PHAS0004 - Atoms, Stars and The Universe
Problem Solving Tutorial Sheet 2
Model Answers

Objectives:

1. Perform a dimensional analysis on Planck's constant.
2. Gain practise with normalising wave-functions and calculating their properties, including expectation values.
3. Practise using the TISE to calculate energies for an unfamiliar potential.
4. Get practise with the integration and differentiation which arises very often in problems of this kind.
5. Gain practise in solving the TISE for different trial solutions and showing that certain functions are not solutions.

Useful definitions

Planck's constant h is 6.6×10^{-34} Js (2 s.f.).

The time-independent Schrödinger equation (TISE) for a particle in one-dimensional potential $V(x)$ with mass m, energy E with wave-function $\psi(x)$ is

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

1: The dimensions of h

In Physics, studying the dimensions of quantities can be a very important way of discovering relationships (or potential relationships) between them. Here we will consider the dimensions arising in Planck-Einstein's photon energy law and Bohr's atomic model.

1.a) Write down the dimensions of Planck's constant h in terms of the fundamental quantities of mass M, length L and time T, taking the definition of h to be through Planck and Einsteins relationship $E = hf$. Why does $\hbar$ have the same dimensions as h?

1.b) Find the dimensions (in terms of mass M, length L and time T) of angular momentum and show that these are the same as those of Plancks constant h. Hence show that Bohrs quantisation assumption $L = n\hbar$ (where L is the angular momentum and n is an integer) is dimensionally consistent.

We shall use square brackets to denote units, e.g. $[h]$ refers to the units of h.

1.a) From Planck-Einstein's formula:

$$[h] = \frac{[E]}{[f]}$$

The units of frequency are Hz or s^-1, hence

$$[f] = [T]^{-1}$$

To express the units of energy in terms of mass $[M]$, length $[L]$ and time $[T]$ we can refer to any equation for energy which contains only these quantities. Kinetic energy will do:

$$\text{K.E} = \frac{1}{2}mv^2$$

and hence

$$[E] = [M][L]^2[T]^{-2}$$

Thus

$$[h] = \frac{[E]}{[f]} = [M][L]^2[T]^{-1}.$$

$\hbar$ has the same dimensions as h since $\hbar = h/2\pi$ and 2π is dimensionless.

1.b) To find the dimensions of angular momentum we can use

$$l = rp$$

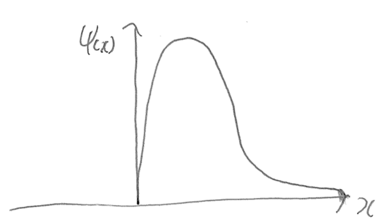
where p is momentum. The dimensions of momentum are $[M][L][T]^{-1}$ from $p = mv$.

Hence

$$[l] = [L][M][L][T]^{-1} = [M][L]^2[T]^{-1}$$

Therefore the left-handside and the right-handside of Bohr's angular momentum assumption are both equal, and $\hbar$ has the same dimension as angular momentum.

2: Calculating properties of wave-functions



(a) Clearly can focus just on $x > 0$. Normalisation:

$$\int_0^\infty |\psi(x)|^2 \, dx = A^2 \int_0^\infty \left(e^{-x} - e^{-2x}\right)^2 dx = 1$$

$$= A^2 \int_0^\infty \left(e^{-2x} - 2e^{-3x} + e^{-4x}\right) dx = 1$$

$$= A^2 \left[-\frac{e^{-2x}}{2} + 2\frac{e^{-3x}}{3} - \frac{e^{-4x}}{4} \right]_0^\infty = 1$$

$$A^2 \left(\frac{1}{2} - \frac{2}{3} + \frac{1}{4} \right) = 1$$

$$A = \sqrt{12}$$

(b)

$$\int_0^\infty x \, |\psi(x)|^2 \, dx = 12 \int_0^\infty \left(xe^{-2x} - 2xe^{-3x} + xe^{-4x}\right) dx$$

Integration by parts:

$$\int_0^\infty xe^{-ax} dx = \left[\frac{xe^{-ax}}{a} \right]_0^\infty + \int_0^\infty \frac{e^{-ax}}{a} dx$$

$$\int_0^\infty xe^{-ax} dx = \left[-\frac{e^{-ax}}{a^2} \right]_0^\infty = \frac{1}{a^2}$$

substituting into above

$$\int_0^\infty x \, |\psi(x)|^2 \, dx = 12 \left(\frac{1}{4} - \frac{2}{9} + \frac{1}{16} \right)$$

$$\int_0^\infty x \, |\psi(x)|^2 \, dx = 12 \left(\frac{5}{16} - \frac{2}{9} \right)$$

$$\int_0^\infty x \, |\psi(x)|^2 \, dx = 12 \left(\frac{45 - 32}{144} \right)$$

$$\int_0^\infty x \, |\psi(x)|^2 \, dx = \frac{13}{12}$$

(c)

