Problem 2.47

Attention: This is a *strictly qualitative* problem—no calculations allowed! Consider the "double square well" potential (Figure 2.20). Suppose the depth V_0 and the width a are fixed, and large enough so that several bound states occur.

(a) Sketch the ground state wave function ψ_1 and the first excited state ψ_2, (i) for the case $b = 0$, (ii) for $b \approx a$, and (iii) for $b \gg a$.

(b) Qualitatively, how do the corresponding energies (E_1 and E_2) vary, as b goes from 0 to ∞? Sketch $E_1(b)$ and $E_2(b)$ on the same graph.

(c) The double well is a very primitive one-dimensional model for the potential experienced by an electron in a diatomic molecule (the two wells represent the attractive force of the nuclei). If the nuclei are free to move, they will adopt the configuration of minimum energy. In view of your conclusions in (b), does the electron tend to draw the nuclei together, or push them apart? (Of course, there is also the internuclear repulsion to consider, but that's a separate problem.)

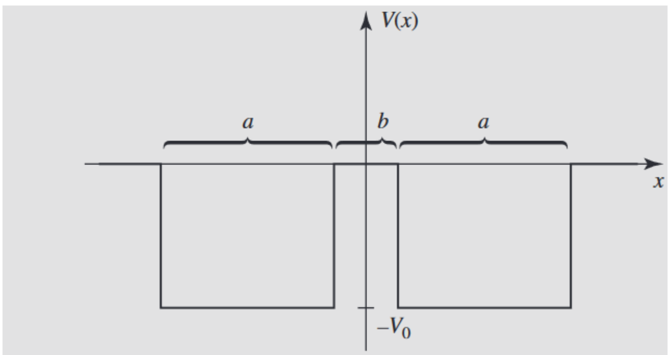


Figure 2.20: The double square well (Problem 2.47).

Solution

Schrödinger's equation describes the time evolution of the wave function $\Psi(x,t)$.

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x,t)\Psi(x,t), \quad -\infty < x < \infty,\ t > 0$$

It is subject to the boundary conditions, $\Psi \to 0$ as $x \to \pm\infty$. For this double square well,

$$V(x,t) = V(x) = \begin{cases} 0 & \text{if } x < -\frac{b}{2} - a \\ -V_0 & \text{if } -\frac{b}{2} - a \leq x \leq -\frac{b}{2} \\ 0 & \text{if } -\frac{b}{2} < x < \frac{b}{2} \\ -V_0 & \text{if } \frac{b}{2} \leq x \leq \frac{b}{2} + a \\ 0 & \text{if } x > \frac{b}{2} + a \end{cases}.$$

Since we're interested in the eigenstates and their corresponding energies, apply the method of separation of variables $[\Psi(x,t) = \psi(x)\phi(t)]$ to reduce the Schrödinger equation to two ODEs, one in t and one in x.

$$\left.\begin{aligned} i\hbar\frac{\phi'(t)}{\phi(t)} &= E \\ -\frac{\hbar^2}{2m}\frac{\psi''(x)}{\psi(x)} + V(x) &= E \end{aligned}\right\}$$

The ODE in x is called the time-independent Schrödinger equation (TISE).

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi(x)$$

Note that for bound states, $-V_0 < E < 0$. On the intervals where $V(x) = 0$, the general solution is

$$\psi(x) = C_1 e^{-\kappa x} + C_2 e^{\kappa x} = C_3 \cosh(\kappa x) + C_4 \sinh(\kappa x), \quad \text{where} \quad \kappa = \frac{\sqrt{-2mE}}{\hbar}.$$

And on the intervals where $V(x) = -V_0$, the general solution is

$$\psi(x) = C_5 e^{-ilx} + C_6 e^{ilx} = C_7 \cos(lx) + C_8 \sin(lx), \quad \text{where} \quad l = \frac{\sqrt{2m(E+V_0)}}{\hbar}.$$

The double square well is an even function, and that means $\psi(x)$ is either an even function or an odd function.

Even Solutions

The general even solution to the TISE that satisfies the boundary condition at infinity is

$$\psi(x) = \begin{cases} \psi(-x) & \text{if } x < 0 \\ A\cosh(\kappa x) & \text{if } 0 < x < \frac{b}{2} \\ B\cos(lx) + C\sin(lx) & \text{if } \frac{b}{2} \le x \le \frac{b}{2} + a \\ De^{-\kappa x} & \text{if } x > \frac{b}{2} + a \end{cases}.$$

Require $\psi(x)$ and its first derivative to be continuous at the interval endpoints.

$$\psi\left(\frac{b}{2}-\right) = \psi\left(\frac{b}{2}+\right): \quad A\cosh\left(\frac{\kappa b}{2}\right) = B\cos\left(\frac{lb}{2}\right) + C\sin\left(\frac{lb}{2}\right)$$

$$\frac{d\psi}{dx}\left(\frac{b}{2}-\right) = \frac{d\psi}{dx}\left(\frac{b}{2}+\right): \quad A\kappa\sinh\left(\frac{\kappa b}{2}\right) = l\left[-B\sin\left(\frac{lb}{2}\right) + C\cos\left(\frac{lb}{2}\right)\right]$$

$$\psi\left[\left(\frac{b}{2}+a\right)-\right] = \psi\left[\left(\frac{b}{2}+a\right)+\right]: \quad B\cos\left[\left(\frac{b}{2}+a\right)l\right] + C\sin\left[\left(\frac{b}{2}+a\right)l\right] = D\exp\left[-\kappa\left(\frac{b}{2}+a\right)\right]$$

$$\frac{d\psi}{dx}\left[\left(\frac{b}{2}+a\right)-\right] = \frac{d\psi}{dx}\left[\left(\frac{b}{2}+a\right)+\right]: \quad l\left\{-B\sin\left[\left(\frac{b}{2}+a\right)l\right] + C\cos\left[\left(\frac{b}{2}+a\right)l\right]\right\} = -\kappa D\exp\left[-\kappa\left(\frac{b}{2}+a\right)\right]$$

Divide the first two equations to eliminate A, and divide the second two equations to eliminate D.

$$\frac{\kappa}{l}\tanh\left(\frac{\kappa b}{2}\right) = \frac{-B\sin\left(\frac{lb}{2}\right) + C\cos\left(\frac{lb}{2}\right)}{B\cos\left(\frac{lb}{2}\right) + C\sin\left(\frac{lb}{2}\right)}$$

$$-\frac{\kappa}{l} = \frac{-B\sin\left[\left(\frac{b}{2}+a\right)l\right] + C\cos\left[\left(\frac{b}{2}+a\right)l\right]}{B\cos\left[\left(\frac{b}{2}+a\right)l\right] + C\sin\left[\left(\frac{b}{2}+a\right)l\right]}$$

Solve this first equation for B,

$$B = C\frac{l\cos\left(\frac{lb}{2}\right) - \kappa\tanh\left(\frac{\kappa b}{2}\right)\sin\left(\frac{lb}{2}\right)}{l\sin\left(\frac{lb}{2}\right) + \kappa\tanh\left(\frac{\kappa b}{2}\right)\cos\left(\frac{lb}{2}\right)},$$

and then substitute it into the second equation.

$$-\frac{\kappa}{l} = \frac{-C\frac{l\cos\left(\frac{lb}{2}\right)-\kappa\tanh\left(\frac{\kappa b}{2}\right)\sin\left(\frac{lb}{2}\right)}{l\sin\left(\frac{lb}{2}\right)+\kappa\tanh\left(\frac{\kappa b}{2}\right)\cos\left(\frac{lb}{2}\right)}\sin\left[\left(\frac{b}{2}+a\right)l\right] + C\cos\left[\left(\frac{b}{2}+a\right)l\right]}{C\frac{l\cos\left(\frac{lb}{2}\right)-\kappa\tanh\left(\frac{\kappa b}{2}\right)\sin\left(\frac{lb}{2}\right)}{l\sin\left(\frac{lb}{2}\right)+\kappa\tanh\left(\frac{\kappa b}{2}\right)\cos\left(\frac{lb}{2}\right)}\cos\left[\left(\frac{b}{2}+a\right)l\right] + C\sin\left[\left(\frac{b}{2}+a\right)l\right]}$$

Cancel C and simplify the right side.

$$-\frac{\kappa}{l} = \frac{-l\sin(la) + \kappa\cos(la)\tanh\left(\frac{\kappa b}{2}\right)}{l\cos(la) + \kappa\sin(la)\tanh\left(\frac{\kappa b}{2}\right)}$$

Further simplify the equation.

$$1 = \frac{l^2\tan(la) - \kappa l\tanh\left(\frac{\kappa b}{2}\right)}{\kappa l + \kappa^2\tan(la)\tanh\left(\frac{\kappa b}{2}\right)} \tag{1}$$

