Problem 6.1 and 6.4a in Griffiths
Delta function perturbation in the center of an infinite square well

\[ hbarc = \hbar \text{times speed of light in eV nm} \]
\[ mc^2 = 511000 \quad \text{Electron rest energy in eV} \]
\[ a = 2 \quad \text{Size of the well in nm} \]
\[ \alpha = 0.02 \quad \text{Strength of the perturbation in eV nm} \]

\[ \psi_0(n, x) := \frac{2}{\alpha} \cdot \sin \left( \frac{n \pi x}{a} \right) \] \quad \text{Eigenstates of the unperturbed infinite square well}

\[ E_0(n) := \frac{\alpha^2 + hbarc^2}{2 \cdot mc^2 \cdot a^2} \] \quad E_0(1) = 0.094 \quad \text{Infinite square well energy eigenvalues}

\[ E_1(n) := \frac{2 \cdot \alpha}{a} \left( \sin \left( \frac{n \pi}{2} \right) \right)^2 \] \quad E_1(1) = 0.02 \quad \text{First order correction to the energy}

\[ E_2(n) := \frac{\alpha}{\pi \cdot hbarc \cdot n} \left( \frac{\alpha}{\pi \cdot hbarc \cdot n} \right)^2 \] \quad E_2(1) = \(-1.067 \times 10^{-3}\) \quad \text{Second order correction}

\[ m = 3, 5, \ldots, 29 \]

\[ \psi_1(x) := \frac{2 \cdot \alpha}{a} \sum_m \left( \frac{\alpha}{\pi \cdot hbarc \cdot n} \right) \cdot \psi_0(m, x) \] \quad \text{First order correction to the ground state wave function. The sum is infinite, but we truncate it at some manageable value and hope for the best.}

Ground State Zeroeth order (red) and 1st-order Perturbed (blue)
Equation for the exact energy eigenvalues in the exact solution, obtained by a piecewise solution matched together properly at the center of the well, where the delta function is:

\[ f_1(E) := \tan \left( \frac{\sqrt{2mc^2E} \cdot a}{2\hbar c} \right) \quad f_2(E) := \frac{-\hbar c}{\alpha} \cdot \sqrt{\frac{2E}{mc^2}} \]

Graphical representation of the solutions for the energy

\[ f(E) := f_1(E) - f_2(E) \]

Find the root numerically for the ground state:

\[ z := 0.1 \quad E_{\text{gnd}} := \text{root}(f(z), z) \quad E_{\text{gnd}} = 0.11267 \]

This compares well with the 2nd-order result from above:

\[ E_0(1) + E_1(1) + E_2(1) = 0.11263 \]

\[ k := \sqrt{\frac{2mc^2E_{\text{gnd}}}{\hbar c}} = 1.723 \quad \text{Ground-state wave number for the exact numerical solution.} \]

\[ \psi_{\text{gnd}}(x) := \begin{cases} \frac{a}{2}, \sin(k \cdot x), \sin[k \cdot (a - x)] \end{cases} \quad \text{Exact solution ground state wave function} \]

\[ \text{Norm} := \int_0^a \left( |\psi_{\text{gnd}}(x)| \right)^2 \, dx = 1.087 \quad \text{Normalization factor for the exact solution} \]
As long as the strength of the perturbation (alpha) is not too large, then we get quite good agreement from just the first-order calculation. But one has to calculate a lot of terms in the sum for the first order correction, as the sum converges rather slowly.
Perturbation theory with a harmonic-oscillator potential

\[ m c^2 = 511000 \]  
Electron rest energy in eV

\[ \hbar c = 197 \]  
Planck’s constant times c, in eV*nm

\[ c = 300 \]  
Speed of light in nm/fs

\[ \omega = 1 \]  
Oscillator classical frequency in rad/fs

\[ \xi(x) := \sqrt{\frac{m c^2 \omega}{c \hbar c}} \cdot x \]  
Dimensionless spatial variable

