Chem 542 Problem Set 1

1. Please show that the wave equation: $\nabla^2 \mathcal{E} = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathcal{E}$ can be derived from Maxwell's equations:

$$\nabla \times \mathcal{E} = -\frac{\partial B}{\partial t}$$

$$\nabla \times B = \frac{1}{c^2}\frac{\partial \mathcal{E}}{\partial t}$$

$$\nabla \cdot \mathcal{E} = 0$$

$$\nabla \cdot B = 0$$

Hint, you should start with $\nabla \times (\nabla \times \mathcal{E})$, and you might need to know that, for a function F:

$$\nabla \times \left(\frac{\partial F}{\partial t}\right) = \frac{\partial}{\partial t}(\nabla \times F) \quad \text{and} \quad \nabla \times \nabla \times F = \nabla(\nabla \cdot F) - \nabla^2 \cdot F.$$

You don't need to know this, but if you forgot a "divergence" is: $\nabla \cdot F = \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\right) F$, "del squared" is: $\nabla \cdot \nabla \cdot F = \nabla^2 \cdot F = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) F$, while a curl is: $\nabla \times F = \left(\frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z}\right)x + \left(\frac{\partial F_x}{\partial z} - \frac{\partial F_z}{\partial x}\right)y + \left(\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y}\right)z$

Answer: We start with: $\nabla \times (\nabla \times \mathcal{E}) = \nabla \times \left(-\frac{\partial B}{\partial t}\right)$. Using the identity we can then show the above is equal to: $-\frac{\partial}{\partial t}(\nabla \times B) = -\frac{\partial}{\partial t}\frac{1}{c^2}\frac{\partial \mathcal{E}}{\partial t} = -\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathcal{E}$. We can also use the second identity to show $\nabla \times (\nabla \times \mathcal{E}) = \nabla(\nabla \cdot \mathcal{E}) - \nabla^2\mathcal{E}$. Since $\nabla \cdot \mathcal{E} = 0$, we are left with $-\nabla^2\mathcal{E}$. Consequently, on the left and right side of is: $\nabla \times (\nabla \times \mathcal{E}) = -\nabla^2\mathcal{E} = -\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathcal{E}$ which reduces to the wave equation:

$$\frac{\partial^2}{\partial x^2}\mathcal{E} = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathcal{E}$$

2. The Dirac delta function $\delta(x - a)$ has the following property when inserted into an integral:

$$\int_{-\infty}^{\infty} f(x)\delta(x - a)\partial x = f(a)$$

Using the above, can you show that:

$$\int_{-\infty}^{\infty} e^{i \cdot (k'-k) \cdot x} \cdot \partial x = 2\pi\delta(k - k')$$

To answer the question, you need to start with the definition of a Fourier transform:

$$F(\lambda) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i \cdot \lambda \cdot x} \cdot f(x) \cdot \partial x$$

And you also need to know that the inverse transform is:

$$f(x) = \int_{-\infty}^{\infty} e^{-i \cdot \lambda \cdot x} \cdot F(\lambda) \cdot \partial \lambda$$

Hint: First, the Fourier transform has an x and λ in it- these need to be changed into other variables to be applicable to the question (note that the question has k's in it). Once you do that you can see that you should insert the Dirac delta function for $f(x)$ in the Fourier transform function and then put that into the inverse transform.

Answer: Starting with the equation for the Fourier transform:

$$F(\lambda) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i \cdot \lambda \cdot x} \cdot f(x) \cdot \partial x$$

First insert $k = x$, $f(x) = \delta(k - k')$, and $\lambda = x$:

$$F(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i \cdot x \cdot k} \cdot \delta(k - k') \cdot \partial k = \frac{1}{2\pi} e^{i \cdot x \cdot k'}$$

which we solved using the definition of what a Dirac Delta function.

Next we insert this into the inverse transform $\int_{-\infty}^{\infty} e^{-i \cdot x \cdot k} \cdot F(x) \cdot \partial x$, and note that we have to set this equal to $f(x) = \delta(k - k')$:

$$f(x) = \delta(k - k') = \int_{-\infty}^{\infty} e^{-i \cdot x \cdot k} \cdot \frac{1}{2\pi} e^{i \cdot x \cdot k'} \cdot \partial x = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i \cdot k \cdot x + i k' x} \cdot \partial x$$

A little simplification yields:

$$2\pi\delta(k - k') = \int_{-\infty}^{\infty} e^{i \cdot (k'-k) \cdot x} \cdot \partial x$$

