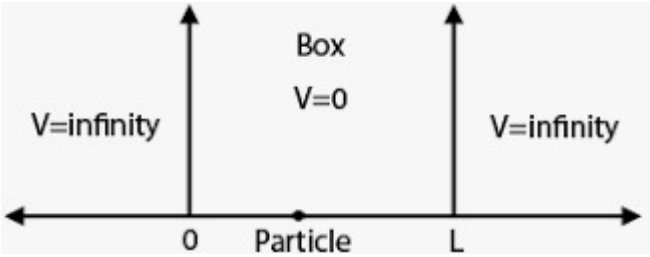
XXIV. Quantum Mechanical Calculations Illuminated with Dirac Notation

The following example is from "*PHYSICAL CHEMISTRY for the Chemical Sciences*", Raymond Chang"

A Particle in a Box in a One Dimensional Box

At the end of the nineteenth century, there were new experimental results that could not be explained by the so-called classical theories of physics. In 1900, the German physicist Max Planck proposed the quantum theory to explain one of these experiments. In this chapter, we take a historical approach and follow the early development of quantum theory.

Consider a particle of mass m confined to a one-dimensional box of length L. We again assume that the particle has zero potential energy inside the box ^ or on the line segment h ; that is, V = 0. The particle has only kinetic energy. At each end of the box is a wall of infinite potential energy, so there is no probability of finding the particle at the walls or outside the box. For simplicity, we chose the line segment to start at the origin, so x is restricted by $0 \le x \le L$, See Figure below. The Schrödinger equation is similar to that for the free particle, with the difference being that the value of x is constrained by the size of the box.



$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \qquad 0 \le x \le L$$

For the particle-in-a-box Schrödinger equation, let us try a trial wave function,

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

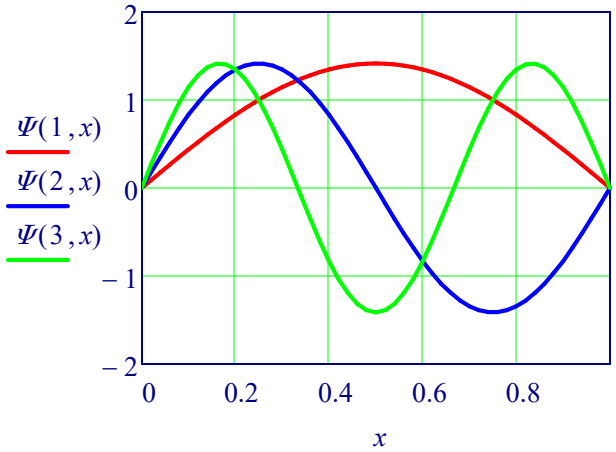
The particle-in-a-box (PIB) problem is exactly soluble and the solution is calculated below for the first 20 eigenstates. All calculations will be carried out in atomic units ($h = 2\pi$) for a particle of unit mass in a 1 D box.

$$n := 1..20 \qquad \Psi(n,x) := \sqrt{2}\cdot\sin(n\cdot\pi\cdot x) \qquad E_n := \frac{n^2\cdot\pi^2}{2}$$

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. $x := 0, .02..1$



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

$$\Phi(x) := \sqrt{30}\cdot\left(x - x^2\right) \qquad \chi(x) := \sqrt{105}\cdot\left(x^2 - x^3\right) \qquad \Gamma(x) := \sqrt{105}\cdot x\cdot(1-x)^2$$

In Dirac bracket notation we can express each of these functions as a linear combination in the basis set. For example, for Φ we have,

$$\langle x|\Phi\rangle = \sum_n \langle x|\Psi_n\rangle\langle\Psi_n|\Phi\rangle = \sum_n \langle x|\Psi_n\rangle\int_0^1 \langle\Psi_n|x\rangle\langle x|\Phi\rangle dx = \sum_n \Psi_n(x)\int_0^1 \Psi_n^*(x)\Phi(x)dx = \sum_n \Psi_n(x)a_n$$

Here both the finite and continuous completeness relations have been used:

$$\sum_n |\Psi_n\rangle\langle\Psi_n| = 1 \quad \text{and} \quad \int |x\rangle\langle x|dx = 1$$

The various overlap integrals for the three trial function (a_n, b_n, and c_n) are evaluated below.

