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:

SECTION A

[Part marks]

1. What relationship did de Broglie postulate between the wavelength of a matter-wave and the momentum of the corresponding particle? **[2]**

   The function
   $$\psi(x) = A\exp(\mathrm{i}kx)$$
   is a solution to the time-independent Schrödinger equation for a free particle of mass m moving in one dimension. How is k related to the de Broglie wavelength? **[1]**

   If the potential energy V is zero everywere, substitute the state ψ into the Schrödinger equation to find the total energy E. Show that your result gives the kinetic energy, assuming de Broglie's hypothesis is correct. **[3]**

2. Write down the time-*dependent* Schrödinger equation for a particle of mass m moving in one dimension in a potential V and wavefunction $\Psi(x, t)$. **[2]**

   Assuming that the potential V is independent of time, find the equation satisfied by the function $\psi(x)$ such that
   $$\Psi(x, t) = \psi(x)\exp(-\mathrm{i}Et/\hbar)$$
   is a solution of the time-dependent Schrödinger equation. **[3]**

   Show that, if Ψ_1 and Ψ_2 are both solutions of the time-dependent Schrödinger equation, so is $c_1\Psi_1 + c_2\Psi_2$ (where c_1 and c_2 are arbitrary constants). **[2]**

3. The expansion postulate says that any function $\psi(x)$ can be expanded in terms of the complete set of eigenfunctions $\phi_n(x)$ of a Hermitian operator $\hat{O}$ in the form

$$\psi(x) = \sum_n c_n \phi_n(x).$$

If the ϕ_n form an orthonormal set and ψ is normalized so

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1,$$

what (according to the postulates of quantum mechanics) is the connection between the coefficients c_n and the probabilities of obtaining different results when the physical quantity corresponding to $\hat{O}$ is measured? (A derivation is *not* required.) **[3]**

Show that in these circumstances the expansion coefficients c_n must satisfy the condition

$$\sum_n |c_n|^2 = 1.$$

[3]

4. The spherical harmonics $Y_l^m(\theta, \phi)$ are simultaneously eigenfunctions of which two angular momentum operators? **[2]**

Give the corresponding eigenvalues of the two operators in terms of the quantum numbers l and m. **[2]**

For a given l, what are the allowed values of m? Give an interpretation of the range of allowed m values within the vector model of angular momentum. **[4]**

5. Far from the nucleus, and in atomic units, the radial part of the Schrödinger equation for a hydrogen atom can be written

$$-\frac{1}{2}\frac{\mathrm{d}^2\chi}{\mathrm{d}r^2} = E\chi.$$

For a bound state ($E < 0$), write down two independent solutions of this equation in terms of the quantity $\kappa = \sqrt{2|E|}$. **[2]**

Which one of your two solutions is physically admissable, and why? **[2]**

What is the energy of the ground state of a hydrogen atom in atomic units? Give also the corresponding value of κ, in atomic units. **[2]**

6. When spin is introduced into quantum physics, the state of an electron is characterized by two new quantum numbers: s and m_s. What is the physical significance of these quantum numbers? **[2]**

One of these quantum numbers always takes the same value for all states of a single electron; which is it? **[1]**

Briefly describe *one* piece experimental evidence for the accepted value of this quantum number. **[4]**

SECTION B

7. A particle of mass m moves in one dimension in an infinite square well extending from $x = -a$ to $x = +a$. Inside the well the potential is zero. Write down the time-independent Schrödinger equation for the particle when it is inside the well, and find the most general solution in this region. **[5]**

What are the boundary conditions on the wave function at $x = \pm a$? By applying these boundary conditions, find the energies and wavefunctions for the square well's *even* stationary states, i.e. those having $\psi(x) = \psi(-x)$. **[5]**

For the case of the ground state (the lowest-energy solution) normalize the wavefunction so that

$$\int_{-\infty}^{\infty} |\psi|^2 \, \mathrm{d}x = 1.$$

[3]

The *expectation value* of a an operator $\hat{O}$ in a quantum system with wavefunction $\psi(x)$ can be written as