3. Powder X-ray diffraction (PXRD) is a method of characterizing nanoparticles of a crystalline material. It is the result of the coherent scattering of high energy (short wavelength) photons off the regular lattice planes of a solid powdered material. Essentially, the nanoparticles act like diffraction gratings. Shown here is the PXRD of gold nanoparticles, where the resonances provide information on the structure of the metal. The "powder" in PXRD implies that there is no overall orientation of the crystals with the incoming X-ray beam.
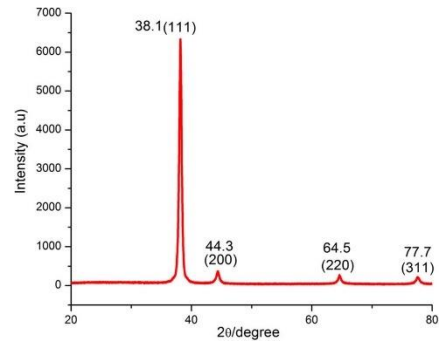
Let's analyze a PXRD spectrum to start applying some programming skills and learn a useful relationship, specifically the Debye equation that describes PXRD intensity:

$$I(s) \approx \sum_m \sum_n f_m(\theta) f_n(\theta) \frac{sin(2\pi s d_{mn})}{2\pi s d_{mn}}$$

where $C(\theta)$ is a function that accounts for intensity variations due to geometry, m and n are atomic labels, $f(\theta)$ is the atomic scattering factor, d_{mn} is the distance between atomic pairs, and $s = \frac{2sin(\theta)}{\lambda}$. A typical operating wavelength in XRD diffractometers is $\lambda = 1.5406$ Å

For this question simply write a code that solves the Debye equation for Au nanoparticles using the coordinates for small (2.3 nm) and larger (4.6 nm) nanoparticles of Au metal that are linked on the website. For this problem submit **(a)** your code, **(b)** the results, and **(c)** suggest a reason that your spectra perfectly match the bulk one shown above. Hint: how does the large vs. small nanoparticle XRD patterns differ? Then apply that reasoning to describe the particles that were used to measure the PXRD pattern above.

Some Matlab hints are provided in the appendix.
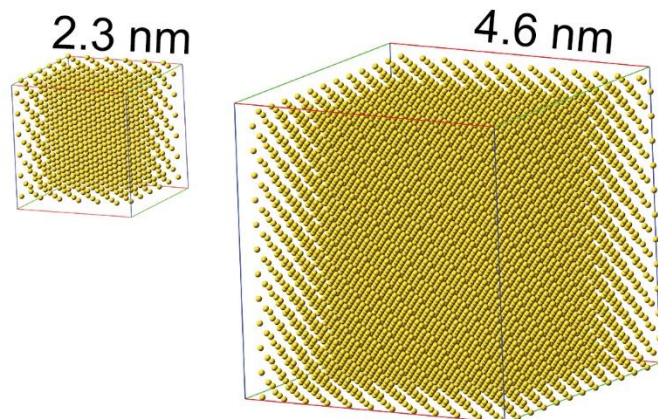
Answer:

a,b) Here is my code for the smaller particle, followed by the results.

```
load coords_small.txt;
xyz=coords_small;
N=max(size(xyz));
lam=1.5406;
spectral_axis=10:0.1:85;
numpoints=max(size(spectral_axis));
for xth=1:numpoints
    %initialize variables
    pxrd(xth)=0;                        %this will be the PXRD spectrum
    twoth(xth)=spectral_axis(xth);   %x-axis of the PXRD spectrum
    theta=twoth(xth)/2/360*2*pi;      %convert 2*angle from degrees to radians
    s=2*sin(theta)/lam;               %s for the Debye equation
    q=4*pi/lam*sin(theta);            %q for the scattering amplitude

    %f1 is gold's scattering amplitude, taken from
http://lampx.tugraz.at/~hadley/ss1/crystaldiffraction/atomicformfactors/formf
actors.php
    f1=16.8819*exp(-0.4611*(q/4/pi)^2)+18.5913*exp(-
8.6216*(q/4/pi)^2)+25.5582*exp(-1.4826*(q/4/pi)^2)+5.86*exp(-
36.3956*(q/4/pi)^2)+12.0658;
    for i=1:N-1
        for j=i+1:N
            d=sqrt((xyz(i,1)-xyz(j,1))^2+(xyz(i,2)-xyz(j,2))^2+(xyz(i,3)-
xyz(j,3))^2);
            pxrd(xth)=pxrd(xth)+f1*f1*sin(2*pi*s*d)/2/pi/s/d;
        end;
    end;
end;
figure;
plot(twoth,pxrd,'b');
```
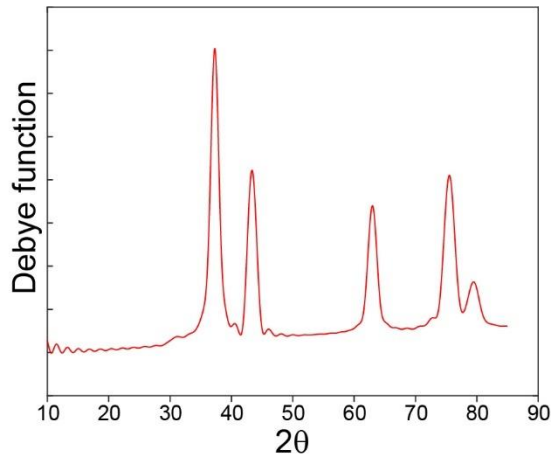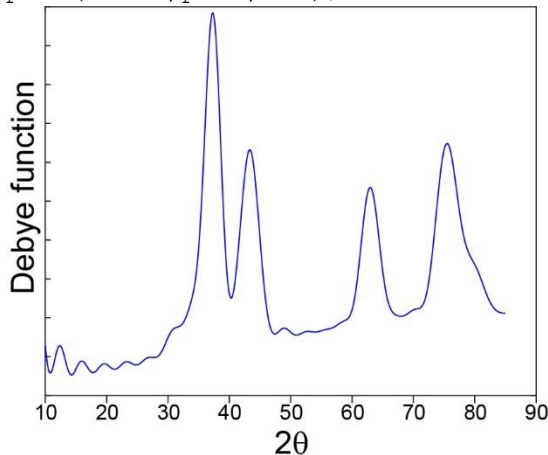

