Problem set 4

P16.1) In this problem, you will calculate the transmission probability through the barrier illustrated in Figure 16.8. We first go through the mathematics leading to the solution. You will then carry out further calculations.

The domain in which the calculation is carried out is divided into three regions for which the potentials are

$$V(x) = 0$$
 for $x \le 0$ Region I
 $V(x) = V_0$ for $0 < x < a$ Region II
 $V(x) = 0$ for $x \ge a$ Region III

The wave functions must have the following form in the three regions if $E < V_0$:

$$\psi(x) = A \exp\left[+i\sqrt{\frac{2mE}{\hbar^2}} x\right] + B \exp\left[-i\sqrt{\frac{2mE}{\hbar^2}} x\right]$$

$$= A e^{+i\kappa x} + B e^{-i\kappa x} \qquad \text{Region I}$$

$$\psi(x) = C \exp\left[-\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} x\right] + D \exp\left[+\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} x\right]$$

$$= C e^{-\kappa x} + D e^{+\kappa x} \qquad \text{Region II}$$

$$\psi(x) = F \exp\left[+i\sqrt{\frac{2mE}{\hbar^2}} x\right] + G \exp\left[-i\sqrt{\frac{2mE}{\hbar^2}} x\right]$$

$$= F e^{+i\kappa x} + G e^{-i\kappa x} \qquad \text{Region III}$$

Assume that the wave approaches the barrier from the negative x direction. The coefficient B cannot be set equal to zero because $Be^{+i\sqrt{(2mE/\hbar^2)}x}$ represents reflection from the barrier. However, G can be set equal to zero because there is no wave incident on the barrier from the positive x direction.

a. The wave functions and their derivatives must be continuous at x = 0 and x = a. Show that the coefficients must satisfy the following conditions:

$$A + B = C + D$$

$$C e^{-ka} + D e^{+ka} = F e^{+ika}$$

$$A - B = -\frac{i\kappa}{k}(-C + D)$$

$$-C e^{-ka} + D e^{+ka} = \frac{ik}{\kappa}F e^{+ika}$$

b. Because the transmission probability is given by |F/A|², it is useful to manipulate these equations to get a relationship between F and A. By adding and subtracting the first pair of equations, A and B can be expressed in terms of C and D. The second pair of equations can be solved individually to give equations for D and C in terms of F. Show that

$$D = \frac{ik \ e^{+ika} + \kappa \ e^{+ika}}{2\kappa \ e^{+\kappa a}} F$$

$$C = \frac{-i \ k \ e^{+ika} + \kappa \ e^{+ika}}{2\kappa e^{-\kappa a}} F, \text{ and }$$

$$A = \frac{(ik - \kappa) C + (ik + \kappa) D}{2ik}$$

Substitute these results for C and D in terms of F into

$$A = \frac{(ik - \kappa)C + (ik + \kappa)D}{2ik}$$

to relate A and F. Show that

$$2ikA = \frac{e^{+ika}}{2\kappa} [(ik - \kappa)(-ik + \kappa)e^{+\kappa a} + (ik + \kappa)(ik + \kappa)e^{-\kappa a}]F$$

d. Using the hyperbolic trigonometric functions

$$\sinh x = \frac{e^x - e^{-x}}{2} \text{ and } \cosh x = \frac{e^x + e^{-x}}{2}$$

and the relationship $\cosh^2 x - \sinh^2 x = 1$, show that

$$\left| \frac{F}{A} \right|^2 = \frac{16(\kappa k)^2}{16(\kappa k)^2 + (4(k^2 - \kappa^2)^2 + 16(\kappa k)^2)\sinh^2(\kappa a)}$$
$$= \frac{1}{1 + [(k^2 + \kappa^2)^2 \sinh^2(\kappa a)]/4(\kappa k)^2}$$

e. Plot the transmission probability for an electron as a function of energy for V₀ = 1.6 × 10⁻¹⁹ J and a = 9.0 × 10⁻¹⁰ m up to an energy of 8 × 10⁻¹⁹ J. At what energy is the tunneling probability 0.1? At what energy is the tunneling probability 0.02?

f. Plot the transmission probability for an electron of energy 0.50×10^{-19} J as a function of the barrier width for $V_0 = 1.6 \times 10^{-19}$ J between 2×10^{-10} and 8×10^{-10} m. At what barrier width is the transmission probability 0.2?

