Chem221a : Solution Set 2

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Problem 1

(a) The hardest part of this one is deciphering the question. Then you just have to wade through some math until you get the right answer.

The question is trying to ask you to assume that we have some state with the momentum wavefunction $g(k)$ (where $k = p/\hbar$). Given that, what's the position (or *spatial*) wavefunction for this state? In other words, do the inverse Fourier transform.

All the $t = 0$ stuff in this first part is just to tell you not to worry about time dependence yet. We'll deal with that in part (b). So, on to the inverse Fourier transform!

$$\psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \mathrm{d}k \, e^{ikx} g(k) \tag{1}$$

$$= \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \mathrm{d}k \, e^{ikx} \frac{\sqrt{a}}{(2\pi)^{1/4}} \exp\left(-\frac{a^2}{4}\,(k-k_0)^2\right) \tag{2}$$

$$= \frac{\sqrt{a}}{(2\pi)^{3/4}} \int_{\mathbb{R}} \mathrm{d}k \, \exp\left(-\frac{a}{4}(k-k_0)^2 + ikx\right) \tag{3}$$

Now we make the substitution $u = k - k_0$, which means $\mathrm{d}u = \mathrm{d}k$ and $k = u + k_0$. That gives us:

$$\psi(x,0) = \frac{\sqrt{a}}{(2\pi)^{3/4}} \int_{\mathbb{R}} \mathrm{d}u \, \exp\left(-\frac{a^2}{4}u^2 + i(u+k_0)x\right) \tag{4}$$

Some of you are clever enough to directly integrate this Gaussian. I'm not, so I'll go through the mess of completing the square and such.[1]

$$\psi(x,0) = \frac{\sqrt{a}}{(2\pi)^{3/4}} e^{ik_0x} \int_{\mathbb{R}} \mathrm{d}u \, \exp\left(-\frac{a^2}{4}u^2 + iux\right) \tag{5}$$

$$= \frac{\sqrt{a}}{(2\pi)^{3/4}} e^{ik_0x} \int_{\mathbb{R}} \mathrm{d}u \, \exp\left(-\left(\frac{a^2}{4}u^2 - iux - \frac{x^2}{a^2} + \frac{x^2}{a^2}\right)\right) \tag{6}$$

$$= \frac{\sqrt{a}}{(2\pi)^{3/4}} e^{ik_0x} \int_{\mathbb{R}} \mathrm{d}u \, \exp\left(-\left(\frac{a}{2}u - i\frac{x}{a}\right)^2\right) \exp\left(-\frac{x^2}{a^2}\right) \tag{7}$$

[1] The only integral I know is $\int_{\mathrm{R}} \mathrm{d}x \, \exp(-ax^2) = \sqrt{\pi/a}$. That's okay: all of modern science is just Taylor expansions and Gaussian integrals.

One more change of variables: let $v = \frac{a}{2}u - i\frac{x}{a}$. That gives us $\mathrm{d}u = \frac{2}{a}\mathrm{d}v$ as well. Plugging those into our wavefunction:

$$\psi(x,0) = \frac{\sqrt{a}}{(2\pi)^{3/4}} e^{ik_0x} e^{-x^2/a^2} \int_{\mathbb{R}} \mathrm{d}v\, \frac{2}{a} \exp\left(-v^2\right) \tag{8}$$

$$= \left(\frac{2}{\pi^3 a^2}\right)^{1/4} e^{ik_0x} e^{-x^2/a^2} \int_{\mathbb{R}} \mathrm{d}v\, \exp(-v^2) \tag{9}$$

$$= \left(\frac{2}{\pi^3 a^2}\right)^{1/4} e^{ik_0x} e^{-x^2/a^2} \sqrt{\pi} \tag{10}$$

$$= \left(\frac{2}{\pi a^2}\right)^{1/4} e^{ik_0x} e^{-x^2/a^2} \tag{11}$$

(b) Now we'll do the same thing as in part (a), but for a time-dependent wavefunction. Using the same $g(k)$ as before, and $\omega(k) = \hbar k^2 t/m$ for a free particle wavepacket, we obtain the following:

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \mathrm{d}k\, \left(\frac{a^2}{2\pi}\right)^{1/4} e^{-\frac{a^2}{4}(k-k_0)^2} e^{i(kx - \hbar k^2 t/2m)} \tag{12}$$

$$= \left(\frac{a^2}{(2\pi)^3}\right)^{1/4} \int_{\mathbb{R}} \mathrm{d}k\, \exp\left(-\frac{a^2}{4}(k-k_0)^2 + ikx - i\frac{\hbar t}{2m}k^2\right) \tag{13}$$

As before, we set $u = k - k_0$. Continuing:

$$\psi(x,t) = \left(\frac{a^2}{(2\pi)^3}\right)^{1/4} \int_{\mathbb{R}} \mathrm{d}k\, \exp\left(-\frac{a^2}{4}u^2 + iux + ik_0x - i\frac{\hbar t}{2m}(u+k_0)^2\right) \tag{14}$$

$$= \left(\frac{a^2}{(2\pi)^3}\right)^{1/4} e^{ik_0x} \int_{\mathbb{R}} \mathrm{d}k\, \exp\left(-\frac{a^2}{4}u^2 + iux - i\frac{\hbar t}{2m}u^2 - i\frac{\hbar t}{m}uk_0 - i\frac{\hbar t}{2m}k_0^2\right) \tag{15}$$

$$= \left(\frac{a^2}{(2\pi)^3}\right)^{1/4} e^{ik_0x} e^{-i\hbar t k_0^2/2m} \int_{\mathbb{R}} \mathrm{d}k\, \exp\left(-\left(\frac{a^2}{4} + \frac{i\hbar t}{2m}\right)u^2 - i\left(x - \frac{\hbar t k_0}{m}\right)u\right) \tag{16}$$

