Basic Mathematics

Mathematics & Quantum Theory

R Horan and M Lavelle

The aim of this package is to provide a short self assessment programme for students who wish to solve problems in introductory quantum theory.

Last Revision Date: November 12, 2001 Version 1.1

Table of Contents

Units

Before getting started, we list the units used in this package.

Energy The Joule (J) is the S.I. unit. The electron volt (eV) is often used at atomic scales. It is the energy gained by an electron accelerated through a one volt potential. $1\,\text{eV} = 1.6 \times 10^{-19}\,\text{J}$.

Planck's Constant This fundamental scale is $h = 6.6 \times 10^{-34}\,\text{Js}$.

Masses The mass of an electron is $m_e = 9.1 \times 10^{-31}\,\text{kg}$, while the mass of a proton is $m_p = 1.7 \times 10^{-27}\,\text{kg}$.

Lengths The following are often used: an Ångstrom is $1\text{Å} = 10^{-10}\,\text{m}$, a nanometre is $1\,\text{nm} = 10^{-9}\,\text{m}$, a micron is $1\,\mu\text{m} = 10^{-6}\,\text{m}$.

Frequency The Hertz is the basic unit of frequency (one oscillation per second). A megahertz is $1\,\text{MHz} = 10^{6}\,\text{Hz}$.

1. Electromagnetic Waves

Light has long been known to have a wave-like character. Frequency, ν, and wavelength, λ, are related by $\nu = c/\lambda$, where c is the speed of light (roughly given by $c \approx 3 \times 10^8 \mathrm{m\,s^{-1}}$).

Example 1

The frequency of BBC Radio 4 on FM is approximately 93 MHz. What is its wavelength?

The frequency is $93 \times 10^6 = 9.3 \times 10^7$ Hz. The wavelength is therefore

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8}{9.3 \times 10^7} = \frac{3 \times 10}{9.3} \approx 3.2\,\mathrm{m}$$

Exercise 1. Various types of electromagnetic radiation are described below. If the frequency is given, calculate the wavelength and vice versa. (Click on the green letters for the solutions.)

(a) Visible light with $\lambda = 600\,\mathrm{nm}$

(b) X-rays with $\nu = 3 \times 10^{18}\,\mathrm{Hz}$

(c) Infra-red radiation with $\lambda = 1.5\,\mu\mathrm{m}$

(d) Gamma rays with $\nu = 10^{21}\mathrm{Hz}$

Quiz Estimate which of the following might emit electromagnetic radiation with frequency $\nu = 10^{16}\,\mathrm{Hz}$.

(a) The sun
(b) An X-ray laser
(c) A gamma ray source
(d) Your body

Quiz If the gap between two planes in a particular crystal is $0.75\,\mathrm{nm}$, what frequency of X-ray would have a wavelength of half this size?

(a) $0.375\,\mathrm{Hz}$
(b) $3 \times 10^{15}\,\mathrm{Hz}$
(c) $1.5 \times 10^{16}\,\mathrm{Hz}$
(d) $8 \times 10^{17}\,\mathrm{Hz}$

2. The Photoelectric Effect

As well as its wave nature, light has a particle like character which is revealed in the photoelectric effect. Einstein's equation for the photoelectric effect reads

$$E = h\nu - W$$

where E is the kinetic energy of electrons emitted from a surface irradiated by light of frequency ν, h ($= 6 \times 10^{-34}$ Js) is Planck's constant and W is a (material specific) constant called the work function.

Example 2 If a metal with $W = 3.3 \times 10^{-19}$J is irradiated by light of frequency $\nu = 10^{15}$Hz, find the energy of the emitted photoelectrons?

$$\begin{aligned} \text{From } E &= h\nu - W \text{ we have :} \\ E &= 6.6 \times 10^{-34} \times 10^{15} - 3.3 \times 10^{-19} \\ &= (6.6 - 3.3) \times 10^{-19} \\ &= 3.3 \times 10^{-19}\text{J} \end{aligned}$$

Note that since one electronvolt of energy is $1\text{eV} = 1.6 \times 10^{-19}\text{J}$, we could reexpress this as $E \approx 2\text{eV}$.

Quiz If the energy of the photoelectrons emitted from a metal is twice the work function, by what factor must the frequency of the incident radiation be increased to double the energy of the photoelectrons?

