ATOMIC and MOLECULAR PROCESSES

Edited by

D. R. BATES

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Department of Applied Mathematics
The Queen's University of Belfast
Belfast, Northern Ireland

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Preface

This compilation, which is designed primarily as a reference book for research scientists, is concerned with radiative and collisional processes involving atoms or molecules. It provides surveys covering the following topics: forbidden and allowed lines and bands, photoionization, photodetachment; recombination, attachment; elastic and inelastic scattering of electrons, energy loss by slow electrons; collision broadening of spectral features; encounters between atomic systems including range, energy loss, excitation, ionization, detachment, charge transfer, elastic scattering, mobility, diffusion, relaxation in gases, and chemical reactions. A chapter is devoted to the use of high temperature shock waves and accounts are given of the other main experimental methods. The relevant theoretical work is also described, detailed mathematics being avoided as far as possible.

The main emphasis is placed on the developments which have taken place in the past decade, that is, since the publication of the first edition of the great treatise by Massey and Burhop *Electronic and Ionic Impact Phenomena*. These developments were stimulated by the growth of interest in such fields as space science, astrophysics, and plasma physics. They were rendered possible by remarkable technical advances which have benefited directly not only experimentalists but also (through fast digital computing) theorists.

Thanks must be given to the staff of the Academic Press for their determined efforts to ensure that a thick volume reviewing work done up to almost the end of 1961 should appear early in 1962.

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1.

Forbidden Transitions

R. H. Garstang

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1 Introduction

1.1 DISCOVERY AND IMPORTANCE OF FORBIDDEN TRANSITIONS

Early in the history of spectroscopy empirical rules were developed to enable the prediction of spectral lines to be accomplished from the energy levels of the atoms. These rules became known as selection rules; they enabled one to select, from all the possible transitions between pairs of energy levels, those which might be expected to be observable. These selection rules were subsequently justified by quantum mechanics. As the subject progressed some lines were discovered which violated the selection rules, and such lines became known as forbidden lines. The first forbidden transitions to be recognized as such were the $^2D - {}^2S$ transitions in the alkali metals, observed by Datta in 1922. Other lines observed in the laboratory were the $6^3P_2 - 6^1S_0$ line of mercury (Rayleigh, 1927), the mercury line $6^3P_0 - 6^1S_0$ by Fukuda (1926), and the auroral line $2p^4\,{}^1S_0 - 2p^4\,{}^1D_2$ of oxygen (McLennan and Shrum, 1925). The study of forbidden lines received its greatest stimulus when Bowen (1928) identified many of the strongest lines in the spectra of gaseous nebulae as being due to forbidden transitions in O II, O III, and N II. Many more forbidden lines were discovered subsequently in celestial objects, and a few were produced in laboratory sources. The appearance of the forbidden lines in celestial objects indicates the presence of unusual physical conditions, particularly low densities, when the frequency of collisional de-excitation of atomic levels is much reduced, and radiative de-excitation by forbidden transitions becomes important. Observations of forbidden lines are thus of importance in astrophysics because of the information which they can yield on the conditions in their source. A number of forbidden transitions were found in molecular spectra from about 1930 onwards. Van Vleck (1934) established the nature of the atmospheric absorption bands of oxygen, Vegard and Kaplan studied forbidden bands in N_2, and others were identified. The occurrence of such bands in the telluric spectrum has led to much of the interest in their study.

1.2 Terminology

A number of definitions of *forbidden* transitions have been proposed. The traditional definition divides spectrum lines into two groups, those which satisfy all the selection rules are termed *permitted lines*, all the others are called *forbidden lines*. This definition is not entirely adequate, for many of the selection rules are only approximate, and the strengths of the forbidden lines vary greatly with atomic number for atoms of the same electronic structure. An alternative definition calls lines forbidden if the probability of their occurrence is very small compared with the probability of the strongest transitions between levels of similar total quantum numbers (Mrozowski, 1944). Other authors refer to those lines which are due to magnetic dipole or electric quadrupole radiation as multipole radiation (Rubinowicz, 1949). Notwithstanding these definitions, a practical terminology has arisen which is described below and used in this chapter.

