: $\dfrac{\langle f_{\text{trial}}|S|f_{\text{trial}}\rangle}{\langle f_{\text{trial}}|\sigma|f_{\text{trial}}\rangle}=\dfrac{\hbar^2}{2m}\left(g+\dfrac{m^2\omega^2/\hbar^2}{4g}\right)\equiv E_{\text{trial}}(g)$

$$g_0=\frac{m\omega}{\hbar} \qquad E_{\text{trial}}(g_0)=\frac{1}{2}\hbar\omega$$

Exact answer

Do you think that there is a reason for getting the correct answer from this method?

a. Chance only
b. Skill

Solution to inhomogeneous problem by using Green's functions

Inhomogenous problem:

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)\varphi(x)=F(x)$$

Green's function :

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)G_\lambda(x,x')=\delta\left(x-x'\right)$$

Formal solution:

$$\varphi_\lambda(x)=\varphi_{\lambda 0}(x)+\int_a^b G_\lambda(x,x')F(x')dx'$$

Solution to homogeneous problem

Formal solution:

$$\varphi_\lambda(x) = \varphi_{\lambda 0}(x) + \int_a^b G_\lambda(x,x')F(x')dx'$$

Solution to homogeneous problem

What is the homogeneous equation psi_0(x)?

Homogenous problem:

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx} + v(x) - \lambda\sigma(x) \right)\varphi_{\lambda 0}(x) = 0$$

In this lecture, we will discuss several methods of finding this Green's function. This topic will also appear in PHY 712

How do we arrive at the formal solution?

Formal solution:

$$\varphi_\lambda(x) = \varphi_{\lambda 0}(x) + \int_a^b G_\lambda(x,x')F(x')dx'$$

Note that this form satisfies the inhomogenous equation

Define $S(x) \equiv -\frac{d}{dx}\tau(x)\frac{d}{dx} + v(x) - \lambda\sigma(x)$

$$S(x)\varphi_\lambda(x) = S(x)\varphi_{\lambda 0}(x) + S(x)\int_a^b G(x,x')F(x')dx'$$

$$S(x)\varphi_\lambda(x) = \quad 0 \quad + \int_a^b \delta(x-x')F(x')dx' = F(x)$$

Using complete set of eigenfunctions to form Green's function --

Suppose that we can find a Green's function defined as follows:

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)G_\lambda(x,x')=\delta\left(x-x'\right)$$

Recall: Completeness of eigenfunctions:

$$\sigma\left(x\right)\sum_n \frac{f_n(x)f_n(x')}{N_n}=\delta\left(x-x'\right)$$

In terms of eigenfunctions:

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)G_\lambda(x,x')=\sigma\left(x\right)\sum_n \frac{f_n(x)f_n(x')}{N_n}$$

$$\Rightarrow G_\lambda(x,x')=\sum_n \frac{f_n(x)f_n(x')/N_n}{\lambda_n-\lambda}$$

By construction

Example Sturm-Liouville problem:

Example: $\tau(x)=1; \quad \sigma(x)=1; \quad v(x)=0; \quad a=0 \quad \text{and} \quad b=L$

$$\lambda=1; \qquad F(x)=F_0 \sin\left(\frac{\pi x}{L}\right)$$

Inhomogenous equation:

$$\left(-\frac{d^2}{dx^2}-1\right)\varphi(x)=F_0 \sin\left(\frac{\pi x}{L}\right)$$

Eigenvalue equation:

$$\left(-\frac{d^2}{dx^2}\right)f_n(x) = \lambda_n f_n(x)$$

Eigenfunctions

$$f_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

Eigenvalues:

$$\lambda_n = \left(\frac{n\pi}{L}\right)^2$$

Completeness of eigenfunctions:

