Atomic field shifts and spectral differences

GRE undergraduate preparation · local supported objectives

Atomic field shifts and spectral differences

- Use the strong-field (**Paschen–Back effect** 帕邢 – 巴克效应) and weak-field Zeeman formulas.
- Calculate the **Landé g-factor** 朗德 g 因子.
- Count spectral lines from level shifts.
- Know when the **Stark effect** 斯塔克效应 is linear.

Strong field: uncoupled labels

- μ_B is the **Bohr magneton 玻尔磁子**. The factor 2 on m_s is the electron spin g-factor.
- When the magnetic energy is much larger than the **spin–orbit coupling 自旋 – 轨道耦合**, L and S act separately:

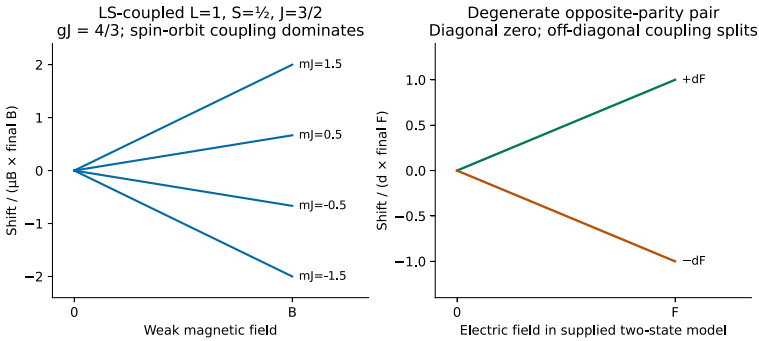
$$\Delta E = \mu_B B(m_l + 2m_s), \qquad \mu_B = 5.79 \times 10^{-5}\ \text{eV/T}$$

Weak field: the Landé g-factor

- For $L = 1$, $S = \frac{1}{2}$: $J = \frac{3}{2}$ has $g_J = \frac{4}{3}$, and $J = \frac{1}{2}$ has $g_J = \frac{2}{3}$.
- Each J level splits into $2J + 1$ equally spaced sublevels.

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

Figure: Weak field: the Landé g-factor



- Weak-field Zeeman shifts are gJ · mJ · μB · B; an electric field splits a degenerate opposite-parity pair linearly
- Read the axes and units first.

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Counting lines

- Normal **Zeeman effect** ($L = 1 \to 0$, spin ignored): $\Delta m_l = 0, \pm 1$ gives three lines, at $-\mu_B B$, 0 and $+\mu_B B$.
- With spin and different g_J in the two levels, the anomalous effect gives more lines.
- Several transitions can share one frequency, so count distinct lines, not levels.

The Stark effect

- A non-degenerate state of definite parity has $\langle z \rangle = 0$: no linear shift, only a smaller quadratic one.
- A degenerate pair of opposite parity, with dipole matrix $\begin{pmatrix} 0 & d \\ d & 0 \end{pmatrix}$, shifts by $\pm dF$: a linear splitting of $2|dF|$. Hydrogen's $n = 2$ level behaves like this.

Which regime?

- Sodium's 3p splitting is 2.1 meV, so $\mu_B B$ matches it only near $B = 36$ T. Laboratory fields of about 1 T are therefore weak.
- In hydrogen, whose fine structure is much smaller, a few tesla already approach the strong-field regime.

Worked example: weak-field shifts

- $m_J = \frac{1}{2}$: $\Delta E = \frac{4}{3} \times \frac{1}{2} \times (5.79 \times 10^{-5}) \times 2.0 = 7.7 \times 10^{-5}$ eV.
- Neighbouring sublevels are $\frac{4}{3}(5.79 \times 10^{-5})(2.0) = 1.5 \times 10^{-4}$ eV apart.
- Four sublevels, at $m_J = \pm\frac{3}{2}, \pm\frac{1}{2}$.

Worked example: the normal triplet

- The outer lines shift by $\pm \mu_B B = \pm 5.79 \times 10^{-5}$ eV.
- $\Delta\lambda = \lambda\, \Delta E / E = 500 \times (5.79 \times 10^{-5}) / 2.48 = 0.012$ nm.
- That is why Zeeman needed a fine grating, and saw only a widening at first.

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Common errors

- Using $g_J m_J$ in a strong field, or $m_l + 2m_s$ in a weak one.
- Forgetting the factor 2 on the spin.
- Giving a photon the shift of one level instead of the difference.

Common errors (2)

- Expecting a linear Stark shift for a non-degenerate state.
- Assuming a 1 T laboratory field is strong for every atom.

Key terms

- **Zeeman effect**: The splitting of spectral lines in a magnetic field.
- **Paschen–Back effect**: The strong-field Zeeman regime, where L and S act separately.
- **Landé g-factor**: g_J, which sets the size of weak-field Zeeman shifts for a level with given L, S, J.
- **Stark effect**: The shift and splitting of energy levels in an electric field.

Check yourself

- What is g_J for $L = 1$, $S = \frac{1}{2}$, $J = \frac{1}{2}$?
- Does the ground state of hydrogen have a linear Stark shift?
- Into how many sublevels does a $J = \frac{5}{2}$ level split in a weak field?