$$\psi(x) = Ae^{-i\sqrt{\frac{2mB}{h^2}}x} + Be^{-i\sqrt{\frac{2mB}{h^2}}x} = Ae^{+ikx} + Be^{-ikx}$$
 Region I

$$\psi(x) = C e^{-\sqrt{\frac{2\pi i(V_0-B)}{\hbar^2}}x} + D e^{+\sqrt{\frac{2\pi i(V_0-B)}{\hbar^2}}x} = C e^{-\kappa x} + D e^{+\kappa x}$$
 Region II

$$\psi(x) = F e^{+i\sqrt{\frac{2\pi dl}{\hbar^2}}x} + G e^{-i\sqrt{\frac{2\pi dl}{\hbar^2}}x} = F e^{+ikx} + G e^{-ikx}$$
 Region III

At x = 0, the boundary between regions I and II, set the amplitudes and the derivatives of the wave functions equal.

$$A+B=C+D$$

Differentiate the wave functions and set x = 0.

$$ikA - ikB = -\kappa C + \kappa D$$

$$A - B = -\frac{i\kappa}{k} (-C + D)$$

At x=a, the boundary between regions II and III, set the amplitudes and the derivatives of the wave functions of the wave functions equal.

$$C e^{-\kappa a} + D e^{+\kappa a} = F e^{+ika}$$

Differentiate the wave functions and set x = a.

a)
$$-\kappa C e^{-\kappa a} + \kappa D e^{+\kappa a} = ikF e^{+ika}$$

$$-C e^{-\kappa s} + D e^{+\kappa s} = \frac{ik}{\kappa} F e^{+iks}$$

b) We begin by eliminating B from the set of equations.

Solving $ikA - ik(C + D - A) = -\kappa C + \kappa D$ for A gives

$$A = \frac{(ik - \kappa)C + (ik + \kappa)D}{2ik}$$

Rewriting $Ce^{-\kappa a} + De^{+\kappa a} = Fe^{ika}$ in the form $C = \frac{Fe^{ika} - De^{+\kappa a}}{e^{-\kappa a}}$ and substituting this result into $-\kappa Ce^{-\kappa a} + \kappa De^{+\kappa a} = ikFe^{ika}$ gives

$$-\kappa \left(\frac{F e^{ika} - D e^{+\kappa a}}{e^{-\kappa a}}\right) e^{-\kappa a} + \kappa D e^{+\kappa a} = i k F e^{ika} \text{ or }$$

 $-\kappa F e^{ika} + 2\kappa D e^{+\kappa a} = i k F e^{ika}$

resulting in an equation relating D and F

$$D = \frac{i k e^{ika} + \kappa e^{ika}}{2\kappa e^{+\kappa a}} F$$

To relate C and F we begin with the two equations

 $C e^{-\kappa a} + D e^{+\kappa a} = F e^{+ika}$ and $-\kappa C e^{-\kappa a} + \kappa D e^{+\kappa a} = i k F e^{+ika}$

Solving the second equation for C and using our result for D, we obtain

$$C = \frac{\kappa D e^{+\kappa a} - i k F e^{+ik a}}{\kappa e^{-\kappa a}} = \frac{\kappa \left(\frac{i k e^{ika} + \kappa e^{ika}}{2\kappa e^{+\kappa a}} F\right) e^{+\kappa a} - i k F e^{+ik a}}{\kappa e^{-\kappa a}}$$

$$C = \frac{-i k e^{+ika} + \kappa e^{+ika}}{2\kappa e^{-\kappa a}} F$$

c) We now use the expressions for C and D in terms of F to express A in terms of F.

We substitute these expressions for C and D into $A = \frac{(ik - \kappa)C + (ik + \kappa)D}{2ik}$ giving

$$A = \frac{(ik - \kappa)\frac{-ike^{+ika} + \kappa e^{+ika}}{2\kappa e^{-\kappa a}}F + (ik + \kappa)\frac{ike^{+ika} + \kappa e^{+ika}}{2\kappa e^{-\kappa a}}F}{2ik}$$

d) To obtain the ratio $\frac{F}{A}$, we proceed as follows.