\[ \psi_0(n, x) := \left( \frac{mc^2 \omega}{\pi c \hbar c} \right)^{1/4} \frac{1}{\sqrt{n!}} \cdot \text{He}(n, \xi(x)) \cdot e^{-\frac{x^2}{2}} \]  
SHO eigenstates

\[ V_0(x) := \frac{1}{2} \cdot mc^2 \cdot \frac{\omega^2}{c^2} \cdot x^2 \]  
SHO potential

\[ E_0(n) := \frac{\hbar c \omega}{c} \left( n + \frac{1}{2} \right) \]  
SHO energy eigenvalues

\[ \frac{2 \cdot E_0(0) \cdot c^2}{mc^2 \cdot \omega^2} = 0.34008 \]  
\[ \psi_{\text{max}} := 1.1 \left( \left| \psi_0(0, 0) \right| \right) = 1.41682 \]  
For setting limits of graphs

\[ x_{\text{max}} := 1.5 \]  
\[ V_{\text{max}} := V_0(x_{\text{max}}) = 6.3875 \]  

Harmonic Oscillator Potential and Some Eigenstates

\[ V_0(x) \]

\[ \omega \]

\[ x \]

\[ \psi_0(n, x) \]

\[ \psi_0(0, x) \]

\[ \psi_0(1, x) \]

\[ \psi_0(2, x) \]

\[ \psi_0(3, x) \]

\[ \psi_0(4, x) \]
Perturbation potential energy function:

\[ a := \frac{x_{\text{max}}}{5} \quad a = 0.3 \]

\[ V_p(x) := \text{if} \left( |x| < a, V_0(a) - V_0(x), 0 \right) \]

The complete potential energy function \( V(x) \)

\[ m := 0 \quad \text{Choose here the eigenstate for which to do the perturbation calculations.} \]

\[ E_{m0} := E_0(m) \quad E_{m0} = 0.32833 \quad \text{Zeroth-order energy} \]

First order energy correction for the \( m \)th eigenstate:

\[ E_{m1} := \int_{-a}^{a} \psi_0(m, x)^2 V_p(x) \, dx \quad E_{m1} = 0.147 \]

Second order energy correction for the \( m \)th eigenstate:

\[ M := 50 \quad \text{Set an upper limit for truncating the infinite sum.} \]

\[ H_p(m, n) := \int_{-a}^{a} \psi_0(m, x) \psi_0(n, x) V_p(x) \, dx \quad \text{Matrix elements} \]

\[ E_{m2} := \sum_{n=0}^{M} \text{if} \left[ m = n, 0, \frac{\left| H_p(m, n) \right|^{2}}{E_0(m) - E_0(n)} \right] \quad \text{Formula for the 2nd-order energy correction} \]

\[ E_{m2} = -5.66889 \times 10^{-3} \]

\[ E_{\text{pert}} := E_{m0} + E_{m1} + E_{m2} \quad \text{Complete 2nd-order energy from perturbation theory} \]

\[ E_{\text{pert}} = 0.46966 \]
Numerical "exact" solution ("wag the dog" or "shooting" method). This program assumes (for simplicity) that the overall potential is symmetric about the origin.

\[ b := x_{max} \quad \text{Upper integration limit} \]

\[ V(x) := V_0(x) + V_p(x) \quad \text{Complete potential energy function} \]

\[ \text{Energy} := 0.469395 \quad \text{Guess the energy for the numerical solution. This guess is refined by hand until the plot below looks correct.} \]

MathCad syntax for defining a set of differential equations to integrate (other options exist in MathCad for solving differential equations, but this is the most visually appealing syntax).

