1. Certain quantities that appear in the theory of hydrogen have wider application in atomic 
physics: the Bohr radius $a_0$, the Rydberg constant $R_\infty$, the fine structure constant $\alpha$ and 
the Bohr magneton $\mu_B$. Give a defining expression for each, and write a sentence explaining 
their significance.

- **Bohr radius** $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 5.29 \times 10^{-11}$ m. The Bohr radius is the typical distance of
  an electron from the nucleus in a hydrogen atom, and larger atoms have an electron 
cloud which extends to several $a_0$.
- **The Rydberg** $R_\infty = \frac{me^4}{8\varepsilon_0\hbar^3c} = 1.097 \times 10^7$ m$^{-1}$ sets the scale of energy levels, and hence 
electronic transitions, in hydrogen. Outer electrons in more complex atoms often have 
ergies typical of higher levels in hydrogen.
- **The fine structure constant** $\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = 137.04^{-1}$ characterises the strength of the
  electromagnetic interaction. In hydrogen, it sets the scale of perturbations to the 
non-relativistic Schrödinger equation.
- **The Bohr magneton** $\mu_B = \frac{e\hbar}{2me} = 9.274 \times 10^{-24}$ J T$^{-1}$ sets the scale for the intrinsic 
magnetic moment of the electron.

2. (a) A muon has a mass 206 times the electron mass, and charge equal to that of an electron. 
The particle may be captured by an atom and the radiation which is emitted as the muon 
cascades through the energy levels can be measured. Assuming the muon-nucleus system 
can be treated as hydrogen-like, find the energy in MeV of the photon emitted as the muon 
goes from a state with principal quantum number 2 to the ground state of lead. Neglect 
the reduced mass correction.

(b) The experimental value is around 5 MeV. This is likely to be significantly different from 
your theoretical value. Which effect(s) might be responsible for the discrepancy? [Hint - 
estimate the typical radius of the muon in its ground state].

- The energy of an electron in the $n$-th energy level of a hydrogen-like ion with nuclear 
charge $Z$ is $E_e(n) = -Z^2hcR_\infty/n^2$. As $R_\infty$ scales as $\sim m_e$, we would expect muon
energies to be $E_\mu(n) = -Z^2 \frac{\hbar c R_\infty}{m_e} / n^2$. Therefore

$$E_\mu(2) - E_\mu(1) = \frac{3}{4} Z^2 \frac{\hbar c R_\infty}{m_e} = 14.1 \text{ MeV}$$  \hspace{1cm} (1)

- The typical radius of the ground state of a hydrogen-like ion is $a_0/Z$. As $a_0$ scales as $\sim 1/m_e$, we would expect the typical radius of a muonic ground state to be $\frac{a_0}{Zm_\mu} \approx 3 \text{ fm}$. The first thing to note is that this is well inside electron orbitals, and hence the muon energy will not be significantly affected by the presence or otherwise of electrons in the system. However, the radius is so small that a muon in this orbit will spend much of its time inside the lead nucleus. The result is that it feels less force than if the nucleus was truly point-like, and hence binding energies (particularly in the ground state) are less than would be expected.

3. A non-mathematical question, which invites you to think about the properties of the hydrogenic wave-functions. Neglecting relativistic and other small effects, the energies of the s,p,d... states in hydrogen for a given value of the principal quantum number $n$ are the same. They have the same potential energy and the same kinetic energy. However, a student argues as follows: *Compared with high angular momentum states of the same $n$, the low angular momentum states have a higher probability of being near the nucleus, so their potential energy must be more negative. Their low angular momentum means they have lower kinetic energy also. So why don’t the low angular momentum state lie deeper in energy?* What is wrong with this argument?

- The first error is that the student assumes that, because low $l$ orbitals have a higher probability of being near the nucleus, they are therefore generally ‘closer’ to the nucleus. In fact, the decay of wavefunctions of small $l$ is slower at large $r$ than those with large $l$: in other words, large $l$ wavefunctions are more sharply peaked around their typical $r$ than small $l$, rather than simply being further from the nucleus. The net consequence is that $\langle 1/r \rangle$ is the same for all orbitals with the same $n$.

- The second issue is that the student forgets the radial contribution to the kinetic energy, which compensates for the decrease in the angular part.

4. Which of the following levels do not exist in hydrogen, and why? $3f^2 F_{3/2}$, $3p^2 P_{3/2}$, $3s^2 S_{3/2}$, $3d^3 D_{3/2}$, $2p^2 D_{3/2}$,

- $3f^2 F_{3/2}$: $s = 1/2$, $l = 3$, $j = 3/2$ – cannot exist because $s, l, j$ do not obey the angular momentum addition rule. For $s, l = 1/2, 3$, the minimum value of $j$ is 5/2. Also, 3f is impossible.

