Answer all questions on this paper. Show all your workings and pay attention to sig. figs and units otherwise you will lose credit. Remember, if you can’t do the problem write down as much as you can that is of relevance to solving the problem so that you get some partial credit.

1. Set up the appropriate integral (but do not solve) for calculating the probability of finding an electron at a distance of greater than $2a_0$ from the nucleus in the hydrogen atom ground state. Show clearly how you construct the hydrogen atom ground state wave function from the relevant tables on your data sheet (starting from the general expression $\psi_{nm}(r, \theta, \phi) = R_n(r)Y_m^m(\theta, \phi)$ - i.e. build the wave function corresponding to the ground state and include it in your final integral). (10 points).

$$\psi_{10} = \frac{1}{\sqrt{\alpha_0}} e^{-r/\alpha_0}$$

To calc. prob. of finding $r$ between $2a_0$ & $\infty$ calc. prob. between $0$ & $2a_0$ & subtract from $1$. Prob. $\text{in } R_{10}^2 Y_0^0 (\theta, \phi) = \int_0^{2\pi} \int_0^\pi \sin \theta \, d\theta \, d\phi ^{1/2} (\frac{1}{2\alpha_0})^3 e^{-2r/\alpha_0} r^2 \, dr$
2. If we calculate the ionization energy of the 1s atom (using the Hamiltonian below) we get a value of 2.00 au.

\[ H = \frac{-2\hbar^2}{2m} (V_2 + V_1) + 2e^2 \frac{2e^2}{4\pi\epsilon_0 r_1 r_2} \]

The experimental value of the ionization energy for this atom is 0.9046 au. Discuss the meaning of each of the various terms in this Hamiltonian and explain the large discrepancy in ionization energy. Indicate what additions we need to make to our Hamiltonian to improve our estimate of this property. What approximate method might be best suited to this calculation? Explain. (10 points)

Kinetic energy of \( \phi_1 \) and \( \phi_2 \)

Coulombic attraction between \( \phi_1 \) and a nucleus

Coulombic attraction between \( \phi_2 \) and a nucleus.

Since there is no \( \phi_1 - \phi_2 \) repulsion, in this case the atom is much more stable (lower E) than it should be (\( \phi_1 - \phi_2 \) rep. is destabilizing interaction). Hence, since the atom is too stable, it’s harder to remove the \( \phi_1 \) than it should be & so IE is too large.

Obviously to improve this situation we need to add an \( \phi_1 - \phi_2 \) rep. term:

\( (\frac{\phi_1^*}{4\pi\epsilon_0 r_1} + \phi_2) \Delta H \)

The perturbation theory is the perfect approach here based on the current Hamiltonian with \( \Delta H \) equal to the \( \phi_1 - \phi_2 \) rep. term.

3. Consider a transition between the \( l = 2 \) and \( l = 3 \) states of a hydrogen atom in an external magnetic field. For each of the possible selection rules (\( \Delta m = 0 \) and \( \Delta m = \pm 1 \)) how many possible transitions are allowed? (Draw a clearly labeled sketch of the energy levels showing all the transitions) (8 points)

Use these sel. rules on 15 pass. tran.
4. The term symbols for an \( nd^2 \) configuration are found to be \( 'S', 'D', 'G', 'P \) and \( 'F'. \)
(a) Calculate all possible values of the \( J \) quantum number associated with each of these term symbols.
(b) Which term symbol represents the ground state? Explain your reasoning. Don't forget to consider the total angular momentum \( (J) \).
(c) How many different possibilities are there for arranging 2 electrons in the five \( d \) orbitals? (You don’t need to show all the configurations, just explain how you arrived at your answer). Hint: you need to do more than just use the equation \( \frac{G!}{N!(G-N)!} \)

\[ \begin{align*}
\text{e) } & S & L = 0 & S = 0 & J = 0 \\
& P & L = 2 & S = 0 & J = 2 \\
& G & L = 4 & S = 0 & J = 4 \\
& P & L = 1 & S = 1 & J = 2, 1, 0 \\
& F & L = 3 & S = 1 & J = 4, 3, 2
\end{align*} \]

b) \( CS = \) triplet state \( 3P \) or \( 3F \) (highest multiplicity). Favor \( 3F \) since \( L \) is larger (\( r, 3N \)). So it’s \( 3F_4, 3F_3, 3F_2 \)

(c) There are 9 orbitals (10 spin orbitals when consider each spatial orbital can contain \( 2 \) or \( 1 \) \( \epsilon \)).