Okay, this time I'm going to cheat and use the integral $\int_{\mathbb{R}} \mathrm{d}x\, \exp(-Ax^2 + Bx) = \sqrt{\frac{\pi}{A}}\exp(\frac{B^2}{4A})$. Identifying $A = \frac{a^2}{4} + \frac{i\hbar t}{2m}$ and $B = -i\left(x - \frac{2\hbar t k_0}{2m}\right)$, we get

$$\psi(x,t) = \left(\frac{a^2}{(2\pi)^3}\right)^{1/4} e^{ik_0x} e^{-i\hbar t k_0^2/2m} \sqrt{\frac{\pi}{\frac{a^2}{4} + \frac{i\hbar t}{2m}}} \exp\left(\frac{\left(-i\left(x - \frac{\hbar t k_0}{m}\right)\right)^2}{4\left(\frac{a^2}{4} + \frac{i\hbar t}{2m}\right)}\right) \tag{17}$$

$$= \left(\frac{a^2}{(2\pi)^3}\right)^{1/4} e^{ik_0x} e^{-i\hbar t k_0^2/2m} \sqrt{\frac{4\pi}{a^2 + \frac{2i\hbar t}{m}}} \exp\left(-\frac{\left(x - \frac{\hbar t k_0}{m}\right)^2}{a^2 + \frac{2i\hbar t}{m}}\right) \tag{18}$$

$$= \left(\frac{16\pi^2 a^2}{(2\pi)^3}\right)^{1/4} e^{ik_0x} e^{-i\hbar t k_0^2/2m} \frac{1}{\sqrt{a^2 + i\frac{2\hbar t}{m}}} \exp\left(-\frac{\left(x - \frac{\hbar t k_0}{m}\right)^2}{a^2 + \frac{2i\hbar t}{m}}\right) \tag{19}$$

At this point, we see that we have *almost* everything correct. The normalization constant will reduce to the right expression, we have two of the phase factors (e^{ik_0x} and $e^{-i\hbar t k_0^2/2m}$), and our Gaussian is right. However, the square root we have above should be the fourth root of the modulus squared of its terms, and we should have this strange phase factor related to $\tan(2\theta)$.

To get these last couple steps, we need to notice that the number in our square root is a complex number (written in Cartesian form). To make the math a little more clear, let's just find polar expression for the square root of a complex number $z = \alpha + i\beta$. First, we want to write z in polar form, $z = re^{i\theta'}$. We know that the modulus of z is $r = \sqrt{\alpha^2 + \beta^2}$ and that the argument of z is given by $\tan(\theta') = \beta/\alpha$. Plugging all of that in gives us:

$$z = \sqrt{\alpha^2 + \beta^2}\; e^{i\tan^{-1}(\beta/\alpha)} \tag{20}$$

Of course, what we want is $\sqrt{z}$:

$$\begin{aligned}
\sqrt{z} = z^{1/2} &= \left(\left(\alpha^2 + \beta^2\right)^{1/2} e^{i\tan^{-1}(\beta/\alpha)}\right)^{1/2} &(21)\\
&= \left(\alpha^2 + \beta^2\right)^{1/4} e^{i\tan^{-1}(\beta/\alpha)/2} &(22)\\
&= \left(\alpha^2 + \beta^2\right)^{1/4} e^{i\theta'/2} &(23)
\end{aligned}$$

Now by identifying $2\theta = \theta'$, we have θ such that $\tan 2\theta = \beta/\alpha$. Using that definition of θ, and using $\alpha = a^2$ and $\beta = \frac{2\hbar t}{m}$, equation (19) gives us:

$$\begin{aligned}
\psi(x,t) &= \left(\frac{2a^2}{\pi}\right)^{1/4} e^{ik_0x} \frac{e^{-i\hbar t k_0^2/2m}}{\left(a^4 + \frac{4\hbar^2 t^2}{m^2}\right)^{1/4} e^{i\theta}} \exp\left(-\frac{\left(x - \frac{\hbar t k_0}{m}\right)^2}{a^2 + \frac{2i\hbar t}{m}}\right) &(24)\\
&= \left(\frac{2a^2}{\pi}\right)^{1/4} e^{ik_0x} \frac{e^{-i\hbar t k_0^2/2m} e^{-i\theta}}{\left(a^4 + \frac{4\hbar^2 t^2}{m^2}\right)^{1/4}} \exp\left(-\frac{\left(x - \frac{\hbar t k_0}{m}\right)^2}{a^2 + \frac{2i\hbar t}{m}}\right) &(25)
\end{aligned}$$

A quick examination of this shows that our θ is the same as the θ described in the problem set (since $\beta/\alpha = \frac{2\hbar t}{ma^2}$) and therefore this expression is the one we were to derive.

(c) After all that ugly math, we get to spend some time thinking exploring what that expression physically tells us. We're asked to use this wavefunction to find a few facts about the physical problem.

The group velocity is just $\frac{\mathrm{d}\omega}{\mathrm{d}k}$, where $-\omega(k)t$ is the time-dependent phase of the wavefunction. In our case, $\omega(k) = \frac{\hbar k^2}{2m}$, so the group velocity $v_g = \hbar k/m$.

The time-dependent spatial extent will show us how the probability density function spreads out as a function of time. We calculate this by taking the modulus square of the wavefunction. Remember, the mod-square is the function times its complex conjugate, so we can immediately cancel out the phase factors to obtain:

$$\begin{aligned}
|\Psi(x,t)|^2 &= \left(\frac{2a^2}{\pi\left(a^4 + \frac{4\hbar^2 t^2}{m^2}\right)}\right)^{1/2} \exp\left(-\frac{\left(x - \frac{\hbar k_0 t}{m}\right)^2}{a^2 + \frac{2\hbar t}{m} i} - \frac{\left(x - \frac{\hbar k_0 t}{m}\right)^2}{a^2 - \frac{2\hbar t}{m} i}\right) &(26)\\
&= \sqrt{\frac{2a^2}{\pi\left(a^4 + \frac{4\hbar^2 t^2}{m^2}\right)}} \exp\left(-\frac{\left(x - \frac{\hbar k_0 t}{m}\right)^2 \left(\left(a^2 - \frac{\hbar k_0 t}{m} i\right) + \left(a^2 + \frac{\hbar k_0 t}{m} i\right)\right)}{a^4 + \frac{4\hbar^2 t^2}{m^2}}\right) &(27)\\
&= \sqrt{\frac{2a^2}{\pi\left(a^4 + \frac{4\hbar^2 t^2}{m^2}\right)}} \exp\left(-\frac{2a^2}{a^4 + \frac{4\hbar^2 t^2}{m^2}} \left(x - \frac{\hbar k_0 t}{m}\right)^2\right) &(28)
\end{aligned}$$