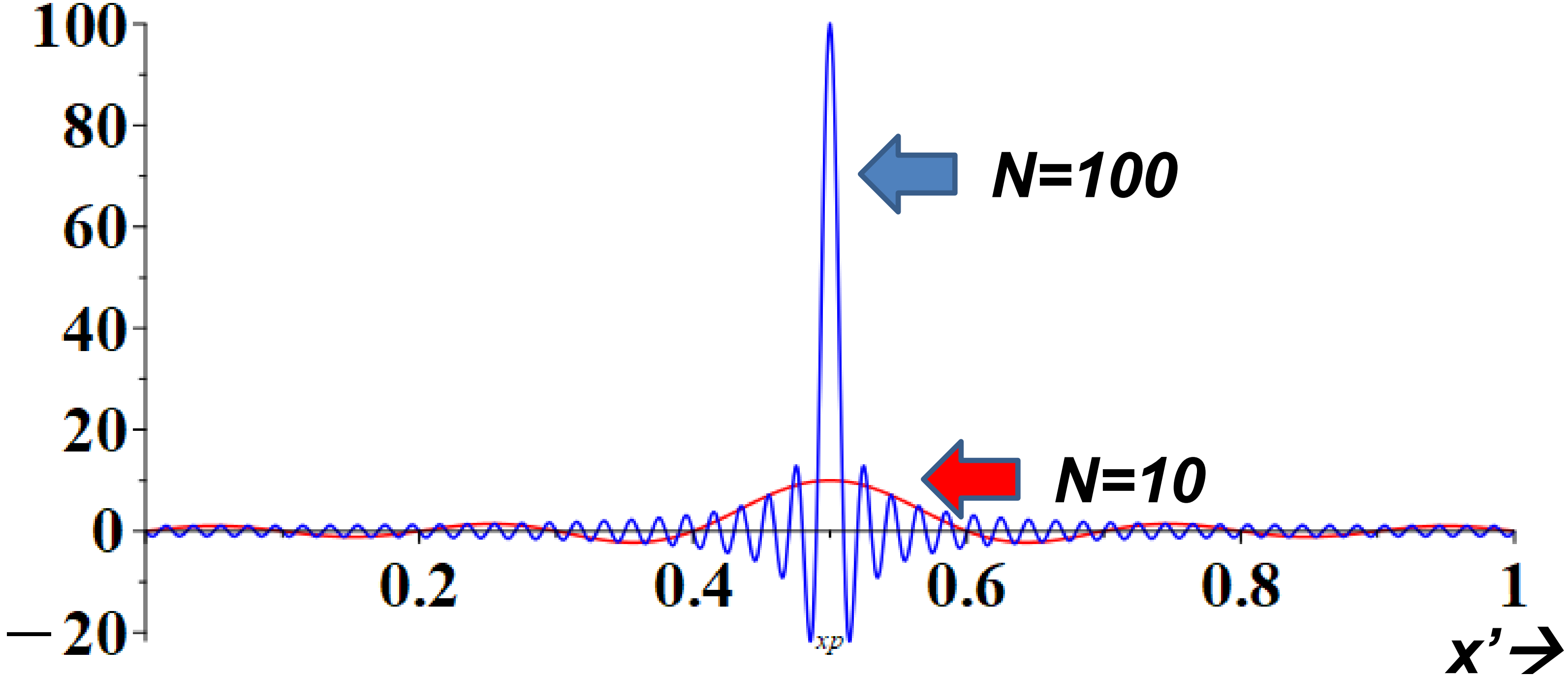
$$\sigma(x)\sum_n \frac{f_n(x)f_n(x')}{N_n} = \delta(x-x')$$

In this example:

$$\frac{2}{L}\sum_{n=1}^{\infty}\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x'}{L}\right) = \delta(x-x')$$

In reality, for finite summation $$\frac{2}{L}\sum_{n=1}^{N}\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x'}{L}\right)=\delta(x-x')$$

x=1/2, L=1



Green's function:

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)G_\lambda(x,x')=\delta(x-x')$$

Green's function for the example:

$$G(x,x')=\sum_n \frac{f_n(x)f_n(x')/N_n}{\lambda_n-\lambda}=\frac{2}{L}\sum_n \frac{\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x'}{L}\right)}{\left(\frac{n\pi}{L}\right)^2-1}$$

Using Green's function to solve inhomogenous equation:

$$\left(-\frac{d^2}{dx^2}-1\right)\varphi(x)=F_0\sin\left(\frac{\pi x}{L}\right)$$ with boundary values $\varphi(0)=\varphi(L)=0$

$$\varphi(x)=\varphi_0(x)+\int_0^L G(x,x')F_0\sin\left(\frac{\pi x'}{L}\right)dx'$$

$$\varphi(x)=\varphi_0(x)+\frac{2}{L}\sum_n\left[\frac{\sin\left(\frac{n\pi x}{L}\right)}{\left(\frac{n\pi}{L}\right)^2-1}\int_0^L\sin\left(\frac{n\pi x'}{L}\right)F_0\sin\left(\frac{\pi x'}{L}\right)dx'\right]$$

$$\varphi(x)=\varphi_0(x)+\frac{F_0}{\left(\frac{\pi}{L}\right)^2-1}\sin\left(\frac{\pi x}{L}\right)$$

Another method of constructing Green's functions -- using two solutions to the homogeneous problem

Green's function :

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)G_\lambda(x,x')=\delta\left(x-x'\right)$$

Two homogeneous solutions

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)g_i(x)=0 \qquad \text{for} \quad i=a,b$$

$$\text{Let}\ \ G_\lambda(x,x')=\frac{1}{W}g_a(x_<)g_b(x_>)$$

$$\text{where } W\equiv\tau(x')\left(g_a(x')\frac{d}{dx}g_b(x')-g_b(x')\frac{d}{dx}g_a(x')\right)$$

Some details:

For $\epsilon \to 0$:

$$\int_{x'-\epsilon}^{x'+\epsilon} dx\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)G_\lambda(x,x')=\int_{x'-\epsilon}^{x'+\epsilon} dx\delta\left(x-x'\right)$$

$$\int_{x'-\epsilon}^{x'+\epsilon} dx\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}\right)\frac{1}{W}g_a(x_<)g_b(x_>)=1$$

$$-\frac{\tau(x)}{W}\left(\frac{d}{dx}g_a(x_<)g_b(x_>)\right)\Bigg]_{x'-\epsilon}^{x'+\epsilon}=\frac{\tau(x')}{W}\left(g_a(x')\frac{d}{dx}g_b(x')-g_b(x')\frac{d}{dx}g_a(x')\right)$$

$$\Rightarrow W=\tau(x')\left(g_a(x')\frac{d}{dx}g_b(x')-g_b(x')\frac{d}{dx}g_a(x')\right)$$

