CHAPTER 7 
Introduction to quantum theory

TOPIC 7A  The origins of quantum mechanics

Discussion questions

7A.1 Summarize the evidence that led to the introduction of quantum mechanics.

7A.2 Explain how Planck’s introduction of quantization accounted for the properties of black-body radiation.

Exercises

7A.1(a) Calculate the size of the quantum involved in the excitation of (i) an electronic oscillation of period 1.0 fs, (ii) a molecular vibration of period 10 fs, (iii) a pendulum of period 1.0 s. Express the results in joules and kilojoules per mole.

7A.1(b) Calculate the size of the quantum involved in the excitation of (i) an electronic oscillation of period 2.5 fs, (ii) a molecular vibration of period 2.21 fs, (iii) a balance wheel of period 1.0 ms. Express the results in joules and kilojoules per mole.

7A.2(a) Calculate the energy per photon and the energy per mole of photons for radiation of wavelength (i) 600 nm (red), (ii) 550 nm (yellow), (iii) 400 nm (blue).

7A.2(b) Calculate the energy per photon and the energy per mole of photons for radiation of wavelength (i) 200 nm (ultraviolet), (ii) 150 pm (X-ray), (iii) 1.0 cm (microwave).

7A.3(a) Calculate the speed to which a stationary H atom would be accelerated if it absorbed each of the photons used in Exercise 7A.2(a).

7A.3(b) Calculate the speed to which a stationary He atom (mass 4.0026 amu) would be accelerated if it absorbed each of the photons used in Exercise 7A.2(b).

7A.4(a) A glow-worm of mass 5.0 g emits red light (650 nm) with a power of 0.1 W entirely in the backward direction. To what speed will it have accelerated after 10 y if released into free space and assumed to live? 10 years.

7A.4(b) A photon-powered spacecraft of mass 10.0 kg emits radiation of wavelength 225 nm with a power of 1.50 kW entirely in the backward direction. To what speed will it have accelerated after 100 y if released into free space?

7A.5(a) A sodium lamp emits yellow light (589 nm). How many photons does it emit each second if its power is (i) 1.0 W, (ii) 100 W?

7A.5(b) A laser used to read CDs emits red light of wavelength 700 nm. How many photons does it emit each second if its power is (i) 0.10 W, (ii) 1.0 W?

7A.6(a) The work function for metallic caesium is 2.14 eV. Calculate the kinetic energy and the speed of the electrons ejected by light of wavelength (i) 700 nm, (ii) 300 nm.

7A.6(b) The work function for metallic rubidium is 2.09 eV. Calculate the kinetic energy and the speed of the electrons ejected by light of wavelength (i) 650 nm, (ii) 195 nm.

7A.7(a) In an X-ray photoelectron experiment, a photon of wavelength 150 pm ejects an electron from the inner shell of an atom and it emerges with a speed of 21.4 Mms⁻¹. Calculate the binding energy of the electron.

7A.7(b) In an X-ray photoelectron experiment, a photon of wavelength 121 pm ejects an electron from the inner shell of an atom and it emerges with a speed of 56.9 Mms⁻¹. Calculate the binding energy of the electron.

7A.8(a) To what speed must an electron be accelerated for it to have a wavelength of 100 pm? What accelerating potential difference is needed?

7A.8(b) To what speed must a proton be accelerated for it to have a wavelength of 100 pm? What accelerating potential difference is needed?

7A.9(a) To what speed must an electron be accelerated for it to have a wavelength of 3.0 cm?

7A.9(b) To what speed must a proton be accelerated for it to have a wavelength of 3.0 cm?

7A.10(a) The fine-structure constant, α, plays a special role in the structure of matter; its approximate value is 1/137. What is the wavelength of an electron travelling at a speed c where c is the speed of light?

7A.10(b) Calculate the linear momentum of photons of wavelength 350 nm. What speed does a hydrogen molecule need to travel to have the same linear momentum?

7A.11(a) Calculate the de Broglie wavelength of (i) a mass of 1.0g travelling at 1.0 cm s⁻¹, (ii) the same, travelling at 1.00 km s⁻¹, (iii) an He atom travelling at 1000 m s⁻¹ (a typical speed at room temperature).

