

# 7.1 Atomic spectra and selection rules

Name: \_\_\_\_\_ Class: \_\_\_\_\_ Date: \_\_\_\_\_

**Total: 10 marks****KEY WORDS** selection rule • Zeeman splitting

## Objective

Relate atomic energies to spectral lines; Apply angular-momentum quantum numbers; Distinguish allowed and forbidden electric-dipole transitions. Original public practice; not an ETS paper.

## 1 Key knowledge and worked examples

For hydrogen-like one-electron ions, the bound energies scale as  $-13.6 Z^2/n^2$  eV in the simplest nonrelativistic model. Emission requires a downward transition and positive photon energy.

Orbital angular momentum has  $l=0,\dots,n-1$  and  $m_l=-l,\dots,l$ . Electron spin adds  $s=1/2$ ; total angular momentum combines orbital and spin contributions.

Electric-dipole selection rules include  $\Delta l=\pm 1$  and  $\Delta m=0,\pm 1$ . These rules concern a specific transition mechanism; forbidden does not mean impossible by every mechanism.

Fine structure, spin-orbit effects and Zeeman splitting refine the simplest hydrogen picture. In many-electron atoms, shielding and electron interactions invalidate direct hydrogen-energy substitution.

### ■ Worked method

For a nonrelativistic one-electron ion, neglecting fine structure,

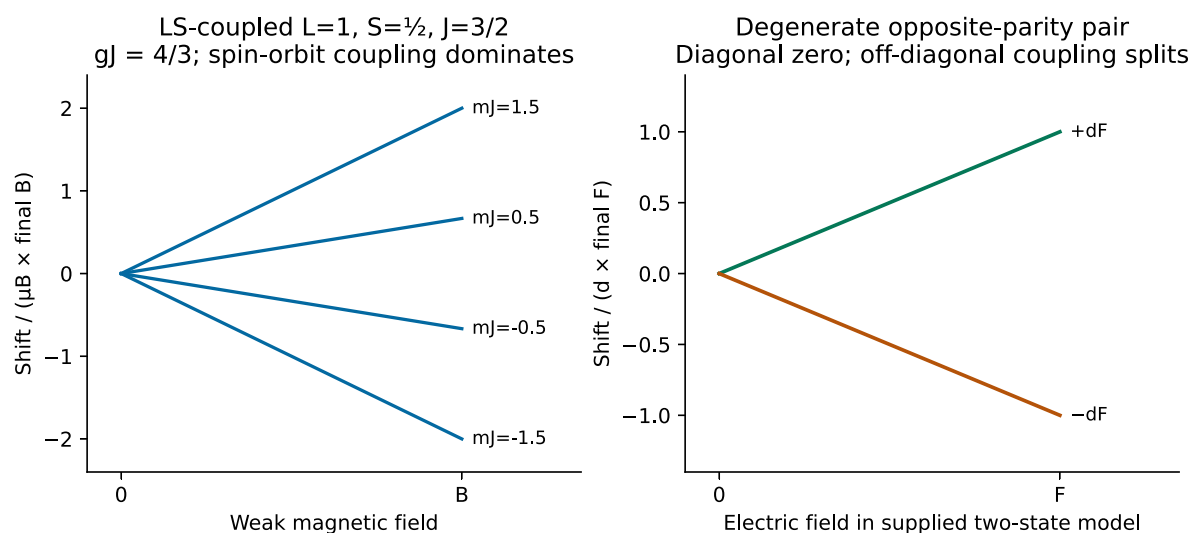
$$E_n = -13.6 \text{ eV } Z^2/n^2.$$

For  $Z = 2$ , an emission from  $n = 3$  to  $n = 2$  gives positive photon energy:

$$E_\gamma = E_3 - E_2 = (13.6 \text{ eV})(2^2)(1/2^2 - 1/3^2) = 7.56 \text{ eV}.$$

$$\lambda = hc/E_\gamma = (1240 \text{ eV nm})/(7.56 \text{ eV}) = 164 \text{ nm}.$$

An energy difference alone does not guarantee an electric-dipole transition; the participating orbital states must satisfy the selection rules.



## 2 Practice

**2.1** Hydrogen  $n=3$  has energy about:

[1]

- A.  $-13.6$  eV
- B.  $-1.51$  eV
- C.  $+1.51$  eV

**2.2** Which  $\Delta l$  is electric-dipole allowed?

[1]

- A. 0
- B. 1
- C. 2

**2.3** For hydrogen  $2 \rightarrow 1$ , the photon energy is \_\_\_\_\_ eV. Show your relation and units.[2]

**2.4** Decide whether this claim is true. Justify it: Electric-dipole forbidden means no emission mechanism can ever exist. [2]

### 3 Exam-style questions

**3.1** A hydrogenic electron is in a 3d state. Under the electric-dipole approximation, which lower principal-level orbital states can it reach in one emission? Explain why the  $n = 1$  level is excluded. Ignore fine structure and spin changes. [4]

## Solutions

---

**2.1** Answer: B. Divide  $-13.6$  by  $9$ .

Compare the rejected options:  $-13.6$  eV;  $+1.51$  eV. Use the stated model and conditions.

**2.2** Answer: B. The orbital rule is  $\Delta l = \pm 1$ .

Compare the rejected options:  $0$ ;  $2$ . Use the stated model and conditions.

**2.3** 10.2. Subtract  $-13.6$  from  $-3.4$ .

**2.4** False. Other mechanisms, such as two-photon emission, can occur.

**3.1** A  $3d$  state has  $l = 2$ . Electric-dipole emission requires  $\Delta l = \pm 1$ , and a lower  $n$  for positive photon energy. At  $n = 2$  only  $l = 0, 1$  exist, so  $2p$  is allowed (with magnetic sublevels obeying  $\Delta m = 0, \pm 1$ ). At  $n = 1$  only  $1s$  exists;  $\Delta l = -2$  forbids that direct electric-dipole transition. Award initial  $l$ , rule,  $2p$  and exclusion of  $1s$ . Higher-order transitions are outside this approximation.