(a) 2/3 (b) 3/2

(c) 5/3 (d) 3/5

3. The de Broglie Wavelength

As well as light having a particle nature, quantum theory says that matter has a wave-like nature. This is expressed for a particle with momentum p by

$$\lambda = \frac{h}{p}$$

where λ is the de Broglie wavelength and h is Planck's constant.

Quiz To understand why we do not see the wave nature of normal matter around us, estimate the wavelength of a 100g pebble thrown through the air with speed, $v = 2\text{ms}^{-1}$.
Recall that momentum and velocity are related by $p = mv$.

(a) $1/100\,\text{m}$
(b) $3 \times 10^{-33}\,\text{m}$
(c) $5 \times 10^{-55}\,\mu\text{m}$
(d) $4 \times 10^{-44}\,\text{m}$

At atomic and subatomic scales we can see wave like properties of matter (e.g., electron diffraction).

Example 3 If in a demonstration of electron diffraction, the electrons' de Broglie wavelength was about 5×10^{-2}Å, find their kinetic energy.

$$\begin{aligned} \text{From } \lambda &= \frac{h}{p} \text{ with } \lambda = 5 \times 10^{-10}\text{m} \\ p &= \frac{h}{\lambda} = \frac{6.6 \times 10^{-34}}{5 \times 10^{-12}} \\ &= 1.3 \times 10^{-22}\,\text{kg m s}^{-1} \end{aligned}$$

The kinetic energy is $E = \frac{1}{2}mv^2 = p^2/(2m)$ and so using the electron mass $m = 9.1 \times 10^{-31}$kg, we get

$$\begin{aligned} E &= \frac{(1.3 \times 10^{-22})^2}{2 \times 9.1 \times 10^{-31}} \\ &= \frac{1.7}{18.2} \times 10^{-13} \approx 9 \times 10^{-15}\,\text{J} \end{aligned}$$

Recalling that $1\text{eV} = 1.6 \times 10^{-19}$J, then, $E \approx 6 \times 10^4$eV.

Quiz What is the wavelength of a 1 keV electron?

(a) 0.4Å (b) 0.04Å (c) 4Å (d) 4nm

Quiz The ratio of the proton and electron masses is given by

$$\frac{m_p}{m_e} = 1836.15$$

If an electron and a proton are to have the same de Broglie wavelength, how must their energies be related?

(a) $\frac{E_p}{E_e} = 1$ (b) $\frac{E_p}{E_e} = 1836.15$

(c) $\frac{E_p}{E_e} = \sqrt{1836.15}$ (d) $\frac{E_p}{E_e} = \frac{1}{1836.15}$

4. The Balmer Series

Quiz Balmer's original formula for the visible lines of the Hydrogen spectrum expressed the wavelengths λ in terms of a constant K

$$\lambda = K\frac{n^2}{n^2-4}$$

for $n = 3, 4 \ldots$. This can also be expressed in terms of the wave number $\bar{\nu} = 1/\lambda$. Which of the formulae below is correct?

(a) $\bar{\nu} = -\frac{1}{4K}$

(b) $\bar{\nu} = K(1 + 4/n^2)$

(c) $\bar{\nu} = \frac{1}{K}\left(1 - \frac{4}{n^2}\right)$

(d) $\bar{\nu} = \frac{1}{K} - \frac{4n^2}{K}$

Quiz What are the shortest and longest wavelengths for lines in the Balmer series?

(a) K and $\frac{9}{5}K$

(b) 0 and $\frac{9}{5}K$

(c) $-\frac{4}{5}K$ and $\frac{4}{5}K$

(d) $\frac{9}{13}K$ and K

5. Rotational and Vibrational Spectra

One of the characteristic predictions of quantum mechanics is that many energies are only allowed to have specific discrete values.
For example the rotational energy levels of linear molecules are roughly

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

where J is an (integer) quantum number and I is the moment of inertia of the molecule.

Quiz What is the difference in the energy between two such adjacent energy levels, $E_{J+1} - E_J$?

(a) $\frac{h^2}{4\pi^2 I}(J+1)(J+2)$

(b) $\frac{h^2}{8\pi^2 I}$

(c) $\frac{h^2}{4\pi^2 I}(J+1)$

(d) $\frac{h^2}{8\pi^2 I}\frac{J+2}{J}$

Quiz A more accurate model of rotating molecules builds in stretching effects via

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - KJ^2(J+1)^2$$

where K is a (small) constant. What is now the difference between two such energy levels?