7A.11(b) Calculate the de Broglie wavelength of an electron accelerated from rest through a potential difference of (i) 100V, (ii) 1.0kV, (iii) 100kV.

Problems

7A.3 The Planck distribution gives the energy in the wavelength range dλ at the wavelength λ. Calculate the energy density in the range 650 nm to 655 nm inside a cavity of volume 100 cm³ when its temperature is (a) 25°C, (b) 3000°C.

7A.4 Demonstrate that the Planck distribution reduces to the Rayleigh–Jeans law at long wavelengths.

7A.5 Derive Wien's law, that λ_max T is a constant, where λ_max is the wavelength corresponding to maximum in the Planck distribution at the temperature T, and deduce an expression for the constant as a multiple of the second radiation constant, c_2 = h c / k.

7A.4 For a black body, the temperature and the wavelength of emission maximum, λ_max, are related by Wien's law, λ_max T = 1/2 c_2 where c_2 = h c / k (see Problem 7A.3). Values of λ_min from a small pinhole in an electrically heated container were determined at a series of temperatures, and the results are given in the following table. Deduce a value for Planck's constant.
<table>
<thead>
<tr>
<th>T (°C)</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
<th>2500</th>
<th>3000</th>
<th>3500</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ_p (nm)</td>
<td>2181</td>
<td>1600</td>
<td>1240</td>
<td>1035</td>
<td>878</td>
<td>763</td>
</tr>
</tbody>
</table>

Solar energy strikes the top of the Earth's atmosphere at a rate of about 100 W/m². About 30% of this energy is reflected directly back into space by the Earth or the atmosphere. The Earth-atmosphere system absorbs the remaining energy and re-radiates it into space as black-body radiation.

What is the average black-body temperature of the Earth? What is the wavelength of the most plentiful of the Earth's black-body radiation? Hint: Use Wien's law, Problem 7A.3.

Use the Planck distribution to deduce the Stefan–Boltzmann law that the total energy density of black-body radiation is proportional to T⁴, and find the constant of proportionality.

Prior to Planck's derivation of the distribution law for black-body radiation, Wien found empirically a closely related distribution function which is very nearly but not exactly in agreement with the experimental results, namely $P = (a/λ) e^{-a/λ}$. This formula shows small deviations from Planck's at long wavelengths. (i) By fitting Wien's empirical formula to Planck's short wavelengths determine the constants $a$ and $b$. (ii) Demonstrate that Wien's formula is consistent with Wien's law (Problem 7A.3) and with the Stefan–Boltzmann law (Problem 7A.6).

The temperature of the Sun's surface is approximately 5800 K. On the assumption that the human eye evolved to be most sensitive at the wavelength of light corresponding to the maximum in the Sun's radiant energy distribution, determine the colour of light to which the eye is most sensitive.

The Einstein frequency is often expressed in terms of an equivalent temperature $T_e$, where $T_e = hν/k$. Confirm that $T_e$ has the dimensions of temperature, and express the criterion for the validity of the high-temperature form of the Einstein equation in terms of $T_e$. Evaluate $T_e$ for (a) diamond, for which $ν = 46.5$ THZ and (b) copper, for which $ν = 7.15$ THZ. What fraction of the Dulong and Petit value of the heat capacity does each substance reach at 25°C?

### TOPIC 7B Dynamics of microscopic systems

#### Discussion questions

7B.1 Describe how a wavefunction summarises the dynamical properties of a system and how those properties may be predicted.

7B.2 Discuss the relation between probability amplitude, probability density, and probability.

#### Exercises

7B.3 (a) Consider a time-independent wavefunction of a particle moving in three-dimensional space. Identify the variables upon which the wavefunction depends.

7B.3 (b) Consider a time-dependent wavefunction of a particle moving in two-dimensional space. Identify the variables upon which the wavefunction depends.

7B.3 (c) Consider a time-independent wavefunction of a hydrogen atom. Identify the variables upon which the wavefunction depends. Use spherical polar coordinates.

7B.3 (d) Consider a time-dependent wavefunction of a helium atom. Identify the variables upon which the wavefunction depends. Use spherical polar coordinates.