Given

\[ \frac{d^2}{dx^2} \Psi(x) + \frac{2mc^2}{\hbar c^2} (\text{Energy} - V(x)) \cdot \Psi(x) = 0 \]

Time independent S.E. in 1D

Conditions for starting the integration. For a symmetric potential, start at the center with \( \psi=1 \), \( \psi'=0 \) for even solutions or \( \psi=0 \), \( \psi'=1 \) for odd solutions. The solution will not be normalized.

\[ \Psi(0) = 1 \quad \Psi'(0) = 0 \]

\[ \Psi := \text{Odesolve}(x, b) \quad \text{Solve the differential equation numerically, starting at } x=0 \text{ and stepping from left to right. By default the Adams/BDF algorithm is used, but by right clicking on Odesolve you can choose other methods, such as 4th order Runge-Kutta with fixed or adaptive step size.} \]

Adjust the Energy above until the plotted wave function asymptotically approaches the x axis on the right-hand-side of the plot. Any desired accuracy can be achieved by expanding the scale to larger values of x and tweaking Energy to make the plot approach the x axis again.

Normalization factor:

\[ \text{Norm} := 2 \int_0^b \Psi(x)^2 \, dx = 0.68631 \]

\[ \Psi_N(x) := \frac{1}{\sqrt{\text{Norm}}} \cdot \Psi(x) \quad \text{Normalized wave function from the numerical integration} \]
First order perturbation correction to the mth wave function

\[ \psi_{m1}(x) := \sum_{n=0}^{M} \text{if } m = n, 0, \frac{\mathcal{H}_p(m,n)}{E_0(m) - E_0(n)} \psi_0(n,x) \quad \text{Series is truncated at } M = 50 \]

Comparing 0th order, 1st order, and numerical solutions

Energy \( E_0(m) = 0.32833 \)

Energy \( E_{\text{pert}} = 0.46966 \)

\( \text{Energy} = 0.4694 \)
Perturbation Theory in a SHO Potential

Describe the SHO potential and eigenstates

\begin{align*}
mc^2 &= 511000; \quad (\text{Electron rest energy in eV }*) \\
hbar c &= 197; \quad (\text{Planck's constant times c in eV nm }*) \\
c &= 300; \quad (\text{Speed of light in nm/fs }*) \\
\omega &= 1; \quad (\text{Natural oscillator frequency in rad/fs }*) \\
\xi[x] &= \sqrt{mc^2 \omega / \hbar c} x; \quad (\text{Dimensionless spatial variable }*) \\
V_0[x] &= \frac{1}{2} mc^2 \left(\frac{\omega}{c}\right)^2 x^2; \quad (\text{SHO potential }*) \\
E_0[n_] &= \frac{\hbar c \omega}{c} (n + 1/2); \quad (\text{SHO Energy Spectrum }*) \\
\psi_0[n_, x_] &= \left(\frac{mc^2 \omega}{\pi c \hbar c}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} \times \text{HermiteH}[n, \xi[x]] \times e^{-\xi[x]^2/2}; \quad (\text{SHO Eigenstates }*) \\
x_{\text{max}} &= 1.5; \quad \psi_{\text{max}} = 1.1 \times \text{Abs}[\psi_0[0, 0.]]; \quad (\text{For setting plotting ranges }*) \\
N &= \sqrt{\frac{2E_0[0] c^2}{mc^2 \omega^2}} \quad (\text{Classical turning point for the ground state }*)
\end{align*}

Out[26]= 0.340082
Plot the SHO eigenstates

```
In[27]:= <<PlotLegends` (* Load the package for plotting legends *)
Plot[{V0[x], ψ0[0, x], ψ0[1, x], ψ0[2, x], ψ0[3, x], ψ0[4, x]},
     {x, -xmax, xmax}, AxesLabel -> {x, ψ}, PlotLabel -> "SHO Eigenstates",
     ImageSize -> 600, PlotRange -> {(-xmax, xmax)}, PlotLegend -> {"V0", "ψ0", "ψ1", "ψ2", "ψ3", "ψ4"},
     LegendPosition -> {1.1, -0.4}, LegendSize -> {0.6, 0.8}]
```

![SHO Eigenstates]