Plugging in the formulas for κ and l results in the following transcendental equation for (half of) the eigenvalues.

$$\boxed{1 = \frac{m(E+V_0)\tan\left[\frac{a\sqrt{2m(E+V_0)}}{\hbar}\right] - \sqrt{-mE}\sqrt{m(E+V_0)}\tanh\left(\frac{b}{\hbar}\sqrt{\frac{-mE}{2}}\right)}{\sqrt{-mE}\sqrt{m(E+V_0)} - mE\tan\left[\frac{a\sqrt{2m(E+V_0)}}{\hbar}\right]\tanh\left(\frac{b}{\hbar}\sqrt{\frac{-mE}{2}}\right)}}$$

In a problem where the constants, m and V_0 and a and b, are given, the eigenvalues can be determined numerically by plotting the functions on both sides versus E and seeing where the curves intersect. For this problem, though, rewrite equation (1).

$$1 = \frac{(la)(la)\tan(la) - (\kappa a)(la)\tanh\left[\frac{\kappa a}{2}\left(\frac{b}{a}\right)\right]}{(\kappa a)(la) + (\kappa a)(\kappa a)\tan(la)\tanh\left[\frac{\kappa a}{2}\left(\frac{b}{a}\right)\right]} \tag{2}$$

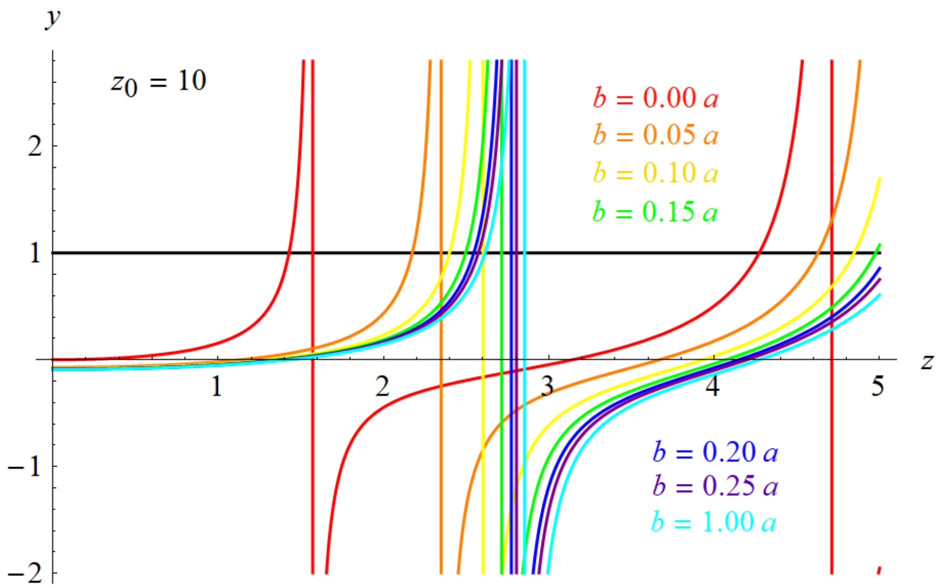
Set $z = la$. Then, since $\kappa^2 + l^2 = 2mV_0/\hbar^2$,

$$\kappa^2 a^2 + l^2 a^2 = \frac{2mV_0 a^2}{\hbar^2} \quad \rightarrow \quad \kappa^2 a^2 = \frac{2mV_0 a^2}{\hbar^2} - l^2 a^2 = z_0^2 - z^2 \quad \rightarrow \quad \kappa a = \sqrt{z_0^2 - z^2}.$$

Substitute these formulas for la and κa into equation (2).

$$1 = \frac{z^2 \tan z - z\sqrt{z_0^2 - z^2} \tanh\left[\frac{\sqrt{z_0^2-z^2}}{2}\left(\frac{b}{a}\right)\right]}{z\sqrt{z_0^2 - z^2} + (z_0^2 - z^2)\tan z \tanh\left[\frac{\sqrt{z_0^2-z^2}}{2}\left(\frac{b}{a}\right)\right]} \tag{3}$$

Graph the functions on both sides versus z for $z_0 = 10$ and various values of b.



The red curve intersects the black curve first at

$$z_1 \approx 1.42755 \quad \Rightarrow \quad E_1 + V_0 \approx \frac{1.01895\hbar^2}{ma^2}.$$

The orange curve intersects the black curve first at

$$z_2 \approx 2.17317 \quad \Rightarrow \quad E_1 + V_0 \approx \frac{2.36134\hbar^2}{ma^2}.$$

The yellow curve intersects the black curve first at

$$z_3 \approx 2.39797 \quad \Rightarrow \quad E_1 + V_0 \approx \frac{2.87513\hbar^2}{ma^2}.$$

The green curve intersects the black curve first at

$$z_4 \approx 2.49581 \quad \Rightarrow \quad E_1 + V_0 \approx \frac{3.11455\hbar^2}{ma^2}.$$

The blue curve intersects the black curve first at

$$z_5 \approx 2.54558 \quad \Rightarrow \quad E_1 + V_0 \approx \frac{3.23998\hbar^2}{ma^2}.$$

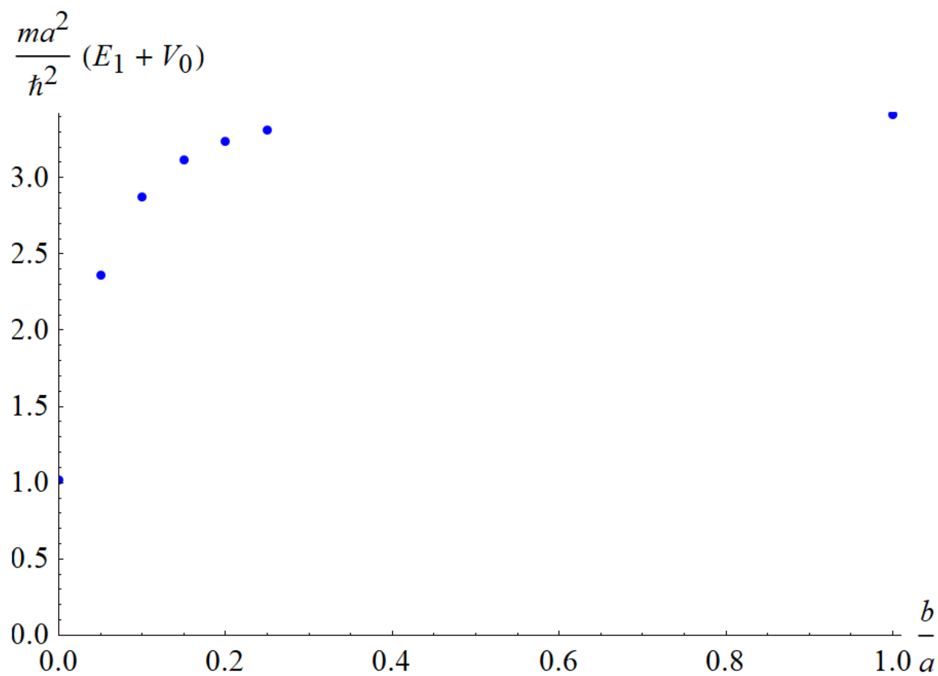
The purple curve intersects the black curve first at

$$z_6 \approx 2.57304 \quad \Rightarrow \quad E_1 + V_0 \approx \frac{3.31026\hbar^2}{ma^2}.$$

The cyan curve intersects the black curve first at

$$z_7 \approx 2.61285 \quad \Rightarrow \quad E_1 + V_0 \approx \frac{3.41350\hbar^2}{ma^2}.$$

The plot below illustrates how the ground state energy above the bottom of the well changes as b increases for $z_0 = 10$.



