ONE HOUR THIRTY MINUTES

A list of constants is enclosed.

UNIVERSITY OF MANCHESTER

Introduction to Quantum Mechanics

16th January 2024, 2.00 p.m. - 3.30 p.m.

Answer **ALL** parts of question 1 and **TWO** other questions

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The use of calculators is permitted, as long as they cannot store text or perform algebra, and have no graphing capability.

The numbers are given as a guide to the relative weights of the different parts of each question.

Formula Sheet

In plane polar coordinates, (r, ϕ), the Laplacian operator is given by

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\,,$$

and the angular momentum operator is given by

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

In spherical polar coordinates, (r, θ, ϕ), the Laplacian operator is given by

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2}\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial \theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\,,$$

and the angular momentum operators are given by

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

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

You may use the following integral without proof:

$$\int_0^\infty x^n\,\mathrm{e}^{-x}\,\mathrm{d}x = n! \quad \text{for integer } n \geq 0.$$

1. a) A particle of mass m is moving in two dimensions in a potential $V(\mathbf{r})$. Write down the time-independent Schrödinger equation of the particle. Explain any symbols you have used.

[4 marks]

b) i) Write down the definition of the momentum operator $\hat{p}_x$ in one dimension. Show that the function

$$\psi(x) = e^{i\alpha x},$$

with constant α, is an eigenfunction of $\hat{p}_x$. Determine the eigenvalue of $\psi(x)$.

ii) A particle is moving in one-dimensional free space and is described by a spatial function

$$\phi(x) = \cos(\beta x),$$

where β is a constant. What are the possible outcomes of a measurement of the particle's momentum and what are their probabilities?

[5 marks]

c) Two operators, $\hat{A}$ and $\hat{B}$, can act on wavefunctions Ψ. Define the commutator of the two operators and explain what the expression $[\hat{A}, \hat{B}]\Psi$ represents.

Show that the commutator of the position and momentum operators in one dimension is given by

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

What is the implication of this result for measurements of these quantities?

[6 marks]

d) Diatomic molecules of nitric oxide gas, NO, absorb infrared light of wavelength $5.4 \times 10^{-6}\,\mathrm{m}$. Use this to estimate the effective spring constant of the bond in a nitric oxide molecule.

You may assume that the atomic masses of nitrogen and oxygen are 14.0 and 16.0 respectively.

[5 marks]

e) Sketch the hydrogen energy-level diagram up to $n = 3$.

Explain which transitions are allowed between these states by the emission or absorption of a single photon and indicate these on your diagram.

Explain why the $2s$ state is much longer-lived than any of the other excited states.

[5 marks]

2. The Hamiltonian operator for a particle moving in three dimensions in a central potential $V(r)$ is given by

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(r).$$

a) Use this, and information on the Formula Sheet, to show that the total angular momentum operator, $\hat{L}^2$, and its component, $\hat{L}_z$, both commute with this Hamiltonian. Explain the physical consequence of these commutations.

[5 marks]

b) Consider separable energy eigenfunctions,

$$\psi(r,\theta,\phi) = R(r)Y_\ell^m(\theta,\phi),$$

where the spherical harmonics $Y_\ell^m(\theta,\phi)$ are eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$.

i) Show that the radial function $R(r)$ depends on the angular momentum quantum number ℓ. Write down the energy eigenvalue equation satisfied by $R(r)$.

[5 marks]

ii) Explain why the ϕ dependence of $Y_\ell^m(\theta,\phi)$ must be equal to $\mathrm{e}^{im\phi}$, where m is an integer.

[3 marks]

c) The Hamiltonian of a three-dimensional simple harmonic oscillator of classical angular frequency ω and mass m is given by

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + \frac{1}{2}m\omega^2 r^2.$$

i) Show that the function $\psi_0(r,\theta,\phi) = A\,\mathrm{e}^{-r^2/2a^2}$ is an eigenfunction of $\hat{L}^2$ and $\hat{L}_z$, and write down its eigenvalues.
Show that this function is also an energy eigenfunction, provided $a = \sqrt{\hbar/m\omega}$, and calculate its energy.

[7 marks]

ii) Show that the function $\psi_1(r,\theta,\phi) = B\,r\sin\theta\cos\phi\,\mathrm{e}^{-r^2/2a^2}$ is an eigenfunction of $\hat{L}^2$ and calculate its eigenvalue.
Show that this function is not an eigenfunction of $\hat{L}_z$.
If a system was in the state described by ψ_1 and the value of L_z was measured, what values could be obtained?

