P8.3) The force constants for H_2 and Br_2 are 575 and 246 N m^{-1}, respectively. Calculate the ratio of the vibrational state populations $\frac{n_1}{n_0}$ and $\frac{n_2}{n_0}$ at $T = 300$ K and $T = 1000$ K.

The vibrational energy is given by $E_n = \left(n + \frac{1}{2}\right)h\nu = \left(n + \frac{1}{2}\right)h\sqrt{\dfrac{k}{\mu}}$

For H_2

$$E_0 = \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} = \frac{1}{2}\times 1.055\times 10^{-34}\text{J s}\times\sqrt{\frac{575\text{ N m}^{-1}}{\dfrac{1.0078\times 1.0078}{1.0078+1.0078}\text{amu}\times 1.661\times 10^{-27}\text{kg amu}^{-1}}} = 4.37\times 10^{-20}\text{J}$$

$$E_1 = \frac{3}{2}\hbar\sqrt{\frac{k}{\mu}} = \frac{3}{2}\times 1.055\times 10^{-34}\text{J s}\times\sqrt{\frac{575\text{ N m}^{-1}}{\dfrac{1.0078\times 1.0078}{1.0078+1.0078}\text{amu}\times 1.661\times 10^{-27}\text{kg amu}^{-1}}} = 1.31\times 10^{-19}\text{J}$$

$$E_2 = \frac{5}{2}\hbar\sqrt{\frac{k}{\mu}} = \frac{5}{2}\times 1.055\times 10^{-34}\text{J s}\times\sqrt{\frac{575\text{ N m}^{-1}}{\dfrac{1.0078\times 1.0078}{1.0078+1.0078}\text{amu}\times 1.661\times 10^{-27}\text{kg amu}^{-1}}} = 2.19\times 10^{-19}\text{J}$$

For Br_2

$$E_0 = \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} = \frac{1}{2}\times 1.055\times 10^{-34}\text{J s}\times\sqrt{\frac{246\text{ N m}^{-1}}{\dfrac{78.9183\times 78.9183}{78.9183+78.9183}\text{amu}\times 1.661\times 10^{-27}\text{kg amu}^{-1}}} = 3.23\times 10^{-21}\text{J}$$

$$E_1 = \frac{3}{2}\hbar\sqrt{\frac{k}{\mu}} = \frac{3}{2}\times 1.055\times 10^{-34}\text{J s}\times\sqrt{\frac{246\text{ N m}^{-1}}{\dfrac{78.9183\times 78.9183}{78.9183+78.9183}\text{amu}\times 1.661\times 10^{-27}\text{kg amu}^{-1}}} = 9.70\times 10^{-21}\text{J}$$

$$E_2 = \frac{5}{2}\hbar\sqrt{\frac{k}{\mu}} = \frac{5}{2}\times 1.055\times 10^{-34}\text{J s}\times\sqrt{\frac{246\text{ N m}^{-1}}{\dfrac{78.9183\times 78.9183}{78.9183+78.9183}\text{amu}\times 1.661\times 10^{-27}\text{kg amu}^{-1}}} = 1.62\times 10^{-20}\text{J}$$

For H_2 at 300 K, $\dfrac{n_1}{n_0} = e^{-\frac{E_1-E_0}{kT}} = e^{-\frac{(1.31-0.437)\times 10^{-19}\text{J}}{1.381\times 10^{-23}\times 300\text{ K}}} = 6.81\times 10^{-10}$

For H_2 at 1000 K, $\dfrac{n_1}{n_0} = e^{-\frac{E_1-E_0}{kT}} = e^{-\frac{(1.31-0.437)\times 10^{-19}\text{J}}{1.381\times 10^{-23}\times 1000\text{ K}}} = 1.78\times 10^{-3}$

For H_2 at 300 K, $\dfrac{n_2}{n_0} = e^{-\frac{E_1-E_0}{kT}} = e^{-\frac{(2.19-0.437)\times 10^{-19}\text{J}}{1.381\times 10^{-23}\times 300\text{ K}}} = 4.65\times 10^{-19}$

