

The Dirac Notation Applied to Variational Calculations

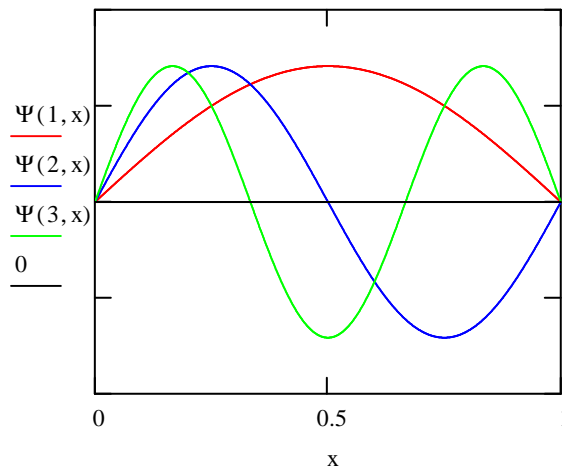
The particle-in-a-box problem is exactly soluble and the solution is calculated below for the first 20 eigens. All calculations will be carried out in atomic units.

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

The first five energy eigenvalues are:

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

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.

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

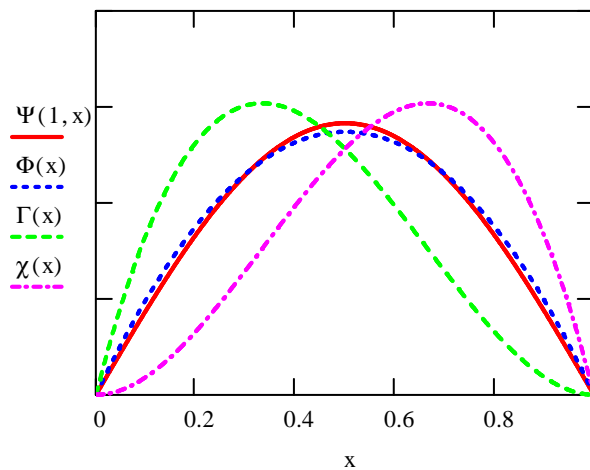
In Dirac bra-ket notation we can express any of these functions as a linear combination in the basis set as follows:

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

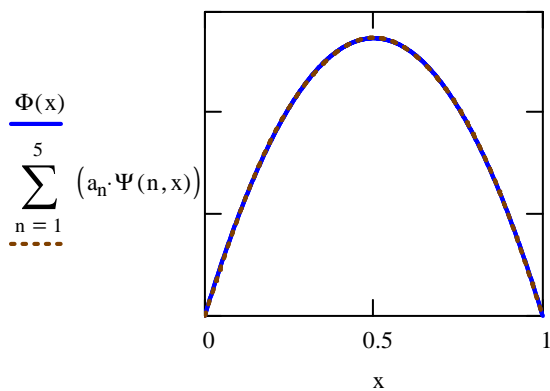
The various overlap integrals for the three trial function are evaluated below.

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

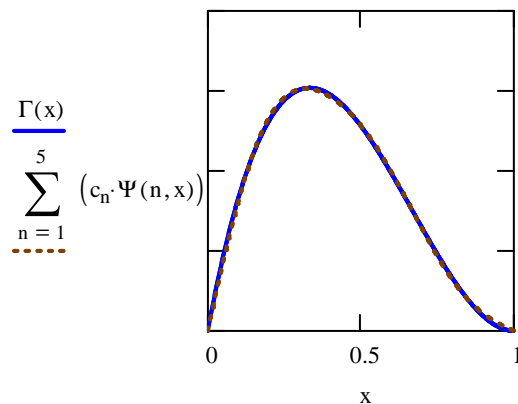
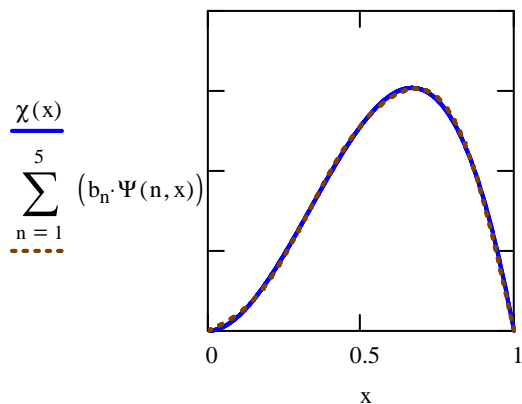
The figure shown below demonstrate that only Φ is a reasonable representative for the ground state wavefunction.



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

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

In Dirac notation we write:

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

Thus we easily show the same result.

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

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

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

In Dirac notation this is formulated as:

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

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

We now calculate some over-lap integrals:

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

In Dirac notation this is formulated as:

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

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