Foundations of Chemistry
https://doi.org/10.1007/s10698-020-09388-y

BOOK REVIEW

Charles S. McCaw: Orbitals with applications in atomic spectra, 2nd edition

World Scientific Press, Singapore, 2020

Eric R. Scerri[1]

As I have written in several publications, a lack of detailed knowledge of the fundamentals of chemistry and its relationship to quantum mechanics among the philosophy of chemistry community has delayed the development of the discipline (Scerri 2017). It has also meant that a good deal of what passes for philosophy of chemistry has been ignored by professional chemists and even by the philosophy of physics fraternity.

The book under review is outstanding and promises to remedy some of this situation, provided that it is read as widely as it deserves to be. Without being an explicitly philosophical treatise Chas McCaw's book, which has now appeared as a second edition, delves into some of the deepest and most difficult aspects of atomic physics and chemistry and its underlying quantum mechanical account.

The six chapters in the book begin with an introduction to the mathematical foundations of quantum mechanics. Chapter 2 is entitled "Orbitals in the Hydrogen atom" and consists of a detailed account of hydrogenic orbitals up to and including the g-orbitals, an aspect that is seldom treated in chemistry textbooks.

In chapter 3, the author moves on to multi-electron atoms. McCaw gives a detailed analysis of the 4 s/3d atomic orbitals conundrum, which has plagued chemical educators for generations (Scerri 2013) and which has only been fully resolved in recent years by the theoretical chemist Eugen Schwarz, who frequently attends and presents at our ISPC international meetings (Wang and Schwarz 2009).

However, there are other approaches to this question, which are equally well reviewed in the book. Similarly, there is a useful section on the anomalous configurations that occur in approximately 20 transition metal and f-block metal atoms have been analyzed through a number of approaches, including those of Schwarz, Rich, and Suter. More recently, the latter approach has been developed further by the Brazilian chemist Eduardo Faria and his colleagues, as our author explains (Orofino et al. 2013). Other topics which are well covered in the same chapter include Slater's rules, electron affinity, including a discussion of the two conventions in use, electron spin and the Pauli Principle.

Chapter 4 provides a review of wave functions in multi-electron atoms, including the question of anti-symmetry, Russell–Saunders coupling, spin–orbit as well as further forms

✉ Eric R. Scerri
scerri@chem.ucla.edu

[1] Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA 90095, USA

Published online: 18 August 2020

of coupling and Hund's rules. The fifth chapter presents a clear and concise account of molecular orbital theory in homonuclear, as well as heteronuclear, molecules before progressing the hybridization of orbitals.

The sixth and final chapter is on Atomic Spectroscopy, the subject of McCaw's own Ph.D. thesis. After explaining the basis of selection rules, the author turns to what he calls simple model systems, such as a particle in a 1D box, followed by the 2D and 3D versions, particle on a ring, and on a sphere. These are all traditional topics but ones that usually appear in a somewhat disconnected fashion in earlier parts of books on quantum chemistry. Instead,McCaw delays in presenting them since they lead naturally on to an analysis of the spectrum of the hydrogen atom. As the author points out, this system is similar to the particle on a sphere model as far as angular momentum is concerned. Finally, the spectra of helium and larger many-electron atoms are examined in a clear way that is reminiscent of the classic quantum mechanics books, such as those of Slater or Condon and Shortley.

One of the many strengths of the book under review is that it takes a rigorous and unflinching look at the necessary mathematical details. In addition, the author, who is the Head of Science at Winchester College in the UK, provides as many as 107 exercises which are interspersed throughout the main text. The detailed solutions are given at the end of the book, over a sequence of about 50 pages. My only slight disappointment was the absence of any treatment of group theory in the book, something that the author readily acknowledges as missing. Perhaps this will be remedied if there is ever to be a third edition of the book, especially given the growing importance of this topic in attempts to explain the periodic table of the elements that go even beyond quantum mechanics (Thyssen and Ceulemans 2017).

References

Orofino, H., Machado, S.P., Faria, R.B.: The use of Rich and Suter diagrams to explain the electron configurations in transition metal atoms. Quim. Nova **36**, 894–896 (2013)

Scerri, E.R.: The trouble with the Aufbau principle. Educ. Chem. **50**(November), 24–26 (2013)

Scerri, E.R.: The Gulf between chemistry and philosophy of chemistry, then and now. Struct. Chem. **28**, 1599–1605 (2017)

Thyssen, P., Ceulemans, A.: Shattered Symmetry: From the Eight-Fold Way to the Periodic Table. Oxford University Press, New York (2017)

Wang, S.-G., Schwarz, W.H.E.: Icon of chemistry: the periodic system of chemical elements in the new century. Angew. Chem. Int. Ed. **48**, 3404–3415 (2009)