Now we can recognize that the Gaussian in x will be of the form $\exp(-x^2/b^2)$, where we identify

$$\frac{1}{b^2} = \frac{2a^2}{a^4 + \frac{4\hbar^2 t^2}{m^2}} \tag{29}$$

In class, we were told to define the "spatial extent" in terms of b as $\Delta x = b/\sqrt{2}$ (see notes from 7 Sept). So we have:

$$\Delta x(t) = \frac{1}{\sqrt{2}} b \tag{30}$$

$$= \frac{1}{\sqrt{2}} \sqrt{\frac{a^4 + \frac{4\hbar^2 t^2}{m^2}}{2a^2}} \tag{31}$$

$$= \frac{1}{2} \sqrt{a^2 + \frac{4\hbar^2 t^2}{a^2 m^2}} \tag{32}$$

We're also asked to show that $g(k,t) = g(k)e^{-i\omega(k)t}$. To show this, we just use the two ways we know to get $\psi(x,t)$. First off, $\psi(x,t)$ is given by the inverse Fourier transform of $g(k,t)$:

$$\psi(x,t) = \frac{1}{2\pi} \int_{\mathbb{R}} \mathrm{d}k\, g(k,t) e^{ikx} \tag{33}$$

We also have the expression which we're given in part (b):

$$\psi(x,t) = \frac{1}{2\pi} \int_{\mathbb{R}} \mathrm{d}k\, g(k) e^{i(kx - \omega(k)t)} \tag{34}$$

$$= \frac{1}{2\pi} \int_{\mathbb{R}} \mathrm{d}k\, g(k) e^{-i\omega(k)t} e^{ikx} \tag{35}$$

Since the inverse Fourier transform is an invertible functional (a one-to-one mapping in function space)[2] we can identify $g(k,t) = g(k)e^{-i\omega(k)t}$. Showing that the magnitude squared of this is time-independent is easy:

$$|g(k,t)|^2 = \left| g(k) e^{-i\omega(k)t} \right|^2 \tag{36}$$

$$= \left(g^*(k) e^{i\omega(k)t} \right) \left(g(k) e^{-i\omega(k)t} \right) \tag{37}$$

$$= g^*(k) g(k) = |g(k)|^2 \tag{38}$$

This is obviously time-independent (there's no dependence on t!)

Problem 2

(a) As an aside, this potential is a great candidate for practice with perturbation theory. But perturbation theory is approximate, and we're looking for an exact solution. So we use the standard method when handling box potentials.

[2] *N.B.*: This kind of identification can only be used when the operation in question can be inverted.

Before actually deriving the energy condition, let's show that it doesn't matter whether $E < V$ or $E > V$. If $E > V$, κ is pure imaginary, so $\kappa = i\,|\kappa|$. A reasoning like what we would get below would tell us that the right side of the odd solution would be $-\,|\kappa|\cot(|\kappa|\,b)$. So how does that relate to the hyperbolic solution? Well, let's write out the above solution:

$$-\,|\kappa|\cot(|\kappa|\,b) = -i\,|\kappa|\,\frac{e^{i|\kappa|b} + e^{-i|\kappa|b}}{e^{i|\kappa|b} - e^{-i|\kappa|b}} \tag{39}$$

$$= -i\,|\kappa|\coth(i\,|\kappa|\,b) \tag{40}$$

$$= \kappa\coth(\kappa b) \tag{41}$$

Similar arguments can be made for the even solutions.

Now let's get to the meat of the problem. First, we write down what the wavefunction would be in each of the three regions described above.

$$\psi_{\mathrm{I}}(x) = A_{\mathrm{I}}e^{ikx} + B_{\mathrm{I}}e^{-ikx} \tag{42}$$

$$\psi_{\mathrm{II}}(x) = A_{\mathrm{II}}e^{\kappa x} + B_{\mathrm{II}}e^{-\kappa x} \tag{43}$$

$$\psi_{\mathrm{III}}(x) = A_{\mathrm{III}}e^{ikx} + B_{\mathrm{III}}e^{-ikx} \tag{44}$$

We're only going to solve for half of the potential, and use the fact that the wavefunction must be either even or odd (since the potential is symmetric) to do the rest for us. Before starting, let's list our boundary conditions:

$$\psi_{\mathrm{I}}(-a) = \psi_{\mathrm{III}}(a) = 0 \tag{45}$$

$$\psi_{\mathrm{II}}(b) = \psi_{\mathrm{III}}(b) \tag{46}$$

$$\psi_{\mathrm{I}}(-b) = \psi_{\mathrm{II}}(-b) \tag{47}$$

$$\psi'_{\mathrm{II}}(b) = \psi'_{\mathrm{III}}(b) \tag{48}$$

$$\psi'_{\mathrm{I}}(-b) = \psi'_{\mathrm{II}}(-b) \tag{49}$$

Before splitting into even and odd wavefunctions, let's apply the boundary condition given by equation (45) at the the point $-a$. This means that we have:

$$\psi_{\mathrm{I}}(-a) = 0 = A_{\mathrm{I}}e^{-ika} + B_{\mathrm{I}}e^{ika} \tag{50}$$

$$B_{\mathrm{I}} = -A_{\mathrm{I}}e^{-2ika} \tag{51}$$

Plugging this back into equation (42), we get

$$\psi_{\mathrm{I}}(x) = A_{\mathrm{I}}e^{ikx} - A_{\mathrm{I}}e^{-2ika}e^{-ikx} \tag{52}$$

$$= A_{\mathrm{I}}e^{-ika}\left(e^{ik(x+a)} - e^{-ik(x+a)}\right) \tag{53}$$

Taking the derivative of that, we obtain:

$$\psi'_{\mathrm{I}}(x) = kA_{\mathrm{I}}\left(e^{ik(x+a)} + e^{-ik(x+a)}\right) \tag{54}$$

This means that the "log-derivative" for $\psi_{\mathrm{I}}(x)$ is

$$\frac{\psi'_{\mathrm{I}}(x)}{\psi'_{\mathrm{I}}(x)} = k\frac{e^{ik(x+a)} + e^{-ik(x+a)}}{e^{ik(x+a)} - e^{-ik(x+a)}} = k\cot(k(x+a)) \tag{55}$$

We can already recognize that this will give us one side of the eigenenergy condition when we plug in $x = -b$. The other side will depend on whether the solution is even or odd.