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

What is the significance of the expectation value in relation to the results of measurements of $\hat{O}$? **[2]**

Using your normalized wavefunction, calculate the expectation value in the ground state of (i) momentum $\hat{p}$, (ii) position $\hat{x}$, (iii) position squared $\hat{x}^2$. **[5]**

You may use without proof the results

$$\int_{-\pi/2}^{\pi/2} \cos^2\theta \, \mathrm{d}\theta = \frac{\pi}{2}; \qquad \int_{-\pi/2}^{\pi/2} \theta^2 \cos^2\theta \, \mathrm{d}\theta = \frac{\pi}{24}(\pi^2 - 6).$$

8. A beam of particles with mass m and energy E is incident from the left on a potential step of height V_0 such that

$$V(x) = \begin{cases} 0 & (x \leq 0) \\ V_0 & (x > 0). \end{cases}$$

Sketch the potential $V(x)$. **[1]**

Assuming that $E > V_0 > 0$ and that the incident beam is normalized so it contains one particle per unit length, write down appropriate solutions for the time-independent Schrödinger equation (a) for $x \leq 0$, (b) for $x > 0$, in terms of the quantities k and k' defined by

$$\frac{\hbar^2 k^2}{2m} = E; \qquad \frac{\hbar^2 k'^2}{2m} = E - V_0.$$

Pay special attention to which terms in your solutions are allowed by the boundary conditions. **[4]**

Write down the matching conditions that must be satisified by the wavefunction at $x = 0$, and use them to find the unkown coefficients in your wave-function. **[6]**

By using your results to compare the probability fluxes in the reflected and incident beams, show that the reflection probability for the particles from the potential step is

$$R = \frac{(k - k')^2}{(k + k')^2}.$$

[3]

For the case where the incident energy is $E = 4V_0/3$, find k' in terms of k. Hence show that to the left of the step ($x \leq 0$) the probability per unit length for finding a particle is $10/9 + 2\cos(2kx)/3$. Also find an expression for the probability per unit length on the right of the step ($x > 0$). **[6]**

[For a stationary state $\psi(x)$ in one dimension, the probability flux is

$$\Gamma(x) = \frac{-i\hbar}{2m}\left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right] = \frac{\hbar}{m}\mathrm{Im}[\psi^* \frac{\partial \psi}{\partial x}]$$

at position x.]

9. Starting from the classical definition of angular momentum $\mathbf{L} = \mathbf{r}\times\mathbf{p}$, show that the quantum mechanical operators for the x- and z-components of angular momentum are

$$\hat{L}_x = -\mathrm{i}\hbar\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]; \quad \hat{L}_z = -\mathrm{i}\hbar\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right].$$

[4]

Verify that the state $\psi = Cxf(r)$, where C is a constant and f is any function of $r = \sqrt{x^2+y^2+z^2}$, is an eigenfunction of $\hat{L}_x$, and find the corresponding eigenvalue. **[3]**

Find the angular part $g(\theta,\phi)$ of the function ψ, using the normal definition of spherical polar coordinates, and show that if we choose $C = \sqrt{\frac{3}{4\pi}}$ then g is normalized so

$$\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \sin\theta\,\mathrm{d}\theta\,|g|^2 = 1.$$

[5]

The completeness postulate implies that g can be expanded in terms of the spherical harmonics

$$g(\theta,\phi) = \sum_{lm} a_{lm} Y_l^m(\theta,\phi),$$

where the a_{lm} are constant expansion coefficients. By inspecting your expression for $g(\theta,\phi)$ and comparing with the expressions given below for the spherical harmonics Y_l^m, find these expansion coefficients. **[4]**

Hence calculate the possible results of measuring the operators $\hat{L}^2$ and $\hat{L}_z$ in the state ψ, and the corresponding probabilities. **[4]**

