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 values:

Planck constant $h = 6.63 \times 10^{-34}\,\mathrm{J\,s}$; $\hbar = 1.05 \times 10^{-34}\,\mathrm{J\,s}$;
Electronic charge $e = 1.60 \times 10^{-19}\,\mathrm{C}$;
Mass of electron $m_e = 9.11 \times 10^{-31}\,\mathrm{kg}$;

SECTION A

[Part marks]

1. The time-dependent Schrödinger equation for a particle moving in one dimension can be written
$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x,t)\Psi(x,t) = \mathrm{i}\hbar\frac{\partial\Psi}{\partial t}.$$
Define the quantities V and Ψ appearing in this equation. **[3]**

   Give an expression involving *one* of the above quantities for the probability that the particle may be found in a small region of space between the positions x and $x + \delta x$. **[3]**

2. The function
$$\psi(x) = C\mathrm{e}^{\mathrm{i}kx},$$
where C and k are constants, is a solution to the time-independent Schrödinger equation for a particle moving in free space in one dimension.

   How is the quantity k related to the de Broglie wavelength of the particle? **[2]**

   The function $\psi(x)$ is an eigenfunction of the momentum operator
$$\hat{p} = -\mathrm{i}\hbar\frac{\partial}{\partial x}.$$
By substituting $\psi(x)$ into the defining equation for an eigenfunction, find the corresponding eigenvalue. **[4]**

3. Let the functions $\{\phi_n\}$ be the eigenfunctions of some Hermitian operator. Explain what is meant if it is stated that this set of functions is *orthonormal.* **[4]**

   The expansion postulate allows us to express an arbitrary function ψ in terms of such a set of eigenfunctions. What is the general form of such an expression? (You are *not* required to evaluate the quantities appearing in it.) **[3]**

4. Define the *commutator* of two operators $\hat{A}$ and $\hat{B}$. **[3]**

   Explain the physical significance of the operators $\hat{L}^2$ and $\hat{L}_z$ in quantum mechanics. **[2]**

   These two operators are *compatible*; what does this mean, and what can you deduce about their commutator? (Detailed mathematical working is *not* required.) **[3]**

5. The *true* potential energy of an electron in a hydrogen atom depends only on its distance from the nucleus. What are the consequences of this fact for the solution of the Schrödinger equation in this system? **[3]**

   The *effective* potential for an electron in a state of orbital angular momentum l in a hydrogen atom can be written as

$$V_{\text{eff}}(r) = \frac{-e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2m_e r^2},$$

   where m_e is the electron mass. What is the physical significance of the two terms in this effective potential? **[4]**

6. In a Stern-Gerlach experiment, a beam of sodium atoms is passed through an inhomogeneous magnetic field. Explain why atoms are attracted into the strong-field or weak-field regions, according to the directions of their magnetic moments. **[2]**

   The experiment divides the atoms into groups according to the value of the z component of the angular momentum of the outermost electron. How many such groups are there? **[2]**

   According to the theory of spin in quantum mechanics, these groups correspond to different values of the quantum number m_s. What are the possible values of m_s for an electron? **[2]**

SECTION B

7. State the condition for the wave function of a particle moving in one dimension to be correctly normalized. **[2]**

At a certain instant a particle has the wave function

$$\psi(x) = \begin{cases} C(a^2 - x^2) & |x| \leq a; \\ 0 & |x| > a. \end{cases}$$

Find a suitable value of the constant C so that ψ obeys the normalization condition. **[4]**

What is the probability that the particle is found between $x = 0$ and $x = a$? **[4]**

The expectation value of an operator $\hat{O}$ in one dimension can be written

$$\langle \hat{O} \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{O} \psi(x) \, \mathrm{d}x.$$

What is the physical significance of the expectation value? **[2]**

Calculate the expectation values of the following quantities, using the normalized wave function $\psi(x)$. You may wish to make use of symmetry arguments where possible to simplify the working.