c) The nanoparticles have resonances that are wider. The smaller one is the widest, which means that the powder pattern shown in the question must be from very large Au particles.

4. For the step potential:

a) What is the formula for the reflectance for an electron with $E<V_0$?

Hint: Reflectance is the amplitude of the left-scattering "B" wave divided by the amplitude of the incoming "A" wave, i.e. $\frac{|B|^2}{|A|^2}$.
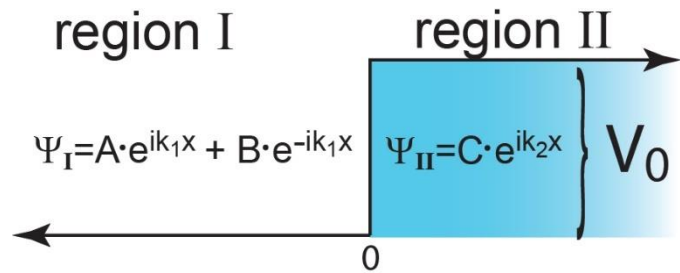
b) What is the formula for the reflectance of an electron with $E>V_0$?

c) Please plot $|\psi|^2$ for $E=1/2V_0$. **Hint**: you can always set the "A" constant equal to 1.0 and then "B" and "C" should be easy to define relative to that. Note some Matlab scripts are attached to assist. Also you should be able to simplify in region 1 into a trigonometric representation such as $|\psi_I|^2 = 2 - 4 \cdot \sin(k_1x)\cos(k_1x) = 2 - 2 \cdot \sin(2k_1x)$. Region 2 will look more like an exponential decay.

d) Please plot $|\psi|^2$ for $E=2V_0$. Hint, $|\psi_{II}|^2$ will be a constant.

Answer: First we note that a wavefunction in region I is : $\psi_I = Ae^{ik_1x} + Be^{-ik_1x}$ and in region II: $\psi_{II} = Ce^{ik_2x}$, where $k_1 = \frac{\sqrt{2mE}}{\hbar}$ and $k_2 = \frac{\sqrt{2m(E-V_0)}}{\hbar}$.

At x=0 the wavefunctions must be smooth and continuous: $Ae^{ik_10} + Be^{-ik_10} = Ce^{ik_20}$ or:

$$A + B = C$$

The continuous stipulation means: $Aik_1e^{ik_10} - Bik_1e^{-ik_10} = Cik_2e^{ik_20}$ or:

$$Ak_1 - Bk_1 = Ck_2$$

Since the reflection is: $\frac{|B|^2}{|A|^2}$ we need to relate A & B through C. To do so look at the second relationship: $Ak_1 - Bk_1 = Ck_2$ which shows that $B = \frac{Ak_1 - Ck_2}{k_1}$. We put this into

$A + B = C$ to yield $A + \frac{Ak_1 - Ck_2}{k_1} = C$ and thus $2Ak_1 = C(k_1 + k_2)$ and $A = \frac{C(k_1+k_2)}{2k_1}$.