In atomic spectroscopy, all transitions which violate the rigorous selection rules for electric dipole radiation in free atoms are termed *forbidden transitions*. This category includes all magnetic dipole and electric quadrupole transitions, two-quantum processes, electric dipole radiation enforced by perturbations external to the atom, and electric dipole radiation caused by the atomic nucleus. Electric dipole transitions which violate only certain approximate selection rules (e.g., $4s^2\,{}^1S_0 - 4s4p\,{}^3P_1$ in Ca I, which violates the rule $\Delta S = 0$) are not called forbidden transitions.

In molecular spectroscopy all transitions which violate any selection rules, whether rigorous or not, are called forbidden. Thus, intercombinations (e.g., ${}^3\Pi - {}^1\Sigma$) are included among forbidden molecular transitions. In polyatomic molecules transitions made possible by vibronic interactions are also included among forbidden transitions.

In atomic spectroscopy forbidden lines are denoted by square brackets, e.g., the auroral line is described as occurring in the spectrum of [O I].

2 *Forbidden Lines in Atomic Spectra*

2.1 Introduction

In accordance with the terminology discussed earlier, all transitions which violate the rigorous selection rules for electric dipole radiation in free atoms are termed forbidden transitions. The selection rules for electric dipole, magnetic dipole, and electric quadrupole radiation are listed in Table I. The notation used is the standard one: L, S, and J are, respectively, the orbital, spin, and total angular momenta of the atomic electrons, M is the magnetic quantum number (component of J) and n is the principal quantum number. The parity is $(-1)^{\Sigma l_i}$ where l_i is the azimuthal quantum number of the ith electron. The selection rules (1), (2), and (3) are rigorous in the absence of nuclear perturbations and two-quantum processes. Rule (4) holds only when configuration interaction is negligible, and rules (5) and (6) hold only for LS-coupling. Forbidden lines may arise from several causes.

(a) The rigorous selection rules, (1)-(3), may be violated for electric dipole radiation, but allowed for magnetic dipole or electric quadrupole radiation.

TABLE I

SELECTION RULES IN ATOMIC SPECTRA

Electric dipole	Magnetic dipole	Electric quadrupole
(1) $\Delta J = 0, \pm 1$	$\Delta J = 0, \pm 1$	$\Delta J = 0, \pm 1, \pm 2$
$(0 \nleftrightarrow 0)$	$(0 \nleftrightarrow 0)$	$(0 \nleftrightarrow 0, \frac{1}{2} \nleftrightarrow \frac{1}{2}, 0 \nleftrightarrow 1)$
(2) $\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1, \pm 2$
(3) Parity change	No parity change	No parity change
(4) One electron jump	No electron jump	One or no electron jump
$\Delta l = \pm 1$	$\Delta l = 0$	$\Delta l = 0, \pm 2$
	$\Delta n = 0$	
(5) $\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
(6) $\Delta L = 0, \pm 1$	$\Delta L = 0$	$\Delta L = 0, \pm 1, \pm 2$
$(0 \nleftrightarrow 0)$		$(0 \nleftrightarrow 0, 0 \nleftrightarrow 1)$

(b) The approximate selection rules, (4)-(6), may be violated.
(c) The atoms may be subject to external perturbations.
(d) Nuclear perturbations may be appreciable.
(e) A two-quantum process may take place.

Lines produced by (b) above [without (a), (c), (d), or (e)] are not usually termed "forbidden" (see § 1.2).

We shall discuss first the general theory of magnetic dipole and electric quadrupole radiation, then consider calculations and observations on individual atoms, and finally discuss the remaining types of forbidden transitions. Review articles on these subjects have been published by Borisoglebskii (1958), Rubinowicz (1949), and Mrozowski (1944).

2.2 THEORY OF MAGNETIC DIPOLE AND ELECTRIC QUADRUPOLE RADIATION

The basic theory of magnetic dipole and electric quadrupole radiation was given by Condon and Shortley (1951). They gave the formulae for transition probabilities in terms of the matrix elements of the magnetic dipole and electric quadrupole moments, and quoted the formulae of Rubinowicz for the relative strengths of the Zeeman components of a line and of the lines of a multiplet in quadrupole radiation. The theory was extended by Shortley (1940), who showed how many of the general methods used for electric dipole intensity calculations could be extended to the electric quadrupole case. In particular, Shortley showed how to perform calculations for the intermediate coupling conditions which are