\( \Rightarrow \) 10 ways to put 1st \( \epsilon \) in \( 1 \) then 9 ways for 2nd \( \epsilon \). \( \Rightarrow 10 \times 9 \times 90 \)

But \( \epsilon \)'s indistinguishable = \( \frac{90}{2} = 45 \)

5. Expand the two electron determinant wavefunction given below and show that it can be factored into a spatial and a spin portion.

\( \psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)x(1) & 2s(1)x(1) \\ 1s(2)x(2) & 2s(2)x(2) \end{vmatrix} \)

\( \psi = \frac{1}{\sqrt{2}} \left[ 1s(1)2s(2) - 2s(1)1s(2) \right] \)

\[ \text{spatial} = \frac{1}{\sqrt{2}} \left[ 1s(1)2s(2) - 2s(1)1s(2) \right] \]

\[ \text{spin} = \]
6. The Hamiltonian operator for a hydrogen atom in an external electric field of strength E is given below.

\[ \hat{H}^{(c)} = -\frac{1}{2}\mu \nabla^2 + e^2 \frac{eE \cos \theta}{4\pi \epsilon_0} \]

(a) Identify the unperturbed Hamiltonian (\(\hat{H}^{(0)}\)) and the perturbation Hamiltonian (\(\hat{H}^{(1)}\)).

(b) Show how to set up the expression that would allow you to determine the first order correction to the energy of a ground state (1s) hydrogen atom in an external electric field of strength E. There is no need to solve this expression. (6 points)

\[ E = \int \psi_{1s}^{(c)} \hat{H}^{(0)} \psi_{1s}^{(c)} \, d\tau \]

\[ = \sum_{\ell} \left( \int \psi_{\ell s}^{(c)} \hat{H}^{(1)} \psi_{\ell s}^{(0)} + s \sum_{\ell} \psi_{\ell s}^{(c)} \hat{H}^{(1)} \psi_{\ell s}^{(0)} \right) \, d\tau \]

[which interestingly, once solved, yields the first order correction to the energy of \(\text{H}_2\).]

7. (a) It is possible (with a little careful thought and Hund’s rules as a guide) to deduce the lowest energy term associated with a \(2p^3\) configuration without tabulating all the possibilities and calculating the individual totals of spin and orbital angular momentum. What is the lowest energy term and how do you determine it? Explain your logic. (5 points)

OK, \(2\hat{S}\) so electron spins will be parallel (11) in which 7
Case \(S^2=1\) or they will be antiparallel (minus case \(S^2=0\).
So \(2S+1\) must either be \(1\) (triplet) or \(\frac{1}{2}\) (triplet). We know from Hund’s rules
that the triplet state will have more energy. For \(2\hat{S}\) to be a singlet (for a
state that has the same energy) the max. value of \(M_s\) will be \(1\) (corresponding to \(1^1S^0\)) so that is an \(L=1\) (P) state. Now we know \(L=2\) & \(S=1\) so possible values of \(J\)
are \(2,1,0\). From Hund’s last rule, for a stateless \(2\hat{S}\), the lowest \(J\) is 0 state. Have \(3P\) corresponds to the ground state term for \(p^3\)
(b) Which of the following terms describe possible states of the carbon atom (with an electronic configuration of \(1s^2\) \(2p^3\))? Explain why the other states are not possible. (5 points)

\[ \begin{array}{c|c|c|c}
\text{(i) } S^2 = 1 & \text{(ii) } S^2 = \frac{1}{2} & \text{(iii) } L = 1 & \text{(iv) } J = \frac{3}{2} \\\n\text{OK} & \text{NO} & \text{NO} & \text{NO} \\
\text{So } S = 1 & \text{So } J = 1,0 & & \\
\text{So } S = 1 & & & \text{not allowed} \\
\end{array} \]

\[ \begin{array}{c|c|c|c}
\text{(i) } S^2 = 1 & \text{(ii) } S^2 = \frac{1}{2} & \text{(iii) } L = 1 & \text{(iv) } J = \frac{3}{2} \\
\text{OK} & \text{NO} & \text{NO} & \text{NO} \\
\text{So } S = 1 & \text{So } J = 1,0 & & \text{not allowed} \\
\end{array} \]
State whether each of the following statements is TRUE or FALSE. Give an explanation for your choice; if you answer FALSE you need to state what the statement should say in that case; if you answer TRUE then support this answer with your reasoning and an explanation of the statement. (Read the statements carefully and be sure that in cases where there are two parts to the statement that both are true)

