

The unperturbed wavefunctions of Hydrogen including spin are $\psi_{n,l,m,m_s}^0 = R_{nl}Y_{lm}X_{\pm}$ where X_+ (spin up) and X_- (spin down) are the common eigenfunctions of the spin operators S^2 and S_z with eigenvalues $s(s+1)\hbar^2 = \frac{3}{4}\hbar^2$ and $m_s\hbar$ for $m_s = \pm\frac{1}{2}$. Similarly, Y_{lm} are the common eigenfunctions of L^2 and L_z with eigenvalues $l(l+1)\hbar^2$ and $m\hbar$, and ψ_{n,l,m,m_s}^0 are the eigenfunctions of H^0 with eigenvalues E_n .

Spin-orbit coupling in Hydrogen gives rise to a perturbation of $H' \propto \underline{L} \cdot \underline{S}$ where \underline{L} and \underline{S} are the orbital and electron spin angular momentum operators, respectively. H^0 , L^2 , L_z , S^2 and S_z all commute with each other.

- (a) The total angular momentum operator $\underline{J} = \underline{L} + \underline{S}$. Evaluate $J^2 = (\underline{L} + \underline{S}) \cdot (\underline{L} + \underline{S})$ to show that $\underline{L} \cdot \underline{S} = \frac{1}{2}(J^2 - L^2 - S^2)$ [1 mark]
- (b) $\underline{L} \cdot \underline{S} = L_x S_x + L_y S_y + L_z S_z$. Show that this can be rewritten using the ladder operators $L_{\pm} = L_x \pm iL_y$ and $S_{\pm} = S_x \pm iS_y$ as $\underline{L} \cdot \underline{S} = \frac{1}{2}(L_+ S_- + L_- S_+) + L_z S_z$ [2 marks]
- (c) Ladder operators raise and lower their associated angular momentum quantum number by unity, so $S_- X_+ = a X_-$ and $S_+ X_- = a X_+$ where $a = \hbar/\sqrt{2}$, and $L_{\pm} Y_{lm} = A_{lm} Y_{l,m\pm 1}$ where $A_{lm} = \hbar\sqrt{l(l+1) - m(m\pm 1)}$. All angular momenta have a maximum value beyond which the upwards ladder operator gives zero, and a minimum below which the downwards ladder operator gives zero.

Use this together with the definition of $\underline{L} \cdot \underline{S}$ in terms of ladder operators in (b) above to show that

$$\underline{L} \cdot \underline{S} \psi_{2,1,-1,1/2}^0 = \frac{\hbar^2}{2}(\psi_{2,1,0,-1/2}^0 - \psi_{2,1,-1,1/2}^0)$$

Are the unperturbed energy eigenfunctions of Hydrogen also eigenfunctions of $\underline{L} \cdot \underline{S}$? [4 marks]

- (d) Use $\underline{L} \cdot \underline{S} = L_x S_x + L_y S_y + L_z S_z$, together with the standard commutation relations for any general angular momenta $[J_x, J_y] = i\hbar J_z$,

$[J_y, J_z] = i\hbar J_x$, $[J_z, J_x] = i\hbar J_y$, (i.e. these relations hold for the components of \underline{L} and \underline{S} as well as \underline{J}) to show that $[\underline{L} \cdot \underline{S}, L_z] \neq 0$ and $[\underline{L} \cdot \underline{S}, S_z] \neq 0$ but that $[\underline{L} \cdot \underline{S}, J_z] = [\underline{L} \cdot \underline{S}, L_z + S_z] = 0$.

Which set of quantum numbers allow the effect of the perturbation to be calculated using non-degenerate perturbation theory? [3 marks]