For H_2 at 1000 K, $\dfrac{n_2}{n_0} = e^{-\frac{E_1-E_0}{kT}} = e^{-\frac{(2.19-0.437)\times 10^{-19}\text{J}}{1.381\times 10^{-23}\times 1000\text{ K}}} = 3.07\times 10^{-6}$

For Br$_2$ at 300 K, $\dfrac{n_1}{n_0} = e^{-\frac{E_1 - E_0}{kT}} = e^{-\frac{(9.70-3.23)\times 10^{-21}J}{1.381\times 10^{-23}\times 300\,K}} = 0.212$

For Br$_2$ at 1000 K, $\dfrac{n_1}{n_0} = e^{-\frac{E_1 - E_0}{kT}} = e^{-\frac{(9.70-3.23)\times 10^{-21}J}{1.381\times 10^{-23}\times 1000\,K}} = 0.628$

For Br$_2$ at 300 K, $\dfrac{n_2}{n_0} = e^{-\frac{E_2 - E_0}{kT}} = e^{-\frac{(1.62-0.323)\times 10^{-20}J}{1.381\times 10^{-23}\times 300\,K}} = 4.50\times 10^{-2}$

For Br$_2$ at 1000 K, $\dfrac{n_2}{n_0} = e^{-\frac{E_2 - E_0}{kT}} = e^{-\frac{(1.62-0.323)\times 10^{-20}J}{1.381\times 10^{-23}\times 1000\,K}} = 0.394$

P8.4)

The $^1H^{35}Cl$ molecule can be described by a Morse potential with $D_e = 7.41 \times 10^{-19}$ J. The force constant k for this molecule is 516.3 N m^{-1} and $\nu = 8.97 \times 10^{13}$ s^{-1}.

a. Calculate the lowest four energy levels for a Morse potential using the formula

$$E_n = h\nu\left(n+\frac{1}{2}\right) - \frac{(h\nu)^2}{4D_e}\left(n+\frac{1}{2}\right)^2.$$

b. Calculate the fundamental frequency ν_0 corresponding to the transition $n=0 \rightarrow n=1$ and the frequencies of the first three overtone vibrations. How large would the relative error be if you assume that the first three overtone frequencies are $2\nu_0$, $3\nu_0$, and $4\nu_0$?

$$E_n = h\nu\left(n+\frac{1}{2}\right) - \frac{(h\nu)^2}{4D_e}\left(n+\frac{1}{2}\right)^2 = 6.626\times 10^{-34}\,J\,s \times 8.97\times 10^{13}s^{-1} \times\left(n+\frac{1}{2}\right)$$

$$-\frac{\left(6.626\times 10^{-34}J\,s \times 8.97\times 10^{13}s^{-1}\right)^2}{4\times 7.41\times 10^{-19}J}$$

$$E_n = 5.944\times 10^{-20}\times\left(n+\frac{1}{2}\right)J - 1.192\times 10^{-21}\times\left(n+\frac{1}{2}\right)^2 J$$

$E_0 = 2.942\times 10^{-20}$ J

$E_1 = 8.647\times 10^{-20}$ J

$E_2 = 1.411\times 10^{-19}$ J

$E_3 = 1.934\times 10^{-19}$ J

$$\nu_{0\rightarrow 1} = \frac{E_1 - E_0}{h} = \frac{8.647\times 10^{-20}J - 2.942\times 10^{-20}J}{6.626\times 10^{-34}J\,s} = 8.61\times 10^{13}s^{-1}$$

$$\nu_{0\rightarrow 2} = \frac{E_1 - E_0}{h} = \frac{14.11\times 10^{-20}J - 2.942\times 10^{-20}J}{6.626\times 10^{-34}J\,s} = 1.69\times 10^{14}s^{-1}$$

$$\nu_{0\rightarrow 3} = \frac{E_1 - E_0}{h} = \frac{19.34\times 10^{-20}J - 2.942\times 10^{-20}J}{6.626\times 10^{-34}J\,s} = 2.47\times 10^{14}s^{-1}$$

$$\text{Error}\left(V_{0\to2}\right) = \frac{V_{0\to2} - 2V_{0\to1}}{V_{0\to2}} = -1.89\%$$

$$\text{Error}\left(V_{0\to3}\right) = \frac{V_{0\to2} - 3V_{0\to1}}{V_{0\to2}} = -4.57\%$$