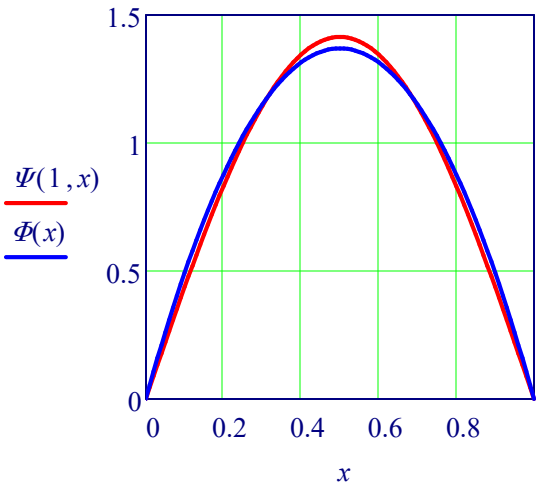
$$a_n := \int_0^1 \Psi(n,x)\cdot\Phi(x)\,dx \qquad b_n := \int_0^1 \Psi(n,x)\cdot\chi(x)\,dx \qquad c_n := \int_0^1 \Psi(n,x)\cdot\Gamma(x)\,dx$$

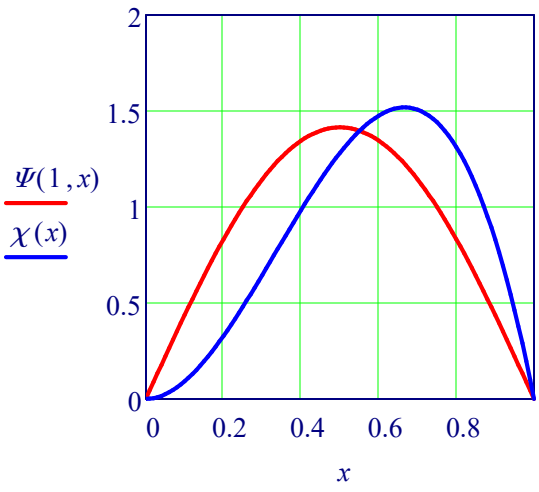
As shown above, these overlap integrals are set up as follows:

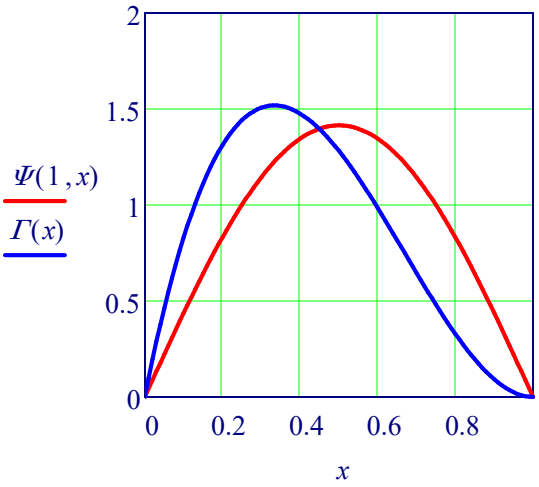
$$a_n = \langle\Psi_n|\Phi\rangle = \int_0^1 \langle\Psi_n|x\rangle\langle x|\Phi\rangle dx = \int_0^1 \Psi_n^*(x)\Phi(x)dx$$