Likewise $A = \frac{Bk_1 + Ck_2}{2k_1}$ and thus $A + B = C$ yields $B = \frac{C(k_1-k_2)}{2k_1}$ and now we see that:

$$\frac{B}{A} = \frac{C(k_1-k_2)}{2k_1} \frac{2k_1}{C(k_1+k_2)} = \frac{k_1-k_2}{k_1+k_2}$$

a) Now if E<V₀, then $k_2 = \frac{\sqrt{2m(E-V_0)}}{\hbar} = \frac{\sqrt{-2m(V_0-E)}}{\hbar} = i\frac{\sqrt{2m(V_0-E)}}{\hbar}$. Let's redefine $k_2 = ik_2'$

with: $k_2' = \frac{\sqrt{2m(V_0-E)}}{\hbar}$. As a result, the reflectance is:

$$\frac{|B|^2}{|A|^2} = \frac{(k_1 - ik_2')^*(k_1 - ik_2')}{(k_1 + ik_2')^*(k_1 + ik_2')} = \frac{(k_1 + ik_2')(k_1 - ik_2')}{(k_1 - ik_2')(k_1 + ik_2')} = \frac{k_1^2 + k_2^2}{k_1^2 + k_2^2} = 1$$

b) If E>V₀ then $\frac{B}{A} = \frac{\sqrt{2mE}-\sqrt{2m(E-V_0)}}{\sqrt{2mE}+\sqrt{2m(E-V_0)}}$, which can be simplified by $\frac{B}{A} = \frac{\sqrt{E}-\sqrt{E-V_0}}{\sqrt{E}+\sqrt{E-V_0}}$.

Thus, $\frac{|B|^2}{|A|^2} = \frac{\left(\sqrt{E}-\sqrt{E-V_0}\right)^2}{\left(\sqrt{E}+\sqrt{E-V_0}\right)^2}$.

c) For E=1/2V₀ we can set A=1, and then $B = \frac{k_1 - ik_2'}{k_1 + ik_2'} = \frac{\sqrt{mV_0}-i\sqrt{mV_0}}{\sqrt{mV_0}+i\sqrt{mV_0}} = \frac{1-i}{1+i}$. You can

simplify this by multiplying top and bottom by $1 - i$: $B = \frac{1-i}{1+i}\left(\frac{1-i}{1-i}\right) = \frac{1-i-i+i^2}{1+i-i-i^2} = \frac{-2i}{2} = -i$.

As a result, the proper wavefunction is $\psi_I = e^{ik_1x} - i \cdot e^{-ik_1x}$. We can simplify it using:

$e^{ik_1x} = \cos(k_1x) + i \cdot \sin(k_1x)$ and $e^{-ik_1x} = \cos(k_1x) - i \cdot \sin(k_1x)$, which gives us:

$$\psi_I = \cos(k_1x) + i \cdot \sin(k_1x) - i\{\cos(k_1x) - i \cdot \sin(k_1x)\}$$
$$= \cos(k_1x) - \sin(k_1x) + i(\sin(k_1x) - \cos(k_1x))$$

Now when you take the absolute value of this:
$\{\cos(k_1x) - \sin(k_1x) + i \cdot \sin(k_1x) - i \cdot \cos(k_1x)\} \cdot \{\cos(k_1x) - \sin(k_1x) - i \cdot \sin(k_1x) + i \cdot \cos(k_1x)\}$

It is: $\cos^2(k_1x) + \sin^2(k_1x) - 2 \cdot \cos(k_1x) \cdot \sin(k_1x) + \sin^2(k_1x) + \cos^2(k_1x) - 2 \cdot \sin(k_1x) \cdot \cos(k_1x) =$

$$|\psi_I|^2 = 2 - 4 \cdot \sin(k_1x) \cdot \cos(k_1x) = 2 - 2 \cdot \sin(2k_1x)$$

For which we used the identity $\sin(2x) = 2\sin(x)\cos(x)$.