P8.11) ~~XXXX~~) An infrared absorption spectrum of an organic compound is shown in the following figure. Using the characteristic group frequencies listed in Section 19.6, decide whether this compound is more likely to be ethyl amine, pentanol, or acetone.
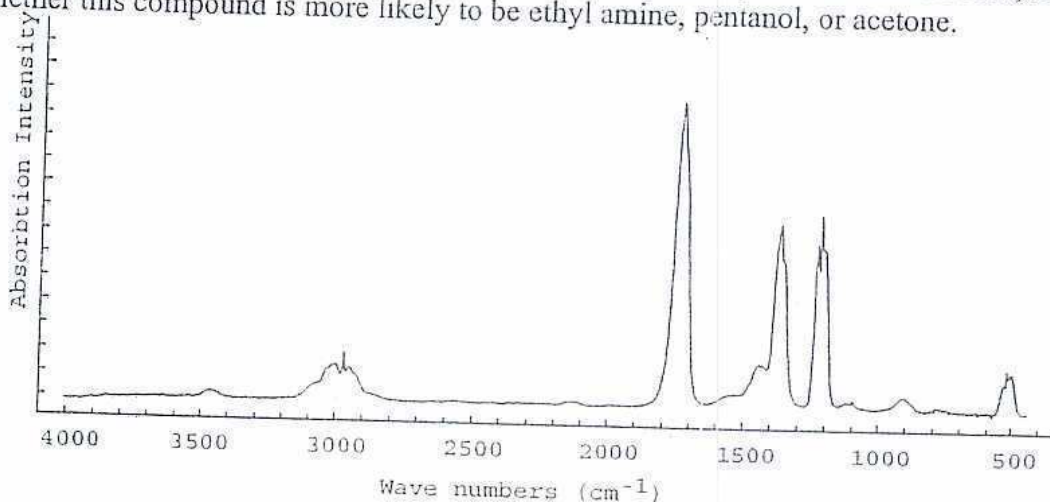
The major peak near 1700 cm^{-1} is the C=O stretch and the peak near 1200 cm^{-1} is a C–C–C stretch. These peaks are consistent with the compound being acetone. Ethyl amine should show a strong peak near 3350 cm^{-1} and pentanol should show a strong peak near 3400 cm^{-1}. Because these peaks are absent, these compounds can be ruled out.

P8.14) ~~wwww~~) The rotational constant for $^{127}\text{I}\,^{79}\text{Br}$ determined from microwave spectroscopy is 0.1141619 cm^{-1}. The atomic masses of ^{127}I and ^{79}Br are 126.904473 amu and 78.918336 amu, respectively. Calculate the bond length in $^{127}\text{I}^{79}\text{Br}$ to the maximum number of significant figures consistent with this information.

$$B = \frac{h}{8\pi^2 \mu r_0^2}; \quad r_0 = \sqrt{\frac{h}{8\pi^2 \mu B}}$$

$$r_0 = \sqrt{\frac{6.6260755\times10^{-34}\,\text{J s}}{8\pi^2 \times \dfrac{126.904473\times78.918336\,\text{amu}}{(126.904473+78.918336)}\times1.6605402\times10^{-27}\text{kg amu}^{-1}\times0.1141619\,\text{cm}^{-1}\times2.99792458\times10^{10}\text{cm s}^{-1}}}$$

$$r_0 = 1.742035\times10^{-10}\,\text{m}$$

P 8.20)

In Problem P19.19 you obtained the result $J_{max} = \frac{1}{2}\left[\sqrt{\dfrac{4I\,kT}{\hbar^2}} - 1\right]$. Using this

result, estimate T for the simulated $^1H^{35}Cl$ rotational spectra in the following figure. Give realistic estimates of the precision with which you can determine T from the spectra.