- $3p^2 P_{3/2}$: $s = 1/2$, $l = 1$, $j = 3/2$ – can exist.

- $3s^2 S_{3/2}$: $s = 1/2$, $l = 0$, $j = 3/2$ – cannot exist because $s, l, j$ do not obey the angular momentum addition rule. For $s, l = 1/2, 0, j = 1/2$. 

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• 3d<sup>3</sup>D<sub>2</sub>: s = 1, l = 2, j = 2 – cannot exist as the spin of a single electron must be s = 1/2.

• 2p<sup>2</sup>D<sub>3/2</sub>: s = 1/2, l = 2, j = 3/2 – cannot exist as the angular momentum state in the configuration (p) must match the total orbital angular momentum in a single-electron atom/ion (which is D in this case).

5. For this question, you need to hand a derivation of the expression for the shifts in the positions of the energy levels of hydrogen-like ions when the spin-orbit interaction is taken into account. The result can be written

\[
\Delta E(n, l, s, j) = \frac{\mu_0}{4\pi} Z^4 g_s \mu_B^2 \frac{1}{n^3 a_0^3 l(l + 1/2)(l + 1)} \frac{j(j + 1) - l(l + 1) - s(s + 1)}{2}.
\]

We are concerned with the physics behind this expression and it derivation.

(a) In simple “vector model” terms, what is the direction of the B-field experienced by the electron, relative to its orbital angular momentum? What is the direction of the intrinsic magnetic moment of the electron relative to its spin angular momentum?

(b) In the light of (a), and given that the interaction is of the form \(-\mu . B\), should the energy by higher or lower for \(j = l + 1/2\) than \(j = l - 1/2\)? Check that your conclusion is correct by inspecting the expression above.

(c) Explain in physical terms where the \(Z^4\) dependence comes from.

• From the perspective of the electron, the nucleus appears as a current heading in the opposite direction from the electron’s tangential velocity. From the good old-fashioned right-hand rule, the B-field is then oriented in the same direction as the electron’s angular momentum. The intrinsic magnetic moment of an electron is aligned oppositely to its spin.

• The form of the interaction indicates that it is negative when \(\mu\) and \(B\) are aligned. Therefore it is negative when spin and \(B\) are anti-aligned, or equivalently when the electron’s spin and orbital angular momenta are oppositely aligned. \(j = l + 1/2\) corresponds to aligned spin and orbital angular momentum: we would therefore expect that the energy is higher for this case than \(j = l - 1/2\). This is confirmed by the positive dependence of \(\Delta E\) on \(j\) for fixed \(n\), \(l\) and \(s\).

• The magnetic field strength can be shown to vary as \((1/r^3)l\) (the electric field varies as \(1/r^2\) and the angular velocity of the electron as \(1/r\)). Thus the final expression contains a factor of \((1/r^3)\) and hence a \(Z^3\) factor appears here. The remaining factor arises because the electric field (and hence the magnetic field from the electron’s perspective) at a given distance \(r\) scales with the nuclear charge \(Z\), of course.

6. Show the splitting due to the spin-orbit interaction between the \(j = 3/2\) and \(j = 1/2\) levels of the 2p configuration in hydrogen is 11GHz. Draw a diagram showing the positions
of the split levels with reference to the unperturbed level, and label the levels with the appropriate quantum numbers. Using the known \( n \)-dependence, find the splitting of the 3p configuration.

- using the given values of \( l \), \( s \) and \( j \), the splitting is seen to be

\[
E_{j=3/2} - E_{j=1/2} = \frac{\mu_0 Z^4 g_s \mu_B^2}{4\pi a_0^3 n^3 (l + 1/2)(l + 1)} \frac{3/2}{n^3 l(l + 1/2)(l + 1)}
\]

(3)

The factor in front of the fraction evaluates to \( 1.162 \times 10^{-22} \) J, and the fraction to 0.0625. Multiply together to give the energy, difference and divide by Planck’s constant \( (\hbar, \text{not } \hbar) \) to give a frequency splitting of 11.0 GHz, as required.

- See figure below for energy level sketch. Note the relative size of the shift.

- The \( n \)-dependence is \( 1/n^3 \), so the 3p level is split by \( (8/27) \times 11.0 = 3.25 \) GHz.

7. A way of studying the small shifts caused by QED is to use high-Z atoms, with all electrons stripped off except one. One method is to take a tunable laser operating in the visible region (say around 600 nm) and excite transitions within the fine structure of the \( n = 2 \) manifold. Using your expression for the spin-orbit splitting as a function of \( Z \), suggest a suitable element for study.