$$2ik A = \frac{e^{+i\kappa a}}{2\kappa} \Big[(ik - \kappa)(-ik + \kappa)e^{+\kappa a} + (ik + \kappa)(ik + \kappa)e^{-\kappa a} \Big] F$$

$$2ik A = \frac{e^{+ika}}{2\kappa} \Big[k^2 e^{+\kappa a} + 2ik\kappa e^{+\kappa a} - \kappa^2 e^{+\kappa a} - k^2 e^{-\kappa a} + 2ik\kappa e^{-\kappa a} + \kappa^2 e^{-\kappa a} \Big] F$$
Using the definitions $\sinh x = \frac{e^x - e^{-x}}{2}$ and $\cosh x = \frac{e^x + e^{-x}}{2}$

$$\frac{F}{A} = \frac{4ik\kappa e^{-ika}}{(k^2 - \kappa^2)(e^{+\kappa a} - e^{-\kappa a}) + 2ik\kappa(e^{+\kappa a} + e^{-\kappa a})} = \frac{4ik\kappa e^{-ika}}{2(k^2 - \kappa^2)\sinh\kappa a + 4ik\kappa\cosh\kappa a}$$

$$\frac{F}{A} = \frac{4ik\kappa e^{-ika}}{2(k^2 - \kappa^2)\sinh\kappa a + 4ik\kappa\cosh\kappa a} \frac{-4ik\kappa e^{+ika}}{2(k^2 - \kappa^2)\sinh\kappa a - 4ik\kappa\cosh\kappa a}$$

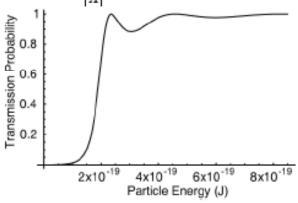
$$\frac{|F|}{A} = \frac{16(k\kappa)^2}{4(k^2 - \kappa^2)^2\sinh^2\kappa a + 16(k\kappa)^2\cosh^2\kappa a}$$

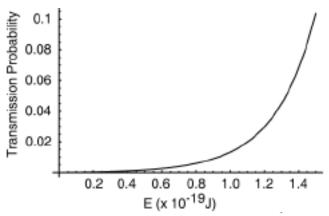
$$= \frac{16(k\kappa)^2}{4(k^2 - \kappa^2)^2\sinh^2\kappa a + 16(k\kappa)^2(1 + \sinh^2\kappa a)}$$

In the last step, we have used the relation $\sinh^2 x + \cosh^2 x = 1$ Our final result is a rather compact equation.

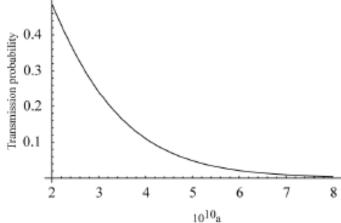
$$\frac{\left|F\right|^2}{\left|A\right|^2} = \left|\frac{F}{A}\right|^2 = \frac{16(\kappa k)^2}{16(\kappa k)^2 + \left[4(k^2 - \kappa^2)^2 + 16(\kappa k)^2\right] \sinh^2(\kappa a)} = \frac{1}{1 + \frac{\left(k^2 + \kappa^2\right)^2 \sinh^2(\kappa a)}{4(\kappa k)^2}}$$

e) Plotting $\left|\frac{F}{A}\right|^2$ as a function of E, we obtain the following graph. By replotting the data over a smaller interval near $E=1\times 10^{-19}$ J, we find that $\left|\frac{F}{A}\right|^2=0.1$ for $E=1.5\times 10^{-19}$ J and 0.02 for $E=1.1\times 10^{-19}$ J.





f) The transmission probability as a function of the barrier width is shown below. The probability is 0.2 for a width of $a = 3.2 \times 10^{-10}$ m.



P16.2) Semiconductors can become conductive if their temperature is raised sufficiently to populate the (empty) conduction band from the highest filled levels in the valence band. The ratio of the populations in the highest level of the conduction band to that of the lowest level in the conduction band is

$$\frac{n_{\text{conduction}}}{n_{\text{valence}}} = \frac{g_{\text{conduction}}}{g_{\text{valence}}} e^{-\Lambda E/kT}$$

where ΔE is the band gap, which is 0.661 eV for Ge and 5.5 eV for diamond. Assume for simplicity that the ratio of the degeneracies is one and that the semiconductor becomes sufficiently conductive when

$$\frac{n_{conduction}}{n_{valence}} = 1.0 \times 10^{-6}$$

At what temperatures will germanium and diamond become sufficiently conductive? Given that the most stable form of carbon at normal pressures is graphite and that graphite sublimates near 3700 K, could you heat diamond enough to make it conductive and not sublimate it?

