Inorganic chemistry

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A Theoretical Approach to Inorganic Chemistry. By A. F. Williams. Pp. 316. (Springer: Berlin, Heidelberg and New York, 1979.) DM98; $53.90.

To my surprise, I greatly enjoyed reading *A Theoretical Approach to Inorganic Chemistry*. Usually when I hear 'theoretical' and 'inorganic' used in conjunction I reach for my revolver. However this admirable book is so full of good sense that all previous prejudices were overcome.

The first chapter contains the essence of quantum mechanics and atomic theory. The only constitutent lacking is the relationship between complex eigenfunctions and the angular momentum operator. The concepts culled from quantum theory are then used to describe polyelectronic atoms and ions, laying to rest in passing such a shibboleth as 'the stability of the half-filled shell'.

The key features of molecular orbital theory are succinctly described in Chapter 2 of which a salutory section discusses hybridisation. The application of molecular orbital theory to the interpretation of the structures of molecules is the subject of Chapter 3 and how best to begin than with a discussion of Walsh diagrams. The section on transition metal compounds is interesting though I was sorry to find the ligand field parameters, Δ and 10Dq, treated as if they are necessarily synonymous; and even more to find the Jahn-Teller effect introduced on page 82 without a proper statement of the theorem. However, the author makes some interesting comments on organometallic compounds, not least the description of the "eighteen-electron rule as an example of electron counting rules that work for no especial reason".

The discussion of electron-deficient compounds (or rather 'compounds for which the theory previously provided was deficient') and cluster compounds is very valuable. It was good to find the same ideas applied to solids, often neglected in popular modern texts. In the chapter on electronic and magnetic properties, the ideas of C. K. Jorgensen find a suitable home; they have long deserved wider exposure. The Jahn-Teller theorem is now discussed more rigorously and as a bonus (?) a brief mention is made of the second-order effect. It is a pity that the author, having kept firmly to SI units in the rest of the book, reverts to c.g.s. units when discussing magnetic properties.

An important chapter contains an account of alternative methods and concepts. Whether the X- method warrants its position at the beginning of the chapter is debatable. The valence bond model and ionic model are well treated and the section on Valence Shell Electron Pair Repulsion should be essential reading for all undergraduates. It is hard to think of an idea that has gained such wide yet uncritical acceptance. The section on "thermodynamics and inorganic chemistry" seems a little out of place in this company especially as it is followed by "Useful Concepts in Inorganic Chemistry". Some might take issue with that title since it includes a description of 'Hardness and Softness' which even warrants a subsection on 'theoretical aspects'. Still, as the author states, "as with other concepts in inorganic chemistry, we should know when they lead us astray". I found the account of "Mechanism and Reactivity" and "Descriptive Chemistry" valuable but that on "Physical and Spectroscopic Methods" less so though even here, the words, though few, are wise. Each chapter has an excellent bibliography.

I have no hesitation in recommending this book to both those who teach and those who study inorganic chemistry. This is especially so for those about to take examinations though by this time it may be too late for the remedial properties of the book to take effect. We should be grateful to the author for sharing his insight with us. □

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Physical principles of photochemistry

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Principles of Photochemistry. By J.A. Barltrop and J.D. Coyle. Pp.213. (Wiley: Chichester, UK and New York, 1979.) £4.95.

THERE are now available several photochemistry textbooks; their emphasis is on photochemical reactions but they deal only briefly with basic photophysics. An alternative approach, such as is in large part provided by Barltrop and Coyle's book, *Principles of Photochemistry,* should be welcomed by undergraduates and postgraduates alike. The emphasis of the book is on photophysics rather than photochemistry (consequently the title is inexact, for only in Chapter 6 is photochemistry really discussed).

After a brief introduction in Chapter 1, Chapter 2 describes time-independent excited-state properties. The Born–Oppenheimer approximation, Franck–Condon factors, spin-orbit coupling, $n\pi^*$, $\pi\pi^*$ and charge transfer transitions are covered. Also included are excited-state geometry changes, acid–base properties and solvent effects. Curiously, though, simple laser theory (which is dealt with too briefly, anyway) is also included in Chapter 2 rather than in Chapter 3, which deals with time-dependent properties, or in Chapter 5, in which techniques for examining reaction mechanisms are explained. Chapter 3 describes excited-state kinetics, fluorescence, phosphorescence, triplet–triplet annihilation and radiationless processes. The last topic is discussed simply but clearly although in a book of this type a more detailed discussion could have been included, especially considering the wealth of information now available. Quenching of excited states by excimer and exciplex formation, electron transfer and electronic energy transfer are treated clearly and concisely in Chapter 4. The kinetics of these quenching mechanisms are also detailed.

Methods of investigating reaction mechanisms, such as trapping intermediates, CIDNP or flash photolysis, occupy half of Chapter 5. No examples of transient flash spectra are given and the most important modern techniques of submicrosecond flash photolysis are only mentioned in passing. Similarly, measurement of singlet lifetimes is hardly mentioned except for an example in Chapter 3 of the rarely used two-photon fluorescence technique. The best feature of this chapter are the pages analysing quenching kinetics leading to nonlinear Stern–Volmer plots.

In summary, this book contains a great deal of useful and, on the whole, carefully presented information on the photophysical properties of excited states. Photochemical reactions are only briefly (12 pages) studied. The description of the experimental techniques is a little out-of-date and excludes important techniques such as single-photon counting and nanosecond and picosecond flash photolysis. The book is, however, well written and easy to read; the problems at the end of the book are also interesting and require some thought. The restriction of mathematical treatments to the minimum while retaining clarity should encourage less mathematically minded students to use this book. □

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