(a) $\frac{h^2}{4\pi^2 I}(J+1) - K(J+1)^2$
(b) $\frac{h^2}{4\pi^2 I}(J+1) - 4K(J+1)^3$
(c) $\frac{h^2}{4\pi^2 I}(J+1) - K(J+2)^2$
(d) $\frac{h^2}{4\pi^2 I}(J+1) - 2K$

Quiz The energy levels of vibrational modes in the simple harmonic oscillator are given by $E_n = (n+\frac{1}{2})h\nu$. What is the difference between two consecutive levels?

(a) 0
(b) $(n - \frac{1}{2})h\nu$
(c) $h\nu$
(d) $(2n+1)h\nu$

6. The Uncertainty Principle

Heisenberg's uncertainty principle tells us that the product of the uncertainty in the position, Δx, and the uncertainty in the momentum, Δp must satisfy

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

where $\hbar = h/2\pi$ (this is pronounced hbar).

Example 4 If an electron is bound in an atom of diameter roughly $1\,\text{Å}$ what is the minimum uncertainty in its velocity?

We read off that $\Delta x \approx 10^{-10}\,\text{m}$. From the uncertainty principle we have

$$\begin{aligned} \Delta p &\geq \frac{\hbar}{2\Delta x} \\ &\geq 5.3 \times 10^{-25}\text{kg}\,\text{m}\,\text{s}^{-1} \end{aligned}$$

Momentum and velocity are related by $p = mv$, the electron mass is 9.1×10^{-31}kg, and so the uncertainty in its velocity must be greater than $\Delta v = \Delta p/m \approx 6 \times 10^{5}\,\text{m}\,\text{s}^{-1}$.

Quiz If the uncertainty in the position of an object is half a micron, which of the following is closest to the minimum uncertainty in its momentum?

(a) 3.314×10^{-39} kg m s^{-1} (b) 10^{-28} kg m s^{-1}
(c) 10^{-33} kg m s^{-1} (d) 10^{-40} kg m s^{-1}

7. Wave Functions and Probabilities

In quantum mechanics the probability density is given by the square modulus of the wave function, ψ:

$$|\psi(x)|^2 = \psi^*(x)\psi(x)\,.$$

see the **Complex Numbers** package for notation.

Quiz In a tunnelling process the wave function may have the form

$$\psi(x) = A\exp(-kx)$$

what is the probability density in this region?

(a) $A^2\exp(-2kx)$
(b) $A^2\exp(2kx)$
(c) $A\exp(kx)$
(d) $2A\exp(kx)$

Quiz If the wave function of a particle moving with a specific momentum in one dimension is $\psi(x,t) = A\exp(-i(kx-\omega t))$ what is its probability density?

(a) $A^2\exp(-(\omega t - kx)^2))$
(b) $A^2\exp(2(\omega t - kx))$
(c) A^2
(d) $A^2\exp(\omega t + kx)$

8. Quantum Quiz

Begin Quiz Choose the solutions from the options given.

1. Estimate the wavelength of a (visible) photon with $\nu = 6\times10^{10}$Hz.

(a) 5Å (b) 2×10^2m
(c) 5×10^{-3}m (d) 6nm

2. Estimate the de Broglie wavelength of 100 eV electrons.

(a) 4km (b) $.25 \times 10^{-6}$m
(c) 10^{-10}m (d) 1.6×10^{-3} Å

3. What is the minimum uncertainty in the momentum of a proton inside a nucleus of radius 1×10^{-15}m?

(a) $5 \times 10^{-20}\,\mathrm{kg\,m\,s^{-1}}$ (b) $3.3 \times 10^{-16}\,\mathrm{kg\,m\,s^{-1}}$
(c) $\hbar\,\mathrm{J\,s}$ (d) 0

4. If $E_l = \frac{\hbar^2}{2I} l(l+1)$ what is E_3/E_2?

(a) $18\hbar^4/I^2$ (b) $3/2$
(c) 2 (d) $6\hbar/I$

End Quiz Score: Correct

Solutions to Exercises

Exercise 1(a) First convert the wavelength into S.I. units:
$600\,\text{nm} = 600 \times 10^{-9} = 6 \times 10^{-7}\,\text{m}$

$$\begin{aligned} \nu &= c/\lambda \\ &= \frac{3 \times 10^{8}}{6 \times 10^{-7}} \\ &= \frac{3 \times 10^{15}}{6} \\ &= 5 \times 10^{14}\,\text{Hz} \end{aligned}$$

Click on the green square to return

Exercise 1(b)

$$\begin{aligned}\lambda &= \frac{c}{\nu} \\ &= \frac{3\times 10^8}{3\times 10^{18}} \\ &= 10^{-10}\,\mathrm{m}\end{aligned}$$

This very small scale, 1 Å, is comparable to atomic spacing in crystals and this fact is the basis of X-ray crystallography.

