Atomic Physics Assignment

Question 1: The Hydrogen Atom and Its Fine Structure

The fine structure of hydrogen arises from three relativistic corrections to the non-relativistic Schrödinger equation: the relativistic kinetic-energy correction, the spin–orbit coupling, and the Darwin term.

This question asks you to examine how these corrections combine and what their consequences are for spectroscopy.

(a) Using first-order perturbation theory, the total fine-structure energy correction for hydrogen is

$$E_{n,j}^{(1)} = -\frac{\alpha^2}{n^2}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right) E_n^{(0)}, \qquad E_n^{(0)} = -\frac{13.6\text{ eV}}{n^2}. \tag{1}$$

For the $n = 2$ level, list all fine-structure states (specifying n, l, j) and calculate their energy splittings in eV. Show explicitly that the states $2p_{1/2}$ and $2s_{1/2}$ are degenerate in this approximation (before the Lamb shift).

(b) Starting from the general expression for the spin–orbit energy in a Coulomb potential, derive the n-dependence of the fine-structure splitting for $l = 1$ states. Hence determine whether the perturbative treatment breaks down at large n or large Z, and identify the relevant dimensionless parameter.

(c) The Lamb shift lifts the degeneracy between $2s_{1/2}$ and $2p_{1/2}$, shifting $2s_{1/2}$ upward by approximately 1058 MHz. Given that the Einstein A coefficient for the $2p \to 1s$ transition is $A \approx 6.3 \times 10^8\ \text{s}^{-1}$, determine whether the $2s_{1/2}$ state is truly metastable. Estimate its natural linewidth (in MHz) and compare it with the Lamb shift to argue whether the Lamb shift is spectroscopically resolvable from the $2s$ level.

(d) Now place the hydrogen atom in a weak external magnetic field B (weak meaning $\mu_B B \ll \Delta_{\text{fs}}$). Write down the energy of each fine-structure sublevel to first order in B using the good quantum numbers in this limit. For the $2p$ manifold, compute the Landé g-factor

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{2}$$

for $2p_{1/2}$ and $2p_{3/2}$. In the weak-field limit, two $n = 2$ states with the same $m_j = +\frac{1}{2}$ but different (l, j) will have different Zeeman shifts. Calculate the field B at which the $2s_{1/2}$, $m_j = \frac{1}{2}$ sublevel crosses the $2p_{3/2}, m_j = -\frac{3}{2}$ sublevel. Express your answer in Tesla and comment on whether this crossing is observable in a laboratory field.

Question 2: Einstein A and B Coefficients, Detailed Balance, and Saturation

Einstein's 1917 derivation of the A and B coefficients was a landmark that prefigured quantum mechanics. This question explores the internal consistency of the coefficient relations, their connection to the oscillator strength, and the impossibility of population inversion in a two-level system.

(a) Consider a two-level atom (ground state $|1\rangle$, excited state $|2\rangle$) with degeneracies g_1 and g_2. In thermal equilibrium with blackbody radiation at temperature T, write down the rate equations for the populations N_1 and N_2 (including absorption, stimulated emission, and spontaneous emission). By requiring $\dot{N}_2 = 0$ and invoking the Boltzmann distribution

$$\frac{N_2}{N_1} = \frac{g_2}{g_1}\, e^{-\hbar\omega/k_B T}, \tag{3}$$

together with the Planck spectral energy density $\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\hbar\omega/k_B T}-1}$, derive the relations between B_{12} & B_{21} and A_{21} & B_{21}

The derivation above assumes that B_{12} and B_{21} are defined per unit spectral energy density $\rho(\omega)$. Repeat the argument when the coefficients are instead defined per unit spectral intensity $I(\nu)$ (per unit frequency $\nu = \frac{\omega}{2\pi}$). Show that the ratio $\frac{A_{21}}{B_{21}}$ changes by a factor of $\frac{8\pi h\nu^3}{c^3}$ vs $\frac{\hbar\omega^3}{\pi^2 c^3}$ and reconcile the two.

(b) The Einstein A coefficient is related to the electric-dipole matrix element (in SI) by

$$A_{21} = \frac{\omega^3}{3\pi\varepsilon_0 \hbar c^3}\left|\langle 2|\, e\mathbf{r}\, |1\rangle\right|^2. \tag{4}$$

The oscillator strength is defined via

$$A_{21} = \frac{e^2\omega^2}{2\pi\varepsilon_0 m_e c^3}\,\frac{g_1}{g_2}\, f_{12}. \tag{5}$$

For a two-level atom with $\lambda = 500$ nm, $A_{21} = 10^8$ s^{-1}, and $g_1 = g_2 = 1$, calculate f_{12} and the magnitude of the transition dipole moment $|\langle 2|er|1\rangle|$ in units of ea_0. Comment on whether this is a strong or weak transition compared with the hydrogen $1s \to 2p$ case ($f \approx 0.416$).

