The Dirac Notation Applied to Variational Calculations

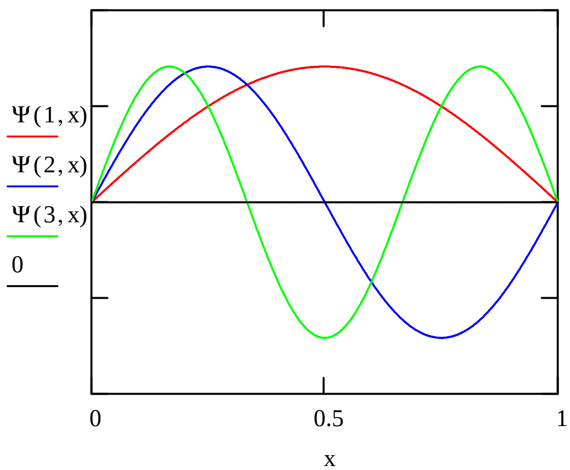
The particle-in-a-box problem is exactly soluble and the solution is calculated below for the first 20 eigens
All calculations will be carried out in atomic units.

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

The first five energy eigenvalues are:

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

The first three eigenfunctions are displayed below.



The set of eigenfunctions forms a complete basis set and any other function can be written as a linear combination 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.

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

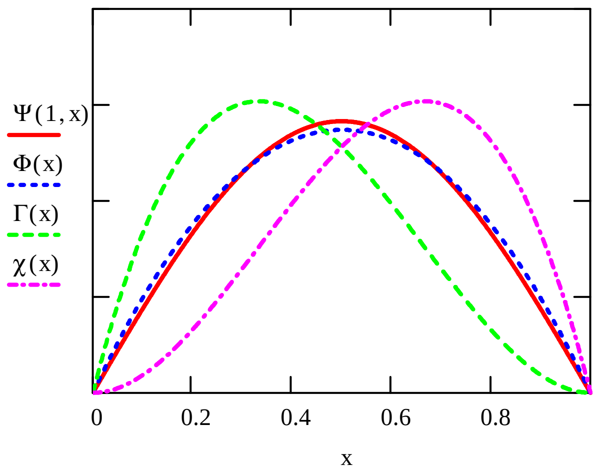
In Dirac bra-ket notation we can express any of these functions as a linear combination in the basis set as follows:

$$\langle x|\Phi\rangle = \sum_n \langle x|\Psi_n\rangle\langle\Psi_n|\Phi\rangle = \sum_n \langle x|\Psi_n\rangle\int_0^1 \langle\Psi_n|x\rangle\langle x|\Phi\rangle\, dx$$

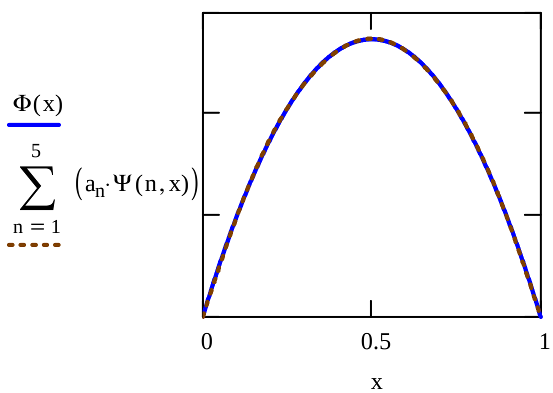
The various overlap integrals for the three trial function are evaluated below.

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

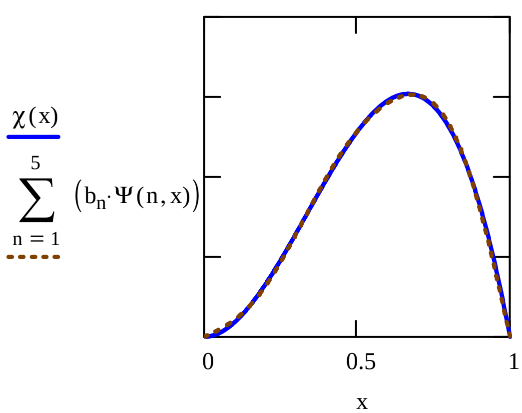
The figure shown below demonstrate that only Φ is a reasonable representative for the ground state wavefunction.

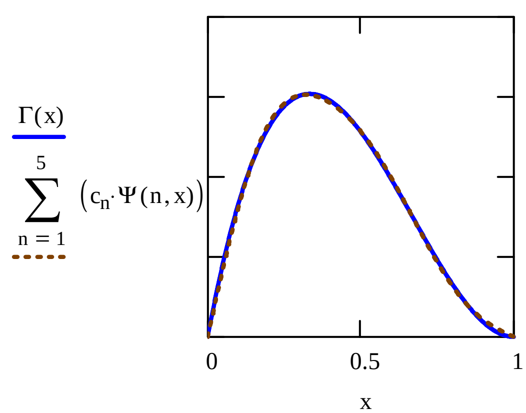


If Φ is written as a linear combination of the first 5 PIB eigenfunctions, one gets two functions that are essentially indistinquishable from one another.



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.

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

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.

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

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 notation this is formulated as:

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

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

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:

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

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