Even Solutions: If the solution is even, then the planewave coefficients in region II are equal (*i.e.*, $A_{\mathrm{II}} = B_{\mathrm{II}}$). Therefore, we can rewrite the wavefunction for region II as

$$\psi_{\mathrm{II}}(x) = A_{\mathrm{II}} \left(e^{\kappa x} + e^{-\kappa x}\right) \tag{56}$$

Its derivative is

$$\psi'_{\mathrm{II}}(x) = \kappa A_{\mathrm{II}} \left(e^{\kappa x} - e^{-\kappa x}\right) \tag{57}$$

Putting these together, the "log-derivative" of the wavefunction in region II is

$$\frac{\psi'_{\mathrm{II}}(x)}{\psi_{\mathrm{II}}(x)} = \kappa \frac{e^{\kappa x} - e^{-\kappa x}}{e^{\kappa x} + e^{-\kappa x}} = \kappa \tanh(\kappa x) \tag{58}$$

Now we're ready to set our first energy condition. At the boundary between regions I and II (namely, when $x = -b$) we know that both the wavefunction and its first derivative must be continuous. This means that the log-derivative must also be continuous:[3]

$$\frac{\psi'_{\mathrm{I}}(-b)}{\psi_{\mathrm{I}}(-b)} = \frac{\psi'_{\mathrm{II}}(-b)}{\psi_{\mathrm{II}}(-b)} \tag{59}$$

$$k \cot(k(a-b)) = \kappa \tanh(\kappa(-b)) \tag{60}$$

$$= -\kappa \tanh(\kappa b) \tag{61}$$

Odd Solutions: For the odd solutions, the sign on the second exponential term switches. This will immediately give us the log-derivative conditions at $-b$:

$$\frac{\psi'_{\mathrm{I}}(-b)}{\psi_{\mathrm{I}}(-b)} = \frac{\psi'_{\mathrm{II}}(-b)}{\psi_{\mathrm{II}}(-b)} \tag{62}$$

$$k \cot(k(a-b)) = -\kappa \coth(\kappa b) \tag{63}$$

Again, we use the fact that cotangent is an odd function.

(b) The first thing to do is to convert the equation we derived in part (a) into a format which we can still into some sort of trancendental equation solver. The trick is to recognize that we're not going to solve directly for the energy, of even for k. No, we're going to use the quantity ka as our variable (and getting that is equivalent to getting the energy, once we know the parameters of the system).

[3]The very observant among you may have noticed that this is not strictly true. The concern is whether the wavefunction can have a node (be equal to zero) at the boundary point, $-b$. When $E < V_0$, this isn't a problem (think about the form of the wavefunction in region II to see why it can't be zero). However, when $E > V_0$, I think you could contrive a particular E based on the values of V_0, a, and b such that $\psi(-b) = 0$. It would require extreme malice, and we'll turn a blind eye to that here.

Here's how we do it for the even solutions. For the odd solutions, just replace tanh with coth:

$$k\cot(k(a-b)) = -\kappa\tanh(\kappa b) \tag{64}$$

$$k\cot(k(a-0.1a)) = -\sqrt{k_0^2-k^2}\tanh(\sqrt{k_0^2-k^2}(0.1a)) \tag{65}$$

$$k\cot(0.9ka) = -\sqrt{k_0^2-k^2}\tanh(0.1\sqrt{(k_0a)^2-(ka)^2}) \tag{66}$$

$$k\cot(0.9ka) = -\sqrt{k_0^2-k^2}\tanh(0.1\sqrt{25-(ka)^2}) \tag{67}$$

We're almost there, but we aren't quite in terms of ka yet. How do we get there? We just multiply by a on both sides!

$$ka\cot(0.9ka) = -\sqrt{k_0^2-k^2}a\tanh(0.1\sqrt{25-(ka)^2}) \tag{68}$$

$$= -\sqrt{25-(ka)^2}\tanh(0.1\sqrt{25-(ka)^2}) \tag{69}$$

Excellent! We can solve that. So let's do it. Remembering how to handle the analytic continuation of the hyperbolic functions (namely, that they become i times the regular trig function when their arguments become imaginary) we can plot the right hand side (RHS) and left hand side (LHS) of the eigenenergy condition as shown in figure 1.

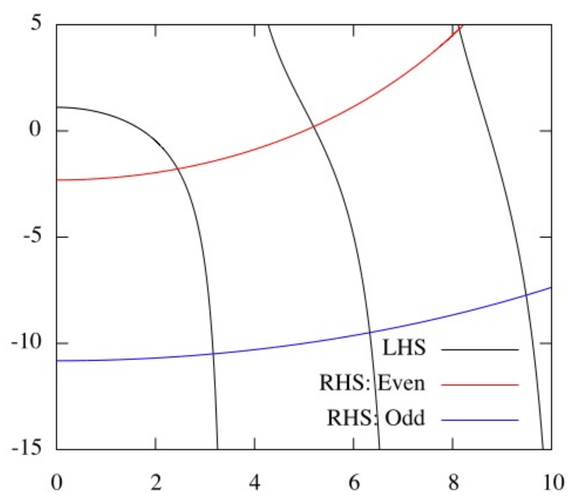

Figure 1: Plot of the transcendental eigenenergy equations. Intersections are allowed energies.

According to my TI-83's "intersect" function (plot the equations, Calc → 5. Intersect) the intersections are located as shown in table 1. Figure 2 gives plots of the first four wavefunctions (yes, those are plots, not just sketches, for $a = 1$. Yes, it was painful.)

