ATOMIC SPECTRA

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To

James Franck

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Preface

When Messrs Longmans asked me, many years ago, to write a book on atomic spectra, I intended to prepare an English version of the book *Atomspektren* which I had written as part of the *Hand-u. Jahrbuch d. Chem. Physik* (Akad. Verl. Ges. 1934). The war, and afterwards various preoccupations, delayed the work so much that the original plan had to be altered. This is a new and essentially different book, taking account of later developments and changed requirements. Some figures and parts of the text of the German book could, however, be used, and the generous permission to do this freely was given by the Akademische Verlags Gesellschaft and is herewith gratefully acknowledged.

There appears to be a need for an up-to-date book on atomic spectra, treating the subject in an introductory manner, yet more thoroughly than general textbooks on modern physics are able to.

The approach is that of the Physicist, not the Mathematician, starting from observed facts and classical concepts, and intentionally stressing the correspondence between classical and quantum Physics. Mathematical concepts are defined and explained as far as they are essential for an understanding of the basic Physics. For complex mathematical techniques the reader is referred to the original literature and to texts such as *Theory of Atomic Spectra* by Condon and Shortley (Cambr. Univ. Press 1935) and *Quantum Theory of Atomic Structure* by J. C. Slater (McGraw-Hill 1960). The theoretical introduction in chapter II is not intended as a textbook of quantum mechanics but tries to collect formulae and methods in the form required in later chapters.

It is hoped that the book will be useful for more advanced undergraduate—and graduate—work, and also to research workers in the fields of Physics, Chemistry and Astronomy. In working for a degree, the student may omit chapter V and some more specialised paragraphs in other chapters without finding the text incoherent. For the benefit of the research worker, many recent developments which could not be fully described have been mentioned with references to the literature.

To aim at completeness in references was obviously impossible in a book of this kind, and the author wishes to apologise for the necessarily somewhat arbitrary selection of references. Apart from especially important papers, those containing full references to other work have been quoted preferentially. The failure to do justice to Russian literature is regretfully admitted; it is entirely due to technical difficulties.

I am profoundly indebted to Dr. G. W. Series who read through almost the entire manuscript and suggested some most valuable improvements, and also to Dr. D. M. Brink who read some sections and gave some valuable advice. I also wish to express my thanks to Prof. S. J. Foster, Prof. R. Gebauer, Dr. G. Herzberg, Dr. F. S. Tomkins and Dr. M. Fred for making prints of spectrograms available for reproduction, and to Mr. C. W. Band for making some excellent photographic reproductions. Mr. D. N. Stacey and Mr. J. M. Vaughan gave valuable help in proof-reading. I specially wish to acknowledge my indebtedness to the publishers whose understanding, helpfulness and efficiency made the work so much easier for the author.

H.G.K.

Balliol College, Oxford.
April 1961.

NOTE TO SECOND IMPRESSION

The second impression has given me an opportunity for eliminating a number of misprints and mistakes. I am indebted to many of my colleagues for pointing out mistakes to me, very particularly to Professor J. E. Mack for his valuable corrections.

H.G.K.

Preface to the Second Edition

Many new developments have been included in this new edition, but by re-writing parts of the text I have tried to avoid an undue increase in the size of the book. Major changes will be found in the sections dealing with highly excited states and autoionisation, isotope shifts and widths of spectral lines, apart from a large number of minor changes and improvements. One substantial addition is the section on radiofrequency spectra in chapter VI. By presenting the fundamental ideas and the scope of the methods of atomic beam resonance, double resonance, level crossing and optical pumping in an elementary way, I have attempted to fill a gap in the textbook literature. In the treatment of highly ionised atoms and isoelectronic sequences it was found difficult to accommodate some of the new material within the framework of this book, and the reader is referred to the authoritative treatment of these topics in the review article by B. Edlén (ref. I, 24). Those interested in the evolution of ideas in the field of atomic spectra will find W. R. Hindmarsh's recent book, *Atomic Spectra* (Pergamon Press 1967) most useful.

In bringing the bibliography up to date it was found necessary to restrict new references to review articles where possible and to a few recent publications containing full references.

I am indebted to many colleagues for corrections and criticism, but very particularly to Dr D. N. Stacey who read through the entire text and not only improved many details but recast some sub-sections completely. For permission to reproduce figures, I am indebted to Professor U. Fano, Drs R. P. Madden and K. Codling, Professor A. Steudel, Professors P. Thaddeus and R. Novik, and Professor H. Griem.

Oxford
February, 1969 H. G. Kuhn

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CHAPTER

I. Introduction

1. The spectroscopic method

The light emitted by atomic gases in a discharge tube is due to the motions of electrons in the atom, and by studying this light we can gain information on the electronic structure which determines the physical and chemical properties of the atom. In principle, we could investigate the light in two different ways; we could set up a very sensitive oscilloscopic apparatus to record the electric vector $\mathbf{E}$ of the radiation field or one of its components, say E_x, as a function of the time t. Alternatively, we could send the light into a spectroscope which effectively carries out a Fourier analysis of the function $E_x(t)$. The "spectrum" can be regarded as a function $A(\nu)$, a record of the amplitude A as a function of the frequency ν.

