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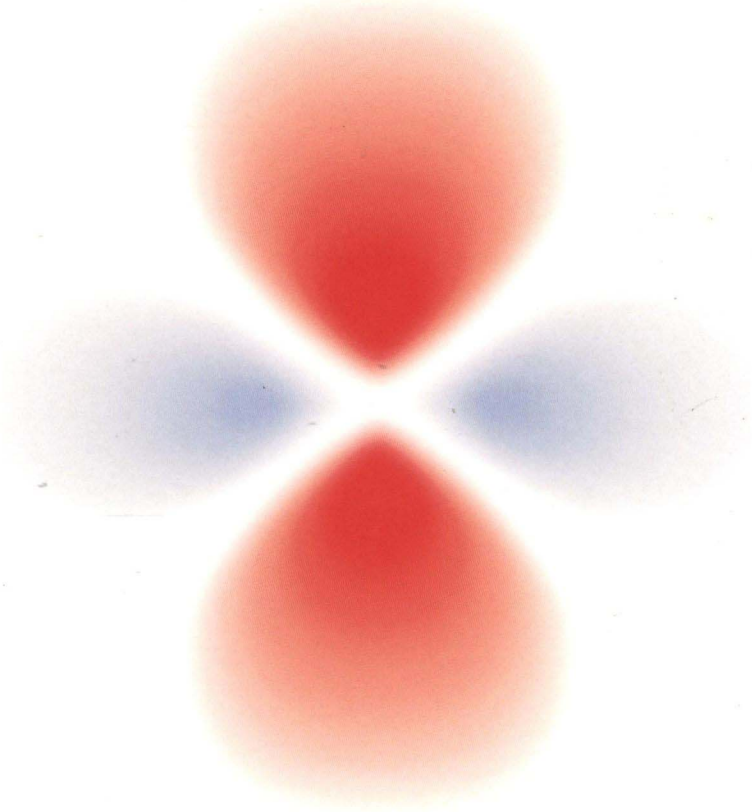
Second edition

# CHEMICAL STRUCTURE and REACTIVITY

## an integrated approach



James Keeler | Peter Wothers

# Chemical Structure and Reactivity:

## an integrated approach

**Second edition**

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Chemical Structure and Reactivity

# Preface

We are pleased to be able to present a second edition of this book, and have taken the opportunity both to make some revisions and changes of our own, as well as to act on the helpful suggestions that a number of people have been kind enough to make. The overall approach and intention are much the same as in the first edition, but we have reorganized some of the material and added two new chapters to Part I. The first of these appears early on and introduces the important topic of molecular symmetry, and the second further develops the general discussion of the kinds of structures which occur when elements bond, first to themselves and then with other elements.

The other main change to the text is the inclusion in each chapter of a number of *Self-test exercises*, the answers to which are given at the end of each chapter. We hope that completing these straightforward problems will help students to get to grips with the material and gain confidence. The *Questions* associated with each chapter now appear in the Online Resource Centre.

## From the preface to the first edition

Our intention in writing this book was to produce a *single* text to accompany the first year, and somewhat beyond, of typical UK degree courses in chemistry. We also had it very much in mind that we wanted to treat the subject *as a whole*, rather than dividing it up in the traditional way. This enables us to emphasize the important connections between different topics, to develop a unified view of the whole subject, and to present the material in rather a different way than is conventional.

Our presentation is very much based on the idea that both structure and reactivity can be understood, or at least rationalized, by thinking about the orbitals (atomic and molecular) involved, their energies, and the way they interact. This is the unifying theme of the whole text, taking us right from the description of the simplest molecules, through to an understanding of reaction mechanisms. This central importance of an orbital description is reflected in the fact that three chapters right at the start of the book are devoted to establishing these ideas.

The quantitative and more theoretical aspects of chemistry are not ignored, but we have been at pains to present these in a way which emphasizes their wider relevance. There are chapters covering the traditional physical chemistry topics of thermodynamics, kinetics, and quantum mechanics, but these are interspersed throughout the book and are strongly connected to the rest of the discussion.