(c) Since $\Psi(x,0) = \frac{1}{\sqrt{2}}(\psi_1(x)+\psi_2(x))$, we know that $\Psi(x,t) = \frac{1}{\sqrt{2}}(\psi_1(x,t)+\psi_2(x,t))$. Of course, since $\psi_1(x)$ and $\psi_2(x)$ are energy eigenstates, their time dependence is just a triv-

Solution	ka	$f(ka)$
Even 1	2.447	-1.789
Odd 1	3.165	-10.49
Even 2	5.194	0.198
Odd 2	6.328	-9.493

Table 1: Allowed values of ka, calculated with a good ol' TI-83.

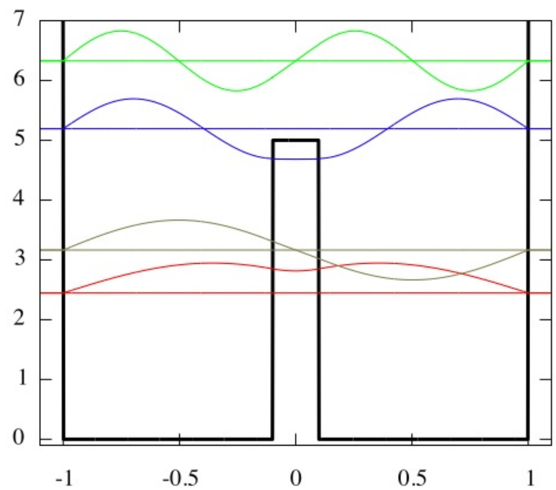

Figure 2: Plots of the first four wavefunctions

ial phase factor. This means that the total time dependent wavefunction is

$$\Psi(x,t) = \frac{1}{\sqrt{2}} \left(\psi_1(x) e^{-iE_1 t/\hbar} + \psi_2(x) e^{-iE_2 t/\hbar} \right) \tag{70}$$

This means that the mod-square of the wavefunction is

$$|\Psi(x,t)|^2 = \frac{1}{2} \left(\psi_1^*(x) e^{iE_1 t/\hbar} + \psi_2^*(x) e^{iE_2 t/\hbar} \right) \left(\psi_1(x) e^{-iE_1 t/\hbar} + \psi_2(x) e^{-iE_2 t/\hbar} \right) \tag{71}$$

$$= \frac{1}{2} \left(|\psi_1(x)|^2 + |\psi_2(x)|^2 + \psi_1^*(x)\psi_2(x) e^{i(E_1 - E_2)t/\hbar} + \psi_2^*(x)\psi_1(x) e^{-i(E_1 - E_2)/\hbar} \right) \tag{72}$$

$$= \frac{1}{2} \left(|\psi_1(x)|^2 + |\psi_2(x)|^2 + 2\Re \left(\psi_1^*(x)\psi_2(x) e^{i(E_1 - E_2)t/\hbar} \right) \right) \tag{73}$$

For the last step, I used the fact that a number plus its complex conjugate is equal to twice its real component. Now using the definition of ω from the problem set, $\omega \equiv (E_1 - E_2)/\hbar$, this becomes:

$$|\Psi(x,t)|^2 = \frac{1}{2} \left(|\psi_1(x)|^2 + |\psi_2(x)|^2 + 2\Re \left(\psi_1^*(x)\psi_2(x) e^{i\omega t} \right) \right) \tag{74}$$

Assuming that the wavefunctions are real (or, more accurately, choosing a phase convention such that $\psi_1^*(x)\psi_2(x)$ is real), we have

$$|\Psi(x,t)|^2 = \frac{1}{2}\left(|\psi_1(x)|^2 + |\psi_2(x)|^2 + 2\psi_1^*(x)\psi_2(x)\cos(\omega t)\right) \tag{75}$$

From this, we can tell that the frequency is ω, which means that the period is $2\pi/\omega$. Now we'll define $\overline{\psi^2}(x) \equiv \frac{1}{2}\left(|\psi_1(x)|^2 + |\psi_2(x)|^2\right)$. Then we have:

$$|\Psi(x,t)|^2 = \overline{\psi^2}(x) + \psi_1^*(x)\psi_2(x)\cos(\omega t) \tag{76}$$

Plugging in the values of t for which we are supposed to plot the wavefunction, this gives us

$$|\Psi(x,t=0)|^2 = \overline{\psi^2}(x) + \psi_1^*(x)\psi_2(x) = \frac{1}{2}|\psi_1(x) + \psi_2(x)|^2 \tag{77}$$

$$|\Psi(x,t=\pi/\omega)|^2 = \overline{\psi^2}(x) - \psi_1^*(x)\psi_2(x) = \frac{1}{2}|\psi_1(x) - \psi_2(x)|^2 \tag{78}$$

$$|\Psi(x,t=2\pi/\omega)|^2 = \overline{\psi^2}(x) + \psi_1^*(x)\psi_2(x) = \frac{1}{2}|\psi_1(x) + \psi_2(x)|^2 \tag{79}$$

From part (b), we'll cheat a little and define units such that $\hbar^2 a^2/2m = 1$ for our system. We can do this because it amounts to defining a unit of length ($a = 1$), a unit of mass ($m = 1/2$) and a unit of time (from $\hbar = 1$). In that case, we have $E = k^2$ and $\Delta E = k_2^2 - k_1^2$. The period will be given by $2\pi\hbar/\Delta E = 2\pi/((3.165)^2 - (2.447)^2) = 1.559$ in whatever these strange units are.

The graphs we were to plot are shown in figure 3. There are only two, because $|\Psi(x,t=0)|^2 = |\Psi(x,t=2\pi/\omega)|^2$.

