Orbitals

With Applications in Atomic Spectra

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by Charles Stuart McCaw (Winchester College, UK)

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With Applications in Atomic Spectra

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*This book is dedicated to the memory of Bob Denning (1938–2013),
my D. Phil. supervisor and a constant source of inspiration.*

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The author used Gnuplot freeware to construct the various kinds of plot and is grateful for the help provided by a couple of sources [1, 2]. The book was written by the author using $\text{\LaTeX}$ freeware, with the assistance of two useful books [3, 4].

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Preface

This book aims to present a modern and mathematically rigorous approach to orbitals in chemistry and apply the concepts to atomic spectra. In the process it should provide a basic introduction to quantum chemistry. It is intended for the book to have wide appeal: orbitals command broad interest across the range of students, teachers and researchers of chemistry in different contexts and at different levels of sophistication.

Electron configurations of transition metals are treated in more detail than in many other books, since this topic raises many interesting and subtle questions about orbitals, starting at the early stages of a UK sixth-form course in chemistry. Rich and Suter diagrams are presented as a useful pedagogical tool, as they provide a more intuitive simple explanation than what is typically seen in textbooks. The limitations of the aufbau principle and of using free atoms to describe electron configurations are discussed and the configuration-average approach of Schwarz is presented. These approaches are little-known and are described here to give a fresh perspective on transition metals; they should be of interest to educators.

There is a discussion of recent research into the visualisation of orbitals, which should be of interest to researchers with an interest in electronic structure. The chapter on orbitals in molecules considers some less common geometries of overlap, and gives a detailed view of π bonding in benzene. The chapter on orbitals in the hydrogen atom considers the f orbitals in both cubic and spherical symmetry. Relativistic effects seen in the s electrons of heavy atoms are explained as far as possible while remaining accessible to most chemists, i.e. without solving the Dirac equation. Electron affinity is considered in the light of data and research that is more recent than some common data books and the approach taken in sixth-form courses.

On first encountering the Schrödinger equation and the mathematical functions describing orbitals of different kinds, many chemistry students are soon confused. Some authors, wanting to protect their readers from

mathematics, present only the most important results, but not knowing their origins can leave the reader unsatisfied. Other authors will present the subject pictorially and communicate qualitative aspects this way. This book aims to present the origins and some important applications of orbitals in as complete a way as possible while explaining everything step-by-step from first principles. The details are either presented in full or left to exercises, which have worked solutions at the back of the book.

Following the recent claim for the discovery of an element with an atomic number of about 122 [5] which, following the aufbau principle and recent relativistic calculations [6], might have a $g_{7/2}$ electron in its ground state configuration, g orbitals are dealt with in this book (albeit in the somewhat idealised sense in a hydrogen atom). They are not, however, presented entirely alongside the better-known atomic orbitals, as they are only of theoretical interest. In this light there is some consideration of the limits of the periodic table and the relativistic factors involved.

Where possible, mathematical group theory is avoided in this book. In keeping with the aims of satisfying the reader that each step is explained in full, examples are chosen to illustrate calculations that do not require group theory. While the author acknowledges the power and elegance of group theory, for many chemists it is a means of arriving at answers to problems rather than a vehicle for gaining deeper understanding.

With over 100 worked solutions to exercises in the appendix, this book should also serve as a tool for learning how to solve problems involving orbitals and atomic spectra, as well as being a textbook.

Most of the material in this book has been taught at various times to able sixth-form students at Winchester College with good training in mathematics; I am grateful to them for their ideas and questions, which have helped in the writing of this book. I believe therefore that it should be accessible to undergraduate chemistry students.