## Content

The content of this book has been tailored to fit in with chemistry courses at UK universities. However, a sufficiently wide range of topics are covered that the text should also be useful in other countries.

Although this book contains a blend of inorganic, organic, and physical chemistry, it is emphatically not a 'general chemistry' text of the type produced for North American universities. Our approach, the content, and the starting point are all significantly different from general chemistry texts. In particular, we have included notably more organic chemistry than one typically finds in such books.

Given that we certainly did not want to produce a book of overwhelming size, we have had to be careful in the selection of the topics which are included and the level to which they are discussed. Our feeling is very much that at this level the most important thing is to understand the key ideas and concepts, and know how to use them. We have therefore devoted a lot of space to setting out these ideas carefully and in detail, so as to provide a sound basis for further study.

Space has not allowed us to include lengthy discussions of the chemistry of each group, nor to explore in detail the subtleties of synthetic organic chemistry, nor to delve deeply into the intricacies of quantum mechanics. Nevertheless, we believe that the material which is presented here forms both a coherent story and a suitable basis on which to begin to get to grips with more advanced chemistry.

## How the text is organized

The book is divided into three parts. The twelve chapters in Part I are closely integrated with one another and designed to be studied in the order they appear. Together, they set out the fundamental ideas needed for the study of chemistry at this level. Although thermodynamics and kinetics appear in Chapters 7 and 12, they are treated with the absolute minimum of mathematics, and in particular without calculus. We have chosen this approach so that those students who are still developing their mathematical skills can nevertheless obtain a good grasp of these essential topics.

The chapters in Part II either introduce further topics or take the discussion started in Part I on to a higher level. For example, with the aid of calculus, Chapter 19 discusses thermodynamics in a somewhat more formal way than was the case in Chapter 7. Similarly, the quantum mechanical ideas which were used qualitatively in Part I are explored in more detail in Chapter 18. Generally speaking, the chapters in Part II can be studied in any order.

In Part III, Chapter 22 is a brief but self-contained exposition of the key mathematical ideas used in the rest of the book. While this chapter is certainly no substitute for an appropriate course in mathematics, we hope that it will be a convenient reference and handy refresher on the key ideas.

Each chapter has associated with it a set of questions, available from the Online Resource Centre, which are designed to test both a basic understanding of the material presented in the chapter, as well as the ability to apply the concepts in more unfamiliar situations. We have also listed in *Further reading* some other texts which can be consulted for an alternative view, or a more advanced or detailed discussion.

## Acknowledgements

We are very grateful to many of our colleagues in the Department of Chemistry for finding the time and patience to answer our questions, direct us to relevant literature, or provide data. In particular we would like to thank both Ruth Lynden-Bell and Anthony Stone for greatly helping our understanding of the underlying theory. Duncan Howe and Paul Skelton from the physical methods section ran many NMR and mass spectra for us with great skill, for which we are most grateful. Alfa Aesar (Heysham, Lancs.) contributed all the samples used to run the NMR spectra, and the GCMS trace shown in Fig. 13.11 was provided by Phil Teale and Simon Hudson (HFL Ltd, Newmarket): we thank them for their contributions.

Several people read and commented on drafts of parts of the book and we remain much indebted to them for their contributions. From Cambridge we would like to acknowledge John Kirkpatrick, Finian Leeper, Rob Paton, Mike Rogers, and Steven Smith. We would also like to acknowledge Michael Clugston (Tonbridge School), Ian Cooper (Newcastle University), Bridgette Duncombe (Imperial College, London), Jason Eames (University of Hull), David McGarvey (Keele University), Ruud Scheek (University of Groningen), Edward Smith (Imperial College, London), Patrick Steel (Durham University), David Worrall (Loughborough University), Rossana Wright (University of Nottingham), and Timothy Wright (University of Nottingham).