#### Problems

7B.1 Normalize the following wavefunctions: (i) $\sin(n\pi x/L)$ in the range $0 \leq x \leq L$, where $n = 1, 2, 3, ...$ (this wavefunction can be used to describe delocalized electrons in a linear polylene), (ii) a constant in the range $-L \leq x \leq L$, (iii) $e^{-x}$ in three-dimensional space (this wavefunction can be used to describe the electron in the ion $He^+$), (iv) $x e^{-x^2}$ in three-dimensional space. Hint: The volume element in three dimensions is $dτ = r dr dθ dφ$, with $0 \leq r < \infty$, $0 \leq θ < π$, $0 \leq φ < 2π$. What is the probability of finding the light atom between $φ = π/2$ and $φ = 3π/2$?

7B.2 Two (unnormalized) excited state wavefunctions of the H atom are

\[ \psi(x) = \left(2 - \frac{x}{\alpha}\right) e^{-x/2\alpha} \]

(a) Normalize both functions to 1. (b) Confirm that these two functions are mutually orthogonal.

7B.3 A particle free to move along one dimension $x$ (with $0 \leq x < \infty$) is described by the unnormalized wavefunction $ψ(x) = e^{-αx}$ with $α = 2 \text{m}^{-1}$. What is the probability of finding the particle at a distance $x = 2\text{m}$?

7B.4 The ground-state wavefunction for a particle confined to a one-dimensional box of length $L$ is $ψ = (2/L)^{1/2} \sin(πx/L)$. Suppose the box is

\[ πr = (a/λ) e^{-a/λ} \]

These problems were supplied by Charles Trapp and Carmen Giunta.
10.0 nm long. Calculate the probability that the particle is (a) between $x=4.95$ nm and 5.05 nm, (b) between $x=1.95$ nm and 2.05 nm, (c) between $x=9.90$ nm and 10.00 nm, (d) in the right half of the box, (e) in the central third of the box.

**7B.5** The ground-state wavefunction of a hydrogen atom is $\psi = (l/\pi a_0) \frac{1}{2} e^{-r/a_0}$, where $a_0 = 53$ pm (the Bohr radius). (a) Calculate the probability that the electron will be found somewhere within a small sphere of radius 1.0 pm centred on the nucleus. (b) Now suppose that the same sphere is located at $r = a_0$. What is the probability that the electron is inside it?

**7B.6** Atoms in a chemical bond vibrate around the equilibrium bond length. An atom undergoing vibrational motion is described by the wavefunction $\psi(x) = \text{Ne}^{-x^2/2\lambda^2}$, where $\lambda$ is a constant and $-$a < x < a. (a) Normalize this function. (b) Calculate the probability of finding the particle in the range $-a < x < a$. Hint: The integral encountered in part (ii) is the error function. It is provided in most mathematical software packages.

**7B.7** Suppose that the state of the vibrating atom in Problem 7B.6 is described by the wavefunction $\psi(x) = \text{Nxe}^{-x^2/2a^2}$. Where is the most probable location of the particle?

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**TOPIC 7C** The principles of quantum theory

**Discussion questions**

**7C.1** Suggest how the general shape of a wavefunction can be predicted without solving the Schrödinger equation explicitly.

**7C.2** Describe the relationship between operators and observables in quantum mechanics.

**Exercises**

**7C.1** (a) Construct the potential energy operator of a particle subjected to a harmonic oscillator potential (see Topic 8B). (b) Construct the potential energy operator of a particle subjected to a Coulomb potential.

**7C.2** (a) Confirm that the kinetic energy operator $-(\hbar^2/2m)d^2/dx^2$, is hermitian. (b) The operator corresponding to the angular momentum of a particle is $(\hbar/2i)d/d\phi$. Is this operator hermitian?

**7C.3** (a) Functions of the form $\sin(n\pi x/L)$ can be used to model the wavefunctions of electrons in a carbon nanotube of length $L$. Show that the wavefunctions $\sin(n\pi x/L)$ and $\sin(m\pi x/L)$, where $n \neq m$, are orthogonal for a particle confined to the region $0 \leq x \leq L$. (b) Functions of the form $\cos(n\pi x/L)$ can be used to model the wavefunctions of electrons in metals. Show that the wavefunctions $\cos(n\pi x/L)$ and $\cos(m\pi x/L)$, where $n \neq m$, are orthogonal for a particle confined to the region $0 \leq x \leq L$.

