Answer TWO questions only.
No marks will be given for attempting a further question.
Each question is marked out of 20. The numbers in square brackets in the right-hand margin indicate the provisional allocation of marks per sub-section of a question.

You may assume the following:

The Hamiltonian for a hydrogenic atom with nuclear charge Z is

$$H_Z = -\frac{1}{2}\nabla^2 + V(r); \qquad V(r) = -\frac{Z}{r}$$

in atomic units (a.u.). The wave function for the ground state with energy $E_Z = -Z^2/2$, is given by

$$\psi_Z(\mathbf{r}) = Z^{3/2} \exp\,(-Zr)/\sqrt{\pi}.$$

The standard integral

$$\int_0^\infty x^n \exp(-ax)dx = n!/a^{n+1}; \qquad \mathcal{R}\rceil\{a\} > 0.$$

1. State the equation that describes the time evolution of a system specified by the time-independent Hamiltonian H. Hence prove that if A is an operator

$$\frac{d\langle A\rangle}{dt} = (i\hbar)^{-1}\langle[A,H]\rangle + \langle\frac{\partial A}{\partial t}\rangle. \qquad [4]$$

Hence derive the equation for A when

a) A does not depend explicitly on time,

b) A commutes with H,

c) $A = H$.

In cases b) and c) what special property of the system does $\langle A\rangle$ represent? [2]

A particle of mass m with position and momentum vectors $\mathbf{r}$ and $\mathbf{p}$ moves in a potential $V(\mathbf{r})$. If $A = \mathbf{r}.\mathbf{p}$, prove that

$$2\langle T\rangle = \langle \mathbf{r}.\nabla V\rangle,$$

where T is the kinetic energy operator and the expectation values are taken with respect to stationary states of the system. [4]

Verify this result for the ground state of a hydrogenic atom. [3]

If the particle has momentum in the range ($\mathbf{p}$,$\mathbf{p}$+d$\mathbf{p}$), the quantum mechanical probability density

$$P_q(\mathbf{p}) = |\phi(\mathbf{p})|^2 \ ,$$

where $\phi(\mathbf{p})$ is the wave function for the particle in momentum space. The corresponding classical probability density, $P_c(\mathbf{p})$, is given by

$$P_c(\mathbf{p}) = \frac{4\pi r_0^2 N}{V'(r_0)} \ ,$$

in a.u., where r_0 is determined from

$$V(r_0) = E - \frac{1}{2}p^2,$$

in which E is the energy and N is a normalisation constant. Calculate $P_q(\mathbf{p})$ and $P_c(\mathbf{p})$ for the ground state of a hydrogenic atom and show that they are identical provided N is suitably chosen. [7]

2. If A and B are operators that commute and A has non-degenerate eigenvalues, prove that the eigenfunctions of A are also eigenfunctions of B. [2]

L is the orbital angular momentum operator with components L_x, L_y and L_z. Prove that

$$[L_x, L_y] = i\hbar L_z; \qquad [L_y, L_z] = i\hbar L_x; \qquad [L_z, L_x] = i\hbar L_y$$

and

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0.$$ [2]

The generalised angular momentum operator **J** together with its components J_x, J_y and J_z satisfy the above commutation relations and the functions $u(jm)$ are simultaneous eigenfunctions of J^2 and J_z with eigenvalues $j(j+1)\hbar^2$ and $m\hbar$. If $J_\pm \equiv J_x \pm \mathrm{i}J_y$, prove that

$$[J_z, J_\pm] = \pm\hbar J_\pm$$

and

$$J_\mp J_\pm = J^2 - J_z^2 \mp \hbar J_z.$$ [3]

Hence show that $J_\pm u(jm)$ are eigenfunctions of J_z with eigenvalues $(m \pm 1)\hbar$ and that

$$J_- J_+ u(jm) = [j(j+1) - m(m+1)]\hbar^2 u(jm).$$ [3]

By using the above results, derive expressions for the non-zero matrix elements of J_x, J_y and J_z and hence obtain matrices representing a spin 1/2 particle. Give an example of a such a particle and indicate how its spin is related to its magnetic moment. [5]

The angular momenta for two independent particles are $\mathbf{J}_1$ and $\mathbf{J}_2$ and their total angular momentum is $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. Prove that

$$J^2 = J_1^2 + J_2^2 + J_{1+}J_{2-} + J_{1-}J_{2+} + 2J_{1z}J_{2z}.$$ [2]

Hence if the whole system is represented by eigenstates $w(j_1 j_2 j m)$ and $v(j_1 m_1 j_2 m_2)$ in the coupled and uncoupled representations, and the two particles each have spin 1/2, show that

$$w(\tfrac{1}{2}\ \tfrac{1}{2}\ 1\ 1) = v(\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2})$$

and

$$\sqrt{2}\, w(\tfrac{1}{2}\ \tfrac{1}{2}\ 1\ 0) = v(\tfrac{1}{2}\ \text{-}\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}) + v(\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\ \text{-}\tfrac{1}{2})$$

Obtain the corresponding expression for the eigenstate $w(\tfrac{1}{2}\ \tfrac{1}{2}\ 0\ 0)$. [3]

3. A system is described by the time-independent Hamiltonian

$$H = H_0 + \lambda V$$

where λV is a small perturbation and H_0 is a Hamiltonian whose eigenvalues E_n^0 and eigenfunctions ψ_n^0, $n = 0,1,2,...$ are known. Develop a time-independent perturbation theory to prove that

$$E_n = E_n^0 + \lambda V_{nn} + O(\lambda^2).$$ [4]

If Ψ is a normalised function that can be varied and that satisfies the appropriate boundary conditions, prove that the ground state energy E_0 satisfies the inequality

$$E_0 \leq \int \Psi^* H \Psi d\tau.$$ [4]

When does equality occur? [1]

The Hamiltonian H (a.u.) is given by

$$H = -\frac{1}{2}\nabla^2 - \frac{Z}{r}\exp(-2r).$$

By choosing $H_0 \equiv H_Z(\mathbf{r})$ show that first-order perturbation theory gives

$$E_0 \simeq \frac{1}{2}Z^2 - \frac{Z^4}{(Z+1)^2},$$ [4]

and also that if $\Psi \equiv \psi_{Z'}(\mathbf{r})$ for a variable nuclear charge Z', the best estimate for E_0 is given by

$$E_0 \simeq \frac{1}{2}Z'^2 - \frac{Z'^3 Z}{(Z'+1)^2}.$$ [4]

Verify that if $Z = 3$, then $Z' \simeq 2.3615$ and obtain estimates from the two results above for E_0. Comment on the relative accuracy of the two results. [3]

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