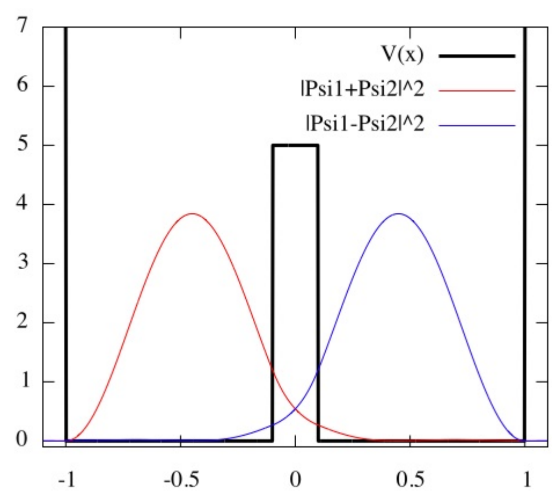

Figure 3: Plots of $|\Psi(x,t)|^2$ at various times.

(d) Although we're told to use the wavefunctions for different systems in this part of the problem, really all we need are the energies — or, more specifically, the differences in energies.

(i) We can approximate the energy levels of a diatomic molecule as rigid rotor energy levels, which are given by $BJ(J+1)$. This means that the difference between the $J = 0$ and $J = 1$ energy level is $\Delta E = B(1)(1+2) - B(0)(0+1) = 2B$. The rotational constant B for a homonuclear diatomic molecule is given by $B = \hbar^2/(mr^2)$, where m is the mass of one of the atoms and r is the distance between them. For H_2, we have $r_{H_2} = 0.742$ Å $= 0.742 \times 10^{-10}$ m[4] and $m_H = 1.0078$ amu $= 1.674 \times 10^{-27}$ kg. Plugging that in, we obtain:

$$B = \frac{\hbar^2}{mr^2} = \frac{(1.055 \times 10^{-34}\ \mathrm{J \cdot s})^2}{(1.674 \times 10^{-27}\ \mathrm{kg})(0.742 \times 10^{-10}\ \mathrm{m})^2} \tag{80}$$

$$= 1.208 \times 10^{-21}\ \mathrm{J} = 60.80\ \mathrm{cm}^{-1} \tag{81}$$

So $\Delta E = 2B = 2.416 \times 10^{-21}$ J, and $\omega = \Delta E/\hbar = 2.290 \times 10^{13}\ \mathrm{s}^{-1}$. The period is just $2\pi/\omega = 2.744 \times 10^{-13}$ s.

(ii) We'll approximate the rotational levels of H_2 as a harmonic oscillator. The energy levels of the harmonic oscillator are given by $E_n = \hbar\omega_{\mathrm{HO}}(n + 1/2)$, so $\Delta E = \hbar\omega_{\mathrm{HO}}(1 + 1/2) - \hbar\omega_{\mathrm{HO}}(0 + 1/2) = \hbar\omega_{\mathrm{HO}}$. So the frequency from the problem is the same as the frequency for the harmonic oscillator: $\omega = \omega_{\mathrm{HO}}$. For the hydrogen molecule, Herzberg tells us that $\hbar\omega_{\mathrm{HO}} = 4395\ \mathrm{cm}^{-1} = 8.730 \times 10^{-20}$ J,[5] which means that our period is $2\pi/\omega = 7.593 \times 10^{-15}$ s.

(iii) The energy levels of the hydrogen atom can be solved exactly. They are given by $E_n = R_H \frac{1}{n^2}$, where $R_H = 2.180 \times 10^{-18}$ J is the Rydberg constant for hydrogen. This means that the energy difference between $n = 2$ and $n = 1$ (between 1s and 2s states) is $\Delta E = R_H \frac{1}{1^2} - R_H \frac{1}{2^2} = \frac{3}{4} R_H = 1.635 \times 10^{-18}$ J. Again, the period is $2\pi\hbar/\Delta E = 4.054 \times 10^{-16}$ s.

Note the difference in timescales, and how that is related to the difference in energy scales between the different states. These differences of scale are also the justification we use for separate the kinds of motion (rotational, vibrational, and electronic).

Problem 3

(a) We'll solve this by using the matrix method described by Professor Neumark in class on 14 September. Many of you probably solved this without using matrices. You'll find that your solutions (assuming you got it right!) are equivalent to what we'll do here, if you look carefully. I just think: (1) this is an easier way to think about the problem, and (B) this prepares you for some of the matrix construction you'll need to get used to in the next few problem sets.

Let's consider an arbitrary wall at $x = \alpha$ where the potential is less than the energy is region I and the potential is greater than the energy in region II (but finite). So we'll use our regular

[4] Get used to looking to Herzberg for this kind of information.
[5] Again, you should make friends with Herzberg.

definitions for k and κ and define the wavefunction in each region as:

$$\psi_{\mathrm{I}}(x) = A_{\mathrm{I}} e^{ikx} + B_{\mathrm{I}} e^{-ikx} \tag{82}$$

$$\psi_{\mathrm{II}}(x) = A_{\mathrm{II}} e^{\kappa x} + B_{\mathrm{II}} e^{-\kappa x} \tag{83}$$

The respective derivatives are therefore

$$\psi_{\mathrm{I}}'(x) = ik\left(A_{\mathrm{I}} e^{ikx} - B_{\mathrm{I}} e^{-ikx}\right) \tag{84}$$

$$\psi_{\mathrm{II}}'(x) = \kappa\left(A_{\mathrm{II}} e^{\kappa x} - B_{\mathrm{II}} e^{-\kappa x}\right) \tag{85}$$

Instead of using the log-derivative, where we combine the equations for the continuity of the wavefunction and of its first derivative, we'll find two different ways to combine those facts to get the coeffiecients in region II in terms of the coeffiecients in region I. We could do this just as easily in the other order, as well (I'll leave that as an exercise to the reader).

