ONE HOUR THIRTY MINUTES

A list of constants is enclosed.

UNIVERSITY OF MANCHESTER

Introduction to Quantum Mechanics

99th January 2022, ?.?? p.m. - ?.?? p.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

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

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

1. a) i) The normalized wavefunction of a particle moving in one dimension is Ψ. Consider an operator $\hat{A}$ associated with a physical measurement, A.
Write down the definition of the expectation value of $\hat{A}$.
Briefly describe the physical meaning of this value and how it is related to the outcomes of particular measurements of A.

[5 marks]

ii) Write down the definition of the Hermitian conjugate, $\hat{A}^\dagger$, of the operator $\hat{A}$.
Show that this definition results in the relation $\left(\hat{A}\hat{B}\right)^\dagger = \hat{B}^\dagger\hat{A}^\dagger$.

[5 marks]

b) A quantum rotor has a moment of inertia of $5 \times 10^{-48}\,\mathrm{kg\,m^2}$. What are the values of the three lowest rotational energy eigenvalues, in eV? What is the degeneracy of each of these three energy levels?

[5 marks]

c) A helium atom has states in which each of the two electrons can be in $1s$, $2s$ or $2p$ orbitals.
Explain how the occupation of these states is affected by the spins of the two electrons.
Explain why the ground state of helium has a total electron spin of $S = 0$.
Explain why the first excited state is $(1s)(2s)$ rather than $(1s)(2p)$.

[5 marks]

d) Write down the atomic ground-state electronic configurations of titanium ($Z = 22$) and nickel ($Z = 28$). Determine the total S, L and J of each of their ground states and write down the corresponding spectroscopic term symbols.

[5 marks]

2. a) Consider a 1D simple quantum harmonic oscillator of classical angular frequency ω.

i) Draw on one sketch, the potential energy function, energy levels, and wavefunctions of the three lowest energy states.

[8 marks]

ii) Calculate the value of the zero-point energy of the oscillator if its classical angular frequency is $2.0 \times 10^{13}\,\mathrm{s}^{-1}$.

[2 marks]

iii) If the particle in the quantum harmonic oscillator is charged, transitions between energy levels can involve the absorption or emission of a single photon.
Explain how the frequency of this photon is related to the classical frequency of the oscillator.

[3 marks]

iv) In a carbon monoxide (CO) molecule, the effective spring constant of the covalent bond has a value of $1860\,\mathrm{N\,m^{-1}}$. Estimate the first excitation energy for vibrational motion of a CO molecule.
You may take the atomic masses of carbon and oxygen to be 12.0 and 16.0 respectively.

[5 marks]

b) Now consider a 2D simple quantum harmonic oscillator of classical angular frequency ω.

i) Write down the general form of a single-valued eigenfunction, $\Phi(\phi)$, of the angular momentum operator $\hat{L}_z$,

$$\hat{L}_z \Phi(\phi) = L_z \Phi(\phi),$$

where ϕ is the polar angle, and state the corresponding value of L_z.

[2 marks]

ii) The following are all energy eigenfunctions of the 2D quantum harmonic oscillator with the same energy, $3\hbar\omega$:

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

$$\psi_{1,1} = B\frac{xy}{a^2} \mathrm{e}^{-(x^2+y^2)/2a^2},$$

where A, B and a are constants. By writing the Cartesian coordinates x and y in plane polar coordinates, show that these states are not eigenfunctions of angular momentum.
Show that they can all be written as superpositions of states with $L_z = 2\hbar$, 0 and $-2\hbar$.

[5 marks]

3. a) For a particle of mass m moving in one dimension, write down the definition of the momentum operator $\hat{p}_x$ and derive the kinetic energy operator $\hat{T}$.
The particle is moving in a region of free space with a wavefunction

$$\psi(x) = A\cos kx,$$

where A and k are constants. Show that $\psi(x)$ is not an eigenfunction of $\hat{p}_x$ but is an eigenfunction of $\hat{T}$.
What are the possible outcomes of a measurement of the particle's momentum?

[9 marks]

b) The magnetic energy operator for an electron in a magnetic field B, pointing in the z direction, is given by

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

where g is the gyromagnetic ratio of the electron, which we will take to be equal to 2, and the other symbols have their usual meanings.

i) When the magnetic field is strong, the quantum numbers m_ℓ and m_s can be assumed to be good quantum numbers. Use this to calculate how many energy levels the $2p$ orbital of hydrogen is split into, in a strong magnetic field.
Calculate the spacing between these energy levels. You may state your answer in terms of Bohr magnetons, or electronvolts.

[4 marks]

ii) When the magnetic field is weak, the quantum numbers m_ℓ and m_s are not good quantum numbers. Explain what this means and why it is the case.
What are the good quantum numbers in this case?

[4 marks]

iii) When the magnetic field is weak, the magnetic energy operator is equivalent to

$$\hat{V}_{mag} = \frac{eB}{2m_e}\, g_L \hat{J}_z,$$

where g_L is the Landé factor,

$$g_L = 1 + \frac{j(j+1) + s(s+1) - \ell(\ell+1)}{2j(j+1)}.$$

For the $2p$ orbital of hydrogen, what values of j are allowed?
For each of these j values, calculate the spacing between the magnetic energy levels. You may state your answer in terms of Bohr magnetons, or electronvolts.

[6 marks]

iv) How would you decide if a given value of magnetic field would be considered "strong" or "weak" in this context?
You do not need to provide a quantitative calculation.

[2 marks]

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

$$\begin{aligned}\psi_A(r,\theta,\phi) &= A\,\mathrm{e}^{-r/a_0},\\ \psi_B(r,\theta,\phi) &= B\left(1-\frac{r}{2a_0}\right)\mathrm{e}^{-r/2a_0},\\ \psi_C(r,\theta,\phi) &= C\left(\frac{r}{a_0}\right)^3\mathrm{e}^{-r/4a_0}\sin^2\theta\cos\theta\,\mathrm{e}^{2i\phi},\end{aligned}$$

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) Sketch the radial probability distribution $P(r)$ corresponding to the wavefunction ψ_B.

[4 marks]

iii) Show that the states ψ_A, ψ_B and ψ_C are all orthogonal to one another. *You may use the result* $\int_0^\infty x^n\,\mathrm{e}^{-x}\,\mathrm{d}x = n!$ *for integer* $n \geq 0$.

[4 marks]

b) i) Write down the quantum operators for the angular momentum components $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$, in terms of $\hat{x}$ and $\hat{p}_x$, etc.

[3 marks]

ii) Given the following commutation relation,

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

use the cyclic rule to write down the other two commutation relations between the angular momentum component operators. Hence show that

$$\left[\hat{L}_z, \hat{L}^+\right] = \hbar\hat{L}^+, \qquad (1)$$

where $\hat{L}^+ = \hat{L}_x + i\hat{L}_y$.

[5 marks]

iii) Use Eq. (1) to show that the wavefunction defined by

$$\hat{L}^+\psi_C,$$

where ψ_C is given in part (a), is also an eigenfunction of $\hat{L}_z$. Find its eigenvalue.

[5 marks]

END OF EXAMINATION PAPER