[5 marks]

3. a) Consider the following wavefunctions of a hydrogen atom

$$\begin{aligned}
\psi_A(r,\theta,\phi) &= A\frac{r}{a_0}\mathrm{e}^{-r/2a_0}\sin\theta\,\mathrm{e}^{i\phi}, \\
\psi_B(r,\theta,\phi) &= B\frac{r}{a_0}\left(6-\frac{r}{a_0}\right)\mathrm{e}^{-r/3a_0}\sin\theta\,\mathrm{e}^{i\phi}, \\
\psi_C(r,\theta,\phi) &= C\left(\frac{r}{a_0}\right)^2\mathrm{e}^{-r/3a_0}\sin\theta\cos\theta\,\mathrm{e}^{i\phi},
\end{aligned}$$

where A, B, C and a_0 are constants.

i) Deduce by inspection the values of the quantum numbers (n, ℓ, m_ℓ) for each of these eigenfunctions.

[6 marks]

ii) Show that the states ψ_A, ψ_B and ψ_C are all orthogonal to each other.

[6 marks]

b) Explain why deuterium (the hydrogen isotope with atomic mass = 2) has a different ground state energy to standard hydrogen (with atomic mass = 1). Calculate the ratio of their ground state energies.

[3 marks]

c) The spin-orbit coupling operator $\hat{V}_{\mathrm{SO}}$ for a hydrogen atom is given by

$$\hat{V}_{\mathrm{SO}} = f(r)\hat{\mathbf{S}}\cdot\hat{\mathbf{L}}\,,$$

with the function $f(r)$ defined as

$$f(r) = \frac{\alpha\hbar}{2m_e^2 c}\frac{1}{r^3},$$

where $\alpha = 1/137$ and all symbols have their usual meanings.

i) The hydrogen atom is in the $3d$ state. Determine the possible values of the total angular momentum quantum number j. Hence determine the eigenvalues of the operator $\hat{\mathbf{S}}\cdot\hat{\mathbf{L}}$.

[6 marks]

ii) Estimate the spin-orbit energy splitting in eV between the states with the j values found in Part (i).
You may use the result that the expectation value for the $3d$ state of hydrogen is

$$\left\langle\frac{1}{r^3}\right\rangle = \frac{1}{405a_0^3},$$

where a_0 is the Bohr radius.

[4 marks]

4. a) Briefly state the physical meanings of the quantum numbers (n, ℓ, m_ℓ, m_s) of a hydrogen atom. Specify their values for a hydrogen atom in its ground state, and their allowed values for excited states.

[5 marks]

b) The operator $\hat{P}$ is defined for a system containing two identical particles as the operator that exchanges all properties (position $\mathbf{r}$ and spin $\mathbf{s}$) of the two particles:

$$\hat{P}\Psi(\mathbf{r}_1, \mathbf{s}_1, \mathbf{r}_2, \mathbf{s}_2) = \Psi(\mathbf{r}_2, \mathbf{s}_2, \mathbf{r}_1, \mathbf{s}_1),$$

for which you may use the shorthand $\hat{P}\Psi(1, 2) = \Psi(2, 1)$.

i) Find the eigenvalues of $\hat{P}$.

[5 marks]

ii) Which of the eigenvalues in Part (i) do electron states have?
If two electrons are in a state with separable position and spin wavefunctions,

$$\Psi(\mathbf{r}_1, \mathbf{s}_1, \mathbf{r}_2, \mathbf{s}_2) = \psi(\mathbf{r}_1, \mathbf{r}_2)\chi(\mathbf{s}_1, \mathbf{s}_2),$$

what does this eigenvalue imply about the functions ψ and χ?

[2 marks]

iii) In a helium atom, the spin wavefunction of the two electrons can be anti-symmetric (parahelium) or symmetric (orthohelium).
Write down the ground-state electronic configurations of parahelium and orthohelium. Which has the lower energy? Explain why.

[5 marks]

iv) In both orthohelium and parahelium, an electronic configuration $(1s)(2s)$ is possible. Which has the lower energy? Explain why.

[5 marks]

c) Explain why the ground state electronic configuration of lithium, Li, is $(1s)^2(2s)$.

[3 marks]

END OF EXAMINATION PAPER