At the boundary, where $x = \alpha$, those four expressions give us the equations

$$A_{\mathrm{I}} e^{ik\alpha} + B_{\mathrm{I}} e^{-ik\alpha} = A_{\mathrm{II}} e^{\kappa\alpha} + B_{\mathrm{II}} e^{-\kappa\alpha} \tag{86}$$

$$\frac{ik}{\kappa}\left(A_{\mathrm{I}} e^{ik\alpha} - B_{\mathrm{I}} e^{-ik\alpha}\right) = A_{\mathrm{II}} e^{\kappa\alpha} - B_{\mathrm{II}} e^{-\kappa\alpha} \tag{87}$$

where the continuity of the first derivative has been divided through by κ. To solve for A_{II}, we add equations (86) and (87):

$$2A_{\mathrm{II}} e^{\kappa\alpha} = \left(1 + \frac{ik}{\kappa}\right) A_{\mathrm{I}} e^{ik\alpha} + \left(1 - \frac{ik}{\kappa}\right) B_{\mathrm{I}} e^{-ik\alpha} \tag{88}$$

$$A_{\mathrm{II}} = \frac{\kappa + ik}{2\kappa} e^{-(\kappa - ik)\alpha} A_{\mathrm{I}} + \frac{\kappa - ik}{2\kappa} e^{-(\kappa + ik)\alpha} B_{\mathrm{I}} \tag{89}$$

We'll solve for B_{II} by subtracting equation (87) from equation (86):

$$2B_{\mathrm{II}} e^{-\kappa\alpha} = \left(1 - \frac{ik}{\kappa}\right) A_{\mathrm{I}} e^{ik\alpha} + \left(1 + \frac{ik}{\kappa}\right) B_{\mathrm{I}} e^{-ik\alpha} \tag{90}$$

$$B_{\mathrm{II}} = \frac{\kappa - ik}{2\kappa} e^{(\kappa + ik)\alpha} A_{\mathrm{I}} + \frac{\kappa + ik}{2\kappa} e^{(\kappa - ik)\alpha} B_{\mathrm{I}} \tag{91}$$

We can combine equations (89) and (91) into a single matrix matrix equation:

$$\begin{pmatrix} A_{\mathrm{II}} \\ B_{\mathrm{II}} \end{pmatrix} = \begin{pmatrix} \frac{\kappa+ik}{2\kappa} e^{-(\kappa-ik)\alpha} & \frac{\kappa-ik}{2\kappa} e^{-(\kappa+ik)\alpha} \\ \frac{\kappa-ik}{2\kappa} e^{(\kappa+ik)\alpha} & \frac{\kappa+ik}{2\kappa} e^{(\kappa-ik)\alpha} \end{pmatrix} \begin{pmatrix} A_{\mathrm{I}} \\ B_{\mathrm{I}} \end{pmatrix} \tag{92}$$

I mentioned above that we could do the same process to solve for the region I coefficients. However, it'll be easier to just use this solution and invert the matrix. In fact, the inverse of a 2x2 matrix $M = \left(\begin{smallmatrix} a & b \\ c & d \end{smallmatrix}\right)$ is given by $M^{-1} = (\det(M))^{-1} \left(\begin{smallmatrix} a & -b \\ -c & d \end{smallmatrix}\right)$. It's pretty easy to see that the determinant of the matrix in equation (92) is $\frac{ik}{\kappa}$, which means that multiplying on the left by the inverse of the matrix in equation (92) will give us

$$\begin{pmatrix} A_{\mathrm{I}} \\ B_{\mathrm{I}} \end{pmatrix} = \begin{pmatrix} \frac{ik+\kappa}{2ik} e^{-(\kappa-ik)\alpha} & \frac{ik-\kappa}{2ik} e^{-(\kappa+ik)\alpha} \\ \frac{ik-\kappa}{2ik} e^{(\kappa+ik)\alpha} & \frac{ik+\kappa}{2ik} e^{(\kappa-ik)\alpha} \end{pmatrix} \begin{pmatrix} A_{\mathrm{II}} \\ B_{\mathrm{II}} \end{pmatrix} \tag{93}$$

Now to apply this to the system in question. From the right, we have a region of type I, then a region of type II, then another region of type I. So, going from right to left, the boundary between region 2 and region 3 will correspond to a matrix like the one in equation (92), and the boundary between region 1 and region 2 will correspond to a matrix like the one in equation (93). The whole problem will amount to solving the equation:

$$\begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = M_{12} M_{23} \begin{pmatrix} A_3 \\ B_3 \end{pmatrix} \tag{94}$$

You may be wondering how we'll get anything useful out of these matrices if they're inverses of each other. The thing to remember is that these matrices are dependent on the location of the boundary, and the two boundaries are at different locations (if they were at the same location, then there would be now intervening region, so it would make sense for it not to change the wavefunction!) We're given the freedom to define our zero anywhere, so let's make the left boundary at $x = 0$ and the right boundary at $x = 2a$, just to make the math easier. Writing out those matrices, along with the boundary condition that we have unit incident flux from the left ($A_1 = 1$ and $B_3 = 0$), we obtain:

$$\begin{pmatrix} 1 \\ B_1 \end{pmatrix} = \frac{1}{4ik\kappa} \begin{pmatrix} ik+\kappa & ik-\kappa \\ ik-\kappa & ik+\kappa \end{pmatrix} \begin{pmatrix} (\kappa+ik)e^{-(\kappa-ik)(2a)} & (\kappa-ik)e^{-(\kappa+ik)(2a)} \\ (\kappa-ik)e^{(\kappa+ik)(2a)} & (\kappa+ik)e^{(\kappa-ik)(2a)} \end{pmatrix} \begin{pmatrix} A_3 \\ 0 \end{pmatrix} \tag{95}$$

$$= \frac{1}{4ik\kappa} \begin{pmatrix} ik+\kappa & ik-\kappa \\ ik-\kappa & ik+\kappa \end{pmatrix} \begin{pmatrix} (\kappa+ik)e^{-(\kappa-ik)(2a)} A_3 \\ (\kappa-ik)e^{(\kappa+ik)(2a)} A_3 \end{pmatrix} \tag{96}$$

$$= \frac{1}{4ik\kappa} \begin{pmatrix} \left((\kappa+ik)^2 e^{-(\kappa-ik)(2a)} - (\kappa-ik)^2 e^{(\kappa+ik)(2a)}\right) A_3 \\ (\kappa-ik)(\kappa+ik)\left(-e^{-(\kappa-ik)(2a)} + e^{(\kappa+ik)(2a)}\right) A_3 \end{pmatrix} \tag{97}$$