The aim now is to determine $\psi(x)$. Plug the formula for B back into the first continuity equation.

$$\begin{aligned} A\cosh\left(\frac{\kappa b}{2}\right) &= B\cos\left(\frac{lb}{2}\right) + C\sin\left(\frac{lb}{2}\right) \\ &= C\frac{l\cos\left(\frac{lb}{2}\right) - \kappa\tanh\left(\frac{\kappa b}{2}\right)\sin\left(\frac{lb}{2}\right)}{l\sin\left(\frac{lb}{2}\right) + \kappa\tanh\left(\frac{\kappa b}{2}\right)\cos\left(\frac{lb}{2}\right)}\cos\left(\frac{lb}{2}\right) + C\sin\left(\frac{lb}{2}\right) \end{aligned}$$

Solve for A and simplify the result.

$$A = C\frac{l\,\mathrm{sech}\left(\frac{\kappa b}{2}\right)}{l\sin\left(\frac{lb}{2}\right) + \kappa\cos\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}$$

Plug the formula for B back into the third continuity equation.

$$\begin{aligned} D\exp\left[-\kappa\left(\frac{b}{2} + a\right)\right] &= B\cos\left[\left(\frac{b}{2} + a\right)l\right] + C\sin\left[\left(\frac{b}{2} + a\right)l\right] \\ &= C\frac{l\cos\left(\frac{lb}{2}\right) - \kappa\tanh\left(\frac{\kappa b}{2}\right)\sin\left(\frac{lb}{2}\right)}{l\sin\left(\frac{lb}{2}\right) + \kappa\tanh\left(\frac{\kappa b}{2}\right)\cos\left(\frac{lb}{2}\right)}\cos\left[\left(\frac{b}{2} + a\right)l\right] + C\sin\left[\left(\frac{b}{2} + a\right)l\right] \end{aligned}$$

Solve for D and simplify the result.

$$D = C\exp\left[\kappa\left(\frac{b}{2} + a\right)\right]\frac{l\cos(la) + \kappa\sin(la)\tanh\left(\frac{\kappa b}{2}\right)}{l\sin\left(\frac{lb}{2}\right) + \kappa\cos\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}$$

Substitute these formulas for A, B, and D into the general solution for $\psi(x)$.

$$\psi(x) = \begin{cases} \psi(-x) & \text{if } x < 0 \\ C\frac{l\operatorname{sech}\left(\frac{\kappa b}{2}\right)}{l\sin\left(\frac{lb}{2}\right)+\kappa\cos\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}\cosh(\kappa x) & \text{if } 0 < x < \frac{b}{2} \\ C\frac{l\cos\left(\frac{lb}{2}\right)-\kappa\tanh\left(\frac{\kappa b}{2}\right)\sin\left(\frac{lb}{2}\right)}{l\sin\left(\frac{lb}{2}\right)+\kappa\tanh\left(\frac{\kappa b}{2}\right)\cos\left(\frac{lb}{2}\right)}\cos(lx) + C\sin(lx) & \text{if } \frac{b}{2} \le x \le \frac{b}{2}+a \\ C\exp\left[\kappa\left(\frac{b}{2}+a\right)\right]\frac{l\cos(la)+\kappa\sin(la)\tanh\left(\frac{\kappa b}{2}\right)}{l\sin\left(\frac{lb}{2}\right)+\kappa\cos\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}e^{-\kappa x} & \text{if } x > \frac{b}{2}+a \end{cases}$$

Rewrite the formula. Note that C is arbitrary and is treated as a normalization constant.

$$\psi(x) = \begin{cases} \psi(-x) & \text{if } x < 0 \\ C\frac{la\operatorname{sech}\left(\frac{\kappa a}{2}\frac{b}{a}\right)}{la\sin\left(\frac{la}{2}\frac{b}{a}\right)+\kappa a\cos\left(\frac{la}{2}\frac{b}{a}\right)\tanh\left(\frac{\kappa a}{2}\frac{b}{a}\right)}\cosh\left(\kappa a\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < \frac{b}{2a} \\ C\frac{la\cos\left(\frac{la}{2}\frac{b}{a}\right)-\kappa a\tanh\left(\frac{\kappa a}{2}\frac{b}{a}\right)\sin\left(\frac{la}{2}\frac{b}{a}\right)}{la\sin\left(\frac{la}{2}\frac{b}{a}\right)+\kappa a\tanh\left(\frac{\kappa a}{2}\frac{b}{a}\right)\cos\left(\frac{la}{2}\frac{b}{a}\right)}\cos\left(la\frac{x}{a}\right) + C\sin\left(la\frac{x}{a}\right) & \text{if } \frac{b}{2a} \le \frac{x}{a} \le \frac{b}{2a}+1 \\ C\exp\left[\kappa a\left(\frac{b}{2a}+1\right)\right]\frac{la\cos(la)+\kappa a\sin(la)\tanh\left(\frac{\kappa a}{2}\frac{b}{a}\right)}{la\sin\left(\frac{la}{2}\frac{b}{a}\right)+\kappa a\cos\left(\frac{la}{2}\frac{b}{a}\right)\tanh\left(\frac{\kappa a}{2}\frac{b}{a}\right)}e^{-\kappa a\frac{x}{a}} & \text{if } \frac{x}{a} > \frac{b}{2a}+1 \end{cases}$$

$$= \begin{cases} \psi(-x) & \text{if } x < 0 \\ C\frac{z\operatorname{sech}\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)}{z\sin\left(\frac{z}{2}\frac{b}{a}\right)+\sqrt{z_0^2-z^2}\cos\left(\frac{z}{2}\frac{b}{a}\right)\tanh\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)}\cosh\left(\sqrt{z_0^2-z^2}\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < \frac{b}{2a} \\ C\frac{z\cos\left(\frac{z}{2}\frac{b}{a}\right)-\sqrt{z_0^2-z^2}\tanh\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)\sin\left(\frac{z}{2}\frac{b}{a}\right)}{z\sin\left(\frac{z}{2}\frac{b}{a}\right)+\sqrt{z_0^2-z^2}\tanh\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)\cos\left(\frac{z}{2}\frac{b}{a}\right)}\cos\left(z\frac{x}{a}\right) + C\sin\left(z\frac{x}{a}\right) & \text{if } \frac{b}{2a} \le \frac{x}{a} \le \frac{b}{2a}+1 \\ C\exp\left[\sqrt{z_0^2-z^2}\left(\frac{b}{2a}+1\right)\right]\frac{z\cos(z)+\sqrt{z_0^2-z^2}\sin(z)\tanh\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)}{z\sin\left(\frac{z}{2}\frac{b}{a}\right)+\sqrt{z_0^2-z^2}\cos\left(\frac{z}{2}\frac{b}{a}\right)\tanh\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)}e^{-\sqrt{z_0^2-z^2}\frac{x}{a}} & \text{if } \frac{x}{a} > \frac{b}{2a}+1 \end{cases}$$

Choose $z_0 = 10$. Then if $b = a$, equation (3) yields $z \approx 2.61285$ for the first eigenvalue.

$$\psi_1(x) = \begin{cases} \psi_1(-x) & \text{if } x < 0 \\ 0.00830432C\cosh\left(9.65262\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < \frac{1}{2} \\ -1.71161C\cos\left(2.61285\frac{x}{a}\right) + C\sin\left(2.61285\frac{x}{a}\right) & \text{if } \frac{1}{2} \le \frac{x}{a} \le \frac{3}{2} \\ 1.00555\times 10^6 Ce^{-9.65262\frac{x}{a}} & \text{if } \frac{x}{a} > \frac{3}{2} \end{cases}$$

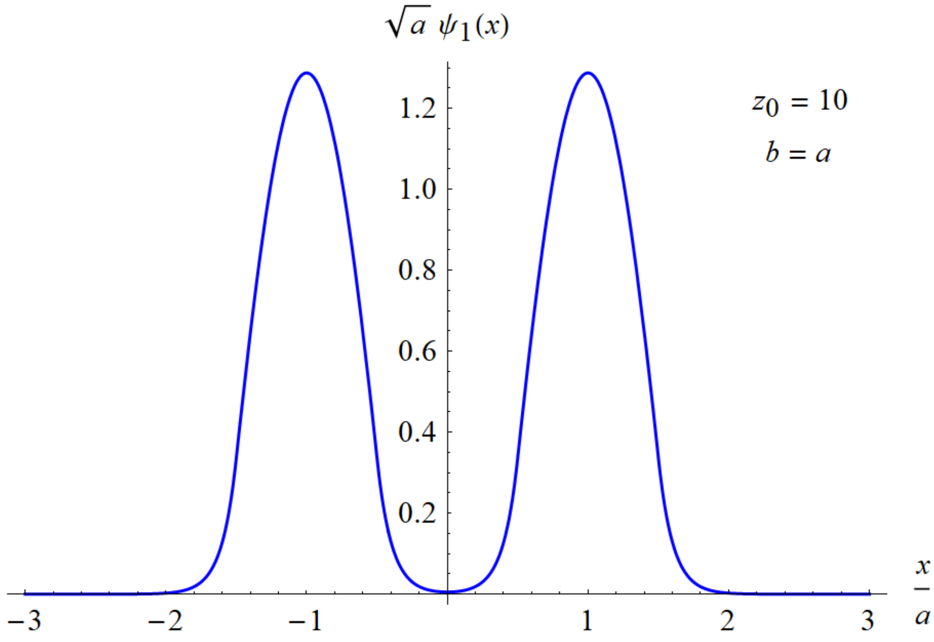
Normalize $\psi_1(x)$ now.

$$1 = \int_{-\infty}^{\infty}[\psi_1(x)]^2\,dx = 2\int_0^{\infty}[\psi_1(x)]^2\,dx \quad\rightarrow\quad 0.5 = \int_0^{\infty}[\psi_1(x)]^2\,dx \quad\Rightarrow\quad C = \pm\frac{0.649302}{\sqrt{a}}$$

Therefore, the ground state for $b = a$ and $z_0 = 10$ is

$$\psi_1(x) = \begin{cases} \psi_1(-x) & \text{if } x < 0 \\ \frac{0.00539202}{\sqrt{a}} \cosh\left(9.65262\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < \frac{1}{2} \\ -\frac{1.11135}{\sqrt{a}} \cos\left(2.61285\frac{x}{a}\right) + \frac{0.649302}{\sqrt{a}} \sin\left(2.61285\frac{x}{a}\right) & \text{if } \frac{1}{2} \le \frac{x}{a} \le \frac{3}{2} \\ \frac{652\,906}{\sqrt{a}} e^{-9.65262\frac{x}{a}} & \text{if } \frac{x}{a} > \frac{3}{2} \end{cases}.$$

Its plot is shown below.