For germanium, we obtain

$$T_{SI} = \frac{-\Delta E}{k \ln \left[\left(\frac{g_{valence}}{g_{conduction}} \right) \left(\frac{n_{conduction}}{n_{valence}} \right) \right]} = \frac{-0.661 \text{eV} \times 1.602 \times 10^{-19} \text{ J eV}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times \ln \left(1.0 \times 10^{-6} \right)} = 555 \text{ K}$$

For diamond, we obtain

$$T_{C} = \frac{-\Delta E}{k \ln \left[\left(\frac{g_{\text{valence}}}{g_{\text{conduction}}} \right) \left(\frac{n_{\text{conduction}}}{n_{\text{valence}}} \right) \right]} = \frac{-5.5 \text{ eV} \times 1.602 \times 10^{-19} \text{ J eV}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times \ln \left(1.0 \times 10^{-6} \right)} = 4.6 \times 10^{3} \text{ K}$$

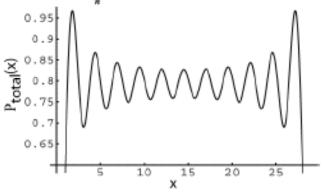
We predict that diamond would not become conductive before it decomposes.

P16.3) For the π-network of β-carotene modeled using the particle in the box, the position-dependent probability density of finding 1 of the 22 electrons is given by

$$P_n(x) = \left| \psi_n(x) \right|^2 = \frac{2}{a} \sin^2 \left(\frac{n\pi x}{a} \right)$$

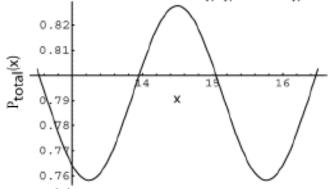
The quantum number n in this equation is determined by the energy level of the electron under consideration. As we saw in Chapter 15, this function is strongly position dependent. The question addressed in this problem is as follows: Would you also expect the total probability density defined by $P_{\text{total}}(x) = \sum_{n} |\psi_{n}(x)|^{2} \text{ to be strongly position dependent? The sum is over all the electrons in the } \pi$ network.

- a. Calculate the total probability density $P_{socal}(x) = \sum_{n} |\psi_{n}(x)|^{2}$ using the box length a = 29.0 nm and plot your results as a function of x. Does $P_{socal}(x)$ have the same value near the ends and at the middle of the molecule?
- b. Determine ΔP_{total}(x)/⟨P_{total}(x)⟩, where ΔP_{total}(x) is the peak-to-peak amplitude of P_{total}(x) in the interval between 12.0 and 16.0 nm.
- c. Compare the result of part (b) with what you would obtain for an electron in the highest occupied energy level.
- d. What value would you expect for $P_{total}(x)$ if the electrons were uniformly distributed over the molecule? How does this value compare with your result from part (a)?
- a) We need to take all the electrons into account and do so by summing the probabilities for each electron. Plotting the data for $P_{total}(x) = \sum |\psi_n(x)|^2$ gives the figure shown below.



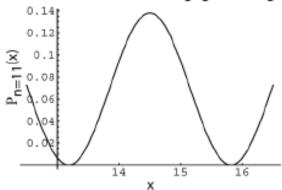
 $P_{total}(x)$ varies more strongly near the ends of the chain than at the middle.

b) Plotting $P_{total}(x)$ over an interval in the middle of the range gives the figure shown below.



From this data, we see that $\frac{\Delta P_{total}(x)}{\langle P_{total}(x) \rangle} = \frac{0.07 \times 10^9 \,\text{m}^{-1}}{0.798 \times 10^9 \,\text{m}^{-1}} = 0.09$

c) Plotting $P_{n=11}(x)$ over an interval in the middle of the range gives the figure shown below.