$$J_{max} = \frac{1}{2}\left[\sqrt{\frac{4I\,kT}{\hbar^2}} - 1\right]; \quad T = \frac{(2J_{max} + 1)^2 \hbar^2}{4I\,k}$$
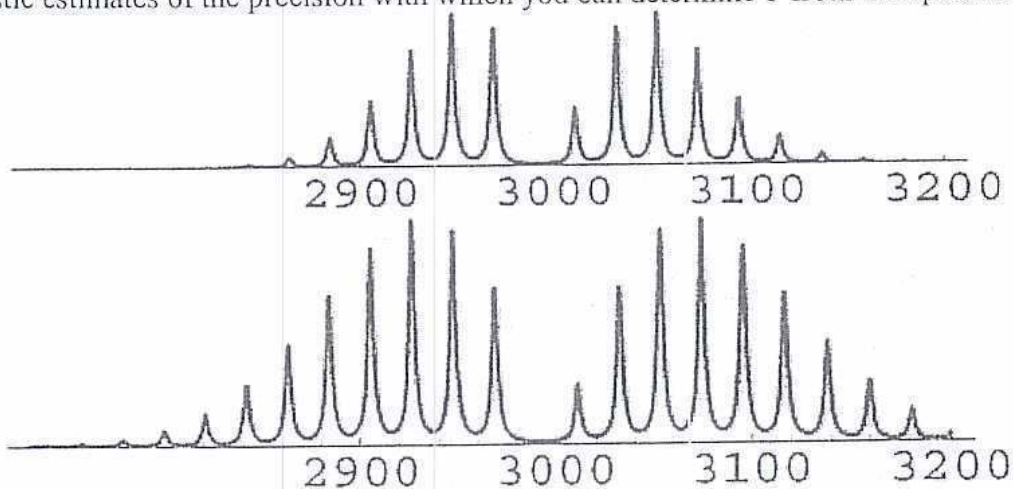
$$T = \frac{(2J_{max} + 1)^2 \hbar^2}{4I\,k}$$

For the upper spectrum, $J_{max} = 2$ in both the P and R branches.

$$T = \frac{5^2 \times \left(1.054 \times 10^{-34}\,\text{J s}\right)^2}{4 \times \dfrac{1.0078 \times 34.9689}{1.0078 \div 34.9689}\,\text{amu} \times 1.1.661 \times 10^{-27}\,\text{kg amu}^{-1} \times \left(1.2746 \times 10^{-10}\,\text{m}\right)^2 \times 1.3807 \times 10^{-23}\,\text{J K}^{-1}}$$

$T = 190\text{ K}$

Setting $J_{max} = 1$ and 3 gives temperatures of 68 K and 372 K. Given an uncertainty of ± 0.5 in J_{max}, a reasonable estimate of the temperature in the upper spectrum is 190 K $\pm$ 70 K.

For the lower spectrum, $J_{max} = 3$ in both the P and R branches, giving $T = 372$ K. Setting $J_{max} = 2$ and 4 gives temperatures of 190 K and 616 K. Given an uncertainty of ± 0.5 in J_{max}, a reasonable estimate of the temperature in the lower spectrum is 372 K $\pm$ 120 K.

Evaluating the intensities for all values of J and not just J_{max} would reduce the uncertainty considerably. The spectra were calculated using values of 150 K and 320 K.

(0) a) In region II (inside the box), the Schrödinger Eq. reads:

$$-\frac{\hbar}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x) \quad [\text{Region II}]$$

The solutions to this diff. eq. are (modulo normalization factor) $\exp(ik(E)x), \exp(-ik(E)x)$; or, equivalently, $\sin(k(E)x), \cos(k(E)x)$, with $k(E) \equiv \sqrt{2mE}/\hbar$.