If instead $b = 100a$, equation (3) yields $z \approx 2.61288$ for the first eigenvalue.

$$\psi_1(x) = \begin{cases} \psi_1(-x) & \text{if } x < 0 \\ 3.66655 \times 10^{-208} C \cosh\left(9.65261\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < 50 \\ 281.737C \cos\left(2.61288\frac{x}{a}\right) + C \sin\left(2.61288\frac{x}{a}\right) & \text{if } 50 \le \frac{x}{a} \le 51 \\ 4.60023 \times 10^{215} C e^{-9.65261\frac{x}{a}} & \text{if } \frac{x}{a} > 51 \end{cases}$$

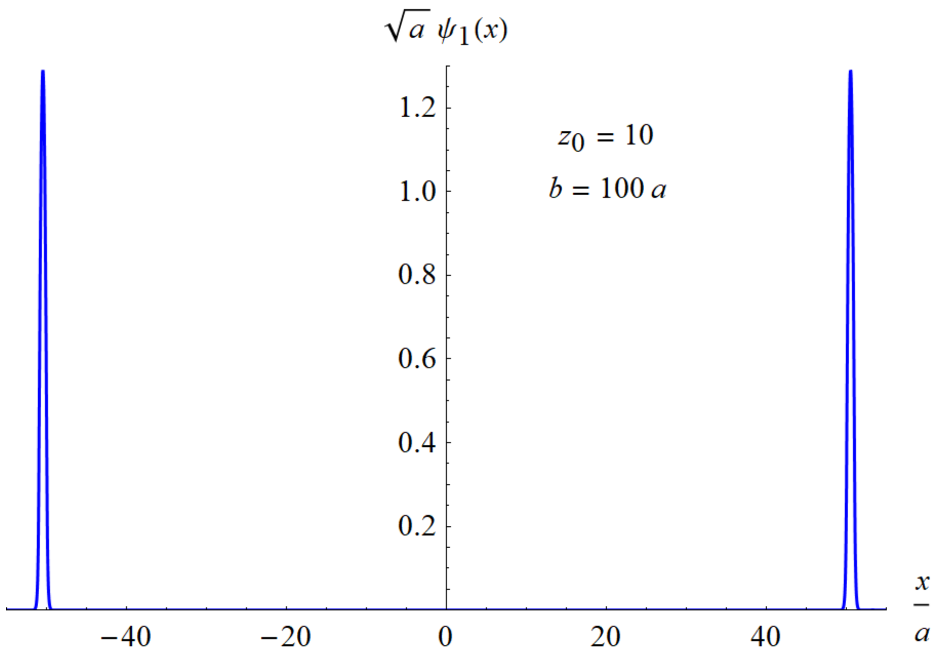
Normalize $\psi_1(x)$ now.

$$1 = \int_{-\infty}^{\infty} [\psi_1(x)]^2\, dx = 2\int_0^{\infty} [\psi_1(x)]^2\, dx \quad \rightarrow \quad 0.5 = \int_0^{\infty} [\psi_1(x)]^2\, dx \quad \Rightarrow \quad C = \pm\frac{0.004582}{\sqrt{a}}$$

Therefore, the ground state for $b = 100a$ and $z_0 = 10$ is

$$\psi_1(x) = \begin{cases} \psi_1(-x) & \text{if } x < 0 \\ \frac{1.68001\times 10^{-210}}{\sqrt{a}} \cosh\left(9.65261\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < 50 \\ \frac{1.29092}{\sqrt{a}} \cos\left(2.61288\frac{x}{a}\right) + \frac{0.004582}{\sqrt{a}} \sin\left(2.61288\frac{x}{a}\right) & \text{if } 50 \le \frac{x}{a} \le 51 \\ \frac{2.10782\times 10^{213}}{\sqrt{a}} e^{-9.65261\frac{x}{a}} & \text{if } \frac{x}{a} > 51 \end{cases}.$$

Its plot is shown below.



If instead $b = 0$, then the potential function changes to a finite square well,

$$V(x) = \begin{cases} 0 & \text{if } x < -a \\ -V_0 & \text{if } -a \le x \le a \\ 0 & \text{if } x > a \end{cases},$$

and the general (even) solution to the TISE changes to

$$\psi(x) = \begin{cases} \psi(-x) & \text{if } x < 0 \\ A\cos(lx) & \text{if } 0 \le x \le a \\ Be^{-\kappa x} & \text{if } x > a \end{cases}.$$

Use the continuity of $\psi(x)$ and its derivative at $x = a$ to determine one of the constants and get an equation for the eigenvalues.

$$\psi(a-) = \psi(a+): \quad A\cos(la) = Be^{-\kappa a}$$

$$\frac{d\psi}{dx}(a-) = \frac{d\psi}{dx}(a+): \quad -lA\sin(la) = -\kappa Be^{-\kappa a}$$

Divide the respective sides of these equations.

$$-l\tan(la) = -\kappa$$

Rewrite the equation.

$$\tan(la) = \frac{\kappa}{l} = \frac{\kappa a}{la}$$

Use $la = z$ and $\kappa a = \sqrt{z_0^2 - z^2}$.

$$\tan z = \frac{\sqrt{z_0^2 - z^2}}{z} = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$$

If $z_0 = 10$, then the first eigenvalue occurs at $z \approx 1.42755$. The first continuity equation implies that $B = Ae^{\kappa a}\cos(la)$. Rewrite the formula for $\psi(x)$ now.

$$\psi(x) = \begin{cases} \psi(-x) & \text{if } x < 0 \\ A\cos\left(la\frac{x}{a}\right) & \text{if } 0 \le \frac{x}{a} \le 1 \\ Ae^{\kappa a}\cos(la)\exp\left(-\kappa a\frac{x}{a}\right) & \text{if } \frac{x}{a} > 1 \end{cases} = \begin{cases} \psi(-x) & \text{if } x < 0 \\ A\cos\left(z\frac{x}{a}\right) & \text{if } 0 \le \frac{x}{a} \le 1 \\ Ae^{\sqrt{z_0^2 - z^2}}\cos(z)\exp\left(-\sqrt{z_0^2 - z^2}\frac{x}{a}\right) & \text{if } \frac{x}{a} > 1 \end{cases}$$

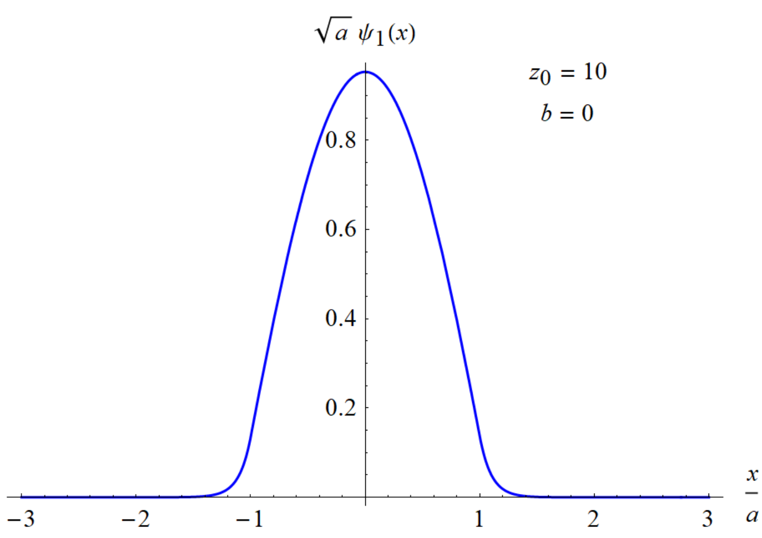
$$\psi_1(x) = \begin{cases} \psi_1(-x) & \text{if } x < 0 \\ A\cos\left(1.42755\frac{x}{a}\right) & \text{if } 0 \le \frac{x}{a} \le 1 \\ 2838.32A\exp\left(-9.89758\frac{x}{a}\right) & \text{if } \frac{x}{a} > 1 \end{cases}$$