**7C.4** (a) An electron in a one-dimensional metal of length $L$ is described by the wavefunction $\psi(x) = \text{N}\cos(n\pi x/L)$. Compute the expectation value of the momentum of the electron. (b) A light atom rotating around a heavy atom to which it is bonded is described by a wavefunction of the form $\psi(\phi) = e^{i\phi}$ with $0 \leq \phi \leq 2\pi$. If the operator corresponding to angular momentum is given by $(\hbar/2i)d/d\phi$, compute the expectation value of the angular momentum of the light atom.

**7C.6** (a) Calculate the minimum uncertainty in the speed of a ball of mass 500 g that is known to be within 1.0 μm of a certain point on a bat. What is the minimum uncertainty in the position of a bullet of mass 3.0 g that is known to have a speed somewhere between 350.000.01 m s$^{-1}$ and 350.000.00 m s$^{-1}$? (b) An electron is confined to a linear region with a length of the same order as the diameter of an atom (about 100 pm). Calculate the minimum uncertainties in its position and speed.

**7C.7** (a) The speed of a certain proton is 0.45 Ms$^{-1}$. If the uncertainty in its momentum is to be reduced to 0.0100 per cent, what uncertainty in its location must be tolerated? (b) The speed of a certain electron is 995 km s$^{-1}$. If the uncertainty in its momentum is to be reduced to 0.0010 per cent, what uncertainty in its location must be tolerated?

**7C.8** (a) Determine the commutators of the operators $i\hbar d/dx$ and $1/x$, (ii) $d/dx$ and $x^2$.

**7C.9** (a) An electron in a carbon nanotube of length $L$ is described by the wavefunction $\psi(x) = (2/L)\sin(n\pi x/L)$. Compute the expectation value of the kinetic energy of the electron. (b) An electron in a carbon nanotube of length $L$ is described by the wavefunction $\psi(x) = (2L)^{1/2}\sin(n\pi x/L)$. Compute the expectation value of the kinetic energy of the electron.

**Problems**

**7C.1** Write the time-independent Schrödinger equations for (a) an electron moving in one dimension about a stationary proton and subjected to a Coulomb potential, (b) a free particle, (c) a particle subjected to a constant, uniform force.

**7C.2** Construct quantum mechanical operators for the following observables: (a) kinetic energy in one and three dimensions, (b) the inverse separation, (c) electric dipole moment in one dimension, (d) the mean square deviations of the position and momentum of a particle in one dimension from the mean values.

**7C.3** Identify which of the following functions are eigenfunctions of the operator $d/dx$: (a) $e^{ikx}$, (b) $k$, (c) $kx$, (d) $e^{-ikx}$. Give the corresponding eigenvalue where appropriate.
4. Determine which of the following functions are eigenfunctions of the momentum operator $i\frac{\partial}{\partial x}$ which has the effect of making the replacement $x \rightarrow -x$:
(a) $x^2$, (b) $\cos x$, (c) $x^2 + 3x - 1$. State the eigenvalue of $i$ when relevant.

5. Which of the functions in Problem 7C.3 are (a) also eigenfunctions of $\frac{d^2}{dx^2}$ and (b) only eigenfunctions of $i\frac{d}{dx}$? Give the eigenvalues where appropriate.

6. Show that the product of a hermitian operator with itself is also a hermitian operator.

7. Calculate the average linear momentum of a particle described by the following wavefunctions: (a) $e^{i\phi}$, (b) $\cos kx$, (c) $e^{-\frac{1}{2}k^2}$, where in each case $x$ ranges from $-\infty$ to $+\infty$.

8. The normalized wavefunctions for a particle confined to move on a circle are $\phi_m(\theta) = (1/2\pi)^{1/2} e^{im\theta}$, where $m = 0, \pm 1, \pm 2, \pm 3, \ldots$ and $0 \leq \rho \leq 2\pi$. Determine $\phi_m$.