[You may assume the results

$$\frac{\partial r}{\partial y} = \frac{y}{r}; \quad \frac{\partial r}{\partial z} = \frac{z}{r}; \quad \int_0^{\pi}\sin^3\theta\,\mathrm{d}\theta = \frac{4}{3}; \quad \int_0^{2\pi}\cos^2\phi\,\mathrm{d}\phi = \pi,$$

and the expressions for the following spherical harmonics Y_l^m*:*

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta; \quad Y_1^1 = -\sqrt{\frac{3}{8\pi}}\sin\theta\exp(\mathrm{i}\phi); \quad Y_1^{-1} = \sqrt{\frac{3}{8\pi}}\sin\theta\exp(-\mathrm{i}\phi).$$

Remember that $\cos\phi = [\exp(\mathrm{i}\phi) + \exp(-\mathrm{i}\phi)]/2$.*]*

10. The time-independent Schrödinger equation for the electron in a hydrogen atom, in atomic units, is

$$-\frac{1}{2}\nabla^2\psi - \frac{1}{r}\psi = E\psi.$$

If a solution ψ is written in spherical polar coordinates (r, θ, ϕ) as

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi),$$

show by substituting into the Schrödinger equation that the angular function Y is an eigenfunction of the total (orbital) angular momentum $\hat{L}^2$. **[5]**

If we neglect spin and all relativistic effects, the allowed energies are determined by a single principal quantum number n. What are the allowed values of n, and what range of l values is found for each value of n? **[3]**

Hence show, again neglecting spin and using the formula for the sum of an arithmetic progression given below, that the total number of solutions to the time-independent Schrödinger equation with the same energy (and hence the same value of n) is

$$\sum_{l=0}^{l=n-1}(2l+1) = n^2.$$

[3]

How does this total number of states change when the electron's spin is accounted for? **[2]**

Including spin, the change in the atom's Hamiltonian when an external magnetic field $(0, 0, B)$ applied in the z-direction is

$$\Delta\hat{H} = \frac{\mu_B B}{\hbar}(\hat{L}_z + g\hat{S}_z),$$

where μ_B is the Bohr magneton, $\hat{L}_z$ and $\hat{S}_z$ are respectively the z-components of the orbital and spin angular momentum of the electron. Taking $g = 2$, explain how the 2p energy levels of a hydrogen atom are split in the presence of such a magnetic field. **[5]**

What are the possible values of the total angular momentum quantum number j that could be obtained by combining the spin and orbital angular momenta for such a 2p electron? **[2]**

[The Laplacian operator may be written in spherical polar coordinates (using atomic units) as

$$\nabla^2 = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left[r^2\frac{\mathrm{d}}{\mathrm{d}r}\right] - \frac{\hat{L}^2}{r^2}.$$

The sum of N terms of an arithmetic progression having first term a and last term b is $N(a+b)/2$.]

11. State the relationship between the eigenfunctions and eigenvalues of an operator $\hat{O}$, and explain their role in quantum mechanics when the physical quantity corresponding to $\hat{O}$ is measured. **[5]**

Two operators $\hat{Q}$ and $\hat{R}$ are said to be *compatible* if they share the same eigenfunctions $\{\phi_n\}$. Use the expansion postulate applied to an arbitrary function ψ to show that

$$[\hat{Q}, \hat{R}]\psi = 0$$

for any pair of compatible operators. **[4]**

According to the measurement postulate of quantum mechanics, what happens if $\hat{Q}$ is measured, followed immediately by a measurement of a compatible quantity $\hat{R}$ and then a further measurement of $\hat{Q}$? (You may assume that the eigenvalues of $\hat{Q}$ and the eigenvalues of $\hat{R}$ are all different.) **[4]**

Which pairs of operators from the set $\{\hat{L}^2, \hat{L}_x, \hat{L}_z\}$ are compatible with one another? **[2]**

An electron in a hydrogen atom is initially in the state

$$\psi = \frac{1}{\sqrt{2}}(\psi_{2,1,1} + \psi_{2,0,0}),$$

where $\psi_{n,l,m}$ denotes the normalized wavefunction with quantum numbers n, l and m. What happens if first $\hat{L}^2$ is measured, then $\hat{L}_z$, and finally $\hat{L}^2$ again? At each stage, give the possible outcomes of the measurement and the associated probabilities, and the state in which the system is left after the measurement. **[5]**