8. The spin multiplicity of every term of an atom with an odd number of electrons will always be an even number. (2 points)

\[ \text{If odd no. of } \ell \text{ is } \leq 5 \text{, spin always be } \frac{1}{2} \text{-integral} \]
\[ \text{so } 2S+1 = \text{always even.} \]

9. The antisymmetric properties of the wavefunction do not need to be considered in the case of the hydrogen atom. (2 points)

\[ \text{only } l \neq 0 \text{ or } \ell \text{ so no need to be concerned with exponents of } \ell \text{s!} \]

10. The spherical harmonic function \( Y_2^0(\theta, \phi) \) is symmetric about the \( z \)-axis. (2 points)

\[ \text{If } m = 0 \text{ then there is no } \phi \text{ dependence} \]
\[ \text{so function is symmetric about } z \text{-axis. (Check it in Table 6.5 - all } m = 0 \text{ functions have no } \phi \text{-derivative.)} \]
\[ \text{This is a } d^0 \text{ orbital in fact.} \]

11. Operation on the 2-electron wavefunction (given below) by the total spin angular momentum operator \( \hat{S}_z \) will give the result \( 3 \) points

\[ \psi = \frac{1}{\sqrt{2}} [1s\alpha(1) - 2s\alpha(2)] \]

This corresponds to a config. where we have 2 spin up \( \ell \)'s, \( \ell \) in the 1s and \( l \) in the 2s.
\[ \text{for } 2 \text{ spin up } \ell \text{s } S_{\text{total}} \text{ is } \frac{1}{2} \text{ (} \ell_{2 \text{h}} \text{ for each).} \]
12. In variation theorem, the energy corresponding to a general trial function \( \phi \) is calculated simply by evaluating the integral \( E = \int \phi^* H \phi \, \mathrm{d}t \) (3 points)

\[
E = \int \phi^* H \phi \, \mathrm{d}t
\]

[Diagram: trial function, usually not normalized, so this needs to be explicitly included.]

13. The integral \( \int \psi_1^* \psi_2 \, \mathrm{d}t \) will equal 1 (where the wave functions describe the hydrogen-like \( 2p_x \) and \( 2p_y \) orbitals respectively). (2 points)

\[ 2p_x \text{ and } 2p_y \text{ are different in one quantum no. } \ell = \text{ no.} \]

[Diagram: orthogonality. Hence \( \int \psi_1^* \psi_2 \, \mathrm{d}t = 0 \) not 1]

14. The average (expectation) value of the angular momentum in the \( x,y \) direction, \( \langle L_x \rangle \) or \( \langle L_y \rangle \), is zero for the hydrogen atom. (3 points)

\[ L_x \text{ and } L_y \text{ commute, so we can know values of } L_x \text{ and } L_y \text{ both at once, but the values of } L_z \text{ are indeterminate or any number.} \]

[Diagram: L_x and L_y are cons. but L_z is undefined. Hence the only values of L_z will be zero.]

15. The atomic transition between the states \( ^2D_{\frac{3}{2}} \rightarrow ^2P_{\frac{1}{2}} \) is a forbidden transition. (3 points)

\[ \Delta S = 0 \text{ and } \Delta J \neq 0 \text{ or } \pm 1 \text{: Both selection rules are obeyed in this case} \]

[The \( \Delta L = \pm 1 \) rule is obeyed.]

16. The wavefunction \( [1s(1) 2s(2) - 2s(1) 1s(2)] \langle \alpha(1) \beta(2) - \beta(1) \alpha(2) \rangle \) is an acceptable wavefunction for the He atom. (3 points)

[Diagram: Both the general and spin parts are antisymmetric w.r.t. exchange of \( \alpha \) and \( \beta \) if we continue antisymmetric tensors, their product will be symmetric w.r.t. exchange (which we know is not acceptable).]