Normalize $\psi_1(x)$ now.

$$1 = \int_{-\infty}^{\infty} [\psi_1(x)]^2\,dx = 2\int_0^{\infty} [\psi_1(x)]^2\,dx \quad \rightarrow \quad 0.5 = \int_0^{\infty} [\psi_1(x)]^2\,dx \quad \Rightarrow \quad A = \pm\frac{0.953014}{\sqrt{a}}$$

As a result,

$$\psi_1(x) = \begin{cases} \psi_1(-x) & \text{if } x < 0 \\ \frac{0.953014}{\sqrt{a}}\cos\left(1.42755\frac{x}{a}\right) & \text{if } 0 \le \frac{x}{a} \le 1 \\ \frac{2704.96}{\sqrt{a}}\exp\left(-9.89758\frac{x}{a}\right) & \text{if } \frac{x}{a} > 1 \end{cases}.$$



Odd Solutions

The general odd solution to the TISE that satisfies the boundary condition at infinity is

$$\psi(x) = \begin{cases} -\psi(-x) & \text{if } x < 0 \\ A\sinh(\kappa x) & \text{if } 0 < x < \frac{b}{2} \\ B\cos(lx) + C\sin(lx) & \text{if } \frac{b}{2} \leq x \leq \frac{b}{2} + a \\ De^{-\kappa x} & \text{if } x > \frac{b}{2} + a \end{cases}.$$

Require $\psi(x)$ and its first derivative to be continuous at the interval endpoints.

$$\psi\left(\frac{b}{2}-\right) = \psi\left(\frac{b}{2}+\right): \quad A\sinh\left(\frac{\kappa b}{2}\right) = B\cos\left(\frac{lb}{2}\right) + C\sin\left(\frac{lb}{2}\right)$$

$$\frac{d\psi}{dx}\left(\frac{b}{2}-\right) = \frac{d\psi}{dx}\left(\frac{b}{2}+\right): \quad A\kappa\cosh\left(\frac{\kappa b}{2}\right) = l\left[-B\sin\left(\frac{lb}{2}\right) + C\cos\left(\frac{lb}{2}\right)\right]$$

$$\psi\left[\left(\frac{b}{2}+a\right)-\right] = \psi\left[\left(\frac{b}{2}+a\right)+\right]: \quad B\cos\left[\left(\frac{b}{2}+a\right)l\right] + C\sin\left[\left(\frac{b}{2}+a\right)l\right] = D\exp\left[-\kappa\left(\frac{b}{2}+a\right)\right]$$

$$\frac{d\psi}{dx}\left[\left(\frac{b}{2}+a\right)-\right] = \frac{d\psi}{dx}\left[\left(\frac{b}{2}+a\right)+\right]: \quad l\left\{-B\sin\left[\left(\frac{b}{2}+a\right)l\right] + C\cos\left[\left(\frac{b}{2}+a\right)l\right]\right\} = -\kappa D\exp\left[-\kappa\left(\frac{b}{2}+a\right)\right]$$

Divide the first two equations to eliminate A, and divide the second two equations to eliminate D.

$$\frac{l}{\kappa}\tanh\left(\frac{\kappa b}{2}\right) = \frac{B\cos\left(\frac{lb}{2}\right) + C\sin\left(\frac{lb}{2}\right)}{-B\sin\left(\frac{lb}{2}\right) + C\cos\left(\frac{lb}{2}\right)}$$

$$-\frac{\kappa}{l} = \frac{-B\sin\left[\left(\frac{b}{2}+a\right)l\right] + C\cos\left[\left(\frac{b}{2}+a\right)l\right]}{B\cos\left[\left(\frac{b}{2}+a\right)l\right] + C\sin\left[\left(\frac{b}{2}+a\right)l\right]}$$

Solve this first equation for B,

$$B = C\frac{-\kappa\sin\left(\frac{lb}{2}\right) + l\cos\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}{\kappa\cos\left(\frac{lb}{2}\right) + l\sin\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)},$$

and then substitute it into the second equation.

$$-\frac{\kappa}{l} = \frac{-C\frac{-\kappa\sin\left(\frac{lb}{2}\right)+l\cos\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}{\kappa\cos\left(\frac{lb}{2}\right)+l\sin\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}\sin\left[\left(\frac{b}{2}+a\right)l\right] + C\cos\left[\left(\frac{b}{2}+a\right)l\right]}{C\frac{-\kappa\sin\left(\frac{lb}{2}\right)+l\cos\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}{\kappa\cos\left(\frac{lb}{2}\right)+l\sin\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}\cos\left[\left(\frac{b}{2}+a\right)l\right] + C\sin\left[\left(\frac{b}{2}+a\right)l\right]}$$

Cancel C and simplify the right side.

$$-\frac{\kappa}{l} = \frac{\kappa\cos(la) - l\sin(la)\tanh\left(\frac{\kappa b}{2}\right)}{\kappa\sin(la) + l\cos(la)\tanh\left(\frac{\kappa b}{2}\right)}$$

Further simplify the equation.

$$1 = \frac{l^2\tan(la)\tanh\left(\frac{\kappa b}{2}\right) - \kappa l}{\kappa l\tanh\left(\frac{\kappa b}{2}\right) + \kappa^2\tan(la)} \tag{4}$$

Plugging in the formulas for κ and l results in the following transcendental equation for (the other half of) the eigenvalues.

$$\boxed{1 = \frac{m(E+V_0)\tan\left[\frac{a\sqrt{2m(E+V_0)}}{\hbar}\right]\tanh\left(\frac{b}{\hbar}\sqrt{\frac{-mE}{2}}\right) - \sqrt{-mE}\sqrt{m(E+V_0)}}{\sqrt{-mE}\sqrt{m(E+V_0)}\tanh\left(\frac{b}{\hbar}\sqrt{\frac{-mE}{2}}\right) - mE\tan\left[\frac{a\sqrt{2m(E+V_0)}}{\hbar}\right]}}$$

In a problem where the constants, m and V_0 and a and b, are given, the eigenvalues can be determined numerically by plotting the functions on both sides versus E and seeing where the curves intersect. For this problem, though, rewrite equation (4).

$$1 = \frac{(la)(la)\tan(la)\tanh\left[\frac{\kappa a}{2}\left(\frac{b}{a}\right)\right] - (\kappa a)(la)}{(\kappa a)(la)\tanh\left[\frac{\kappa a}{2}\left(\frac{b}{a}\right)\right] + (\kappa a)(\kappa a)\tan(la)} \tag{5}$$

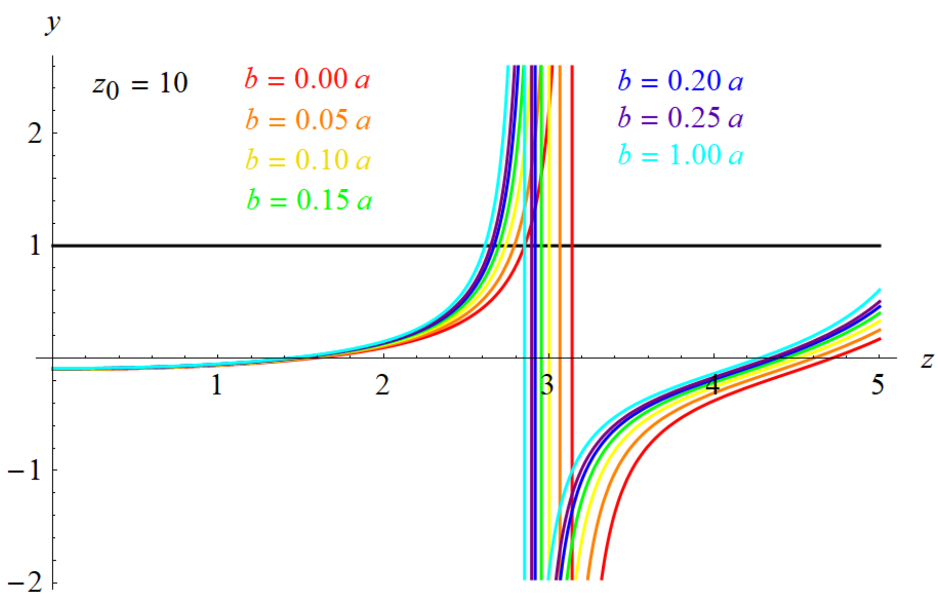
Set $z = la$. Then, since $\kappa^2 + l^2 = 2mV_0/\hbar^2$,

$$\kappa^2a^2 + l^2a^2 = \frac{2mV_0a^2}{\hbar^2} \quad \to \quad \kappa^2a^2 = \frac{2mV_0a^2}{\hbar^2} - l^2a^2 = z_0^2 - z^2 \quad \to \quad \kappa a = \sqrt{z_0^2 - z^2}.$$

Substitute these formulas for la and κa into equation (5).

$$1 = \frac{z^2\tan z\tanh\left[\frac{\sqrt{z_0^2-z^2}}{2}\left(\frac{b}{a}\right)\right] - z\sqrt{z_0^2-z^2}}{z\sqrt{z_0^2-z^2}\tanh\left[\frac{\sqrt{z_0^2-z^2}}{2}\left(\frac{b}{a}\right)\right] + (z_0^2-z^2)\tan z} \tag{6}$$

Graph the functions on both sides versus z for $z_0 = 10$ and various values of b.