(a) The position $\hat{x}$; **[2]**

(b) The momentum $\hat{p}$; **[2]**

(c) The kinetic energy $\hat{p}^2/2m$, where m is the particle's mass. **[4]**

8. A particle of mass m moves in a finite one-dimensional rectangular well, located between $x = -a$ and $x = +a$, such that the potential is

$$V(x) = \begin{cases} 0 & (|x| \leq a); \\ V_0 & (|x| > a), \end{cases} \qquad \text{with} \quad V_0 > 0.$$

Sketch a graph of the potential $V(x)$. **[2]**

The time-independent Schrödinger equation inside the well is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \quad (|x| \leq a).$$

Write down the general solution to this equation for positive energies E in terms of the wavenumber k. How is k related to E? **[4]**

What is the Schrödinger equation in the barrier region $|x| > a$? **[2]**

Assuming the energy E is less than V_0, the general solution in the barrier regions can be written

$$\psi(x) = C\mathrm{e}^{\kappa x} + D\mathrm{e}^{-\kappa x}, \quad (|x| > a)$$

where C and D are arbitrary constants. Find the value of the constant κ in terms of the energy E, and show that

$$k^2 + \kappa^2 = k_0^2, \quad \text{where} \quad \frac{\hbar^2 k_0^2}{2m} = V_0.$$

[4]

Consider the right-hand barrier region ($x > a$). One of the two terms in the general solution can be ruled out on physical grounds; which is it, and why? **[3]**

What *two* conditions do the solutions for ψ in the different regions have to satisfy at the edges of the well $x = \pm a$? **[2]**

In the case of even solutions where $\psi(x) = \psi(-x)$, these two conditions can be shown to require that

$$k\tan(ka) = \kappa = \sqrt{k_0^2 - k^2}.$$

Suppose the particle concerned is an electron. Working in atomic units ($\hbar = m_e = 1$) find the depth V_0 of a well having $a = 1$ unit, given that it possesses an even stationary state with energy $E = 0.125$ units. **[3]**

9. To which physical quantity does the Hamiltonian operator $\hat{H}$ correspond in quantum mechanics? Write down the form of the Hamiltonian for a particle moving in one dimension in a time-independent potential, and give the equation defining an eigenfunction ψ_n of the Hamiltonian and its corresponding eigenvalue E_n. **[4]**

A solution of the full time-*dependent* Schrödinger equation can be constructed by taking

$$\Psi_n(x,t) = \exp(-\mathrm{i}E_n t/\hbar)\psi_n(x).$$

By substituting into the time-dependent Schrödinger equation, show that any linear combination of two such solutions, in the form $c_1\Psi_1(x,t) + c_2\Psi_2(x,t)$ where c_1 and c_2 are constants, is also a solution. **[4]**

In atomic units and spherical polar coordinates, the 1s and 2s stationary-state wave functions of the electron in a hydrogen atom can be written respectively as

$$\psi_{1s}(r,\theta,\phi) = 2\mathrm{e}^{-r}Y_{00}(\theta,\phi); \quad \psi_{2s}(r,\theta,\phi) = \frac{1}{\sqrt{2}}(1-\frac{r}{2})\mathrm{e}^{-r/2}Y_{00}(\theta,\phi).$$

What are the corresponding energies E_{1s} and E_{2s}, also in atomic units? Hence write down the corresponding time-dependent solutions $\Psi_{1s}(r,\theta,\phi,t)$ and $\Psi_{2s}(r,\theta,\phi,t)$. **[4]**

Suppose the electron's wave function at time $t=0$ is

$$\Psi(r,\theta,\phi,t=0) = \frac{1}{3}\psi_{1s}(r,\theta,\phi) + \frac{2\sqrt{2}}{3}\psi_{2s}(r,\theta,\phi).$$

What is the wave function at subsequent times t? **[4]**

Hence show that the probability per unit volume (in atomic units) of finding the electron near the nucleus (at $r=0$) varies with time as

$$|\Psi(r=0,\theta,\phi,t)|^2 = \frac{4}{9\pi}\cos^2\left(\frac{3t}{16}\right).$$

[4]

[The $(l=0, m=0)$ spherical harmonic is $Y_{00}(\theta,\phi) = 1/\sqrt{4\pi}$. The energy eigenvalue of a hydrogen-atom stationary state having principal quantum number n is $E_n = -1/2n^2$, in atomic units. You may assume that

$$\hbar = 1; \quad m_e = 1; \quad \frac{e^2}{4\pi\epsilon_0} = 1$$

in atomic units.]