For the second region we start with: $A + B = C$, and if we let A=1 and we already know that $B = -i$, then $C = 1 - i$. As a result, $\psi_{II} = (1 - i)e^{ik_2x}$. As $k_2 = ik_2'$ with $k_2' = \frac{\sqrt{2m(V_0-E)}}{\hbar}$, then we have $\psi_{II} = (1 - i)e^{-k_2'x}$
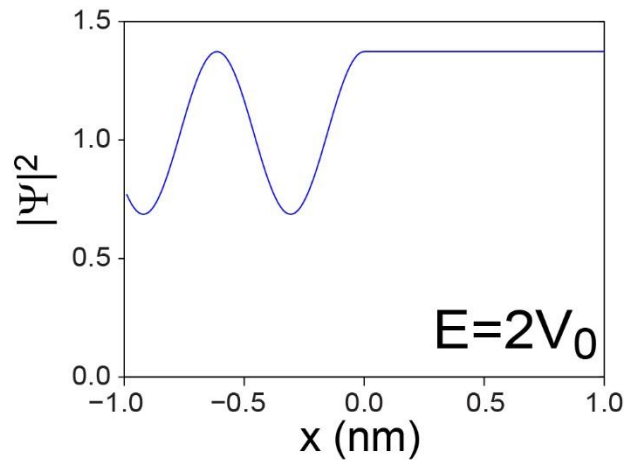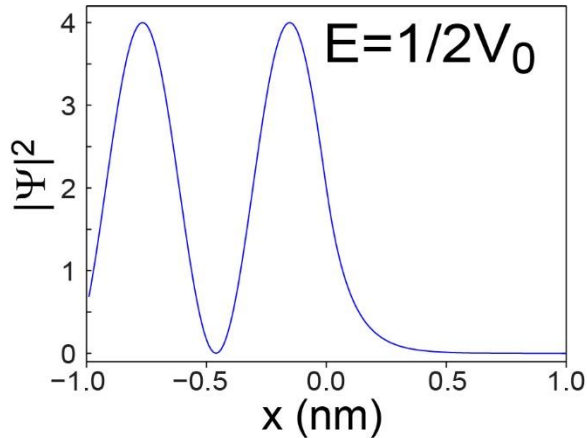
As a result, $|\psi_{II}|^2 = \{(1 - i)e^{-k_2'x}\}^*\{(1 - i)e^{-k_2'x}\} = (1 + i)(1 - i)e^{-2k_2'x} = 2e^{-2k_2'x}$

We can plot this using Matlab as:

```
hbar=1.0546e-34;
m=9.109e-31;
en=1.602e-19;
v=en*2;
k1=sqrt(2*m*en)/hbar;  k2=sqrt(2*m*(v-en))/hbar;
for x2=1:200
    x(x2)=(x2-100)*0.1e-10;
    if (x(x2)<=0)
        wfsq(x2)=2-2*sin(2*k1*x(x2));
    end;
    if (x(x2)>0)
        wfsq(x2)=2*exp(-2*k2*x(x2));
    end;
end;
plot(x,wfsq);
```


d) If E=$2V_0$, and we set A=1, then $B = \frac{\sqrt{2V_0}-\sqrt{V_0}}{\sqrt{2V_0}+\sqrt{V_0}} = \frac{\sqrt{2}-1}{\sqrt{2}+1}$. First, we can simplify the expression:

$$|\psi_I|^2 = \left(e^{ik_1x} + Be^{-ik_1x}\right)^*\left(e^{ik_1x} + Be^{-ik_1x}\right) = \left(e^{-ik_1x} + Be^{ik_1x}\right)\left(e^{ik_1x} + Be^{-ik_1x}\right)$$
$$= e^{-ik_1x}e^{ik_1x} + e^{-ik_1x}Be^{-ik_1x} + B^*e^{ik_1x}e^{ik_1x} + Be^{ik_1x}Be^{-ik_1x}$$
$$= e^{-ik_1x+ik_1x} + Be^{-ik_1x-ik_1x} + Be^{ik_1x+ik_1x} + B^2e^{ik_1x-ik_1x}$$
$$= e^0 + Be^{-2ik_1x} + Be^{2ik_1x} + B^2e^0 = 1 + B^2 + Be^{-2ik_1x} + Be^{2ik_1x}$$

Here we recognize that $e^{-2ik_1x} + e^{2ik_1x} = 2 \cdot cos(2k_1x)$ which gives a final result of:

$$|\psi_I|^2 = 1 + B^2 + 2B \cdot cos(2k_1x)$$

You could have tried to solve this problem using entirely trigonometric functions as follows:

$$|\psi_I|^2 = \left(e^{ik_1x} + Be^{-ik_1x}\right)^*\left(e^{ik_1x} + Be^{-ik_1x}\right) = \left(e^{-ik_1x} + Be^{ik_1x}\right)\left(e^{ik_1x} + Be^{-ik_1x}\right)$$
$$= \{\cos(k_1x) - i \cdot \sin(k_1x) + B\cos(k_1x) + B \cdot i \cdot \sin(k_1x)\}\{\cos(k_1x) + i$$
$$\cdot \sin(k_1x) + B\cos(k_1x) - B \cdot i \cdot \sin(k_1x)\}$$
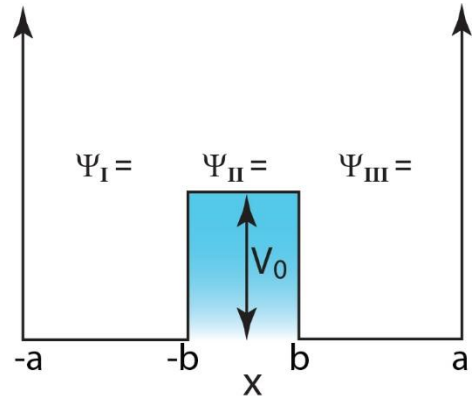$$= 1 + B^2 + 2B\{\cos^2(k_1x) - \sin^2(k_1x)\} = 1 + B^2 + 2B \cdot \cos(2k_1x)$$

