ONE HOUR THIRTY MINUTES

A list of constants is enclosed.

UNIVERSITY OF MANCHESTER

Introduction to Quantum Mechanics

18th January 2023, 9:45a.m. - 11:15a.m.

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

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Electronic calculators may be used, provided that they cannot store text.

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) Electrons with a kinetic energy of 3 eV are passing through a slit of width 1.2 nm. Are the wave properties of these electrons important? Give your reason.

[3 marks]

b) A particle is in the following mixed state

$$\Psi(x,t) = \frac{1}{\sqrt{5}}\Psi_1(x,t) + \frac{2}{\sqrt{5}}\Psi_2(x,t),$$

where $\Psi_n(x,t) = \psi_n(x)\mathrm{e}^{-iE_nt/\hbar}$ are stationary states.

What are the possible outcomes of a measurement of the particle's energy?

Determine the expectation value of the energy of the particle.

[4 marks]

c) Specify the allowed values of the quantum numbers (n, ℓ, m_ℓ, m_s) of a hydrogen atom. Briefly state their physical meanings.

Calculate how many different states have the same quantum number n.

Explain briefly why different states with the same value of n do not all have the same energy.

[7 marks]

d) State the definition of the Hermitian conjugate, $\hat{A}^\dagger$, of an operator $\hat{A}$, and the definition of a Hermitian operator.

Show that the momentum operator $\hat{p}_x$ is a Hermitian operator.

[7 marks]

e) Write down the atomic ground-state electronic configuration of carbon ($Z = 6$). Determine the total S, L and J of its ground state and write down the corresponding spectroscopic term symbol.

[4 marks]

2. a) Consider a 1D simple quantum harmonic oscillator of classical angular frequency ω. Draw on one sketch, the potential energy function, energy levels, and wavefunctions of the three lowest energy states.

[8 marks]

b) Vibrations of a diatomic molecule such as carbon monoxide can be considered to be approximately simple harmonic. With the help of a sketch of the potential energy as a function of the distance between a carbon atom and an oxygen atom, explain why this is the case.

What feature of this function determines the effective spring constant?

Explain briefly why the bond energy (the energy required to separate the atoms in a diatomic molecule from each other) is different quantum mechanically from the one that would be expected from a classical calculation with the same potential energy function.

[6 marks]

c) Now consider a 1D oscillator consisting of a mass on a spring that can be extended elastically, but not compressed, corresponding to a potential energy function:

$$V(x) = \begin{cases} \frac{1}{2}m\omega^2 x^2 & \text{if } x > 0, \\ \infty & \text{if } x \leq 0. \end{cases}$$

Write down the full set of energy eigenvalues of this oscillator and sketch the eigenfunction of its ground state. Find the first excitation energy (i.e. the difference between the energies of the ground state and first excited state). Briefly state the reasoning behind your results.

[6 marks]

d) One of the energy eigenfunctions of a 2D simple harmonic oscillator is given by

$$\psi_{1,0} = A\frac{x}{a}\exp\left(\frac{-(x^2+y^2)}{2a^2}\right),$$

where A and a are constants. By writing the Cartesian coordinates x and y in plane polar coordinates, show that this is not an eigenfunction of angular momentum.

Determine the values of angular momentum that could be obtained from a measurement of this state.

[5 marks]

3. a) Use the following commutation relations

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z, \quad \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x, \quad \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y,$$

to show that $\left[\hat{L}^2, \hat{L}_z\right] = 0$. What is the significance of this result?

Explain why $\hat{L}^2$ and $\hat{L}_z$ also commute with the Hamiltonian for a central potential.

[7 marks]

b) Use the expression for $\hat{L}^2$ in spherical polar coordinates on the Formula Sheet to show that the spherical harmonic

$$Y(\theta, \phi) = \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \, \mathrm{e}^{i\phi}$$

is an eigenfunction of $\hat{L}^2$ and find the corresponding eigenvalue.

[8 marks]

c) Consider the following wavefunctions of a hydrogen atom

$$\begin{aligned}
\psi_A(r, \theta, \phi) &= A\,\mathrm{e}^{-r/a_0}, \\
\psi_B(r, \theta, \phi) &= B\left(1 - \frac{r}{2a_0}\right)\mathrm{e}^{-r/2a_0}, \\
\psi_C(r, \theta, \phi) &= C\left(\frac{r}{a_0}\right)^2 \mathrm{e}^{-r/3a_0} \sin\theta \cos\theta \, \mathrm{e}^{i\phi},
\end{aligned}$$

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.

[4 marks]

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

[2 marks]

d) A lithium atom has three electrons. Use your knowledge of the energy levels and eigenfunctions of hydrogen to explain why:

The first ionization energy of lithium (the energy required to remove one electron from a neutral lithium atom) is around 5 eV;

The last ionization energy of lithium (the energy required to remove the one remaining electron from a Li^{2+} ion) is around 120 eV.

[4 marks]

4. a) The total angular momentum operator is given by

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}},$$

where $\hat{\mathbf{L}}$ is the orbital angular momentum operator and $\hat{\mathbf{S}}$ is the spin operator.

Explain how the quantum numbers that describe $\hat{\mathbf{J}}$ are related to those that describe $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$.

[5 marks]

b) For a state specified by fixed values of ℓ and s, show that the number of (m_ℓ, m_s) combinations is $(2\ell+1)(2s+1)$.

Show that the number of (j, m_j) combinations is also $(2\ell+1)(2s+1)$.

[6 marks]

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

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

with the function $f(r)$ given by

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

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

i) The hydrogen atom is in the $2p$ 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 between states with the j values you found in Part (i). You may use the result that the expectation value for the $2p$ state of hydrogen is

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

where a_0 is the Bohr radius.

[4 marks]

d) The magnetic energy operator for an electron in a magnetic field B, pointing in the z direction, is approximately

$$\hat{V}_{mag} = \frac{eB}{2m_e}\left(\hat{L}_z + 2\hat{S}_z\right).$$

Use this to discuss the number of energy levels the $2p$ orbital of hydrogen is broken into by both strong and weak magnetic fields.

[4 marks]

END OF EXAMINATION PAPER