In regions I,III (outside the box), the Schrödinger Eq. reads:

$$-\frac{\hbar}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V_0\psi(x) = E\psi(x) \quad [\text{Regions I,III}]$$

The solutions to this diff. eq. for $E < V_0$ are (modulo normalization factor) $\exp(\kappa(E)x), \exp(-\kappa(E)x)$, with $\kappa(E) \equiv \sqrt{2m(V_0 - E)}/\hbar$.

Now, in region III, the $\exp(\kappa(E)x)$ term must be disregarded (it blows up as $x \to \infty$). In region II, the $\cos(k(E)x)$ must be discarded, since we are seeking odd-parity solutions. Thus $\psi_{II}(x) = \sin(kx)$. (We can choose the scale factor in front of the sin function to be 1, since we are not concerned here with the overall normalization of the eigenfunction.) And: $\psi_{III}(x) = Ae^{-\kappa x}$. [Note: the scale factor A is not arbitrary in this region, but must be chosen so that $\psi(x)$ is continuous at $x = a/2$.] Finally, in region I, the $\exp(-\kappa(E)x)$ term must be discarded (it blows up as $x \to -\infty$). Thus we obtain $\psi_I(x) = -Ae^{\kappa x}$. [Note: If a particular constant A "works" for the matching of solutions at $x = a/2$, then $-A$ will work at $x = -a/2$, and the overall eigenfunction $\psi(x)$ will have odd parity.]

b) Match $\psi, d\psi/dx$ at $x=a/2$:

(i) $\psi(a/2)$: $\sin(ka/2) = A\exp(-\kappa a/2)$

(ii) $d\psi(a/2)/dx$: $k\cos(ka/2) = -\kappa A\exp(-\kappa a/2)$

Dividing (ii)/(i) leads to the equation: $\cot(ka/2) = -\kappa/k$.

Then, utilizing the definition of k, κ noted above, we obtain: $\cot(\frac{\sqrt{2mE}a}{2\hbar}) = -\sqrt{\frac{V_0 - E}{E}}$, QED.

[Note: performing the same matching process at $x=-a/2$ leads to the same quantization condition.]

c) Converting the quantization condition obtained in b) to the dimensionless form

$$-\cot(\frac{\pi}{2}\sqrt{\varepsilon}) = \sqrt{\frac{v_0 - \varepsilon}{\varepsilon}} \qquad [A1]$$

(see the PS statement for the definition of v_0), we plot the l.h.s. vs. the r.h.s. of this equation for $v_0 = 30$ in Fig. A1:
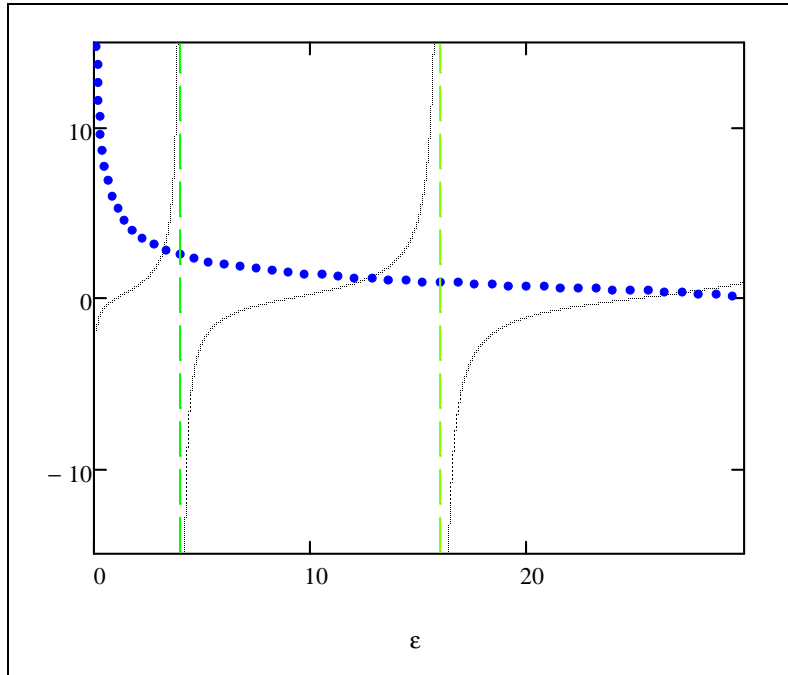

Fig. A1. l.h.s. of Eq. A1: solid black line; r.h.s. of Eq. A1: dotted blue line. [Dashed green lines indicate the values $\varepsilon = 4,16$.] Note maximum abscissa value is $\varepsilon = 30$.