(c) The condition for population inversion is $N_2/g_2 > N_1/g_1$. Using the rate equations from (a) with a single monochromatic field of spectral energy density ρ, show that a two-level atom *cannot* achieve population inversion in steady state regardless of how strong the driving field is. Find the maximum achievable excited-state fraction $N_2/(N_1 + N_2)$ in the saturation limit ($\rho \to \infty$), and express it in terms of the degeneracies. What does this tell you about the impossibility of lasing on a two-level transition?

(d) When a coherent monochromatic field drives the transition, the atom undergoes Rabi oscillations with Rabi frequency

$$\Omega_R = \frac{eE_0\,|\langle 2|r|1\rangle|}{\hbar}, \tag{6}$$

where E_0 is the field amplitude. Derive a condition on the field intensity I (in $\mathrm{W\,m^{-2}}$) such that Rabi oscillations are observable, i.e. $\Omega_R \gtrsim A_{21}$. Express this as a saturation intensity I_{sat}, and discuss what happens to the population dynamics when $I \gg I_{\mathrm{sat}}$ versus $I \ll I_{\mathrm{sat}}$.

Question 3: The Optical Bloch Equations and Their Steady-State Solutions

The optical Bloch equations (OBEs) generalise the two-level dynamics to include both coherent driving and incoherent decay via the density matrix. This question builds the OBEs, finds their steady-state solutions, and extracts the physics of absorption, dispersion, and the ac Stark shift.

(a) The density matrix for a two-level system is $\rho = \begin{pmatrix} \rho_{22} & \rho_{21} \\ \rho_{12} & \rho_{11} \end{pmatrix}$ with $\rho_{11} + \rho_{22} = 1$. Under a coherent drive of Rabi frequency Ω and detuning $\Delta = \omega - \omega_0$, with spontaneous decay at rate $\Gamma = A_{21}$, write down the OBEs in the rotating frame (after making the rotating-wave approximation). Defining the Bloch vector components

$$u = 2\,\mathrm{Re}(\tilde{\rho}_{12}), \quad v = 2\,\mathrm{Im}(\tilde{\rho}_{12}), \quad w = \rho_{22} - \rho_{11}, \tag{7}$$

(where $\tilde{\rho}_{12}$ is the slowly varying coherence in the rotating frame), show the OBEs in terms of u, v and w. Comment on the physical importance of v and u in the context of atomic polarisation.

(b) Find the steady-state solutions ($\dot{u} = \dot{v} = \dot{w} = 0$) for u, v, and w. Show that the steady-state excited-state population is

$$\rho_{22}^{\mathrm{ss}} = \frac{\Omega^2/2}{\Delta^2 + \Gamma^2/4 + \Omega^2/2}. \tag{8}$$

Define the on-resonance saturation parameter $s_0 = 2\Omega^2/\Gamma^2$ and rewrite ρ_{22}^{ss} in terms of s_0 and Δ. Verify that on resonance ($\Delta = 0$), $\rho_{22} \to \frac{1}{2}$ as $s_0 \to \infty$, consistent with your result in Q2(c).

(c) The imaginary part v is proportional to the absorption coefficient and the real part u to the dispersion. From your steady-state solutions, write the lineshapes $\chi''(\Delta)$ (absorption) and $\chi'(\Delta)$ (dispersion) as functions of detuning. Show that in the

weak-driving limit ($\Omega \to 0$), the absorption profile is a Lorentzian of half-width $\Gamma/2$. For strong driving (large Ω), show that the effective linewidth becomes

$$\Gamma_{\text{eff}} = \sqrt{\Gamma^2 + 2\Omega^2}\,, \tag{9}$$

which is the phenomenon of *power broadening*. Calculate the percentage increase in linewidth when $s_0 = 3$ (i.e. $\Omega^2 = 3\Gamma^2/2$).

(d) In the dressed-state picture, the eigenstates of the combined atom–field system have energies $\pm\frac{\hbar}{2}\sqrt{\Delta^2 + \Omega^2}$, and the ground-state energy acquires an ac Stark shift (light shift)

$$\delta E_g \approx \frac{\hbar\Omega^2}{4\Delta}, \qquad |\Delta| \gg \Omega. \tag{10}$$

Using this result and your steady-state coherence u from (b), show that the light shift is consistent with the dispersive component of the atomic polarisation. Then estimate δE_g in Hz for sodium ($\lambda = 589$ nm, $\Gamma = 2\pi \times 9.8$ MHz, $|\langle 2|er|1\rangle| = 3.5\,ea_0$) driven 1 GHz off resonance at intensity $I = 10\ \text{mW cm}^{-2}$. Comment on whether this shift is detectable relative to the linewidth of a modern atomic clock.

Question 4: Hyperfine Structure and the Zeeman Effect in the Ground State of Hydrogen

The ground state of hydrogen ($1s_{1/2}$) has nuclear spin $I = 1/2$, giving rise to two hyperfine levels $F = 0$ and $F = 1$ separated by the famous 21 cm (1420 MHz) transition. This question traces the evolution of these levels from zero field to the Paschen–Back regime.