As for region II we have: $|\psi_{II}|^2 = \left\{(1+B)e^{ik_2x}\right\}^*\left\{(1+B)e^{ik_2x}\right\} =$

$$\left(e^{-ik_2x} + Be^{-ik_2x}\right)\left(e^{ik_2x} + Be^{ik_2x}\right) = 1 + 2B + B^2$$

5. For the double square well potential shown here:

Note that $k_1 = \frac{\sqrt{2mE}}{\hbar}$ and $k_2 = \frac{\sqrt{2m(V_0-E)}}{\hbar}$

a) Determine what should be reasonable
wavefunctions in regions 1, 2 and 3. Hint: Good
candidates include $e^{-kx} + e^{kx}$, $\sin(k(x - x_0))$, and
$\cos(k(x - x_0))$ weighted with appropriate constants,
i.e. "A", "B" etc.

b) Show that the energy can be calculated for an
even parity solution using the transcendental
equation:

$$k_1 \cdot cotan\left(k_1(a - b)\right) = -k_2 \cdot tanh\,(k_2b)$$

And that the odd parity solution is:

$$k_1 \cdot cotan\left(k_1(a - b)\right) = -k_2 \cdot coth\,(k_2b)$$

Hint: First, these questions are all about developing an equation with k_1 and k_2 without
the "A" and "B" coefficients etc. A good way to do that is to specify that the
wavefunctions must be smooth and continuous at each boundary, i.e.:

$$\frac{\frac{\partial\psi_I(\text{boundary})}{\partial x}}{\psi_I(\text{boundary})} = \frac{\frac{\partial\psi_{II}(\text{boundary})}{\partial x}}{\psi_{II}(\text{boundary})}$$

Here are some useful identities: $tanh(x) = \frac{sinh(x)}{cosh(x)} = \frac{e^x - e^{-x}}{e^x + e^{-x}}$ and $coth(x) = \frac{cosh(x)}{sinh(x)} = \frac{e^x + e^{-x}}{e^x - e^{-x}}$

c) Show that if $V_0 \rightarrow \infty$ then you get the regular particle in a box energy with an added factor of degeneracy:

$E_n = \frac{\pi^2 \hbar^2 n^2}{2mL^2}$ where n=1, 2, 3… and L=b-a, the length of the "trap".

Answer:

a) First, we have to define the wavefunctions in each of the three regions, with k_2 being imaginary since the energy is below the potential. This is actually made somewhat easy because we know that the wavefunction has to be 0 at point -a, which allows us to use a sine function:

$$\psi_I = A \cdot sin(k_1(x + a))$$

Region II will be the usual decaying exponentials:

$$\psi_{II} = B \cdot e^{-k_2 x} + C \cdot e^{k_2 x}$$

And region III will be:

$$\psi_{III} = D \cdot sin(k_1(x - a))$$

b) At the boundary x=-b we will stipulate smooth and continuous conditions:

$\psi_I(-b) = \psi_{II}(-b)$ and $\frac{\partial \psi_I(-b)}{\partial x} = \frac{\partial \psi_{II}(-b)}{\partial x}$ which means:

$$A \cdot sin\big(k_1(a - b)\big) = B \cdot e^{k_2 b} + C \cdot e^{-k_2 b}$$

and

$$A \cdot k_1 \cdot cos\big(k_1(a - b)\big) = -B \cdot k_2 \cdot e^{k_2 b} + C \cdot k_2 \cdot e^{-k_2 b}$$

We can divide the two relationships to show:

$$\frac{\frac{\partial \psi_I(-b)}{\partial x}}{\psi_I(-b)} = \frac{\frac{\partial \psi_{II}(-b)}{\partial x}}{\psi_{II}(-b)} = \frac{A \cdot k_1 \cdot cos\big(k_1(a - b)\big)}{A \cdot sin\big(k_1(a - b)\big)} = \frac{C \cdot k_2 \cdot e^{-k_2 b} - B \cdot k_2 \cdot e^{k_2 b}}{B \cdot e^{k_2 b} + C \cdot e^{-k_2 b}}$$