The red curve intersects the black curve first at

$$z_1 \approx 2.85234 \quad \Rightarrow \quad E_2 + V_0 \approx \frac{4.06793\hbar^2}{ma^2}.$$

The orange curve intersects the black curve first at

$$z_2 \approx 2.79045 \quad \Rightarrow \quad E_2 + V_0 \approx \frac{3.89330\hbar^2}{ma^2}.$$

The yellow curve intersects the black curve first at

$$z_3 \approx 2.73773 \quad \Rightarrow \quad E_2 + V_0 \approx \frac{3.74759\hbar^2}{ma^2}.$$

The green curve intersects the black curve first at

$$z_4 \approx 2.69704 \quad \Rightarrow \quad E_2 + V_0 \approx \frac{3.63701\hbar^2}{ma^2}.$$

The blue curve intersects the black curve first at

$$z_5 \approx 2.66790 \quad \Rightarrow \quad E_2 + V_0 \approx \frac{3.55884\hbar^2}{ma^2}.$$

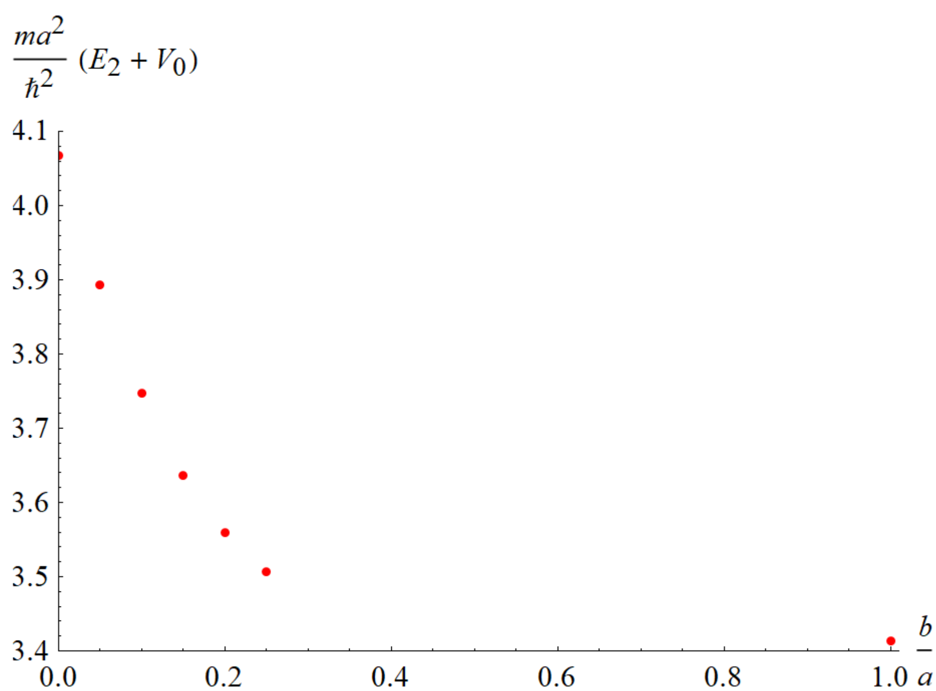
The purple curve intersects the black curve first at

$$z_6 \approx 2.64810 \quad \Rightarrow \quad E_2 + V_0 \approx \frac{3.50623\hbar^2}{ma^2}.$$

The cyan curve intersects the black curve first at

$$z_7 \approx 2.61291 \quad \Rightarrow \quad E_2 + V_0 \approx \frac{3.41364\hbar^2}{ma^2}.$$

The plot below illustrates how the first excited state energy above the bottom of the well changes as b increases for $z_0 = 10$.



The aim now is to determine $\psi(x)$. Plug the formula for B back into the first continuity equation.

$$\begin{aligned}A\sinh\left(\frac{\kappa b}{2}\right) &= B\cos\left(\frac{lb}{2}\right) + C\sin\left(\frac{lb}{2}\right)\\ &= C\frac{-\kappa\sin\left(\frac{lb}{2}\right) + l\cos\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}{\kappa\cos\left(\frac{lb}{2}\right) + l\sin\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}\cos\left(\frac{lb}{2}\right) + C\sin\left(\frac{lb}{2}\right)\end{aligned}$$

Solve for A and simplify the result.

$$A = C\frac{l\,\operatorname{sech}\left(\frac{\kappa b}{2}\right)}{\kappa\cos\left(\frac{lb}{2}\right) + l\sin\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}$$

Plug the formula for B back into the third continuity equation.

$$\begin{aligned}D\exp\left[-\kappa\left(\frac{b}{2}+a\right)\right] &= B\cos\left[\left(\frac{b}{2}+a\right)l\right] + C\sin\left[\left(\frac{b}{2}+a\right)l\right]\\ &= C\frac{-\kappa\sin\left(\frac{lb}{2}\right) + l\cos\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}{\kappa\cos\left(\frac{lb}{2}\right) + l\sin\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}\cos\left[\left(\frac{b}{2}+a\right)l\right] + C\sin\left[\left(\frac{b}{2}+a\right)l\right]\end{aligned}$$

Solve for D and simplify the result.

$$D = C\exp\left[\kappa\left(\frac{b}{2}+a\right)\right]\frac{\kappa\sin(la) + l\cos(la)\tanh\left(\frac{\kappa b}{2}\right)}{\kappa\cos\left(\frac{lb}{2}\right) + l\sin\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}$$

Substitute these formulas for A, B, and D into the general solution for $\psi(x)$.

$$\psi(x) = \begin{cases} -\psi(-x) & \text{if } x < 0 \\ C\frac{l\,\operatorname{sech}\left(\frac{\kappa b}{2}\right)}{\kappa\cos\left(\frac{lb}{2}\right)+l\sin\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}\sinh(\kappa x) & \text{if } 0 < x < \frac{b}{2} \\ C\frac{-\kappa\sin\left(\frac{lb}{2}\right)+l\cos\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}{\kappa\cos\left(\frac{lb}{2}\right)+l\sin\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}\cos(lx) + C\sin(lx) & \text{if } \frac{b}{2} \le x \le \frac{b}{2}+a \\ C\exp\left[\kappa\left(\frac{b}{2}+a\right)\right]\frac{\kappa\sin(la)+l\cos(la)\tanh\left(\frac{\kappa b}{2}\right)}{\kappa\cos\left(\frac{lb}{2}\right)+l\sin\left(\frac{lb}{2}\right)\tanh\left(\frac{\kappa b}{2}\right)}e^{-\kappa x} & \text{if } x > \frac{b}{2}+a \end{cases}$$

$$= \begin{cases} -\psi(-x) & \text{if } x < 0 \\ C\frac{la\,\operatorname{sech}\left(\frac{\kappa a}{2}\frac{b}{a}\right)}{\kappa a\cos\left(\frac{la}{2}\frac{b}{a}\right)+la\sin\left(\frac{la}{2}\frac{b}{a}\right)\tanh\left(\frac{\kappa a}{2}\frac{b}{a}\right)}\sinh\left(\kappa a\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < \frac{b}{2a} \\ C\frac{-\kappa a\sin\left(\frac{la}{2}\frac{b}{a}\right)+la\cos\left(\frac{la}{2}\frac{b}{a}\right)\tanh\left(\frac{\kappa a}{2}\frac{b}{a}\right)}{\kappa a\cos\left(\frac{la}{2}\frac{b}{a}\right)+la\sin\left(\frac{la}{2}\frac{b}{a}\right)\tanh\left(\frac{\kappa a}{2}\frac{b}{a}\right)}\cos\left(la\frac{x}{a}\right) + C\sin\left(la\frac{x}{a}\right) & \text{if } \frac{b}{2a} \le \frac{x}{a} \le \frac{b}{2a}+1 \\ C\exp\left[\kappa a\left(\frac{b}{2a}+1\right)\right]\frac{\kappa a\sin(la)+la\cos(la)\tanh\left(\frac{\kappa a}{2}\frac{b}{a}\right)}{\kappa a\cos\left(\frac{la}{2}\frac{b}{a}\right)+la\sin\left(\frac{la}{2}\frac{b}{a}\right)\tanh\left(\frac{\kappa a}{2}\frac{b}{a}\right)}e^{-\kappa a\frac{x}{a}} & \text{if } \frac{x}{a} > \frac{b}{2a}+1 \end{cases}$$

