ONE HOUR THIRTY MINUTES

A list of constants is enclosed.

UNIVERSITY OF MANCHESTER

Introduction to Quantum Mechanics

17 January 2020, 14.00 - 15.30

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.

1. a) Show how the method of separation of variables can be used for the time-dependent Schrödinger equation (TDSE) if the potential energy function is time-independent, to give the time-independent Schrödinger equation.
Solve the differential equation for the time dependence and hence write down the general solution of the TDSE.

[7 marks]

b) Two wavefunctions of a system, $\psi_1(x)$ and $\psi_2(x)$, have the same definite energy, but different values of some observable A, represented by the operator $\hat{A}$, A_1 and A_2 respectively. The system is in a mixed state $\psi(x) = a_1\psi_1(x) + a_2\psi_2(x)$, where a_1 and a_2 are complex numbers. If A is measured, what outcomes are possible and what are their probabilities?
If A is measured a second time, how does the result of the first measurement affect the second measurement?

[5 marks]

c) Show that the commutator of the position and momentum operators is given by

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

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

[4 marks]

d) The angular momentum operator $\hat{\mathbf{J}}$ is given in terms of the orbital angular momentum operator $\hat{\mathbf{L}}$ and the spin operator $\hat{\mathbf{S}}$ by

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

Explain how the quantum numbers j and m_j are related to $\hat{\mathbf{J}}$.
For the case $l = 2$, $s = 1$, enumerate the possible values of j and m_j. Show that the number of states is equal to $(2l + 1)(2s + 1)$.

[5 marks]

e) Write down the atomic ground-state electronic configurations of boron ($Z = 5$) and gallium ($Z = 31$). Determine the total S, L and J of the ground state of boron and write down the corresponding spectroscopic term symbol.

[4 marks]

2. a) 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. Show that

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

[6 marks]

b) Show that in polar coordinates r, θ, ϕ,

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

Show that the wavefunction

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{im\phi}$$

is an eigenfunction of $\hat{L}_z$ and explain why only integer values of m are allowed.

[6 marks]

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

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \frac{1}{2}m\omega^2\left(x^2 + y^2 + z^2\right).$$

i) Write down its energy eigenvalues as a function of quantum numbers n_x, n_y and n_z. What are the lowest three energy levels and the corresponding degeneracies?

[6 marks]

ii) Show that $\hat{L}_z$ commutes with $\hat{H}$. What is the significance of this? You may use the following formula without proof:

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right).$$

[3 marks]

d) Show that the wavefunction

$$\psi(x, y, z) = A\,x\,\mathrm{e}^{-(x^2+y^2+z^2)/2a^2}$$

is not an eigenfunction of $\hat{L}_z$. What values of L_z could be obtained from a measurement of the oscillator in a state with this wavefunction?

[4 marks]

3. a) Two real eigenfunctions of the time-independent Schrödinger equation for an electron in a potential $V(x)$ are $\psi_1(x)$ and $\psi_2(x)$ with eigenvalues E_1 and E_2 respectively. At time $t = 0$, the electron is in a state

$$\psi(x) = \frac{1}{\sqrt{2}}\Big[\psi_1(x) + \psi_2(x)\Big].$$

i) Write down the electron's wavefunction $\Psi(x,t)$ at time $t > 0$.

[2 marks]

ii) Determine the energy uncertainty ΔE in the state $\Psi(x,t)$.

[4 marks]

iii) Show that the probability density $|\Psi(x,t)|^2$ is an oscillatory function in time and find the period τ. Calculate $\tau\,\Delta E$ and comment on your value.

[4 marks]

b) The following wavefunctions are energy eigenfunctions of the hydrogen atom,

$$\begin{aligned}
\psi_1(r,\theta,\phi) &= A_1\,\mathrm{e}^{-r/a_0}, \\
\psi_2(r,\theta,\phi) &= A_2\left(\frac{r}{a_0}\right)\mathrm{e}^{-r/2a_0}\sin\theta\,\mathrm{e}^{-i\phi}, \\
\psi_3(r,\theta,\phi) &= A_3\left(\frac{r}{a_0}\right)^2\mathrm{e}^{-r/3a_0}\sin\theta\cos\theta\,\mathrm{e}^{-i\phi},
\end{aligned}$$

where A_1, A_2 and A_3 are normalization constants and a_0 is the Bohr radius.

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

[6 marks]

ii) What are the energy eigenvalues of these three states in eV? If a hydrogen atom makes a transition from state ψ_2 to state ψ_1 by emitting a photon, calculate the frequency of the photon.

[5 marks]

iii) Show that these states are all orthogonal to one another.

[4 marks]

4. a) Give the definition of a Hermitian operator that acts on wavefunctions in one dimension. Show that the momentum operator is Hermitian.

[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 $\hat{P}\Psi(1, 2) = \Psi(2, 1)$. By applying $\hat{P}$ twice to $\Psi(1, 2)$, find its eigenvalues, λ.

[5 marks]

c) Which of these eigenvalues 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]

d) Explain briefly how first order perturbation theory can be used to estimate the energy levels of helium from hydrogen atom wavefunctions.

[3 marks]

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

[5 marks]

f) In both orthohelium and parahelium, a configuration $1s2s$ is possible. Which has the lower energy? Explain why.

[5 marks]

END OF EXAMINATION PAPER