Click on the green square to return

Exercise 1(c) Note that the wavelength was given in μm! We need to first convert it into metres by dividing by a factor of 10^6, i.e., $\lambda = 1.5 \times 10^{-6}$m.

$$\begin{aligned} \nu &= c/\lambda \\ &= \frac{3 \times 10^8}{1.5 \times 10^{-6}} \\ &= 2 \times 10^{14}\text{Hz} \end{aligned}$$

Click on the green square to return □

Exercise 1(d)

$$\begin{aligned}\lambda &= \frac{c}{\nu} \\ &= \frac{3 \times 10^{8}}{3 \times 10^{21}} \\ &= 3 \times 10^{-13}\text{m}\end{aligned}$$

Click on the green square to return □

Solutions to Quizzes

Solution to Quiz: This frequency corresponds to $\lambda \approx 3 \times 10^{-8}\,\text{m}$. It is thus ultra-violet radiation, which is emitted by the sun.

End Quiz

Solution to Quiz:
Convert the gap into metres: $0.75\,\mathrm{nm} = 7.5 \times 10^{-10}\,\mathrm{m}$
So half this is $\frac{1}{2} \times 7.5 \times 10^{-10}\,\mathrm{m}$ and the equivalent frequency is:

$$\begin{aligned} \nu &= \frac{c}{\lambda} \\ &= \frac{3 \times 10^1 0}{\frac{1}{2} \times 7.5 \times 10^{-8}} \\ &= 8 \times 10^{17}\,\mathrm{Hz} \end{aligned}$$

End Quiz

Solution to Quiz:
We are told that $E = 2W$. Therefore $2W = h\nu - W$, so

$$h\nu = 3W$$

If we want to double the energy of the photoelectrons, then the new energy must be $E' = 4W$. This implies

$$h\nu' = 4W + W = 5W$$

So the necessary ratio of the frequencies is given by

$$\frac{h\nu'}{h\nu} = \frac{\nu'}{\nu} = \frac{5W}{3W} = \frac{5}{3}\,.$$

End Quiz

Solution to Quiz: First re-express the mass in S.I. units:
$m = 100/1000 = 0.1\,\mathrm{kg}$. Therefore

$$p = mv = 0.1 \times 2 = 0.2\mathrm{kg\,m\,s^{-1}}$$

and so

$$\begin{aligned} \lambda &= \frac{h}{p} \\ &= \frac{6.6 \times 10^{-34}}{0.2} \\ &\approx 3 \times 10^{-33}\mathrm{m} \end{aligned}$$

which is clearly much smaller than we can hope to measure.

End Quiz

Solution to Quiz: From $E = p^2/(2m)$, we have $p = \sqrt{2mE}$ and so

$$\lambda = \frac{h}{p} = \frac{6.6 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-16}}}$$

where we used that $1000\,\mathrm{eV} = 1.6 \times 10^{-16}\,\mathrm{J}$.

This corresponds to $\lambda \approx 0.4\,\text{Å}$. End Quiz

Solution to Quiz: If they have the same wavelengths, then they must have the same momentum, p. So their kinetic energies are given by

$$E_p = \frac{p^2}{2m_p} \qquad \text{and} \qquad E_e = \frac{p^2}{2m_e}$$

Thus their ratio is

$$\frac{E_p}{E_e} = \frac{m_e}{m_p} = \frac{1}{1836.15}$$

End Quiz

Solution to Quiz: We have to invert both sides of the given formula

$$\begin{aligned}\bar{\nu} = \frac{1}{\lambda} &= \frac{1}{K}\frac{n^2 - 4}{n^2} \\ &= \frac{1}{K}\left[1 - \frac{4}{n^2}\right]\end{aligned}$$

End Quiz

Solution to Quiz: We have the expression

$$\lambda = K\frac{n^2}{n^2 - 4}$$

and the smallest wavelength is found for the largest value of n, i.e., $n \to \infty$. For very large n the fraction tends to one and we get $\lambda = K$.