From Fig. A1, we see that there are 3 intersections of the l.h.s. and r.h.s. of Eq. A1 in the range $0 < \varepsilon < v_0$, and thus there are 3 odd-parity eigenfunctions confined within this bos.

(1) Basic Principles of Rotational Spectra

P8.19)

Because the intensity of a transition to first order is proportional to the population of the originating state, the J value for which the maximum intensity is observed in a rotational-vibrational spectrum is not generally $J = 0$. Treat J in the equation $\dfrac{n_J}{n_0} = \dfrac{g_J}{g_0} e^{-(\varepsilon_J - \varepsilon_0)/kT} = (2J+1)e^{-\hbar^2 J(J+1)/2IkT}$ as a continuous variable.

a. Show that

$$\frac{d\left(\dfrac{n_J}{n_0}\right)}{dJ} = 2e^{-\hbar^2 J(J+1)/2IkT} - \frac{(2J+1)^2 \hbar^2}{2IkT} e^{-\hbar^2 J(J+1)/2IkT}$$

$$\frac{d\left(\dfrac{n_J}{n_0}\right)}{dJ} = 2e^{-\hbar^2 J(J+1)/2IkT} + (2J+1)e^{-\hbar^2 J(J+1)/2IkT} \frac{d\left(-\hbar^2 J(J+1)/2IkT\right)}{dJ}$$

$$= 2e^{-\hbar^2 J(J+1)/2IkT} + (2J+1)e^{-\hbar^2 J(J+1)/2IkT}\left(-\frac{\hbar^2 (2J+1)}{2IkT}\right)$$

$$= 2e^{-\hbar^2 J(J+1)/2IkT} - \frac{(2J+1)^2 \hbar^2}{2IkT} e^{-\hbar^2 J(J+1)/2IkT}$$

b) Show that setting $\dfrac{d\left(\dfrac{n_J}{n_0}\right)}{dJ} = 0$ gives the equation $2 - \dfrac{(2J_{max}+1)^2 \hbar^2}{2IkT} = 0$

$$\frac{d\left(\dfrac{n_J}{n_0}\right)}{dJ} = 2e^{-\hbar^2 J(J+1)/2IkT} - \frac{(2J+1)^2 \hbar^2}{2IkT} e^{-\hbar^2 J(J+1)/2IkT} = 0$$

cancelling $e^{-\hbar^2 J(J+1)/2IkT}$ on both sides of the equation, $2 - \dfrac{(2J+1)^2 \hbar^2}{2IkT} = 0$

c) Show that the solution of this quadratic equation is $J_{max} = \dfrac{1}{2}\left[\sqrt{\dfrac{4IkT}{\hbar^2}} - 1\right]$

$$2 - \frac{(2J+1)^2 \hbar^2}{2IkT} = 0; \quad -\frac{2\hbar^2}{IkT} J^2 - \frac{2\hbar^2}{IkT} J - \frac{2\hbar^2}{IkT} + 2 = 0$$

Solving this quadratic equation, $J_{max} = -\dfrac{1}{2} \pm \dfrac{\sqrt{2}}{2}\sqrt{\dfrac{2IkT}{\hbar^2}}$

