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## Book Review: *The Theory of Atomic Structure and Spectra* by Robert D. Cowan

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## Atomic Spectroscopy

Book Review: *The Theory of Atomic Structure and Spectra*, by Robert D. Cowan. University of California Press, Berkeley, CA, 1981. xviii, 732 pp., illus. \$45. Los Alamos Series in Basic and Applied Sciences.

The field of atomic spectroscopy is currently experiencing a resurgence of interest owing on the one hand to its applications in astrophysics, plasma physics, and other fields and on the other hand to the development of new experimental tools to probe atomic structures. One example of the latter is the use of tunable lasers to study highly excited atoms in the presence of strong external electric and magnetic fields. Another is the use of synchrotron radiation to probe with increasing detail the inner shell structure of rare earth, actinide, and other heavy atoms.

The theoretical foundations of atomic spectroscopy were given in a classic 1935 book, *The Theory of Atomic Spectra* by Condon and Shortley. It served the physics community for decades and is still useful today. The development of powerful techniques of tensor analysis by Racah in the 1940s has prompted a number of authors to write books on the theory of atomic spectra from this more modern point of view. The most recent of these books is that of Robert D. Cowan. His gives probably the most practical detail of all the recent books on the subject; it will therefore prove invaluable to those who plan to carry out numerical calculations and will be useful generally to all who wish examples of how well modern theoretical calculations compare with experimental data.

Cowan has made his career as a theorist in the field of atomic spectroscopy, and his book contains much of the wealth of practical experience he has acquired. The book is based on lectures he gave at Purdue University in spring 1971 and at the University of New Mexico in spring 1972. Though Cowan has greatly expanded the lectures, the book is still intended for possible use as a graduate-level textbook. Thus, all of the theory is developed from an elementary point of view, and there are suggested exercises at the end of many sections of the book. Though the theories of antisymmetric  $N$ -electron wavefunctions, irreducible tensor operators, radiative transitions, and so on are all included, the emphasis is on the actual numerical calculation of atomic energy levels. Flow charts of computer programs, detailed comparison with experimental data, extensive tabular material in the appendixes, and much advice on numerical procedures make this book especially useful.

Cowan's book treats topics in an amount of detail that is not easily found outside the research literature. For example, anyone who has ever studied atomic structure knows Hund's rule, which states that for a given configuration the

lowest energy term is the one with the largest value of  $S$  having the largest value of  $L$ . Most books give the rule and explain its plausibility. Cowan gives a critique of it. He writes:

With the limited amount of experimental evidence available at that time, Hund thought the above relations to be quite general. Although they are now known to be misleading more often than not (note the two points of disagreement in Fig. 4-4), they are still sometimes invoked in an attempt to predict the lowest term of a complex configuration. Hund's rule can safely be applied only to configurations with a single open subshell or with one subshell plus an  $s$  electron, and then only in the restricted form: *The lowest-energy term of a configuration  $l^n$  or of  $l^n s$  is that term of maximum  $S$  which has the largest value of  $L$*  [pp. 124-125].

Cowan then compares this restricted rule with experimental evidence and discusses its plausibility.

Other topics treated in similarly useful detail are the numerical solution of the Hartree-Fock equations and the complications and instabilities that can occur (sections 7-5 and 7-6), the use of nonorthogonal basis states in atomic structure calculations (section 13-2), and the effects of cancellation on theoretically calculated oscillator strengths (section 14-15). The theory of continuum wavefunction normalization is treated very satisfyingly for students: all the limiting procedures used to obtain the end result—which are glossed over in most quantum mechanics textbooks—are spelled out (section 18-3).

Three topics of current interest are discussed in the last chapters of the book. Chapter 19 reviews highly ionized atomic spectra, of interest, for example, in plasma physics. Chapter 20 discusses rare earth and transition element spectra, which are of interest because of their unique properties associated with the filling of  $f$  and  $d$  subshells. Chapter 21 discusses statistical distributions of atomic energy levels and applications of the theory in analyzing plasma spectra.

Despite the size of the book, Cowan omits many topics that are now subfields of atomic structure theory. Thus no discussion is given of group theory, accurate methods for treating few-electron atoms, or accurate methods for treating electron correlations in many-electron atoms. Rather Cowan has chosen to emphasize less powerful but more straightforward theoretical procedures that permit the theorist to analyze a broad range of experimental spectral data. In its emphasis on comparing theory with experiment Cowan's book is probably closest in spirit of any of the modern books on atomic spectroscopy to Condon and Shortley's classic work.

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