

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,

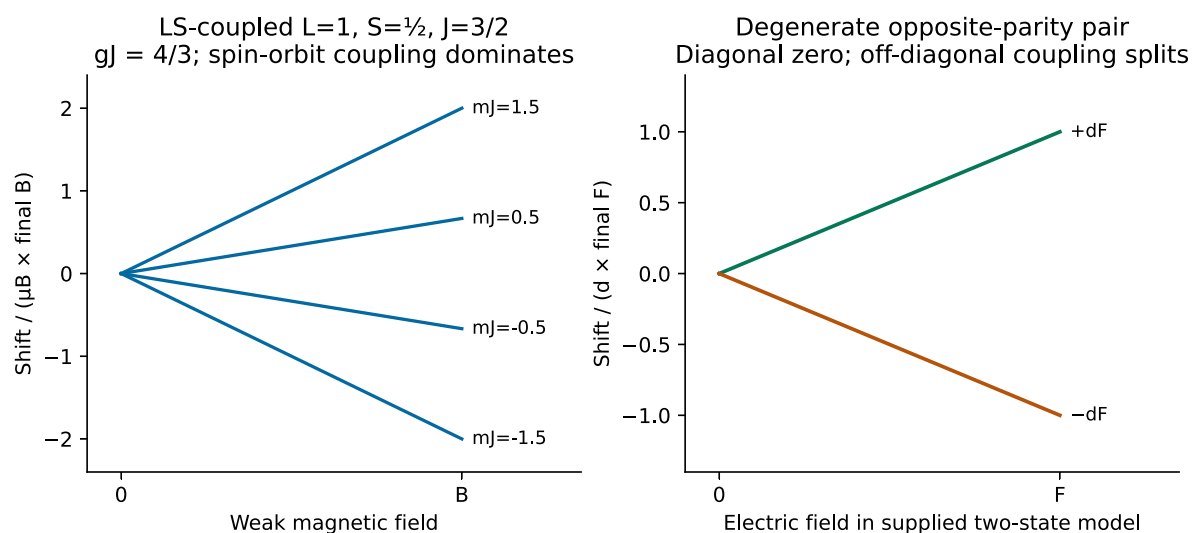
$$E_n = -13.6 \text{ eV } Z^2/n^2.$$

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 Choose one answer. Hydrogen $n=3$ has energy about:

[1]

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

2.2 Choose one answer. Which Δl 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 B Divide -13.6 by 9 .

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

2.2 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.