Finding Roots

The attempt to find analytical solutions to Schrodinger's equation for some problems yields transcendental equations which must be solved by a combination of graphical and numerical techniques. Mathcad is particularly well-suited for such applications.

Solving Schroedinger's equation for the particle in the box with an internal barrier yields the trancendental equation f(E) shown below. This equation is solved by plotting f(E) vs E to find the approximate values of the bound energy states.

The box is 1 bohr wide and the barrier is 0.1 bohr thick and located in the center of the box.

Vo is the barrier height in hartrees. $Vo := 100$

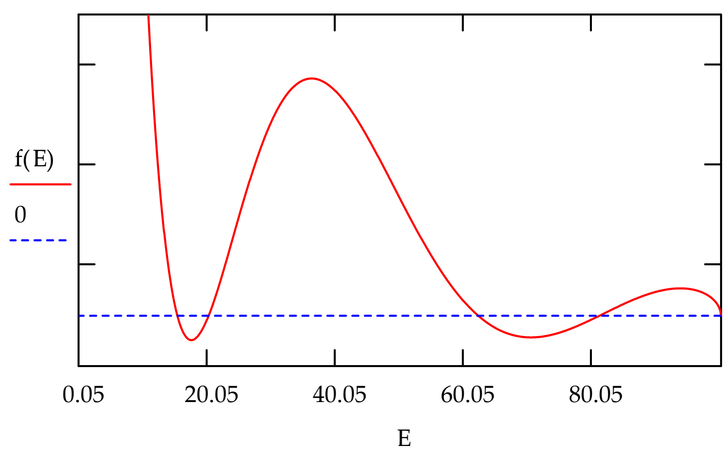
The barrier thickness in bohrs. $BT := .1$

Left barrier boundary in bohrs. $LB := .45$

$E := 0.05, .1 .. 100$

$$f(E) := \tanh\left[BT\cdot\sqrt{2\cdot(Vo - E)}\right]\cdot\left(\frac{Vo - E}{E}\cdot\sin\left(LB\cdot\sqrt{2\cdot E}\right)^2 + \cos\left(LB\cdot\sqrt{2\cdot E}\right)^2\right) \ldots$$
$$+ 2\cdot\sqrt{\frac{Vo - E}{E}}\cdot\sin\left(LB\cdot\sqrt{2\cdot E}\right)\cdot\cos\left(LB\cdot\sqrt{2\cdot E}\right)$$

For a derivation of this formula see: Johnson and Williams, Amer. J. Phys. **1982**, *50*, 239-244.



By inspection of the graph one can see that there are roots at approximately 15, 20, 62, and 80. The exact energy is found with Mathcad's ***root*** function using the approximate energy as a seed value as illustrated below.

$E := 15$ $\quad$ $\mathrm{root}(f(E), E) = 15.43$

$E := 20$ $\quad$ $\mathrm{root}(f(E), E) = 20.29$

$E := 62$ $\quad$ $\mathrm{root}(f(E), E) = 62.24$

$E := 80$ $\quad$ $\mathrm{root}(f(E), E) = 81.07$

This exercise can be extended by noting that this problem can also be solved by numerical integration of Schrodinger's equation. Comparisions of this sort help are helpful in strengthening the students understanding of the computational techniques available to the quantum chemist. Below the problem is solved by numerical integration of Schroedinger's equation.

Integration limit: $x_{max} := 1$ Effective mass: $\mu := 1$ Barrier height: $V_0 := 100$

Barrier boundaries: $lb := .45$ $rb := .55$ Potential energy: $V(x) := \text{if}\left[(x \ge lb)\cdot(x \le rb), V_0, 0\right]$

Numerical integration of Schrodinger's equation: Enter energy guess: $E := 15.43$

Given $$\frac{-1}{2\cdot\mu}\cdot\frac{d^2}{dx^2}\Psi(x) + V(x)\cdot\Psi(x) = E\cdot\Psi(x) \qquad \Psi(0) = 0 \qquad \Psi'(0) = 0.1$$

$\Psi := \text{Odesolve}\left(x, x_{max}\right)$ Normalize wave function: $$\Psi(x) := \frac{\Psi(x)}{\sqrt{\int_0^{x_{max}} \Psi(x)^2\, dx}}$$