Only the + solution gives $J > 0$

$$J_{max} = \frac{1}{2}\left[\sqrt{\frac{4IkT}{\hbar^2}} - 1\right]$$

P5.6) (2) Quantum Mechanical Tunneling through a 1D Potential Energy Barrier:

a)

$$\psi(x) = A e^{+i\sqrt{\frac{2mE}{\hbar^2}}\,x} + B e^{-i\sqrt{\frac{2mE}{\hbar^2}}\,x} = A e^{+ikx} + B e^{-ikx} \qquad \text{Region I}$$

$$\psi(x) = C e^{-\sqrt{\frac{2m(V_0-E)}{\hbar^2}}\,x} + D e^{+\sqrt{\frac{2m(V_0-E)}{\hbar^2}}\,x} = C e^{-\kappa x} + D e^{+\kappa x} \qquad \text{Region II}$$

$$\psi(x) = F e^{+i\sqrt{\frac{2mE}{\hbar^2}}\,x} + G e^{-i\sqrt{\frac{2mE}{\hbar^2}}\,x} = F e^{+ikx} + G e^{-ikx} \qquad \text{Region III}$$

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

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

Differentiate the wave functions and set $x = a$.

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

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

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 $C e^{-\kappa a} + D e^{+\kappa a} = F e^{ika}$ in the form $C = \dfrac{F e^{ika} - D e^{+\kappa a}}{e^{-\kappa a}}$

and substituting this result into $-\kappa C e^{-\kappa a} + \kappa D e^{+\kappa a} = ik e^{ika}$ gives

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

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

resulting in an equation relating D and F

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

To relate C and F we begin with the two equations

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

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

we obtain

$$C = \frac{\kappa D e^{+\kappa a} - ikF e^{+ika}}{\kappa e^{-\kappa a}} = \frac{\kappa \left(\dfrac{ike^{ika} + \kappa e^{ika}}{2\kappa e^{+\kappa a}} F \right) e^{+\kappa a} - ikF e^{+ika}}{\kappa e^{-\kappa a}}$$

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

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

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

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

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

$$2ikA = \frac{e^{+ika}}{2\kappa}\left[k^2 e^{-\kappa a} + 2ik\kappa e^{+\kappa a} - \kappa^2 e^{+\kappa a} + 2ik\kappa e^{-\kappa a} + \kappa^2 e^{-\kappa a} \right] F$$

Using the definitions $\sinh x = \dfrac{e^x - e^{-x}}{2}$ and $\cosh x = \dfrac{e^x + e^{-x}}{2}$

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

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

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

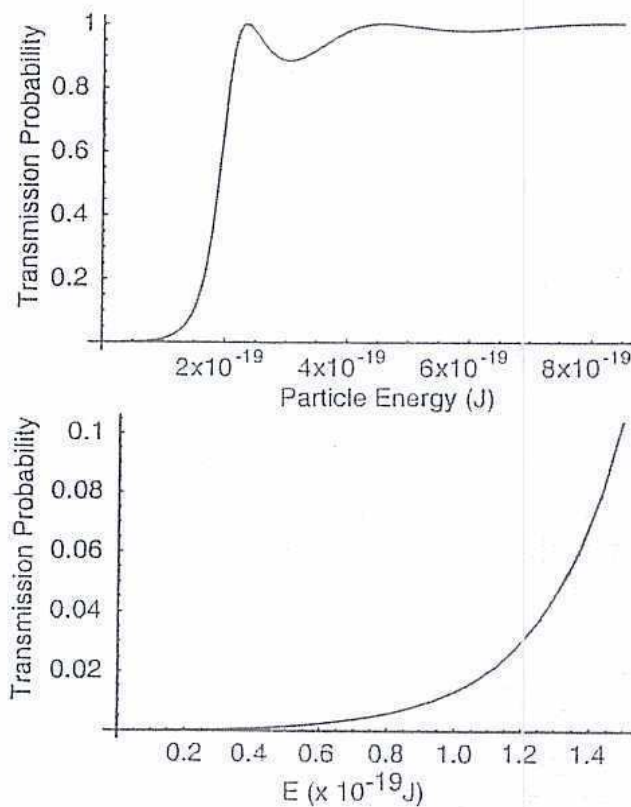⟶ In the last step, we have used the relation $-\sinh^2 x + \cosh^2 x = 1$

Our final result is a rather compact equation.