9. A particle freely moving in one dimension with $0 \leq x < \infty$ is in a state described by the wavefunction $\psi(x) = \alpha x^3 e^{-\beta x^2}$, where $\alpha$ is a constant. Determine the expectation value of the position operator.

10. The wavefunction of an electron in a linear accelerator is $\psi(x) = \chi_0 e^{ikx} + \sin \chi_0 e^{-i\chi_0}$, where $k$ is a parameter. (i) What is the probability that the electron will be found with a linear momentum (a) $+kh$, (b) $-kh$? (c) What form would the wavefunction have if it were 90 per cent certain that the electron had linear momentum $+kh$? (c) Evaluate the kinetic energy of the electron.

11. Two (unnormalized) excited state wavefunctions of the H atom are (i) $\psi = (2 - r/a_0)e^{-r/2a_0}$, and (ii) $\psi = r\sin \theta \cos \theta e^{-r/2a_0}$. (a) Normalize both functions to 1. (b) Confirm that these two functions are mutually orthogonal. (c) Evaluate the expectation values of $r$ and $r^2$ for the atom.

12. The ground-state wavefunction of a hydrogen atom is $\psi = (1/\pi a_0)^{1/2} e^{-r/\alpha_0}$, where $a_0$ is a constant and $0 \leq r < \infty$. Calculate (a) the mean potential energy and (b) the mean kinetic energy of an electron in the ground state of a hydrogenic atom.

13. Show that the expectation value of an operator that can be written as the square of an hermitian operator is positive.

14. A particle is in a state described by the wavefunction $\psi(x) = (2a)^{1/4} e^{-x^2}$, where $a$ is a constant and $0 \leq x < \infty$. Verify that the value of the product $\Delta x \Delta p$ is consistent with the predictions from the uncertainty principle.

15. A particle is in a state described by the wavefunction $\psi(x) = (2a)^{1/4} e^{-x^2}$, where $a$ is a constant and $0 \leq x < \infty$. Determine the expectation value of the commutator of the position and momentum operators.

16. Evaluate the commutators (a) $[\hat{H}, \hat{p}_x]$ and (b) $[\hat{H}, \hat{x}]$ where $\hat{H} = \hat{p}_x^2/2m + V(x)$. Choose (i) $V(x) = V_0$, a constant, (ii) $V(x) = \frac{1}{2} k x^2$.

17. (a) Given that any operators used to represent observables must satisfy the commutation relation in eqn 7C.16, what would be the operator for position if the choice had been made to represent linear momentum parallel to the x-axis by multiplication by the linear momentum. These different choices are all valid 'representations' of quantum mechanics. (b) With the identification of $x$ in this representation, what would be the operator for $1/x$? Hint: Think of $1/x$ as $x^{-1}$.

### Integrated activities

2.4 A star too small and cold to shine has been found by S. Kulkarni et al. (Science 270, 1478 (1995)). The spectrum of the object shows the presence of methane which, according to the authors, would not exist at temperatures much above 1000 K. The mass of the star, as determined from its gravitational effect on a companion star, is roughly 20 times the mass of Jupiter. The star is considered to be a brown dwarf, the coolest ever found. (a) From available thermodynamic data, test the stability of methane at temperatures above 1000 K. (b) What is $L_{\text{eff}}$ for this star? (c) What is the energy density of the star relative to that of the Sun (6000 K)? (d) To determine whether the star will shine, estimate the fraction of the energy density of the star in the visible region of the spectrum.

7.2 Suppose that the wavefunction of an electron in a carbon nanotube is a linear combination of $\cos(nx)$ functions. (a) Use mathematical software, a spreadsheet, or the Living graphs on the web site of this book to construct superpositions of cosine functions as

$$\psi(x) = \frac{1}{N} \sum_{n=1}^{N} \cos(k_n x)$$

where the constant $1/N$ is introduced to keep the superpositions with the same overall magnitude. Set $x = 0$ at the centre of the screen and build the superposition there. (b) Explore how the probability density $\psi^2(x)$ changes with the value of $N$. (c) Evaluate the root mean square location of the packet, $(x^2)^{1/2}$. (d) Determine the probability that a given momentum will be observed.