From this data, we see that $\frac{\Delta P_{m=11}(x)}{\left\langle \Delta P_{total}(x) \right\rangle} = \frac{0.14 \times 10^9 \,\mathrm{m}^{-1}}{0.07 \times 10^9 \,\mathrm{m}^{-1}} = 2$ The variation of the probability density for

the highest occupied state is approximately 20 times as large as that for the probability density for all electrons.

d) There would be 22 electrons uniformly distributed over a length of 29 nm. Therefore the probability density would be 0.76. This is very close to the average value obtained in part (a).

P16.5) Calculate the energy levels of the π-network in octatetraene, C₈H₁₀, using the particle in the box model. To calculate the box length, assume that the molecule is linear and use the values 135 and 154 pm for C=C and C-C bonds. What is the wavelength of light required to induce a transition from the ground state to the first excited state?

The length of the box is $a = 4 \times 135 \,\text{pm} + 3 \times 154 \,\text{pm} = 1002 \,\text{pm}$. The energy levels are given by $E_n = \frac{n^2 h^2}{8 \,m \,a^2}$ and the transition is between n = 4 and n = 5.

$$\lambda = \frac{c}{v} = \frac{c}{E/h} = \frac{8 \, \text{m} \, a^2 c}{h \left(n_2^2 - n_1^2\right)} = \frac{8 \times 9.11 \times 10^{-31} \, \text{kg} \times \left(10.02 \times 10^{-10} \, \text{m}\right)^2 \times 2.998 \times 10^8 \, \text{m s}^{-1}}{6.626 \times 10^{-34} \, \text{J s} \times \left(5^2 - 4^2\right)}$$
= 368 nm

P16.7) In this problem, you will solve for the total energy eigenfunctions and eigenvalues for an electron in a finite depth box. We first go through the calculation for the box parameters used in Figure 16.1. You will then carry out the calculation for a different set of parameters.

We describe the potential in this way:

$$V(x) = V_0$$
 for $x \le -\frac{a}{2}$ Region I
 $V(x) = 0$ for $-\frac{a}{2} < x < \frac{a}{2}$ Region II
 $V(x) = V_0$ for $x \ge \frac{a}{2}$ Region III

The eigenfunctions must have the following form in these three regions:

$$\psi(x) = B \exp\left[+ \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} x \right] + B' \exp\left[-\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} x \right]$$

$$= Be^{+\kappa x} + B'e^{-\kappa x} \qquad \text{Region I}$$

$$\psi(x) = C \sin\sqrt{\frac{2mE}{\hbar^2}} x + D \cos\sqrt{\frac{2mE}{\hbar^2}} x$$

$$= C \sin kx + D \cos kx \qquad \text{Region II}$$

$$\psi(x) = A \exp\left[-\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} x \right] + A' \exp\left[+\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} x \right]$$

$$= A e^{-\kappa x} + A' e^{+\kappa x} \qquad \text{Region III}$$

So that the wave functions remain finite at large positive and negative values of x, A' = B' = 0. An additional condition must also be satisfied. To arrive at physically meaningful solutions for the eigenfunctions, the wave functions in the separate regions must have the same amplitude and derivatives at the values of x = a/2 and x = -a/2 bounding the regions. This restricts the possible values for the coefficients A, B, C, and D. Show that applying these conditions gives the following equations:

$$Be^{-\kappa(a/2)} = -C\sin k \frac{a}{2} + D\cos k \frac{a}{2}$$

$$B\kappa e^{-\kappa(a/2)} = Ck\cos k \frac{a}{2} + Dk\sin k \frac{a}{2}$$

$$Ae^{-\kappa(a/2)} = C\sin k \frac{a}{2} + D\cos k \frac{a}{2}$$

$$-A\kappa e^{-\kappa(a/2)} = Ck\cos k \frac{a}{2} - Dk\sin k \frac{a}{2}$$

These two pairs of equations differ on the right side only by the sign of one term. We can obtain a set of

equations that contain fewer coefficients by adding and subtracting each pair of equations to give

$$(A+B)e^{-\kappa(a/2)} = 2D\cos\left(k\frac{a}{2}\right)$$

$$(A-B)e^{-\kappa(a/2)} = 2C\sin\left(k\frac{a}{2}\right)$$

$$(A+B)\kappa e^{-\kappa(a/2)} = 2Dk\sin\left(k\frac{a}{2}\right)$$

$$-(A-B)\kappa e^{-\kappa(a/2)} = 2Ck\cos\left(k\frac{a}{2}\right)$$

At this point we notice that by dividing the equations in each pair, the coefficients can be eliminated to give

$$\kappa = k \tan\left(k\frac{a}{2}\right) \text{ or } \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} = \sqrt{\frac{2mE}{\hbar^2}} \tan\left(\sqrt{\frac{2mE}{\hbar^2}} \frac{a}{2}\right) \text{ and}$$