Perturbation Potential Energy Function

```
In[29]:= a := xmax / 5.;
Vp[x_] := If[Abs[x] < a, V0[a] - V0[x], 0];
V[x_] := V0[x] + Vp[x];
Plot[V[x], {x, -xmax, xmax}, AxesLabel -> {x, V},
     PlotLabel -> "Complete Potential Energy Function"]
```

![Complete Potential Energy Function]
Calculate Perturbation Corrections to the Energy

\(m := 0; M := 50;\)
\(E_{m0} := \text{E0} [m];\)
\(E_{m1} := \text{NIntegrate} [\psi_0 [m, x] \times Vp [x], \{x, -a, a\}];\)
\(H_p [m_, n_] := \text{NIntegrate} [\psi_0 [m, x] \psi_0 [n, x] Vp [x], \{x, -a, a\}, \text{AccuracyGoal} \to 6];\)
\(E_{m2} := \sum_{n=0}^{m} \text{If} [m = n, 0, (\text{Abs}[H_p [m, n]])^2 / (E_0 [m] - E_0 [n])];\)
\(E_{pert} = E_{m0} + E_{m1} + E_{m2} \) (* Complete 2nd-order energy estimate *)

Out[38] = 0.328333
Out[39] = 0.146997
Out[40] = -0.00566889
Out[41] = 0.469662

Numerical "Exact" Solution by the "Shooting" Method

\(b := x_{max};\) (* Upper integration limit *)
\(\text{Energy} := 0.469395;\) (* Guess for the energy of the numerical solution. This must be refined by hand until the plot below looks correct *)
\(\text{WaveFun} = \)
\(\text{First}[\psi \, \text{/. NDSolve} \left[[\psi''[x] = \frac{2 mc^2}{\hbar a^2} (V[x] - \text{Energy}) \times \psi[x], (* Time independent S.E. *) \right.\]
\(\psi[0] = 1, \psi'[0] = 0\}, (* wave function and its derivative at the start of the integration *) \]
\(\psi, \{x, 0, b\}]];\)
\(\text{Plot}[\text{WaveFun}[x], \{x, 0, b\}, \text{AxesLabel} \to \{x, \psi\}, \text{PlotLabel} \to \text{"Shooting-Method Wave Function"}];\)

Shooting-Method Wave Function
First-order perturbation correction to the mth wave function

\begin{align*}
\text{pnts} & := \text{Table}[\text{WaveFun}[x], \{x, 0, b, 0.01]\}; \\
\psi_{\text{numeric}} & := \frac{\text{pnts}}{\sqrt{\text{normalization}}}; \\
\psi_{m1}[x] & := \sum_{n=0}^{M} \text{If}[m = n, 0, \frac{\text{Hp}[m, n]}{E_0[m] - E_0[n]} \times \psi_0[n, x]]; \\
\text{ListLinePlot}[\{\psi_{\text{numeric}}, \text{Table}[\psi_0[m, x], \{x, 0, b, 0.01]\}], \\
\text{Table}[\psi_0[m, x] + \psi_{m1}[x], \{x, 0, b, 0.05]\}], \text{AxesLabel} \rightarrow \{x, \psi\}, \text{PlotRange} \rightarrow (-0.5, 1.5), \\
\text{DataRange} \rightarrow (0, b), \text{PlotLegend} \rightarrow \{\text{"numeric"}, \text{"0th order"}, \text{"1st order"}\}, \\
\text{LegendPosition} \rightarrow (1.1, -0.4), \text{LegendSize} \rightarrow \{0.6, 0.8\}, \text{ImageSize} \rightarrow 800, \\
\text{PlotLabel} \rightarrow \text{"Comparing the 'exact' and perturbative wave functions"}
\end{align*}

(* Here I plot lists instead of the functions in order to speed up the execution. Otherwise Mathematica tries to calculate too many points. *)

Comparing the 'exact' and perturbative wave functions

Energy

(* Compare the energy results for the numerical integration versus 2nd-order perturbative *)

\begin{align*}
\text{Epert} & := 0.525144 \\
& := 0.525846
\end{align*}