Maximum probability corresponds to $\frac{d|\psi(x)|^2}{dx} = 0$

$$\frac{d \, |\psi(x)|^2}{dx} = 0$$

$$\frac{d\left|\psi(x)\right|^2}{dx} = 12\frac{d\left[e^{-2x} - 2e^{-3x} + e^{-4x}\right]}{dx}$$

$$0 = 12\left[-2e^{-2x} + 6e^{-3x} - 4e^{-4x}\right]$$

Removing common terms

$$0 = \left[-1 + 3e^{-x} - 2e^{-2x}\right]$$

factorises to

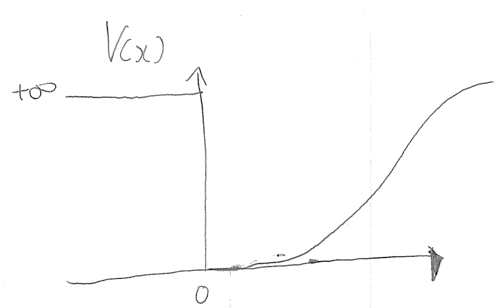
$$0 = \left(2e^{-x} - 1\right)\left(1 - e^{-x}\right)$$

the right term is only zero at $x = 0$, which is outside the allowed range. Which leaves:

$$x = \ln 2$$

This is not the same as the expectation value. Mean and peak values are not the same for skewed distributions .

(d)



$V(x) = \infty$ for $x < 0$

$V(x)$ is finite and small for low x

$V(x)$ is very large for high x

3: Which functions are valid wave-functions? (seen)

To represent a physical particle, wave-functions must be continuous and normalisable. Consider the following functions. Can they represent a wave-function for a physical system? If not, explain why.

3a)

$$f_1(x) = \cos(px/\hbar)$$

As we saw in lectures,

$$\int_{-\infty}^{\infty} \sin^2(px/\hbar)dx$$

diverges to infinity, the same is true of

$$\int_{-\infty}^{\infty} \cos^2(px/\hbar)dx$$

and therefore this function cannot be normalised and cannot represent a physical state.

3b)

$$f_2(x) = \begin{cases} \cos(4\pi x) - \cos(2\pi x) & \text{if } 0 \le x \le 1 \\ 0 & \text{otherwise} \end{cases}$$

Yes - this is a physical wavefunction. It is continuous, and normalisable, and so satisfies the criteria in the question.

Give yourself a bonus mark if you noted that this wavefunction is also continuous in its first derivative. Since in the middle region,

$$\frac{df_3(x)}{dx} = -4\pi\sin(4\pi x) + 2\pi\sin(2\pi x)$$

which at $x = 0$ is equal to 0 and at $x = 1$ is also equal to 0, matching the zero first derivative of the constant wavefunction outside this region.

3c)

$$f_3(x) = \begin{cases} \cos(\pi x) & x \le 0 \\ \sin(\pi x) & x > 0 \end{cases}$$

This is not a valid wave-function since it is *not continuous*. $\sin(0) = 0$ but $\cos(0) = 1$ hence there is a discontinuity at $x = 0$.

3d)

$$f_4(x) = e^{-x}$$

This wave-function blows up to infinity as x gets large and negative, and thus the normalisation integral also blows up to infinity. This wavefunction cannot be normalised and is unphysical.

4: Ground state of a chemical bond

A chemical bond can be approximated by a simple spring between two masses (which represent the atoms), the potential energy of which depends on their separation x, according to:

$$V(x) = \frac{1}{2}kx^2$$

where k is the spring constant. If we solve the TISE for such a potential, the lowest energy state has a wave function of the form:

$$\psi(x) = A\exp[-\alpha^2 x^2/2]$$

where $\alpha = \sqrt{m\omega/\hbar}$ and $\omega = \sqrt{k/m}$.

4a) Use the TISE to compute the energy of wavefunction $\psi(x)$.

The TISE for this potential is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x)$$

We know that $\psi(x)$ is a solution to this, so by substituting it into the TISE we can compute the energy.

We need to compute

$$\frac{d^2\psi(x)}{dx^2} = \frac{d}{dx}A\left(\frac{-2x\alpha^2}{2}\right)\exp[-\alpha^2x^2/2] = -A\alpha^2\frac{d}{dx}\left(x\exp[-\alpha^2x^2/2]\right)$$

$$= -A\alpha^2\left(\exp[-\alpha^2x^2/2] + \frac{-2\alpha^2}{2}x^2\exp[-\alpha^2x^2/2]\right) = A(\alpha^4x^2 - \alpha^2)\exp[-\alpha^2x^2/2]$$

where we used the chain rule and the product rule.

Hence we obtain:

$$-\frac{\hbar^2}{2m}A(\alpha^4x^2-\alpha^2)\exp[-\alpha^2x^2/2]+\frac{1}{2}kx^2A\exp[-\alpha^2x^2/2]=EA\exp[-\alpha^2x^2/2]$$

and after cancellations

$$-\frac{\hbar^2}{2m}(\alpha^4x^2-\alpha^2)+\frac{1}{2}kx^2=E$$

$$\left(-\frac{\hbar^2}{2m}\alpha^4+\frac{1}{2}k\right)x^2=(E-\frac{\hbar^2}{2m}\alpha^2)$$

When we substitute for the values of α and ω given above the LHS cancels to zero. Hence

$$(E-\frac{\hbar^2}{2m}\alpha^2)=0$$

$$E=\frac{\hbar^2\alpha^2}{2m}=\frac{\hbar^2 m\omega}{2m\hbar}=\frac{\hbar\omega}{2}$$

4b) Use the symmetry of the wave-function to determine the expectation value for separation x.