Some simplification yields:

$k_1 \cdot cotan\big(k_1(a - b)\big) = k_2 \frac{C \cdot e^{-k_2 b} - B \cdot e^{k_2 b}}{B \cdot e^{k_2 b} + C \cdot e^{-k_2 b}}$ **(1)**

When you do the same for the 2nd boundary condition you find:

$\psi_{II}(b) = \psi_{III}(b)$ and $\frac{\partial \psi_{II}(b)}{\partial x} = \frac{\partial \psi_{III}(b)}{\partial x}$ which means:

$$D \cdot sin(k_1(b - a)) = B \cdot e^{-k_2 b} + C \cdot e^{k_2 b}$$

and

$$D \cdot k_1 \cdot cos(k_1(b - a)) = -B \cdot k_2 \cdot e^{-k_2 b} + C \cdot k_2 \cdot e^{k_2 b}$$

We can divide the two relationships to show:

$$\frac{\frac{\partial \psi_{III}(b)}{\partial x}}{\psi_{III}(b)} = \frac{\frac{\partial \psi_{II}(b)}{\partial x}}{\psi_{II}(b)} = \frac{D \cdot k_1 \cdot cos(k_1(b - a))}{D \cdot sin(k_1(b - a))} = \frac{C \cdot k_2 \cdot e^{k_2 b} - B \cdot k_2 \cdot e^{-k_2 b}}{B \cdot e^{-k_2 b} + C \cdot e^{k_2 b}}$$

Some simplification yields:

$$k_1 \cdot cotan(k_1(b - a)) = k_2 \frac{C \cdot e^{k_2 b} - B \cdot e^{-k_2 b}}{B \cdot e^{-k_2 b} + C \cdot e^{k_2 b}}$$

Since $cotan(-x) = -cotan(x)$ we can say the following:

$$-k_1 \cdot cotan(k_1(a - b)) = k_2 \frac{C \cdot e^{k_2 b} - B \cdot e^{-k_2 b}}{B \cdot e^{-k_2 b} + C \cdot e^{k_2 b}} \qquad \textbf{(2)}$$

Now if you equate both the right-hand sides of (1) and (2):

$$-k_2 \frac{C \cdot e^{-k_2 b} - B \cdot e^{k_2 b}}{B \cdot e^{k_2 b} + C \cdot e^{-k_2 b}} = k_2 \frac{C \cdot e^{k_2 b} - B \cdot e^{-k_2 b}}{B \cdot e^{-k_2 b} + C \cdot e^{k_2 b}}$$

Divide out k_2:

$$-\frac{C \cdot e^{-k_2 b} - B \cdot e^{k_2 b}}{B \cdot e^{k_2 b} + C \cdot e^{-k_2 b}} = \frac{C \cdot e^{k_2 b} - B \cdot e^{-k_2 b}}{B \cdot e^{-k_2 b} + C \cdot e^{k_2 b}}$$

Now we can simplify via:

$$-(C \cdot e^{-k_2 b} - B \cdot e^{k_2 b})(B \cdot e^{-k_2 b} + C \cdot e^{k_2 b}) = (C \cdot e^{k_2 b} - B \cdot e^{-k_2 b})(B \cdot e^{k_2 b} + C \cdot e^{-k_2 b})$$

When you multiply this out, on the left:

$$-(C \cdot e^{-k_2 b} - B \cdot e^{k_2 b})(B \cdot e^{-k_2 b} + C \cdot e^{k_2 b}) = -CB \cdot e^{-2k_2 b} - C^2 + B^2 + BC \cdot e^{2k_2 b}$$

and on the right:

$$(C \cdot e^{k_2 b} - B \cdot e^{-k_2 b})(B \cdot e^{k_2 b} + C \cdot e^{-k_2 b}) = CB \cdot e^{2k_2 b} + C^2 - B^2 - CB \cdot e^{-2k_2 b}$$

Put them together to show:

$$-CB \cdot e^{-2k_2 b} - C^2 + B^2 + BC \cdot e^{2k_2 b} = CB \cdot e^{2k_2 b} + C^2 - B^2 - CB \cdot e^{-2k_2 b}$$

$$+2B^2 = +2C^2$$

And you are left with:

$$+2B^2 = +2C^2$$

$$B^2 = C^2$$

Now there are two sets of solutions, if $B = -C$ (odd parity) and you plug that into (1):

$$\left(\frac{1}{k_1}\right) \cdot cotan\big(k_1(a-b)\big) = k_2 \frac{-e^{-k_2 b} - e^{k_2 b}}{e^{k_2 b} - e^{-k_2 b}} = -k_2 \frac{e^{k_2 b} + e^{-k_2 b}}{e^{k_2 b} - e^{-k_2 b}}$$