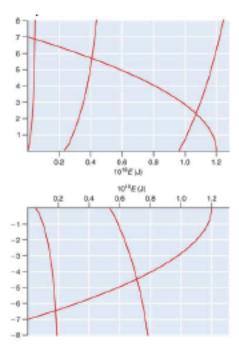
$$-\kappa = k \cot \left(k \frac{a}{2}\right) \text{ or } -\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} = \sqrt{\frac{2mE}{\hbar^2}} \cot \left(\sqrt{\frac{2mE}{\hbar^2}} \frac{a}{2}\right)$$

Multiplying these equations on both sides by a/2 gives dimensionless parameters and the final equations are

$$\sqrt{\frac{m(V_0-E)a^2}{2\hbar^2}} = \sqrt{\frac{mEa^2}{2\hbar^2}} \tan \sqrt{\frac{mEa^2}{2\hbar^2}} \quad \text{and} \quad$$

$$-\sqrt{\frac{m(V_0 - E)a^2}{2\hbar^2}} = \sqrt{\frac{mEa^2}{2\hbar^2}} \cot \sqrt{\frac{mEa^2}{2\hbar^2}}$$

The allowed energy values E must satisfy these equations. They can be obtained by graphing the two sides of each equation against E. The intersections of the two curves are the allowed energy eigenvalues. For the parameters in the caption of Figure 16.1, $V_0 = 1.20 \times 10^{-18}$ J and $a = 1.00 \times 10^{-9}$ m, the following two graphs are obtained:



The five allowed energy levels are at 4.61×10^{-20} , 4.09×10^{-19} , and 1.07×10^{-18} J (top figure), and 1.84×10^{-19} and 7.13×10^{-19} J (bottom figure).

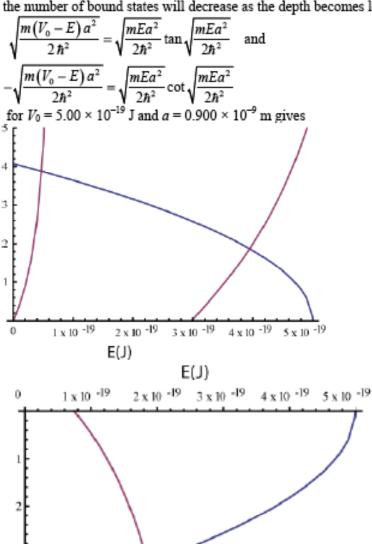
- a. Given these values, calculate λ for each energy level. Is the relation λ = 2a/n (for n an integer) that arose from the calculations on the infinitely deep box still valid? Compare the values with the corresponding energy level in the infinitely deep box. Explain why the differences arise.
- b. Repeat this calculation for $V_0 = 5.00 \times 10^{-19}$ J and $a = 0.900 \times 10^{-9}$ m. Do you think that there will be fewer or more bound states than for the problem just worked out? How many allowed energy levels are there for this well depth and what is the energy corresponding to each level?

there for this well depth and what is the energy corresponding to each level? a) Using the equation $\frac{n}{a} = \frac{n}{a\sqrt{2 m E}}$ we obtain the following values

E	Nα	λ/a for infinite box
4.61 × 10 ⁻²⁰ J	2.29	2.00
1.84 × 10 ⁻¹⁹ J	1.15	1.00
4.09 × 10 ⁻¹⁹ J	0.768	0.667
7.13 × 10 ⁻¹⁹ J	0.582	0.500
1.07 × 10 ⁻¹⁸ J	0.475	0.400

We see that λ/a is always greater for the finite depth box. This is necessary if the particle is to have a finite probability of being outside of the box. Note that if λ/a is less than that for the infinitely deep box, additional nodes are introduced inside the box.

b) Because a finite depth box has fewer bound states than an infinitely deep box, one should expect that the number of bound states will decrease as the depth becomes less. Graphing the equations



There are 3 bound states whose energies are 4.76×10^{-20} J, 1.86×10^{-19} J, and 3.95×10^{-19} J.