1.27: The Dirac Notation Applied to Variational Calculations

The particle-in-a-box problem is exactly soluble and the solution is calculated below for the first 20 eigenstates. All calculations will be carried out in atomic units.

$$\psi(n, x) = \sqrt{2}\sin(n\pi x)$$

$$E_n = \frac{n^2\pi^2}{2}$$

with $n = 1, 2, \ldots, 20$

The First five EigenValues

The first five energy eigenvalues are:

$$E_1 = 4.935 \; E_2 = 19.739 \; E_3 = 44.413 \; E_4 = 78.957 \; E_5 = 123.37$$

The first three eigenfunctions are displayed below:

```
%matplotlib inline

import matplotlib.pyplot as plt
import numpy as np

t = np.linspace(0,1,100)
t1 = t*np.pi
t2 = t*np.pi*2
t3 = t*np.pi*3
a = np.sin(t1)
b = np.sin(t2)
c = np.sin(t3)
plt.xlim(0,1)
plt.plot(t,a,color = "red", label= "\u03C8 (1,x)")
plt.plot(t,b,color = "blue",label = "\u03c8 (2,x)")
plt.plot(t,c,color = "limegreen",label = "\u03c8 (3,x)")
plt.plot(t,(t*0), color ="black")

plt.xticks([0,0.5,1])
plt.yticks([-.5,0,.5],[])
plt.xlabel("x")
leg = plt.legend(loc = "center", bbox_to_anchor=[-.11,.5],frameon=False)
plt.tick_params(top=True,right=True,direction="in")

plt.show()
```

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The set of eigenfunctions forms a complete basis set and any other functions can be written as a linear combinations in this basis set. For examples, Φ, χ, and Γ are three trial functions that satisfy the boundary conditions for the particle in a 1 bohr box.

$$\Phi(x) = \sqrt{30}(x - x^2)$$

$$\chi(x) = \sqrt{105}(x^2 - x^3)$$

$$\Gamma(x) = \sqrt{105}x(1 - x)^2$$

In Dirac bra-ket notation we can express and of these functions as a linear combination in the basis set as follows:

$$\langle x|\Phi\rangle = \sum_n^{\infty} \langle x|\psi_n\rangle\langle\psi_n|\Phi\rangle \tag{1.27.1}$$

$$= \sum_n^{\infty} \langle x|\psi_n\rangle \int_0^1 \langle\psi_n|x\rangle\langle x|\Phi\rangle dx \tag{1.27.2}$$

The various overlap integral for the three trial function are evaluated below.

$$a_n = \int_0^1 \psi(n,x)\Phi(x)dx$$

$$b_n = \int_0^1 \psi(n,x)\chi(x)dx$$

$$c_n = \int_0^1 \psi(n,x)\Gamma(x)dx$$

```
%matplotlib inline

import matplotlib.pyplot as plt
import numpy as np
import math

t = np.arange(0,1,.001)
plt.plot(t,math.sqrt(2)*np.sin(t*np.pi),color = "red", label = "\u03C8 (1,x)")
plt.plot(t,math.sqrt(30)*(t-t**2),color ="blue", linestyle = "--",label = "\u03A6(x)"
plt.plot(t,math.sqrt(105)*t*(1-t)**2,color = "lime", linestyle = "--", label = "\u0393
plt.plot(t,math.sqrt(105)*(t**2 - t**3),color = "magenta", linestyle = "-.", label = '
plt.xticks([0.2,0.4,0.6,0.8])
plt.yticks([.5,1,1.5],[ ])
plt.tick_params(direction="in")
plt.xlabel("x")
leg = plt.legend(loc = "center",bbox_to_anchor=[-.11,.5], frameon=False)
plt.tick_params(top=True, right=True)
plt.xlim(0,1)
plt.ylim(0,2)
plt.show()
```

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The figure shown below demonstrate that only Φ is a reasonable representative for the ground state wavefunction.

First Five Particle in a BOx EigenFunctions

If χ is written as a linear combination of the first 5 PIB eigenfunctions, one gets two functions that are essentially indistinguishable from one another.
The same, of course, is true for χ and Γ, as is demonstrated in the graphs shown below.

Traditionally we use energy as a criterion for the quality of a trial wavefunction by evaluating the variational integral in the following way.

$$\int_0^1 \Phi(x) - \frac{1}{2}\cdot\frac{d^2}{dx^2}\Phi(x)dx = 5 \quad \int_0^1 \chi(x) - \frac{1}{2}\cdot\frac{d^2}{dx^2}\chi(x)dx = 7 \quad \int_0^1 \Gamma(x)\cdot\frac{1}{2}\cdot\frac{d^2}{dx^2}\Gamma(x)dx = 7$$

In Dirac notation we write:

$$\langle E\rangle = \langle\Phi|\hat{H}|\Phi\rangle = \sum_n \langle\Phi|\hat{H}|\Psi_n\rangle\,\langle\Psi_n|\Phi\rangle = \sum \langle\Phi|\Psi_n\rangle E_n\,\langle\Psi_n|\Phi\rangle = \sum_n a_n^2 E_n$$

Thus we easily show the same result.

$$\sum_{\mathrm{n}}\left[(\mathrm{a_n})^2\cdot \mathrm{E_n}\right]=5 \quad \sum_{\mathrm{n}}\left[(\mathrm{b_n})^2\cdot \mathrm{E_n}\right]=6.999 \quad \sum_{\mathrm{n}}\left[(\mathrm{c_n})^2\cdot \mathrm{E_n}\right]=6.999$$

We now show, belatedly, that the three trial functions are normalized by both methods.

$$\int_0^1 \Phi(x)^2 dx=1 \quad \int_0^1 \chi(x)^2 dx=1 \quad \int_0^1 \Gamma(x)^2 dx=1$$

In Dirac notation this is formulated as:

$$\langle\Phi|\Phi\rangle=\sum_n \langle\Phi|\Psi_n\rangle\langle\Psi_n|\Phi\rangle=\sum_n a_n^2$$

$$\sum_{\mathrm{n}}(a_n)^2=1 \quad \sum_n (b_n)^2=1 \quad \sum_n (c_n)^2=1$$

We now calculate some over-lap integrals:

$$\int_0^1 \Phi(x)\cdot\chi(x)dx=0.935 \qquad \int_0^1 \Phi(x)\cdot\Gamma(x)dx=0.935 \quad \int_0^1 \chi(x)\cdot\Gamma(x)dx=0.75$$

In Dirac notation this is formulated as:

$$\langle\Phi|\Gamma\rangle=\sum_n \langle\Phi|\Psi_n\rangle\langle\Psi_n|\Gamma\rangle=\sum_n a_n c_n$$

$$\sum_{\mathrm{n}}(\mathrm{a_n}\cdot \mathrm{b_n})=0.935 \quad \sum_{\mathrm{n}}(\mathrm{a_n}-\mathrm{c_n})=0.935 \quad \sum_{\mathrm{n}}(\mathrm{b_n}-\mathrm{c_n})=0.75$$

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