10. (a) In spherical polar coordinates, the operator $\hat{L}_z$ can be written

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

Show that any function of the azimuthal angle ϕ of the form

$$f_m(\phi) = C\mathrm{e}^{\mathrm{i}m\phi}$$

is an eigenfunction of $\hat{L}_z$; find the corresponding eigenvalue, and explain why m must be an integer. **[4]**

(b) Now look for eigenfunctions of the operator $\hat{L}^2$, having eigenvalue λ, which are also eigenfunctions of $\hat{L}_z$, in the following way. Try a solution of the form,

$$Y(\theta,\phi) = \Theta(\theta)\mathrm{e}^{\mathrm{i}m\phi},$$

and show that

(i) Y is indeed still an eigenfunction of $\hat{L}_z$; **[2]**

(ii) The unknown function Θ obeys the equation **[4]**

$$-\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + m^2\Theta = \frac{\lambda}{\hbar^2}\sin^2\theta\Theta.$$

(c) The solutions to this equation which are finite at $\theta = 0$ and $\theta = \pi$ are the associated Legendre functions

$$\Theta(\theta) = P_l^m(\cos\theta);$$

the eigenvalues are $\lambda = l(l+1)\hbar^2$, where l is a non-negative integer ($l = 0, 1, 2, \ldots$). Using the information about these functions given below, identify the values of l and m, and the corresponding eigenvalues of $\hat{L}_z$ and $\hat{L}^2$, for the following two eigenfunctions (which are not normalized): **[6]**

$$Y^{(1)} = \sin\theta\mathrm{e}^{\mathrm{i}\phi}; \quad Y^{(2)} = \sin\theta\mathrm{e}^{-\mathrm{i}\phi}.$$

(d) The angular part of a particle's wave-function is given by

$$\psi(\theta,\phi) = A + B\sin\theta\cos\phi.$$

What would be the possible results of measuring the particle's total orbital angular momentum $\hat{L}^2$ and its z-angular momentum $\hat{L}_z$? **[4]**

[The operator $\hat{L}^2$ can be written in spherical polar coordinates as

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right].$$

You may use without proof the expressions

$$P_0^0(\cos\theta) = 1; \quad P_1^{\pm1}(\cos\theta) = \sqrt{1-\cos^2\theta} = \sin\theta; \quad P_1^0(\cos\theta) = \cos\theta$$

for the first few associated Legendre functions.]

11. Consider a particle of mass m moving freely in two dimensions but confined within a rectangular box by infinitely high potential walls at $x = \pm a$ and $y = \pm b$.

(a) Write down the time-independent Schrödinger equation satisfied by the wave function $\psi(x, y)$ inside the box (i.e. for $-a \leq x \leq a; -b \leq y \leq b$). (You may take the value of the potential energy to be zero in this region.) **[4]**

(b) Write down the boundary conditions obeyed by ψ at the edges of the box, explaining the reasons for them. **[4]**

(c) Show that, by writing

$$\psi(x, y) = X(x)Y(y),$$

you can separate the Schrödinger equation into one part depending only on x and one part only on y. Hence show that

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = E_xX,$$

where E_x is a constant whose origin you should explain, and find a corresponding equation satisfied by Y. **[5]**

(d) Solve the equations for X and Y, subject to the boundary conditions you found in part (b). **[4]**

(e) Hence show that the lowest energy eigenvalue of the system is

$$\frac{\hbar^2\pi^2}{8m}\left[\frac{1}{a^2} + \frac{1}{b^2}\right]$$

Give an expression for the corresponding ground-state wave function $\psi(x, y)$. (It need not be normalized.) **[3]**