

Atomic field shifts and spectral differences

GRE undergraduate preparation · local supported objectives

Choose the physical question

Reasoning

The same magnetic field needs different quantum labels when its energy scale crosses the spin-orbit splitting. Calculate orbital and spin magnetic shifts in the appropriate coupling regime Find photon-energy shifts from allowed upper-minus-lower level changes Contrast parity cancellation with degenerate electric-field splitting

Choose magnetic quantum labels

Reasoning

An electron has a negative magnetic moment: $\mu_L = -\mu_B L/\hbar$ and $\mu_S \approx -2\mu_B S/\hbar$. With B along positive z , the interaction $-\mu \cdot B$ therefore gives $H_Z = \mu_B B(L_z + 2S_z)/\hbar$. $\mu_B \approx 5.788 \times 10^{-5}$ eV/T. In an uncoupled basis with orbital projection m_l and spin projection $m_s = \pm 1/2$, the shift is $\mu_B B(m_l + 2m_s)$. Use this uncoupled rule when the magnetic interaction is large relative to the relevant spin-orbit splitting but still small relative to orbital energy gaps, so quadratic diamagnetic and orbital restructuring effects can be neglected. Large and small are comparisons of energies, not universal Tesla thresholds. In the opposite weak-field regime, m_l and m_s are not independently conserved labels for an LS-coupled eigenstate.

Resolve a weak-field multiplet

Reasoning

When LS coupling dominates a weak magnetic perturbation, $J=L+S$ and m_J label the multiplet. The first-order shift is $\mu_B B g_J m_J$, with $g_J = 1 + [J(J+1) + S(S+1) - L(L+1)] / [2J(J+1)]$ in the approximation $g_s = 2$. L, S, J here are dimensionless quantum numbers. For $L=1, S=1/2$, $J=3/2$ gives $g_J = 4/3$ and shifts $-2, -2/3, +2/3, +2$ times $\mu_B B$. $J=1/2$ gives $g_J = 2/3$ and shifts $\pm \mu_B B/3$. Do not substitute $J=0$ into the singular formula; a $J=0$ state has no first-order vector projection shift. Intermediate fields require a coupled Hamiltonian rather than mixing weak-field and uncoupled formulas.

Subtract the two level shifts

Reasoning

A photon's energy is the upper atomic energy minus the lower energy. Its field-induced change is therefore $\Delta E_\gamma = \Delta E_{\text{upper}} - \Delta E_{\text{lower}}$. Count allowed transitions using the stated selection rules as well as the two level patterns. Several transitions can share one frequency; the number of split states is not automatically the number of spectral lines. In a spin-neglected orbital model, an upper $L=1$ triplet has shifts $m_l \mu_B$ with $m_l = -1, 0, +1$, and a lower $L=0$ state has zero shift. Electric-dipole $\Delta m_l = 0, \pm 1$ permits three photon shifts $-\mu_B, 0, +\mu_B$. This normal-triplet model does not describe every real atom or fine-structure multiplet. Polarisation and observation direction can change which components are detected.

Use electric-field symmetry and degeneracy

Reasoning

In a uniform electric field F along z , an electron's perturbation is $+eFz$ for the stated electrostatic potential convention. A nondegenerate parity eigenstate has $\langle z \rangle = 0$, so its first-order diagonal Stark shift vanishes, although a quadratic shift can remain. Exactly degenerate opposite-parity states instead allow an off-diagonal dipole matrix element. In an original two-state model, suppose the dipole matrix is $[[0, d], [d, 0]]$, with real d in charge $\times$ length units. The perturbation F times this matrix has eigenvalues $\pm dF$ and opposite superpositions of the two states. Changing a basis phase changes the off-diagonal sign but not the splitting $2|dF|$. Actual near-degenerate atoms require comparison with fine structure and other small splittings before an exactly degenerate approximation is adopted; this supplied matrix is not a universal hydrogen coefficient.

Worked reasoning 1

Reasoning

In weak LS-coupled magnetic fields, the Zeeman effect uses J , not uncoupled m_l and m_s .

Worked relation 2

Reasoning

Apply this relation only under the conditions just stated.

$$\Delta E = \mu_B B g_J m_J, \quad g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}.$$

Worked reasoning 3

Reasoning

For $L = 1$, $S = 1/2$ and $J = 3/2$, $g_J = 4/3$.

Worked relation 4

Reasoning

Apply this relation only under the conditions just stated.

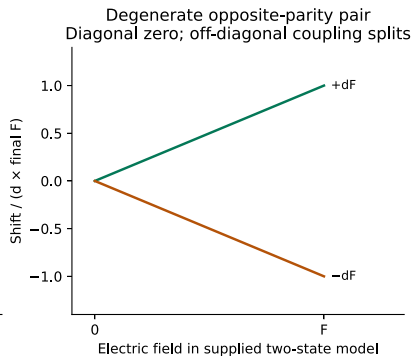
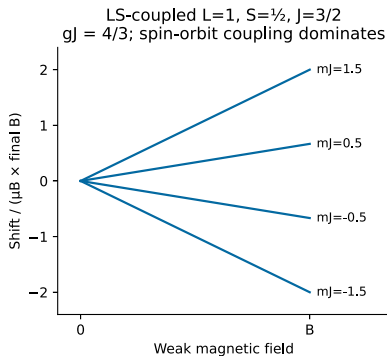
$$\Delta E = \mu_B B g_J m_J = (5.788 \times 10^{-5} \text{ eV/T})(2 \text{ T})(4/3)(1/2) = 7.72 \times 10^{-5} \text{ eV}.$$

Worked reasoning 5

Reasoning

Select the field regime before inserting quantum numbers. Photon shifts subtract the lower-level shift.

Read the original diagram



- Original GRE teaching diagram: Atomic field shifts and spectral differences
- Identify the axes, units, directions and the stated model.

Independent transfer · attempt

Reasoning

Two opposite-parity degenerate states have dipole perturbation matrix $\begin{pmatrix} 0 & dF \\ dF & 0 \end{pmatrix}$.
Find energies and eigenstates to first order. Compare with two such states separated by a large unperturbed gap Δ . **[5]**

Independent transfer · reasoning

Reasoning

Degenerate shifts are $\pm dF$, with eigenstates $(1, \pm 1)/\sqrt{2}$; splitting is $2|dF|$. With a large gap, each parity state's first-order diagonal shift is zero. Off-diagonal coupling instead gives ground shift approximately $-(dF)^2/\Delta$. Award shifts, states, splitting, vanishing nondegenerate first order and quadratic correction/condition.

Check assumptions and limits

Reasoning

Declare the coupling regime, keep the negative electron moment sign, and subtract lower-level shifts. Zero diagonal dipole expectation does not exclude degenerate mixing or quadratic shifts.

Keep the technical distinctions

Reasoning

Landé factor : Projection factor relating a weak-field LS-coupled magnetic shift to $g_J m_J$. Stark splitting : Electric-field-induced separation of atomic energy levels, with symmetry and degeneracy controlling leading order.

Check yourself

- Define Landé factor and give its condition of use.
- Define Stark splitting and give its condition of use.
- Redo the original transfer with a changed parameter; check a limiting case.