$\langle x\rangle=0$. The wavefunction $\psi(x)$ is an even function. Therefore the probability density $|\psi(x)|^2$ is also even. The integral:

$$\langle x\rangle=\int_{-\infty}^{\infty}x|\psi(x)|^2dx.$$

is an integral over the odd function $x|\psi(x)|^2$ which evaluates to zero.

4c) Find the value of A which normalises this wavefunction.

You may find the following integral useful

$$\int_{-\infty}^{\infty}e^{-y^2}dy=\sqrt{\pi}$$

To find A we solve:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

Hence

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = A^2 \int_{-\infty}^{\infty} \exp[-\alpha^2 x^2] dx$$

To use the given integral I need to change variables: $y = \alpha x$ and hence $dy = \alpha dx$.

$$A^2 \int_{-\infty}^{\infty} \exp[-\alpha^2 x^2] dx = \frac{A^2}{\alpha} \int_{-\infty}^{\infty} \exp[-y^2] dy = \frac{A^2}{\alpha} \sqrt{\pi}.$$

Hence

$$A = \frac{\sqrt{\alpha}}{\pi^{1/4}}.$$

5: Solving the Time Independent Schrödinger Equation for a free particle (unseen)

In lectures we saw that a general sinusoidal function:

$$\psi(x) = A \sin\left(\frac{2\pi(x-\phi)}{\lambda}\right)$$

was a solution of the TISE for a free particle, and we calculated the associated energy. In this question, you are going to attempt to solve the TISE for a free particle yourselves, using a variety of trial functions.

The TISE for a free particle is:

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

5a) In lectures you heard that the only classes of functions which are proportional to their second derivative have sine-like and exponential-like forms. Let's look at some other functions and see how they fail. First let's consider

$$\psi(x) = x^2$$

Show that this function is *not* a solution to the free particle TISE.

$$\frac{d\psi(x)}{dx} = 2x$$
$$\frac{d^2\psi(x)}{dx^2} = 2$$

2 is a constant and is not proportional to x^2. Therefore x^2 cannot be a solution to the TISE.

5b) Is there any (finite) value of n for which

$$\psi(x) = x^n$$

could be a solution to the TISE for a free particle?

It is the same argument but more general.

$$\frac{d\psi(x)}{dx} = nx^{n-1}$$
$$\frac{d^2\psi(x)}{dx^2} = n(n-1)x^{n-2}$$

$n(n-1)x^{n-2}$ is not proportional to x^n (question to the students - why?). Therefore x^n cannot be a solution to the TISE for any n.

It is not a coincidence that solutions to the TISE are functions such as sine and cos which have infinitely many terms in their power series expansion.

5c) Now consider the following function:

$$\psi(x) = A\sin(ax) + B\cos(bx)$$

Find an expression for the ratio

$$\frac{d^2\psi(x)}{dx^2} \div \psi(x).$$

Show that if $b = a$ this ratio is a constant, and that the wavefunction is solution to the TISE and calculate the energy of the particle as a function of parameters a, A and B.

$$\frac{d\psi(x)}{dx} = Aa\cos(ax) - Bb\sin(bx)$$
$$\frac{d^2\psi(x)}{dx^2} = -Aa^2\sin(ax) - Bb^2\cos(bx)$$

Let's rewrite the TISE in a more convenient form:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x)$$

We need to check whether $\frac{d^2\psi(x)}{dx^2}$ can be proportional to (with a negative constant of proportionality) $\psi(x)$.

To simplify notation let $\kappa = \frac{2mE}{\hbar^2}$. Hence we want our wavefunction to satisfy:

$$\frac{d^2\psi(x)}{dx^2} = -\kappa\psi(x)$$

$$-Aa^2\sin(ax) - Bb^2\cos(bx) = -(Aa^2\sin(ax) + Bb^2\cos(bx)) = -\kappa(A\sin(ax) + B\cos(bx))$$

we can rewrite this:

$$\kappa = \frac{Aa^2\sin(ax) + Bb^2\cos(bx)}{A\sin(ax) + B\cos(bx)}$$

If $b = a$

$$\kappa = \frac{Aa^2\sin(ax) + Ba^2\cos(ax)}{A\sin(ax) + B\cos(ax)} = \frac{a^2(A\sin(ax) + B\cos(ax))}{A\sin(ax) + B\cos(ax)} = a^2$$

To calculate the energy, recall that:

$$\kappa = \frac{2mE}{\hbar^2} = a^2$$

Hence

$$E = \frac{\hbar^2 a^2}{2m}$$

NB the energy does not depend on A or B.

Ryan Nichol, October 2018