(a) Write down the hyperfine Hamiltonian $\hat{H}_{\text{hf}} = A\,\hat{\mathbf{I}}\cdot\hat{\mathbf{J}}$ for the $1s_{1/2}$ state of hydrogen. Using the identity

$$\hat{\mathbf{I}}\cdot\hat{\mathbf{J}} = \tfrac{1}{2}\big[F(F+1) - I(I+1) - J(J+1)\big], \tag{11}$$

find the energies of the $F = 1$ and $F = 0$ states in terms of A. Given that the 1420 MHz transition corresponds to the $F = 1 \to F = 0$ splitting, determine A in MHz. Verify that the centre-of-gravity condition $\sum_F (2F+1)\,E_F = 0$ holds.

(b) In a weak magnetic field ($\mu_B B \ll A\hbar$), F is a good quantum number. Derive the energy of each $|F, M_F\rangle$ sublevel to first order in B, expressing your answer in terms of g_F and $\mu_B B$.

By projecting the magnetic moment operator $\boldsymbol{\mu} \approx -g_J\mu_B\mathbf{J}$ onto the total angular momentum $\mathbf{F}$ using the Wigner–Eckart theorem, derive the expression for g_F and evaluate it for both $F = 1$ and $F = 0$.

(c) In a strong field ($\mu_B B \gg A\hbar$, the Paschen–Back limit for hyperfine structure), F is no longer a good quantum number. The good quantum numbers become m_J and m_I. Write down the energy eigenvalues in this regime (including both the Zeeman energy and the hyperfine interaction to first order) and enumerate all four states using (m_J, m_I). Identify which states are weak-field seeking (energy increasing with B) and which are strong-field seeking (noting the relevance for magnetic trapping experiments).

(d) For the states connecting to $|F = 1, M_F = 0\rangle$ and $|F = 0, M_F = 0\rangle$ at zero field, show that their exact energies at an arbitrary field B can be written as

$$E = -\frac{A}{4} \pm \frac{A}{2}\sqrt{1 + x^2}, \qquad x = \frac{2\mu_B B}{A\hbar} \quad \text{(specify any overall constants)}. \tag{12}$$

(This is a special case of the Breit–Rabi formula.) At what field strength does the frequency of the $M_F = 0 \leftrightarrow M_F = 0$ transition have its minimum sensitivity to B? Explain why this is the operating point for hydrogen masers and atomic clocks.

Question 5: Multi-Electron Atoms: From LS to jj Coupling

The two idealised coupling limits, LS (Russell–Saunders) and jj, represent opposite extremes of the competition between inter-electron electrostatic repulsion and the spin–orbit interaction. Real atoms often lie between these extremes. This question explores the competition using the carbon-like np^2 configuration.

(a) For two equivalent p-electrons (configuration np^2), enumerate all possible two-electron states using the Pauli exclusion principle and LS coupling. List all valid (L, S) terms, justify which are excluded by antisymmetry, and write down the spectroscopic notation. Using Hund's rules, identify the ground term.

(b) The LS ground term of np^2 is a ${}^3P$ term, split by spin–orbit interaction into levels $J = 0, 1, 2$. The Landé interval rule gives

$$\Delta E(J,\, J-1) \equiv E(J) - E(J-1) = A_{\mathrm{LS}} \cdot J. \tag{13}$$

Show that the intervals $E(1) - E(0)$ and $E(2) - E(1)$ are in the ratio $1 : 2$. For carbon ($n = 2$), the ${}^3P_1 - {}^3P_0$ splitting is approximately 16.4 cm^{-1}. Determine A_{LS} for carbon and predict the ${}^3P_2 - {}^3P_1$ splitting. Is the multiplet normal or inverted, and why?

(c) Now consider the analogous configuration in a heavy atom (e.g. Pb, $Z = 82$, configuration $6p^2$). In the jj-coupling limit, each p-electron has definite $j = \frac{1}{2}$ or $j = \frac{3}{2}$. Enumerate the possible jj-coupled states $(j_1, j_2)_J$ for the two p-electrons (applying Pauli exclusion), and write down their spectroscopic labels. Show that

the total number of distinct J-levels is the same as in LS coupling — verify this is a general consequence of the fact that both schemes span the same Hilbert space.

(d) As Z increases from light to heavy atoms, the spin–orbit parameter $\zeta \propto Z^4$ grows faster than the electrostatic repulsion $K \propto Z$. In intermediate coupling the levels are labelled by J only; two levels of the same J arising from different LS terms undergo an *avoided level crossing* as ζ/K increases. Identify which pair of J-levels (from your results in parts (a)–(c)) undergoes such a crossing in the np^2 sequence, and qualitatively sketch their energies as a function of increasing ζ/K, with K held fixed. Identify which quantum numbers are preserved throughout.