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

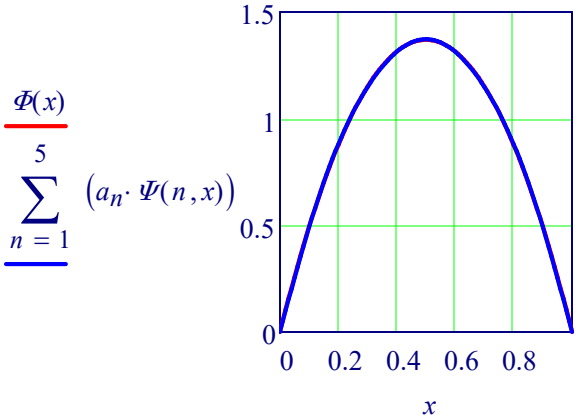
$$x := 0, .01 .. 1$$



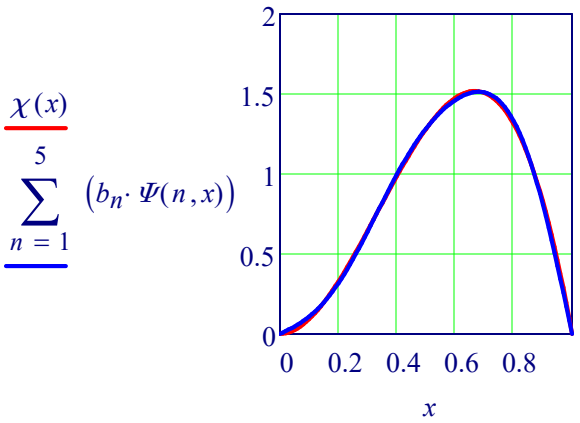


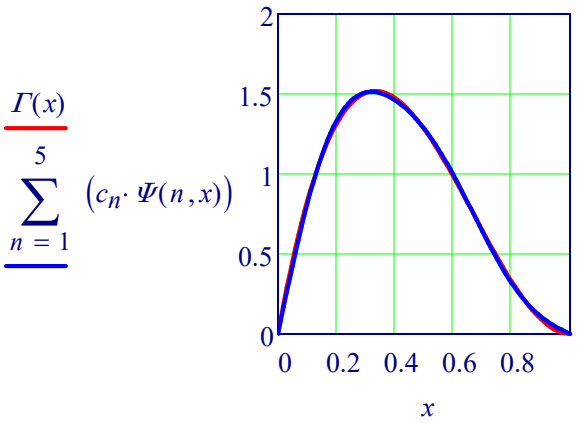


However, if Φ is written as a linear combination of the first 5 PIB eigenfunctions, one gets two functions that are essentially indistinguishable from one another.



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. Φ(x) is the best trial function because it gives the lowest energy.

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

With Dirac notation we would write:

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

Thus we easily show the same result.

$$\sum_n \left[(a_n)^2\cdot E_n\right] = 5 \qquad \sum_n \left[(b_n)^2\cdot E_n\right] = 6.999 \qquad \sum_n \left[(c_n)^2\cdot E_n\right] = 6.999$$

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

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

In Dirac bracket notation this is written as: $\langle\Phi|\Phi\rangle = \sum_n \langle\Phi|\Psi_n\rangle\langle\Psi_n|\Phi\rangle = \sum_n a_n^2$

$$\sum_n (a_n)^2 = 1 \qquad \sum_n (b_n)^2 = 1 \qquad \sum_n (c_n)^2 = 1$$

We now calculate some over-lap integrals:

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

In Dirac notation this is formulated as: $\langle\Phi|\Gamma\rangle = \sum_n \langle\Phi|\Psi_n\rangle\langle\Psi_n|\Gamma\rangle = \sum_n a_n c_n$

$$\sum_n (a_n\cdot b_n) = 0.935 \qquad \sum_n (a_n\cdot c_n) = 0.935 \qquad \sum_n (b_n\cdot c_n) = 0.75$$

As a final exercise we calculate the expectation value for position using the three trial wave functions. In bracket notation this calculation is set up most directly as follows.

$$\langle\Phi|\hat{x}|\Phi\rangle = \int_0^1 \langle\Phi|\hat{x}|x\rangle\langle x|\Phi\rangle\,dx = \int_0^1 \langle\Phi|x\rangle x\langle x|\Phi\rangle\,dx = \int_0^1 \Phi(x)^* x\,\Phi(x)dx$$

where we have employed the eigenvalue equation for the position operator: $\hat{x}|x\rangle = |x\rangle x$

Evaluation of the integral on the right for each trial function is shown below. Naturally the results are consistent with the shapes of the trial wave functions shown in the first figure.

$$\int_0^1 \Phi(x)\cdot x\cdot \Phi(x)\,dx = 0.5 \qquad \int_0^1 \chi(x)\cdot x\cdot \chi(x)\,dx = 0.625 \qquad \int_0^1 \Gamma(x)\cdot x\cdot \Gamma(x)\,dx = 0.375$$

Although it is computationally less expedient, it is instructive to expand these calculations in terms of the PIB eigenfunctions.

$$\langle \Phi | \hat{x} | \Phi \rangle = \sum_m \sum_n \int_0^1 \langle \Phi | \Psi_m \rangle \langle \Psi_m | x \rangle x \langle x | \Psi_n \rangle \langle \Psi_n | \Phi \rangle dx = \sum_m \sum_n a_m^* a_n \int_0^1 \sqrt{2}\sin(m\pi x) x \sqrt{2}\sin(n\pi x)\,dx$$

Truncating the calculation after five PIB eigenfunctions yields the same results as obtained with the integrals above.

$$\sum_{m=1}^{5}\sum_{n=1}^{5}\left(a_m\cdot a_n\cdot\int_0^1 \sqrt{2}\cdot sin(m\cdot\pi\cdot x)\cdot x\cdot\sqrt{2}\cdot sin(n\cdot\pi\cdot x)\,dx\right) = 0.5$$

$$\sum_{m=1}^{5}\sum_{n=1}^{5}\left(b_m\cdot b_n\cdot\int_0^1 \sqrt{2}\cdot sin(m\cdot\pi\cdot x)\cdot x\cdot\sqrt{2}\cdot sin(n\cdot\pi\cdot x)\,dx\right) = 0.625$$

$$\sum_{m=1}^{5}\sum_{n=1}^{5}\left(c_m\cdot c_n\cdot\int_0^1 \sqrt{2}\cdot sin(m\cdot\pi\cdot x)\cdot x\cdot\sqrt{2}\cdot sin(n\cdot\pi\cdot x)\,dx\right) = 0.375$$