Atomic spectra and selection rules

GRE undergraduate preparation · local supported objectives

Atomic spectra and selection rules

- Find photon energies and wavelengths from hydrogen-like levels.
- Count states with the **quantum numbers 量子数**.
- Apply electric-dipole **selection rules 选择定则**.
- Know how **fine structure**, the **Zeeman effect** and shielding change the simple picture.

Hydrogen-like energies

- The photon energy is the positive difference $E_\gamma = E_i - E_f$.
- The **ionisation energy 电离能** from the ground state is $13.6\,Z^2$ eV: 13.6 eV for H, 54.4 eV for He^+.
- Every level of He^+ ($Z = 2$) is four times deeper than the matching level of hydrogen.

$$E_n = -\frac{13.6\,Z^2}{n^2}\ \text{eV}, \qquad \lambda = \frac{hc}{E_\gamma}, \quad hc \approx 1240\ \text{eV nm}$$

Spectral series

- Lyman series: down to $n = 1$, in the ultraviolet ($2 \to 1$ is 10.2 eV, 122 nm).
- Balmer series: down to $n = 2$, mostly visible ($3 \to 2$ is the red line at 656 nm).
- Paschen series: down to $n = 3$, in the infrared.

Quantum numbers

- Level n holds $2n^2$ states: 2, 8, 18, ...
- The total angular momentum is $\mathbf{J} = \mathbf{L} + \mathbf{S}$; for one electron with $l > 0$, $j = l \pm \frac{1}{2}$.
- Letters: $l = 0, 1, 2, 3$ are s, p, d, f.

Electric-dipole selection rules

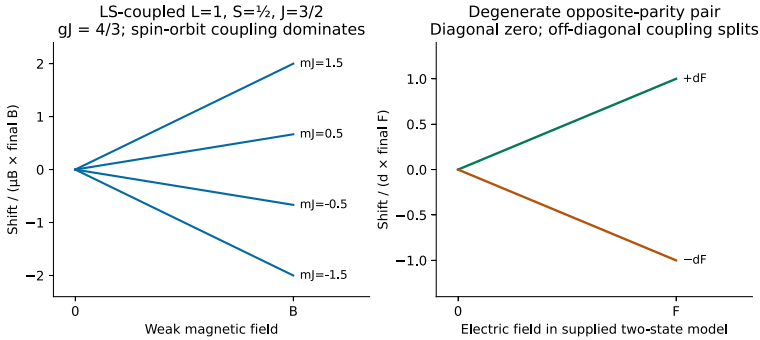
- $\Delta l = \pm 1$, $\Delta m_l = 0, \pm 1$, and no change of spin.
- $2p \to 1s$ $(\Delta l = -1)$ is allowed and fast. $2s \to 1s$ $(\Delta l = 0)$ is forbidden, so 2s is **metastable 亚稳态的**: it decays slowly, by emitting two photons.
- "Forbidden" means forbidden for this mechanism, not impossible.

Fine structure and the Zeeman effect

- For $^2P_{3/2}$ ($L = 1$, $S = 1/2$, $J = 3/2$), $g_J = 4/3$, and there are four equally spaced sublevels.
- An electric field splits a degenerate pair of opposite-parity states linearly in the field (the linear Stark effect of hydrogen).

$$\Delta E = g_J m_J \mu_B B, \qquad \mu_B = 5.79 \times 10^{-5}\ \text{eV/T}$$

Figure: Fine structure and the Zeeman effect



- 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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Many-electron atoms

- Shielding breaks the l-degeneracy: in sodium, 3s lies below 3p. The 3p $\to$ 3s jump gives the yellow D line at 589 nm.
- You cannot put $Z = 11$ into $-13.6Z^2/n^2$ for sodium's outer electron.
- The Pauli principle fills states in order, giving the periodic table.

Worked example: Balmer's red line

- Hydrogen: $E_\gamma = 13.6\left(\frac{1}{4} - \frac{1}{9}\right) = 1.89$ eV, so $\lambda = 1240/1.89 = 656$ nm.
- He^+ $4 \to 2$: $E_\gamma = 13.6 \times 4\left(\frac{1}{4} - \frac{1}{16}\right) = 10.2$ eV, the same as hydrogen's Lyman-alpha (122 nm).
- Check with Balmer's formula: $B \times 9/5 = 364.6 \times 1.8 = 656$ nm.

Worked example: Zeeman splitting

- Neighbouring sublevels: $g_J \mu_B B = \frac{4}{3}(5.79 \times 10^{-5})(1.0) = 7.7 \times 10^{-5}$ eV apart.
- Largest shift ($m_J = 3/2$): $\frac{4}{3} \times \frac{3}{2} \times 5.79 \times 10^{-5} = 1.16 \times 10^{-4}$ eV.
- These shifts are tiny next to the 2 eV photon energies of visible light, so the lines split only slightly.

Common errors

- Giving a negative photon energy, or using $E_f - E_i$.
- Forgetting the factor Z^2 for hydrogen-like ions.
- Calling a $\Delta l = 0$ or $\Delta l = 2$ transition allowed.

Common errors (2)

- Counting n^2 states per level instead of $2n^2$, which includes spin.
- Using the hydrogen formula for outer electrons of many-electron atoms.

Key terms

- **quantum numbers**: The labels n, l, m_l, m_s (and j, m_J) that identify an electron state.
- **selection rules**: Conditions on quantum-number changes that a given transition mechanism allows.
- **ionisation energy**: The energy needed to remove an electron completely.
- **spectral series**: All the lines that end on the same lower level.

Check yourself

- What is the **ionisation energy** of ground-state He^+?
- Is the transition 3d $\rightarrow$ 2s allowed for electric-dipole emission?
- How many electron states does the $n = 3$ level hold?