Substitute $z = la$ and $\kappa a = \sqrt{z_0^2 - z^2}$. Note that C is arbitrary and is treated as a normalization constant.

$$\psi(x) = \begin{cases} -\psi(-x) & \text{if } x < 0 \\ C\dfrac{z\,\text{sech}\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)}{\sqrt{z_0^2-z^2}\cos\left(\frac{z}{2}\frac{b}{a}\right)+z\sin\left(\frac{z}{2}\frac{b}{a}\right)\tanh\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)}\sinh\left(\sqrt{z_0^2-z^2}\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < \frac{b}{2a} \\ C\dfrac{-\sqrt{z_0^2-z^2}\sin\left(\frac{z}{2}\frac{b}{a}\right)+z\cos\left(\frac{z}{2}\frac{b}{a}\right)\tanh\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)}{\sqrt{z_0^2-z^2}\cos\left(\frac{z}{2}\frac{b}{a}\right)+z\sin\left(\frac{z}{2}\frac{b}{a}\right)\tanh\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)}\cos\left(z\frac{x}{a}\right) + C\sin\left(z\frac{x}{a}\right) & \text{if } \frac{b}{2a} \le \frac{x}{a} \le \frac{b}{2a}+1 \\ C\exp\left[\sqrt{z_0^2-z^2}\left(\frac{b}{2a}+1\right)\right]\dfrac{\sqrt{z_0^2-z^2}\sin(z)+z\cos(z)\tanh\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)}{\sqrt{z_0^2-z^2}\cos\left(\frac{z}{2}\frac{b}{a}\right)+z\sin\left(\frac{z}{2}\frac{b}{a}\right)\tanh\left(\frac{\sqrt{z_0^2-z^2}}{2}\frac{b}{a}\right)}e^{-\sqrt{z_0^2-z^2}\frac{x}{a}} & \text{if } \frac{x}{a} > \frac{b}{2a}+1 \end{cases}$$

Choose $z_0 = 10$. Then if $b = a$, equation (6) yields $z \approx 2.61291$ for the first eigenvalue.

$$\psi_2(x) = \begin{cases} -\psi_2(-x) & \text{if } x < 0 \\ 0.00830485C\sinh\left(9.65260\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < \frac{1}{2} \\ -1.71194C\cos\left(2.61291\frac{x}{a}\right) + C\sin\left(2.61291\frac{x}{a}\right) & \text{if } \frac{1}{2} \le \frac{x}{a} \le \frac{3}{2} \\ 1.0057\times 10^6 Ce^{-9.65260\frac{x}{a}} & \text{if } \frac{x}{a} > \frac{3}{2} \end{cases}$$

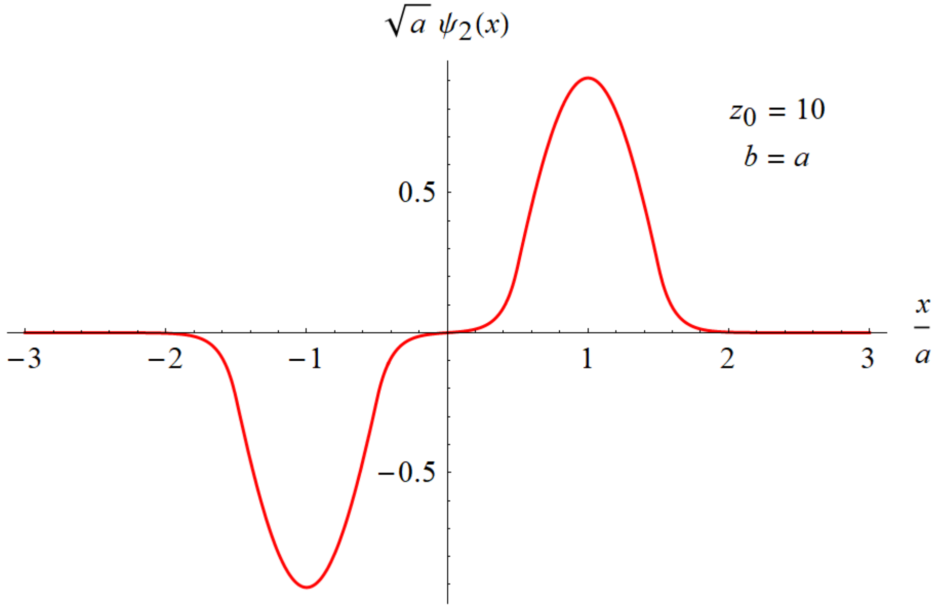
Normalize $\psi_2(x)$ now.

$$1 = \int_{-\infty}^{\infty}[\psi_2(x)]^2\,dx = 2\int_0^{\infty}[\psi_2(x)]^2\,dx \quad\rightarrow\quad 0.5 = \int_0^{\infty}[\psi_2(x)]^2\,dx \quad\Rightarrow\quad C = \pm\frac{0.459067}{\sqrt{a}}$$

Therefore, the first excited state for $b = a$ and $z_0 = 10$ is

$$\psi_2(x) = \begin{cases} -\psi_2(-x) & \text{if } x < 0 \\ \frac{0.00381249}{\sqrt{a}}\sinh\left(9.65260\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < \frac{1}{2} \\ -\frac{0.785898}{\sqrt{a}}\cos\left(2.61291\frac{x}{a}\right) + \frac{0.459067}{\sqrt{a}}\sin\left(2.61291\frac{x}{a}\right) & \text{if } \frac{1}{2} \le \frac{x}{a} \le \frac{3}{2} \\ \frac{461\,685}{\sqrt{a}}e^{-9.65260\frac{x}{a}} & \text{if } \frac{x}{a} > \frac{3}{2} \end{cases}.$$

Its plot is shown below.



If instead $b = 100a$, equation (6) yields $z \approx 2.61288$ for the first eigenvalue.

$$\psi_2(x) = \begin{cases} -\psi_2(-x) & \text{if } x < 0 \\ 3.66655 \times 10^{-208} C \sinh\left(9.65261\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < 50 \\ 281.737C\cos\left(2.61288\frac{x}{a}\right) + C\sin\left(2.61288\frac{x}{a}\right) & \text{if } 50 \leq \frac{x}{a} \leq 51 \\ 4.60023 \times 10^{215} C e^{-9.65261\frac{x}{a}} & \text{if } \frac{x}{a} > 51 \end{cases}$$

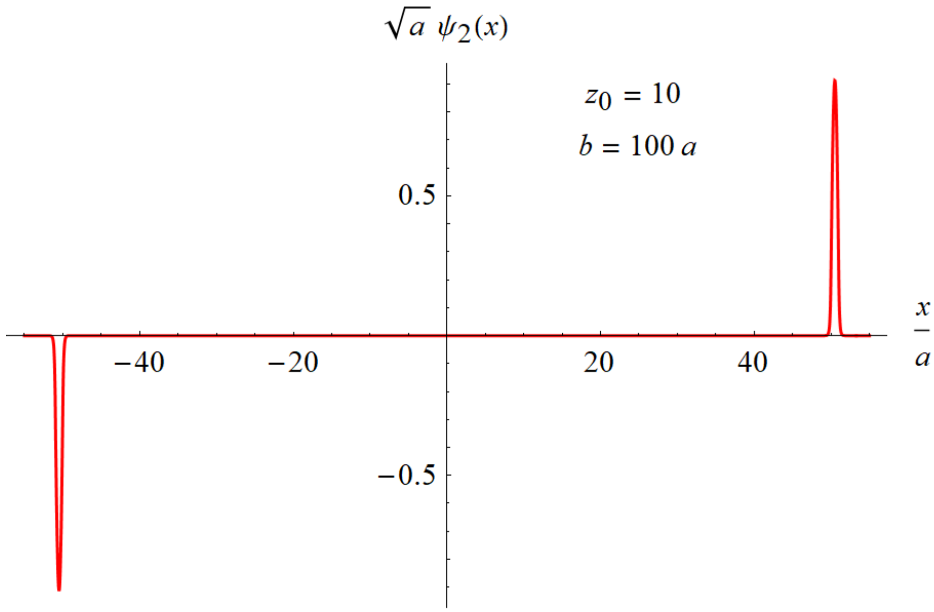
Normalize $\psi_2(x)$ now.

$$1 = \int_{-\infty}^{\infty} [\psi_2(x)]^2\,dx = 2\int_0^{\infty} [\psi_2(x)]^2\,dx \quad \rightarrow \quad 0.5 = \int_0^{\infty} [\psi_2(x)]^2\,dx \quad \Rightarrow \quad C = \pm\frac{0.00323996}{\sqrt{a}}$$

Therefore, the first excited state for $b = 100a$ and $z_0 = 10$ is

$$\psi_2(x) = \begin{cases} -\psi_2(-x) & \text{if } x < 0 \\ \frac{1.18795\times 10^{-210}}{\sqrt{a}} \sinh\left(9.65261\frac{x}{a}\right) & \text{if } 0 < \frac{x}{a} < 50 \\ \frac{0.912818}{\sqrt{a}}\cos\left(2.61288\frac{x}{a}\right) + \frac{0.00323996}{\sqrt{a}}\sin\left(2.61288\frac{x}{a}\right) & \text{if } 50 \leq \frac{x}{a} \leq 51 \\ \frac{1.49046\times 10^{213}}{\sqrt{a}} e^{-9.65261\frac{x}{a}} & \text{if } \frac{x}{a} > 51 \end{cases}.$$

Its plot is shown below.