To obtain the largest wavelength we insert the smallest possible value of n, which, in the Balmer series, is $n = 3$. The fraction becomes $9/5$ and we have $\lambda = 9K/5$.

Note that the largest wavelength corresponds to a photon with enough energy to excite an electron into the next state, while a photon with the shortest wavelength in the series can eject an electron from the atom (ionisation).

End Quiz

Solution to Quiz:

If $E_J = \dfrac{h^2}{8\pi^2 I} J(J+1)$, then $E_{J+1} = \dfrac{h^2}{8\pi^2 I}(J+1)(J+2)$, so we have

$$\begin{aligned} E_{J+1} - E_J &= \frac{h^2}{8\pi^2 I}(J+1)(J+2) - \frac{h^2}{8\pi^2 I} J(J+1) \\ &= \frac{h^2}{8\pi^2 I}(J+1)\left[(J+2) - J\right] \\ &= \frac{h^2}{8\pi^2 I}(J+1)2 \\ &= \frac{h^2}{4\pi^2 I}(J+1) \end{aligned}$$

where we have factored out the common term $\dfrac{h^2}{8\pi^2 I}(J+1)$.

End Quiz

Solution to Quiz: The first term in all the answers is just the answer of the previous quiz. What we need to calculate is the difference between the correction terms, $-KJ^2(J+1)^2$. In the next level, $J \to J+1$, this term reads $-K(J+1)^2(J+2)^2$, so the difference is

$$\begin{aligned} -K(J+1)^2(J+2)^2 - \left(-KJ^2(J+1)^2\right) &= -K(J+1)^2(J+2)^2 \\ &\quad +KJ^2(J+1)^2 \end{aligned}$$

This can now be simplified using the techniques from the package on **Factorisation**

$$\begin{aligned} &= -K(J+1)^2\left[(J+2)^2 - J^2\right] \\ &= -K(J+1)^2\left[J^2+4J+4-J^2\right] \\ &= -K(J+1)^2(4J+4) \\ &= -4K(J+1)^3 \end{aligned}$$

where, to expand the quadratic, we used the FOIL technique (see the package on **Brackets**) End Quiz

Solution to Quiz: The consecutive energy levels are:

$$E_{n+1} = (\{n + 1\} - \frac{1}{2})h\nu = (n + \frac{1}{2})h\nu)$$

and

$$E_n = (n - \frac{1}{2})h\nu$$

so their difference is

$$\begin{aligned} E_{n+1} - E_n &= [n + \frac{1}{2} - (n - \frac{1}{2})]h\nu \\ &= [n + \frac{1}{2} - n + \frac{1}{2}]h\nu \\ &= h\nu \end{aligned}$$

This result is just the expression of the equal spacing of energy levels in such oscillators. End Quiz

Solution to Quiz: From the uncertainty principle

$$\Delta p \geq \frac{\hbar}{2\Delta x}$$

and since $\hbar \approx 10^{-34}\,\mathrm{J\,s}$ and Δx is given as $5 \times 10^{-7}\,\mathrm{m}$ the answer follows directly. This is incredibly tiny: for comparison the diameter of an atomic nucleus is about $10^{-14}\,\mathrm{m}$. End Quiz

Solution to Quiz: Here the wave function is real. So we just need to square it:

$$\begin{aligned} |\psi(x)|^2 &= A\exp(-kx) \times A\exp(-kx) \\ &= A^2\exp(-kx - kx) \\ &= A^2\exp(-2kx) \end{aligned}$$

where we used the rule $a^m a^n = a^{(m+n)}$, see the package on **Powers**.

End Quiz

Solution to Quiz: Here the wave function is complex. We replace $i \to -i$ to form its conjugate:

$$\psi^*(x,t) = A\exp(+i(kx - \omega t))$$

so multiplying ψ and ψ^* gives:

$$\begin{aligned} |\psi(x,t)|^2 &= A\exp(i(kx-\omega)) \times A\exp(-i(kx-\omega t)) \\ &= A^2\exp(0) \\ &= A^2 \end{aligned}$$

where we again used the rule $a^m a^n = a^{(m+n)}$.

Note that the probability density is independent of x and t, i.e., we have no information about where the particle is. This is a consequence of the uncertainty principle, since we know its momentum exactly and cannot know both quantities at once! End Quiz