Answer ALL SIX questions from Section A and THREE questions from Section B.

The numbers in square brackets at the right-hand margin indicate the provisional allocation of marks per sub-section of a question.

You may assume the following value:

$$\text{Planck constant } h = 6.63 \times 10^{-34}\,\text{J s}; \ \hbar = 1.05 \times 10^{-34}\,\text{J s}$$

<div align="center">

SECTION A

</div>

[Part marks]

1. What relationship did de Broglie suggest between the wavelength of a matter wave and the momentum of the corresponding particles? [2]

   Briefly and qualitatively describe *one* experiment that provided confirmation of de Broglie's hypothesis via interference of matter waves. [5]

2. Explain what is meant by the requirement that the wavefunction of a one-dimensional quantum system be *normalized*. How is this requirement connected to the relationship between the wavefunction and the probability density? [3]

   Find a possible value for the constant C such that the wavefunction

$$\psi(x) = Cx \exp(-\beta x^2)$$

   is correctly normalized. [4]

   [*You may use the following result:*

$$\int_{-\infty}^{\infty} x^2 \exp(-x^2/a^2)\,\mathrm{d}x = \frac{\sqrt{\pi}a^3}{2}.]$$

3. What is meant by the *zero-point energy* of a quantum simple harmonic oscillator, and how is it related to the classical frequency of that oscillator? [3]

   Calculate the zero-point energy of a one-dimensional molecular vibration having a classical frequency $\nu = 10^{13}\,\text{Hz}$. [3]

4. Define the *eigenvalues* and *eigenfunctions* of a linear operator. [3]

   According to the postulates of quantum mechanics, what role do the eigenvalues and eigenfunctions of an operator play when the corresponding quantity is measured? [4]

5. What is meant by the *commutator* $[\hat{A}, \hat{B}]$ of two operators $\hat{A}$ and $\hat{B}$? **[3]**

By defining the position and momentum operators in the x-direction as

$$\hat{x} = x; \qquad \hat{p}_x = -i\hbar \frac{\partial}{\partial x},$$

show that

$$[\hat{x}, \hat{p}_x] = i\hbar.$$

[4]

6. What is value of the the spin quantum number s for an electron? **[1]**

What is the value of the orbital angular momentum quantum number l for an electron in the 4f state of hydrogen? **[1]**

What are the possible values of the total angular momentum quantum number j that could be produced by combining these orbital and spin angular momenta? What is the range of total magnetic quantum numbers m_j associated with each possibility? **[4]**

SECTION B

7. Consider a particle of mass m moving in one dimension in an infinite square well, such that its potential energy is

$$V(x) = \begin{cases} 0 & \text{if } -a < x < +a \\ +\infty & \text{otherwise.} \end{cases}$$

Write down the time-independent Schrödinger equation for the particle when it is inside the well ($-a < x < +a$), and find its general solution. [5]

State the boundary conditions that the wave-function $\psi(x)$ has to satisfy at $x = \pm a$, and hence find the wave-function of the lowest energy eigenstate $\psi_1(x)$, and the corresponding energy E_1. [5]

Normalize the wavefunction ψ_1, and hence write down the probability density per unit length of finding the particle near position x in this state. [3]

Suppose the particle has wavefunction $\psi_1(x)$ when the potential is suddenly changed, so that the well now extends from $x = -2a$ to $x = +2a$. Using your previous results, write down the lowest-energy normalized wavefunction $\phi_1(x)$ in the new well (you do not need to repeat the detailed working). [2]

The expansion postulate of quantum mechanics states that the original wavefunction may be expanded in terms of the normalized energy eigenfunctions $\{\phi_n(x)\}$ of the new well as

$$\psi_1(x) = \sum_{n=1}^{\infty} a_n \phi_n(x).$$

Evaluate the coefficient a_1 in this expansion. [3]

Hence show that, if the particle's energy is measured immediately after the well has changed, the probability the particle is found in the lowest-energy state of the new (larger) well is $64/(3\pi)^2$. [2]

[*You may use the following integrals in your answer:*

$$\int_{-\pi/2}^{\pi/2} \cos^2\theta \, \mathrm{d}\theta = \frac{\pi}{2};$$
$$\int_{-\pi/2}^{\pi/2} \cos\theta \cos(\theta/2) \, \mathrm{d}\theta = \frac{4\sqrt{2}}{3}.]$$

8. What is the definition of a *Hermitian operator*? [3]

Show that the function $f_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp(\mathrm{i}m\phi)$ (where ϕ is the azimuthal angle about the z-axis) is an eigenfunction of the angular momentum operator $\hat{L}_z$, and find the corresponding eigenvalue. (An expression for $\hat{L}_z$ is given at the end of the question.) [3]

Why must m be an integer in order for this to be a physically acceptable eigenfunction? [2]

Show the functions f_m are orthogonal for different values of m, and are normalized so that

$$\int_0^{2\pi} \mathrm{d}\phi \, [f_m(\phi)]^* f_{m'}(\phi) = \delta_{m,m'},$$

where $\delta_{m,m'} = 0$ if $m \neq m'$, and 1 if $m = m'$. [3]

Suppose a particle has the wave-function

$$g(\phi) = \sqrt{\frac{1}{5\pi}}[\cos\phi + 2\sin(2\phi)].$$

By inspection, or otherwise, write $g(\phi)$ as a linear combination of eigenfunctions of $\hat{L}_z$. [4]