Before we get too carried away with these matrices, let's remember what we're looking for. We want the transmission, which is given by the expression

$$T = \frac{k_3}{k_1} \frac{|A_3|^2}{|A_1|^2} \tag{98}$$

The fact that we'll be dividing by $|A_1|^1$ is what allowed us to take $A_1 = 1$ earlier, and since $k_1 = k_3$, we have the (unusual) case that $T = |A_3|^2$. So we don't need to calculate B_1, which means that only the first line of our matrix equation actually matters. So let's just take that, and mess with it a little:

$$1 = \frac{1}{4ik\kappa} \left((\kappa+ik)^2 e^{-(\kappa-ik)(2a)} - (\kappa-ik)^2 e^{(\kappa+ik)(2a)}\right) A_3 \tag{99}$$

$$= \frac{1}{4ik\kappa} \left((\kappa^2 + 2ik\kappa - k^2) e^{-2\kappa a} e^{2ika} - (\kappa^2 - 2ik\kappa - k^2) e^{2\kappa a} e^{2ika}\right) A_3 \tag{100}$$

$$= \frac{e^{2ika}}{4ik\kappa} \left((\kappa^2 - k^2)(e^{-2\kappa a} - e^{2\kappa a}) + 2ik\kappa(e^{-2\kappa a} + e^{2\kappa a})\right) A_3 \tag{101}$$

$$= e^{2ika} \left(\frac{\kappa^2 - k^2}{2k\kappa} \frac{1}{2i}(e^{-2\kappa a} - e^{2\kappa a}) + \frac{1}{2}(e^{2\kappa a} + e^{-2\kappa a})\right) A_3 \tag{102}$$

$$= e^{2ika} \left(\frac{1}{2}\left(\frac{\kappa}{k} - \frac{k}{\kappa}\right) \frac{1}{2}(e^{2\kappa a} - e^{-2\kappa a}) i + \frac{1}{2}(e^{2\kappa a} + e^{2\kappa a})\right) A_3 \tag{103}$$

$$= e^{2ika} \left(\frac{\varepsilon}{2} \sinh(2\kappa a) i + \cosh(2\kappa a)\right) A_3 \tag{104}$$

We've identified ε as given in the problem. Also note that we used the identity $1/i = -i$ to get our signs right for the sinh function. This pretty quickly gives us the rest of the problem. Immediately, we have

$$A_3 = \frac{1}{e^{2ika}\left(\frac{\varepsilon}{2}\sinh(2\kappa a)i + \cosh(2\kappa a)\right)} \tag{105}$$

From our determination of T in terms of A_3, we also have

$$\begin{aligned}
T &= |A_3|^2 \quad (106)\\
&= \frac{1}{e^{2ika}\left(\frac{\varepsilon}{2}\sinh(2\kappa a)i + \cosh(2\kappa a)\right)} \frac{1}{e^{-2ika}\left(-\frac{\varepsilon}{2}\sinh(2\kappa a)i + \cosh(2\kappa a)\right)} \quad (107)\\
&= \frac{1}{\cosh^2(2\kappa a) + \frac{\varepsilon^2}{4}\sinh^2(2\kappa a)} \quad \square \quad (108)
\end{aligned}$$

(b) Once we have the expression from part (a), this is just a matter of rewriting a few things and taking the limit as κa goes to infinity.

$$\begin{aligned}
T &= \left(\cosh^2(2\kappa a) + \frac{\varepsilon^2}{4}\sinh^2(2\kappa a)\right)^{-1} \quad (109)\\
&= \left(\left(\frac{1}{2}(e^{2\kappa a} + e^{-2\kappa a})\right)^2 + \frac{\varepsilon^2}{4}\left(\frac{1}{2}(e^{2\kappa a} - e^{-2\kappa a})\right)^2\right)^{-1} \quad (110)\\
&= \left(\frac{1}{4}\left(\left(e^{4\kappa a} + 2 + e^{-4\kappa a}\right) + \frac{\varepsilon^2}{4}\left(e^{4\kappa a} - 2 + e^{-4\kappa a}\right)\right)\right)^{-1} \quad (111)
\end{aligned}$$

Now we go ahead and take the limit as $\kappa a \to \infty$. The constant terms and the terms of the form $e^{-4\kappa a}$ all become neglible compared to the terms of the form $e^{4\kappa a}$:

$$\begin{aligned}
T &\to \left(\frac{1}{4}\left(e^{4\kappa a} + \frac{\varepsilon^2}{4}e^{4\kappa a}\right)\right)^{-1} \quad (112)\\
&= \left(\frac{1}{4}e^{4\kappa a}\left(1 + \frac{\varepsilon^2}{4}\right)\right)^{-1} \quad (113)
\end{aligned}$$

At this point, we need to plug the definition of ε back in. You'll also see a common math trick that switches $(a-b)^2$ to $(a+b)^2$. Any time you see a switch like that, you should look for a way to add in a factor of $4ab$.

$$T \to \left(\frac{1}{4}e^{4\kappa a}\left(1+\frac{1}{4}\left(\frac{\kappa}{k}-\frac{k}{\kappa}\right)^2\right)\right)^{-1} \tag{114}$$

$$= \left(\frac{1}{4}e^{4\kappa a}\left(1+\frac{1}{4}\left(\frac{\kappa^2-k^2}{k\kappa}\right)^2\right)\right)^{-1} \tag{115}$$

$$= \left(\frac{1}{4}e^{4\kappa a}\left(\frac{4k^2\kappa^2}{4k^2\kappa^2}+\frac{\kappa^4-2k^2\kappa^2+k^4}{4k^2\kappa^2}\right)\right)^{-1} \tag{116}$$

$$= \left(\frac{1}{4}e^{4\kappa a}\frac{\kappa^4+2k^2\kappa^2+k^4}{4k^2\kappa^2}\right)^{-1} \tag{117}$$

$$= \left(\frac{1}{16}e^{4\kappa a}\frac{\left(\kappa^2+k^2\right)^2}{k^2\kappa^2}\right)^{-1} \tag{118}$$

$$= 16e^{-4\kappa a}\left(\frac{k\kappa}{k^2+\kappa^2}\right)^2 \quad \square \tag{119}$$