If instead $b = 0$, then the potential function changes to a finite square well,

$$V(x) = \begin{cases} 0 & \text{if } x < -a \\ -V_0 & \text{if } -a \le x \le a \\ 0 & \text{if } x > a \end{cases},$$

and the general (odd) solution to the TISE changes to

$$\psi(x) = \begin{cases} -\psi(-x) & \text{if } x < 0 \\ A\sin(lx) & \text{if } 0 \le x \le a \\ Be^{-\kappa x} & \text{if } x > a \end{cases}.$$

Use the continuity of $\psi(x)$ and its derivative at $x = a$ to determine one of the constants and get an equation for the eigenvalues.

$$\psi(a-) = \psi(a+): \quad A\sin(la) = Be^{-\kappa a}$$

$$\frac{d\psi}{dx}(a-) = \frac{d\psi}{dx}(a+): \quad Al\cos(la) = -\kappa Be^{-\kappa a}$$

Divide the respective sides of these equations.

$$\frac{1}{l}\tan(la) = -\frac{1}{\kappa}$$

Rewrite the equation.

$$\tan(la) = -\frac{l}{\kappa} = -\frac{la}{\kappa a}$$

Use $la = z$ and $\kappa a = \sqrt{z_0^2 - z^2}$.

$$\tan z = -\frac{z}{\sqrt{z_0^2 - z^2}}$$

If $z_0 = 10$, then the first eigenvalue occurs at $z \approx 2.85234$. The first continuity equation implies that $B = Ae^{\kappa a}\sin(la)$. Rewrite the formula for $\psi(x)$ now.

$$\psi(x) = \begin{cases} -\psi(-x) & \text{if } x < 0 \\ A\sin\left(la\frac{x}{a}\right) & \text{if } 0 \le \frac{x}{a} \le 1 \\ Ae^{\kappa a}\sin(la)e^{-\kappa a\frac{x}{a}} & \text{if } \frac{x}{a} > 1 \end{cases} = \begin{cases} -\psi(-x) & \text{if } x < 0 \\ A\sin\left(z\frac{x}{a}\right) & \text{if } 0 \le \frac{x}{a} \le 1 \\ Ae^{\sqrt{z_0^2-z^2}}\sin(z)e^{-\sqrt{z_0^2-z^2}\frac{x}{a}} & \text{if } \frac{x}{a} > 1 \end{cases}$$

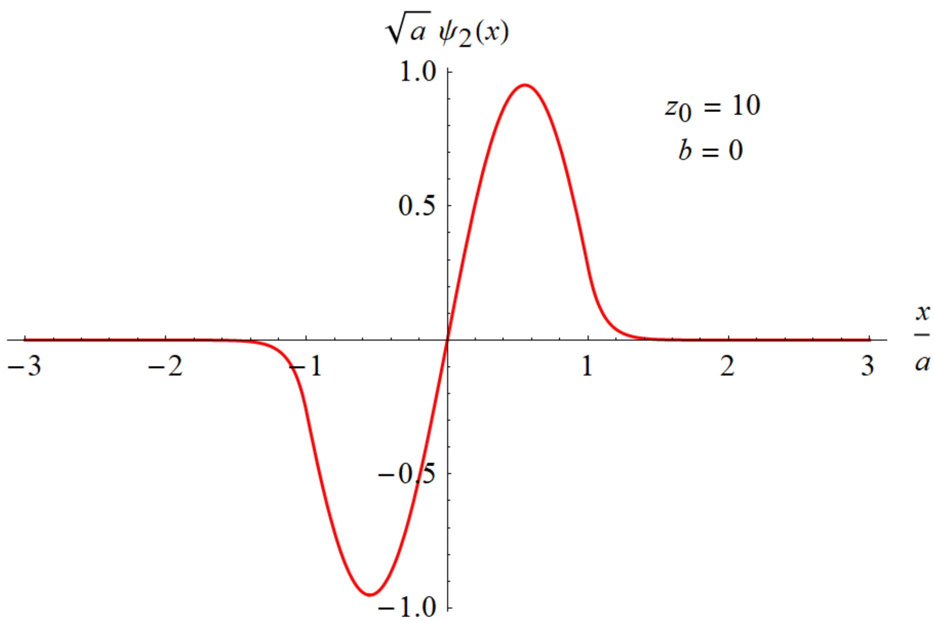
$$\psi_2(x) = \begin{cases} -\psi_2(-x) & \text{if } x < 0 \\ A\sin\left(2.85234\frac{x}{a}\right) & \text{if } 0 \le \frac{x}{a} \le 1 \\ 4146.97Ae^{-9.58458\frac{x}{a}} & \text{if } \frac{x}{a} > 1 \end{cases}$$

Normalize $\psi_2(x)$ now.

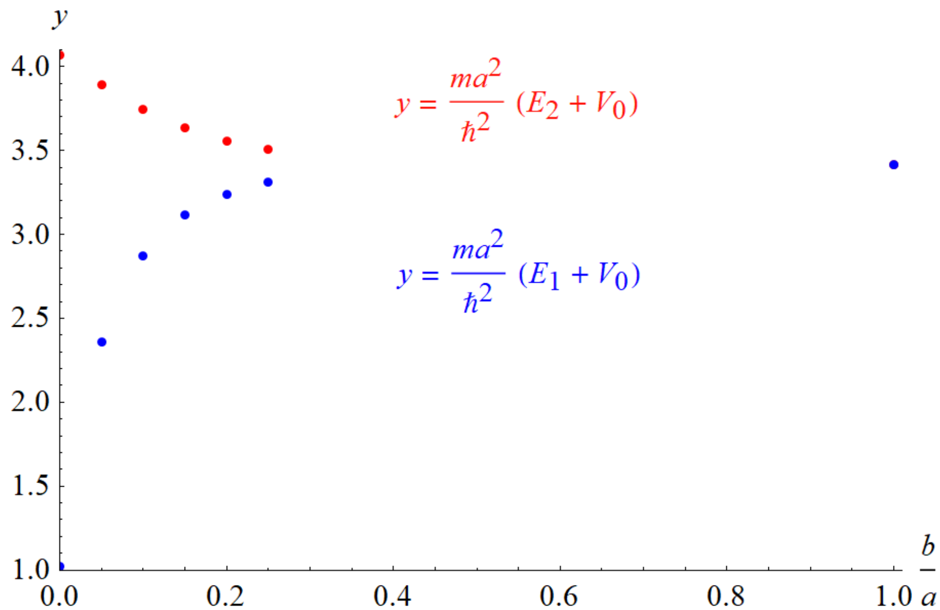
$$1 = \int_{-\infty}^{\infty} [\psi_2(x)]^2\,dx = 2\int_0^{\infty} [\psi_2(x)]^2\,dx \quad \rightarrow \quad 0.5 = \int_0^{\infty} [\psi_2(x)]^2\,dx \quad \Rightarrow \quad A = \pm\frac{0.951589}{\sqrt{a}}$$

As a result,

$$\psi_2(x) = \begin{cases} -\psi_2(-x) & \text{if } x < 0 \\ \frac{0.951589}{\sqrt{a}}\sin\left(2.85234\frac{x}{a}\right) & \text{if } 0 \le \frac{x}{a} \le 1 \\ \frac{3946.22}{\sqrt{a}}\exp\left(-9.58458\frac{x}{a}\right) & \text{if } \frac{x}{a} > 1 \end{cases}.$$



Superimpose the graphs of the ground state energy (in blue) and the first excited state energy (in red) above the bottom of the well as b increases.



In the ground state the energy is minimum when b is as close to zero as possible; that is, the electron tends to pull the nuclei together to form a stable molecule. In the first excited state, though, the energy is minimum when b is as large as possible; that is, the electron tends to push the nuclei away.