Since $coth(x) = \frac{cosh(x)}{sinh(x)} = \frac{e^x + e^{-x}}{e^x - e^{-x}}$

$$k_1 \cdot cotan\big(k_1(a-b)\big) = -k_2 \cdot coth\,(k_2 b)$$

If we use $B = C$ (even parity) and you plug that into (1):

$$k_1 \cdot cotan\big(k_1(a-b)\big) = k_2 \frac{e^{-k_2 b} - e^{k_2 b}}{e^{k_2 b} + e^{-k_2 b}} = -k_2 \frac{e^{k_2 b} - e^{-k_2 b}}{e^{k_2 b} + e^{-k_2 b}}$$

Since $tanh(x) = \frac{sinh(x)}{cosh(x)} = \frac{e^x - e^{-x}}{e^x + e^{-x}}$

$$k_1 \cdot cotan\big(k_1(a-b)\big) = -k_2 \cdot tanh\,(k_2 b)$$

c) If $V_0 \to \infty$ then $k_2 \to \infty$. If we plug that into our transcendental equation:

$$\left(\frac{1}{k_1}\right) \cdot tan\big(k_1(a-b)\big) = \left(\frac{-1}{k_2}\right) tanh(k_2 b) = 0$$

The function tan is 0 when its argument is $n\pi$. Thus,

$$k_1(a-b) = \frac{\sqrt{2mE}}{\hbar}(a-b) = n\pi$$

Solving for E yields: $\sqrt{2mE} = \frac{n\pi\hbar}{(a-b)}$ and thus: $2mE = \frac{n^2\pi^2\hbar^2}{2mL^2}$, where L=b-a (the fact that it is squared removed the negative sign from this definition of length).

Appendix: Example Matlab scripts

a. Plotting wavefunctions:

```
hbar=1.0546e-34;
m=9.109e-31;
en=1.602e-19;
v=en*2;
k1=sqrt(2*m*en)/hbar;
k2=sqrt(2*m*(v-en))/hbar;
B=(sqrt(2)-1)/(sqrt(2)+1);
for x2=1:200
    x(x2)=(x2-100)*0.1e-10;
    if (x(x2)<=0)
        wfsq(x2)=2-2*sin(2*k1*x(x2));
        wfsq2(x2)=1+B*B+2*B*cos(2*k1*x(x2));
    end;
    if (x(x2)>0)
        wfsq(x2)=2*exp(-2*k2*x(x2));
        wfsq2(x2)=(1+B)^2;
    end;
end;
plot(x,wfsq,'b');
hold on;
plot(x,wfsq2,'r');
```

b. Debye example and Au scattering factor:

The Au scattering factor is solved using a combination of three exponential functions and depends on the wavelength of light (1.5406 Å in most XRD spectrometers) as shown here:

$$f_{au} = \sum_{i=1}^{4} A_i \cdot exp\left(-b_i \left(\frac{q}{4\pi}\right)^2\right) + c$$

where A, b, and c are constants from the website and $q = \frac{4\pi}{\lambda} sin(\theta)$.

Below is an example script that will help you initialize your Matlab script and calculate the PXRD spectra of the two nanoparticles (small and large), the coordinates for which are linked in the assignment.

```
load coords_small.txt;
xyz=coords_small;
N=max(size(xyz));
lam=1.5406;                          %wavelength in angstroms
spectral_axis=10:0.1:85;             %The PXRD angle (x) axis
numpoints=max(size(spectral_axis));  %The number of datapoints
for xth=1:numpoints
    %initialize variables
    pxrd(xth)=0;                     %this will be the PXRD spectrum
    twoth(xth)=spectral_axis(xth);   %x-axis of the PXRD spectrum
    theta=twoth(xth)/2/360*2*pi;     %convert 2*angle from degrees to radians
    s=;                              %s for the Debye equation
    q=;                              %q for the scattering amplitude
```

```matlab
    %f1 is gold's scattering amplitude, taken from
http://lampx.tugraz.at/~hadley/ss1/crystaldiffraction/atomicformfactors/formf
actors.php
    f_au=16.8819*exp(-0.4611*(q/4/pi)^2)+18.5913*exp(-
8.6216*(q/4/pi)^2)+25.5582*exp(-1.4826*(q/4/pi)^2)+5.86*exp(-
36.3956*(q/4/pi)^2)+12.0658;
    for i=1:N-1
        for j=i+1:N
            d=;
            pxrd(xth)=;
        end;
    end;
end;
figure;
plot(twoth,pxrd,'b');
```