Basic Mathematics

Mathematics & Quantum Theory

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

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The full range of these packages and some instructions, should they be required, can be obtained from our web page Mathematics Support Materials.

1. Electromagnetic Waves

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

Example 1

The frequency of BBC Radio 4 on FM is approximately 93MHz. 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 $\lambda = 600$nm
(b) X-rays with $\nu = 3 \times 10^{18}$ Hz
(c) Infra-red radiation with $\lambda = 1.5\mu$m
(d) Gamma rays with $\nu = 10^{21}$Hz

Quiz From the data above estimate which of the following might emit electromagnetic radiation with frequency $\nu = 10^{-16}$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 0.75nm, what frequency of X-ray would have a wavelength of half this size?

(a) 0.375Hz
(b) 3×10^{15}Hz
(c) 1.5×10^{16}Hz
(d) 2×10^{16}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 ($\approx 6 \times 10^{-34}$ 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, what energy have 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*.

Exercise 2. To see why we do not see the wave nature of normal matter around us:

(a) Calculate 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 $p = mv$.
(Click on the green letter for the solution.)

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

Example 3 In the first ever demonstration of electron diffraction, their wavelength was about 5×10^{-2}Å, what was their kinetic energy?

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

So from $E = p^2/(2m)$, we get

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

where we used that the electron mass is 9.1×10^{-31}kg. Recalling that $1\text{eV} = 1.6 \times 10^{19}$J, we see that, in more natural units, $E \approx 6 \times 10^4$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) $\frac{E_p}{E_e} = 5 \times 10^{-4}$

4. The Balmer Series

Quiz Balmer's original formula for part of the Hydrogen spectrum read

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

for $n = 3, 4 \ldots$. This can be also 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. E.g., 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 Vibrational modes in the simple harmonic oscillator have energies given by $E_n = (n + \frac{1}{2})h\nu$. What is the difference between two consecutive levels?

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

6. The Uncertainty Principle

One way to state Heisenberg's uncertainty principle is to note that the product of the uncertainty in the position, Δx, and and the uncertainty in the momentum, Δp must satisfy

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

where $\hbar = h/2\pi$.

Example 4 If an electron is bound in an atom of diameter roughly 1 Å what is the minimum uncertainty in its velocity?

Since its position is known up to a scale of 10^{-10} m, we have $\Delta x \approx 10^{-10}$ m. From the uncertainty principle we have

$$\begin{aligned} \Delta p &\geq \frac{\hbar}{2\Delta x} \\ &\geq 6.6 \times 10^{-24} \text{kgms}^{-1} \end{aligned}$$

Since the electron mass is 9.1×10^{-31}kg, and using $p = mv$, this yields an uncertainty in its velocity of $\Delta v = \Delta p/m = 7 \times 10^{6}\,\text{ms}^{-1}$.

Quiz If the uncertainty in the position of a body is 0.01m, which of the following is closest to the minimum uncertainty in its momentum?

(a) $0.01\,\text{kg m s}^{-1}$
(b) $10^{32}\,\text{kg m s}^{-1}$
(c) $10^{-32}\,\text{kg m s}^{-1}$
(d) $10^{-36}\,\text{kg m s}^{-1}$

7. Hueckel Theory

Hueckel theory is an approximation used in quantum chemistry to find the electron energy levels in molecules.

Quiz In ethylene Hueckel theory yields the quadratic equation:

$$(\alpha - W)^2 - \beta^2 = 0$$

which of the following expressions for α in terms of W and β is correct?

(a) $\sqrt{\beta^2 + W^2}$ (b) $W \pm \beta$
(c) $\beta - W$ (d) β / W

Quiz In butadiene Hueckel theory yields the equation:

$$x^4 - 3x^2 + 1 = 0$$

This is a quadratic equation in x^2 and can be solved using standard methods. What are the two roots in terms of x^2 to two decimal places?

(a) $(4.80\,,\ 1.20)$ (b) $(1.88\,,\ 4.12)$
(c) $(1.61\,,\ 0.62)$ (d) $(0.38\,,\ 2.62)$

8. Wave Functions and Probabilities

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

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

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) $A^2\exp(-2x)$
(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 $\psi(x,t) = A\exp(i(\omega t - kx))$ 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) $A^2\exp(\omega t + kx)$

9. 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. What is the de Broglie wavelength of 40keV electrons?

(a) 4km (b) $.25 \times 10^{-6}$m
(c) 10^{-15}m (d) 5×10^{-2}Å

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

(a) $2 \times 10^{-19}\,\mathrm{kg\,m\,s^{-1}}$ (b) $3.3 \times 10^{-16}\,\mathrm{kg\,m\,s^{-1}}$
(c) $\hbar$ (d) 0

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

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

End Quiz Score: Correct

Solutions to Exercises

Exercise 1(a) First convert the wavelength into SI 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)

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

This very small scale is comparable to atomic spacing in crystals and this 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 □

Exercise 2(a) First re-express the mass in SI units: $m = 100/1000 = 0.1\text{Kg}$. Therefore

$$p = mv = 0.1 \times 2 = 0.2\text{ms}^{-1}$$

and so

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

which is clearly much smaller than we can distinguish. Click on the green square to return

Solutions to Quizzes

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

End Quiz

Solution to Quiz:

Convert the gap into metres: $0.75\text{nm} = 7.5 \times 10^{-8}\text{m}$

So half this is $\frac{1}{2} \times 7.5 \times 10^{-8}\text{m}$ and the equivalent frequency is:

$$\begin{aligned}\nu &= \frac{c}{\lambda} \\ &= \frac{3 \times 10^{8}}{\frac{1}{2} \times 7.5 \times 10^{-8}} \\ &= 8 \times 10^{15}\text{Hz}\end{aligned}$$

End Quiz

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

$$h\nu = 3W$$

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

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

So the necessary ratio of the frequencies is

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

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 1000eV$= 1.6 \times 10^{-16}$J. This corresponds to $\lambda \approx 0.4\mathring{A}$.

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

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

Thus their ratio is

$$\frac{E_p}{E_e} = \frac{m_e}{m_p} = \frac{1}{1836.15} \approx 5 \times 10^{-4}$$

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 $\lambda = 9K/5$. End Quiz

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

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

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

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

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

where, to expand the quadratic, we used the FOIL technique (see the package on ???) 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

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

and since $\hbar \approx 10^{-34}$ Js and Δx is given as 0.01 m the answer follows directly. This is incredibly tiny. End Quiz

Solution to Quiz: Taking β^2 to the other side we get:

$$(A - W)^2 = \beta^2$$

upon taking the square root we have:

$$A - W = \pm\beta$$

and the result follows. End Quiz

Solution to Quiz: Let $x^2 = y$. The quadratic then reads:

$$y^2 - 3y + 1 = 0$$

Completing the square we write this as:

$$(y - \frac{3}{2})^2 + 1 - \frac{9}{4} = 0$$

and so

$$(y - \frac{3}{2})^2 = \frac{5}{4}$$

which implies

$$y = \frac{3}{2} \pm \sqrt{\frac{5}{4}} = \frac{3}{2} \pm \frac{\sqrt{5}}{2}$$

which immediately yields the result.

Note that x is then $\pm$ each of these two values, i.e., there are four allowed values of x. 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 $a^m a^n = a^{(m+n)}$. End Quiz

Solution to Quiz: Here the wave function is complex. Its conjugate is:

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

so multiplying ψ and ψ^* gives:

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

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. End Quiz