Hence state what the possible results of a measurement of L_z in this state would be, and what would be the corresponding probabilities of obtaining each one (given that $g(\phi)$ is correctly normalized). [5]

[*The operator $\hat{L}_z$ can be written in spherical polar coordinates as*

$$\hat{L}_z = -\mathrm{i}\hbar\frac{\partial}{\partial\phi}.]$$

9. (a) What is meant by the *expectation value* of an observable quantity O in quantum mechanics? How can it be calculated from a knowledge of the corresponding operator $\hat{O}$ and the wave-function, ψ, of the system? [5]

Calculate the expectation value of the one-dimensional kinetic energy operator

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

in the state

$$\psi(x) = (2\beta/\pi)^{1/4}\exp(-\beta x^2).$$

You may assume ψ is correctly normalized. You may also use the results:

$$\int_{-\infty}^{\infty} \exp(-x^2/a^2)\,\mathrm{d}x = \sqrt{\pi}a; \qquad \int_{-\infty}^{\infty} x^2\exp(-x^2/a^2)\,\mathrm{d}x = \frac{\sqrt{\pi}a^3}{2}.$$

[6]

It may be shown, from the time-dependent Schrödinger equation, that for an operator $\hat{O}$ that does not explicitly depend on time, the time-derivative of the expectation value is

$$\frac{\mathrm{d}\langle\hat{O}\rangle}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar}\langle[\hat{O},\hat{H}]\rangle.$$

Consider the case where $\hat{O}$ is the momentum operator

$$\hat{p}_x = -\mathrm{i}\hbar\frac{\partial}{\partial x},$$

and where $\hat{H}$ is the one-dimensional Hamiltonian for a particle of mass m moving in a potential $V(x)$:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + V(x).$$

By considering the action of $[\hat{p}_x, \hat{H}]$ on a general state, show that

$$[\hat{p}_x, \hat{H}] = -\mathrm{i}\hbar\frac{\mathrm{d}V}{\mathrm{d}x}.$$

Hence find an expression for the rate of change of $\langle\hat{p}_x\rangle$. [6]

How does your result show that classical and quantum mechanics are connected in the limit where the uncertainty in momentum becomes negligible? [3]

10. A particle of mass m moving in one dimension has potential energy $V(x) = \frac{1}{2}m\omega_0^2 x^2$. Explain the significance of the quantity ω_0 in classical mechanics. **[2]**

Write down the time-independent Schrödinger equation for this system. State the energy eigenvalues of this system according to quantum mechanics. **[4]**

Verify that

$$\psi_0 \propto \exp(-m\omega_0 x^2/2\hbar) \quad \text{and} \quad \psi_1 \propto x\exp(-m\omega_0 x^2/2\hbar),$$

are both solutions of the time-independent Schrödinger equation, and find the corresponding energy eigenvalues. **[4]**

What are the corresponding solutions of the *time-dependent* Schrödinger equation? **[2]**

The particle is initially prepared in the state

$$\Psi(x,0) = (a + bx)\exp(-m\omega_0 x^2/2\hbar),$$

where a and b are real constants chosen in such a way that Ψ is correctly normalized. Show that after a time t has elapsed, the probability density per unit length of finding the particle near position x is

$$[a^2 + b^2 x^2 + 2abx\cos(\omega_0 t)]\exp(-m\omega_0 x^2/\hbar).$$

[5]

For the case where a and b are both positive, sketch this probability density at (a) $t = 0$, (b) $t = \pi/\omega_0$; (c) $t = 2\pi/\omega_0$. **[3]**

11. Write down the three-dimensional time-independent Schrödinger equation for the electron in a hydrogen atom, using atomic units ($\hbar = m_e = e^2/(4\pi\epsilon_0) = 1$) and spherical polar coordinates (r, θ, ϕ), under the assumption of a fixed and point-like nucleus. [3]

Write the wavefunction as $\psi(r, \theta, \phi) = R(r)Y_l^m(\theta, \phi)$ (where Y_l^m is a spherical harmonic). Hence show that if the radial wavefunction R is written as

$$R(r) = \frac{\chi(r)}{r},$$

then $\chi(r)$ satisfies the equation

$$\frac{-1}{2}\frac{d^2\chi}{dr^2} + \left[\frac{l(l+1)}{2r^2} - \frac{1}{r}\right]\chi = E\chi. \tag{1}$$

(An expression for the operator ∇^2 in spherical polar coordinates is given at the end of the question.) [5]

Show that far from the atom (i.e. as $r \to \infty$) the possible solutions to equation (1) for a bound state ($E < 0$) are

$$\chi(r) \propto \exp(\pm\kappa r),$$

and show how κ is related to the energy E. [4]

Which one of these solutions is physically acceptable, and why? [2]

Verify that the hydrogen 2s wave-function (in atomic units)

$$\chi_{2s}(r) = rR_{2s}(r) = 2^{-1/2}r\left(1 - \frac{r}{2}\right)\exp(-r/2)$$

is a solution to equation (1) with $l = 0$, and calculate the corresponding energy E. [4]

What is the probability density per unit volume (once again, in atomic units) for finding an electron in the 2s state of hydrogen at the position of the nucleus ($r = 0$)?

[2]

[*The $l = 0$, $m = 0$ spherical harmonic is $Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$. The Laplacian operator in spherical polar coordinates can be written as*

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] - \frac{\hat{L}^2}{r^2},$$

where $\hat{L}^2$ is the operator representing the square of the total angular momentum and atomic units have been used.]