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

e) Plotting $\left|\dfrac{F}{A}\right|^2$ 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 $\left|\dfrac{F}{A}\right|^2 = 0.1$ 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.
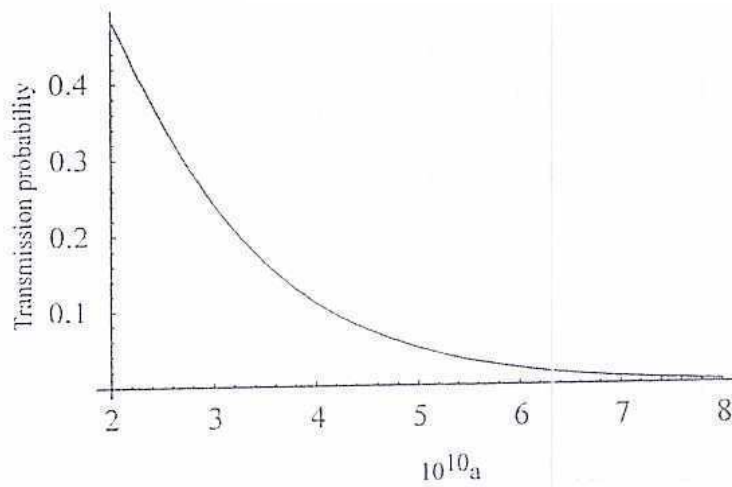
Additional part to 5.6)

For $\kappa a \gg 1$, $\sinh(\kappa a) \cong \exp(\kappa a)/2$. Thus:

$$\frac{1}{1+[(k^2+\kappa^2)^2 \sinh^2(\kappa a)]/4(\kappa k)^2} \cong \frac{1}{1+\dfrac{(k^2+\kappa^2)^2 \exp(2\kappa a)}{16k^2\kappa^2}} \cong \frac{1}{\dfrac{(k^2+\kappa^2)^2 \exp(2\kappa a)}{16k^2\kappa^2}}$$

The final approximation follows since $\dfrac{(k^2+\kappa^2)^2 \exp(2\kappa a)}{16k^2\kappa^2} \gg 1$ for $\kappa a \gg 1$. QED.

A plot of the exact vs. the approximate transmission probability formulae is provided in Fig. A2 for one set of system parameters. Note that the approximate formula works well except when the system energy is nearly equal to the barrier height. (Why?)
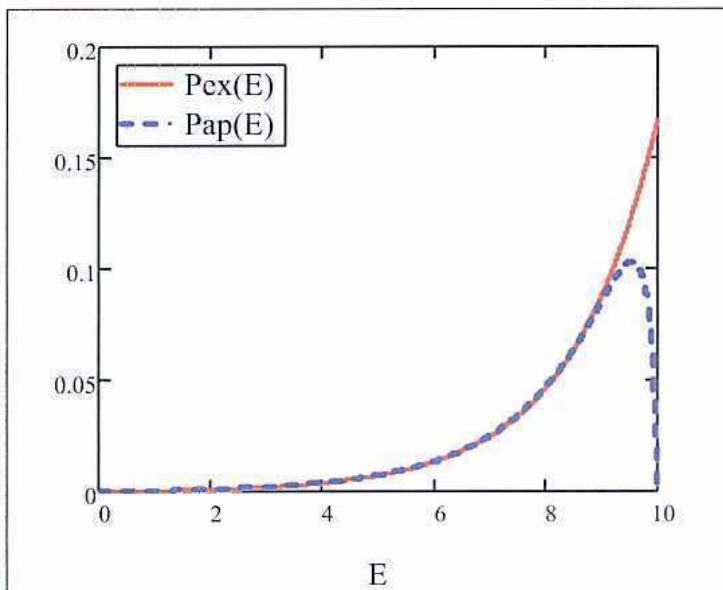

Fig. A2. Plot of exact transmission probability formula, Pex, vs. approximate transmission probability formula, Pap, as function of energy E. System parameters are: $m = h = 1; a = 1; V_0 = 10$.