The way in which the characteristic features of mechanical motion can be impressed on a light wave and then deduced from the spectrum may be illustrated by the following experiment which could be carried out in actual fact. Light from a highly monochromatic source, of frequency ν_0, is passed through a device which modulates its amplitude E at the frequency δ. It may be imagined as a uniformly rotating disk whose optical density varies sinusoidally as a function of the angle of azimuth or, more realistically, as an electro-optical Kerr cell operated by a radio-frequency generator. The amplitude of the emergent light is then given by

$$\begin{aligned} E(t) &= (a_0 + a_1 \cos 2\pi\delta t) \sin 2\pi\nu_0 t \\ &= a_0 \sin 2\pi\nu_0 t + \tfrac{1}{2}a_1 \sin 2\pi(\nu_0+\delta)t + \tfrac{1}{2}a_1 \sin 2\pi(\nu_0-\delta)t. \end{aligned} \tag{1}$$

If the light enters a spectroscope of extremely high resolving power, three spectral lines of frequencies ν_0, $\nu_0+\delta$ and $\nu_0-\delta$ and intensities $a_0{}^2$, $(a_1/2)^2$ and $(a_1/2)^2$ will be observed. Eq. (1) can be regarded as a simple example of a Fourier expansion of the function $E(t)$. The statement that the amplitude function $A(\nu)$ has finite values only for the three values ν_0, $\nu_0+\delta$ and $\nu_0-\delta$ of the variable ν and assumes the values a_0, $a_1/2$ and $a_1/2$ specifies the function $E(t)$ completely, except for the phases which are often unimportant.

If the motion happened to be of a more complicated type, but still periodic, lines of frequencies $\nu_0 \pm 2\delta$, $\nu_0 \pm 3\delta$, .. would be observed, and a knowledge of their amplitudes and phases would enable us to derive the function $E(t)$.

If the motion is not strictly periodical, the spectroscope will no longer show perfectly "sharp" spectral lines. If the frequency or transparency of the Kerr cell drifts slowly or if it changes abruptly after long intervals of constancy, the spectrum will be continuous with pronounced peaks at approximately the frequencies of the spectral lines observed for strictly periodic motion.

Of the two kinds of information mentioned, the second one which consists in the knowledge of the Fourier amplitudes $A(\nu)$ or their squares $I(\nu)$, is not only easier to obtain for light emitted by atoms, but also proves to be of a specially useful and convenient form: atomic spectra are found to consist, to a high degree of approximation, mostly of spectral lines. The Fourier analysis performed by the spectroscope shows essentially a "discrete" spectrum, a number of definite values of ν for which the intensity $I(\nu)$ is finite while practically vanishing for other values of ν.

In any mechanical system, a discrete spectrum of frequencies is characteristic of periodic motions which are confined to a definite part of space, such as planetary motions in contrast to cometary motions; they are conveniently referred to as *bounded* motions.

It was the principal aim of the early spectroscopists to find an interpretation of the spectra of atoms in terms of a *model*, by applying the classical laws of mechanics and electrodynamics to the motion of particles having suitably chosen properties. Even in this general form, the problem led to difficulties of a fundamental nature: the integral ratios of frequencies (higher harmonics) which every classical model would yield, were not found in atomic spectra. But further difficulties arose when classical laws were applied to the more definite model which Lord Rutherford and others had evolved on the basis of well-established experimental facts such as the scattering of α-particles by atoms.

The atom is now known to consist of a nucleus, of positive electric charge Ze, and of Z electrons, each of which has the charge $-e = -4{\cdot}8029 \times 10^{10}$ esu and the mass $m = 9{\cdot}1091 \times 10^{-28}$ gm. The atomic number Z assumes all integral values from hydrogen, $Z = 1$, to the heaviest element known at present, $Z = 102$. Even for the lightest elements, the nucleus is so heavy, compared with the electrons, that it can be regarded as a fixed centre of attraction, except for the description of some very fine details of spectra. All the main properties of each atom are therefore determined by the single parameter Z.

Goudsmit and Uhlenbeck(1) later extended the model by replacing the *point electron* by the *spinning electron*, endowed with an intrinsic angular momentum as well as with mass and charge.

Under the influence of the electrostatic attraction by the nucleus, together with their mutual repulsion, the electrons would be expected to carry out complicated, planetary motions. But, as one can most easily see for the hydrogen atom with one electron, the gradual loss of energy by radiation would cause the electron to approach the nucleus more and more closely, emitting light of continually increasing frequency, and finally to fall into the nucleus.

The laws of classical mechanics thus proved to be incapable of explaining either the structure of spectra or the stability of atoms, and new and more general laws had to be evolved. The empirically found relationships in atomic spectra, more than any other facts, showed the way to these new laws of quantum physics. The "old" quantum theory of Bohr and Sommerfeld which formed the first step in this development is still frequently used, mainly because of its close relation to classical mechanics. For rigorous, quantitative work, it has been superseded by the more complete and self-consistent methods of quantum mechanics. It appears that quantum mechanics in its present form is capable of describing the structure of spectra in their essential features. Numerically, however, the computations are extremely complicated and have not yet been carried very far. It is likely that semi-empirical methods, combining spectroscopic data with theoretical concepts, will continue to play a great part in the study of atoms.

A new phase in atomic spectroscopy started with the discovery of hyperfine structures and isotope shifts of spectral lines. They are caused by properties of nuclei other than their charges, such as angular momenta, magnetic moments and the distribution of charge and magnetism in the nucleus, and the study of these structures has become a means of exploring both atomic and nuclear structure.

Though this book deals primarily with optical spectra of atoms, a term intended to include infra-red and ultra-violet, and even X-ray spectra, results from radio-frequency methods will be referred to frequently. In view of the rapid development of radio-frequency resonance methods for measurement of hyperfine and fine structures, a section describing the main features of the various methods has been added to chapter VI.