- Spin-orbit splitting scales as \( Z^4 \). We know that the splitting of the relevant levels in hydrogen is 11 GHz, which translates to 2.73 \( \times 10^{-2} \) m. To get to 600 nm, we need an increase in splitting of energy levels, and hence \( Z^4 \), by 4.56 \( \times 10^4 \). This would suggest the use of an element with \( Z \sim 15 \), or phosphorus.

8. (a) Explain qualitatively why the energy required to remove one electron from the ground state of the helium atom is much larger than that in hydrogen, whole for other states the hydrogenic value is quite a good approximation, e.g. the 1s2s levels in helium have energies very similar to the 2s in hydrogen.

(b) The 1s2s configuration in helium is split into two levels. Explain briefly the physical origin of the splitting, and how it comes about that these different energies should be associated with different relative orientations of the intrinsic spins of the two electrons (so that one of the levels is called a ‘singlet’ and the other a ‘triplet’).
• If we ignored electron-electron repulsion, both electrons would behave independently (ignoring, for now, the Pauli exclusion principle) and the ionization energy of the helium atom would be the same as the helium ion (i.e., 4 times that of a hydrogen atom due to the \( Z^2 \) dependence of energy levels in single-electron ions). However, electron-electron repulsion makes the binding of electrons much less strong. When both are in the 1s orbital, each electron is partially ‘shielded’ from the extra charge in the nucleus (relative to hydrogen) by the other electron. Therefore the ionization energy is somewhere between that for a helium ion and a hydrogen atom (the electrons ‘see’ an effective charge somewhere between 1 and 2). When we consider one electron in a higher-\( n \) shell, however, that electron is much more effectively screened from the extra charge in the nucleus by the other electron inside it in the 1s orbital. As a consequence, the outer electron behaves as if it sees a charge of \( \sim 1 \) at the nucleus, and hence the energies are hydrogen-like. If you feel that this argument is a bit rough, you are right – we will deal with multi-electron atoms more formally in the coming term.

• The 1s2s configuration has two possible product wavefunctions (ignoring spin for now): \( \psi_{1s}(r_1)\psi_{2s}(r_2) \) and \( \psi_{2s}(r_1)\psi_{1s}(r_2) \). These are eigenstates of the system if we ignore electron-electron repulsion, but not when we include it. If we include the electrostatic interaction, it turns out that the appropriate eigenstates (for the application of perturbation theory) for the 1s2s configuration are

\[
\Psi_{\pm} = \frac{1}{\sqrt{2}} \left( \psi_{1s}(r_1)\psi_{2s}(r_2) \pm \psi_{2s}(r_1)\psi_{1s}(r_2) \right).
\]  

(4)

We don’t actually need to go into much detail to prove this: electron-electron repulsion must be symmetric with respect to the interchange of the spatial coordinates of the particles. Therefore our eigenstates should be chosen as eigenstates of the spatial exchange operator – these are exactly those eigenstates. There is of course, no reason why \( \Psi_+ \) and \( \Psi_- \) should have the same energies, and indeed they don’t. But I stress that this is due to the difference in the radial separation of the electrons in the two cases, and the resultant impact on the repulsion.

Now we worry about spin and the Pauli exclusion principle. Our spatial eigenstates are already fixed by the coulomb interaction, so we include spin by multiplying our \( \Psi_{\pm}(r_1, r_2) \) by some spin-states \( \chi(s_1, s_2) \). But what should these spin states be? The exchange principle tells us that any state of electrons must be antisymmetric with respect to exchange of all coordinates (spatial and spin). We have spatial wavefunctions that are symmetric (\( \Psi_+ \)) and antisymmetric (\( \Psi_- \)), so we need to combine them with antisymmetric (\( \chi_A \)) and symmetric (\( \chi_S \)) spin states respectively. So, our eigenstates are:

\[
\Psi_+(r_1, r_2)\chi_A(s_1, s_2) \quad \text{and} \quad \Psi_-(r_1, r_2)\chi_S(s_1, s_2).
\]  

(5)
We know that the symmetric spin states for two spin-1/2 particles are

$$
\chi_S(s_1, s_2) = \uparrow_1 \uparrow_2, \quad \frac{1}{\sqrt{2}}(\uparrow_1 \downarrow_2 + \downarrow_1 \uparrow_2), \quad \downarrow_1 \downarrow_2,
$$

which all have total spin 1. The antisymmetric spin state is

$$
\chi_A(s_1, s_2) = \frac{1}{\sqrt{2}}(\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2),
$$

which has total spin of 0. Therefore the different total spin states are associated with spatial wave functions of different symmetry due to the exchange principle. These spatial wavefunctions have different energies when the coulomb repulsion of electrons is considered, and hence the different spin states are associated with different energies, even though spin itself has not (yet) entered the Hamiltonian.