Note -- W (Wronskian) is constant, since $\dfrac{dW}{dx'}=0.$

$\Rightarrow$ Useful Green's function construction in one dimension:

$$G_\lambda(x,x')=\frac{1}{W}g_a(x_<)g_b(x_>)$$

$$\left(-\frac{d}{dx}\tau(x)\frac{d}{dx}+v(x)-\lambda\sigma(x)\right)\varphi(x)=F(x)$$

Green's function solution:

$$\varphi_\lambda(x)=\varphi_{\lambda 0}(x)+\int_a^b G_\lambda(x,x')F(x')dx'$$

$$=\varphi_{\lambda 0}(x)+\frac{g_b(x)}{W}\int_a^x g_a(x')F(x')dx'+\frac{g_a(x)}{W}\int_x^b g_b(x')F(x')dx'$$

Note that the integral has to be performed in two parts. While the eigenfunction expansion method can be generalized to 2 and 3 dimensions, this method only works for one dimension.

Example from previous discussion:

$$\left(-\frac{d^2}{dx^2}-1\right)\varphi(x)=F_0\sin\left(\frac{\pi x}{L}\right)\qquad \text{with boundary values } \varphi(0)=\varphi(L)=0$$

Using: $G(x,x')=\frac{1}{W}g_a(x_<)g_b(x_>)$ for $0\le x\le L$

$$\left(-\frac{d^2}{dx^2}-1\right)g_i(x)=0 \qquad \Rightarrow g_a(x)=\sin(x); \qquad g_b(x)=\sin(L-x);$$

$$W=g_b(x)\frac{dg_a(x)}{dx}-g_a(x)\frac{dg_b(x)}{dx}=\sin(L-x)\cos(x)+\sin(x)\cos(L-x)$$

$$=\sin(L)$$

$$\varphi(x)=\varphi_0(x)+\frac{\sin(L-x)}{\sin(L)}\int_0^x \sin(x')F_0\sin\left(\frac{\pi x'}{L}\right)dx'$$

$$+\frac{\sin(x)}{\sin(L)}\int_x^L \sin(L-x')F_0\sin\left(\frac{\pi x'}{L}\right)dx'$$

$$\varphi(x)=\varphi_0(x)+\frac{F_0}{\left(\frac{\pi}{L}\right)^2-1}\sin\left(\frac{\pi x}{L}\right)$$

(Actually the algebra is painful). But, hurray! Same result as before.

Another example --

$$\frac{d^2}{dx^2}\Phi(x) = -\rho(x)/\epsilon_0$$ electrostatic potential for charge density $\rho(x)$

Homogeneous equation:

$$\frac{d^2}{dx^2} g_{a,b}(x) = 0$$

Let $g_a(x) = x \qquad g_b(x) = 1$

Wronskian:

$$W = g_a(x)\frac{dg_b(x)}{dx} - g_b(x)\frac{dg_a(x)}{dx} = -1$$

Green's function:

$$G(x, x') = -x_<$$

$$\Phi(x) = \Phi_0(x) + \frac{1}{\epsilon_0}\int_{-\infty}^{x} dx'\,x'\rho(x') + \frac{x}{\epsilon_0}\int_{x}^{\infty} dx'\rho(x')$$

Example -- continued

$$\frac{d^2}{dx^2}\Phi(x) = -\rho(x)/\epsilon_0$$ electrostatic potential for charge density $\rho(x)$

$$\Phi(x) = \Phi_0(x) + \frac{1}{\epsilon_0}\int_{-\infty}^{x} dx'\, x'\rho(x') + \frac{x}{\epsilon_0}\int_{x}^{\infty} dx'\rho(x')$$

Suppose $$\rho(x) = \begin{cases} 0 & x \le -a \\ \rho_0 x/a & -a \le x \le a \\ 0 & x \ge a \end{cases}$$

$$\Phi(x) = \Phi_0(x) + \begin{cases} 0 & x \le -a \\ \dfrac{\rho_0}{\epsilon_0 a}\left(\dfrac{a^3}{3} + \dfrac{xa^2}{2} - \dfrac{x^3}{6}\right) & -a \le x \le a \\ \dfrac{2}{3\epsilon_0}\rho_0 a^2 & x \ge a \end{cases}$$

$$\Phi(x)=\begin{cases}0 & x\le -a\\ \dfrac{\rho_0}{\epsilon_0 a}\left(\dfrac{a^3}{3}+\dfrac{xa^2}{2}-\dfrac{x^3}{6}\right) & -a\le x\le a\\ \dfrac{2}{3\epsilon_0}\rho_0 a^2 & x\ge a\end{cases}$$