Steven Smith has also prepared, with great skill and care, a significant part of the solutions manual. Stephen Elliott contributed a great deal to the development of the Online Resource Centre, and we are very grateful to him for producing some really outstanding resources.

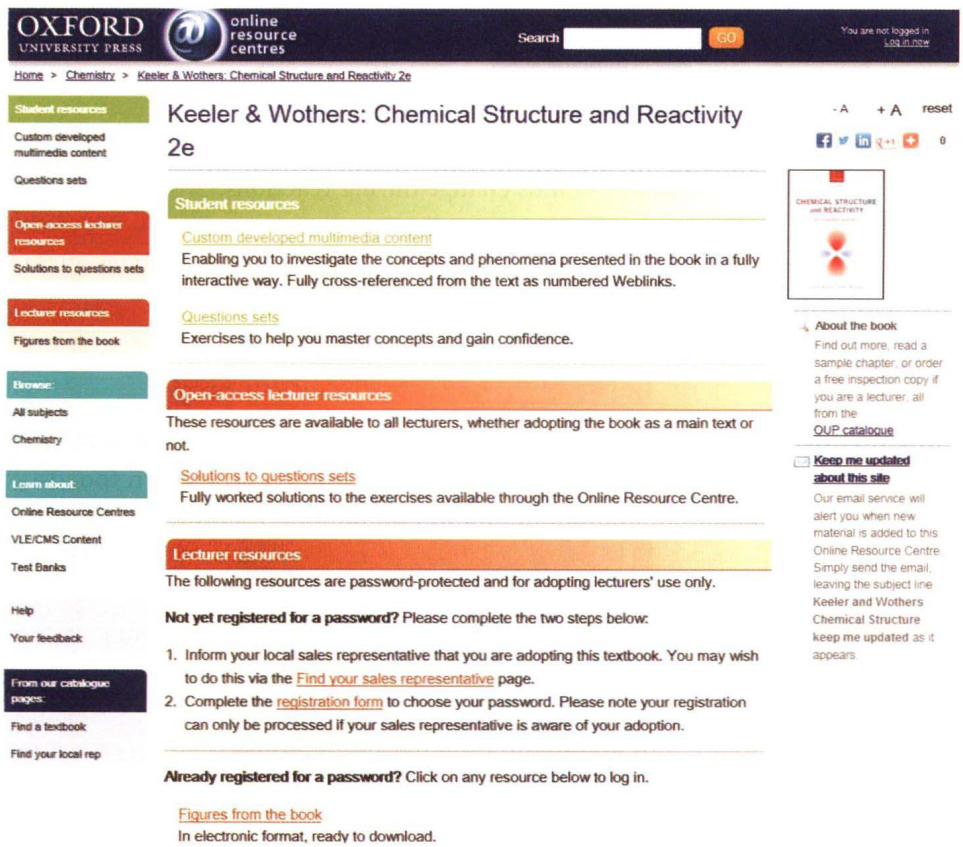
This book has been typeset by the authors using the LaTeX text processing system, in the implementation distributed by MiKTeX (`http://miktex.org/`). We acknowledge the exceptional and continuing effort of the many people throughout the world who have contributed to the LaTeX system and made it freely available.

*Cambridge*, August 2013

# Online Resource Centre

The Online Resource Centre provides both students and teachers with additional materials to complement and extend the text. It also provides a mechanism for all users of the book to feed back their comments and observations to the authors.

**www.oxfordtextbooks.co.uk/orc/keeler2e/**




## For students

Each chapter has associated with it a set of *Questions* which can be downloaded from the resource centre.

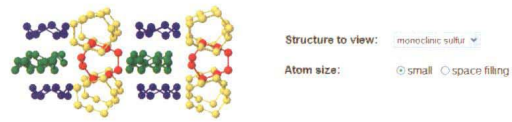
Throughout the text, relevant online resources are indicated by *Weblink* boxes in the margin. On the website the links are arranged according to chapter, so you should easily be able to navigate to the particular link you are looking for.

*Weblink 1.1*

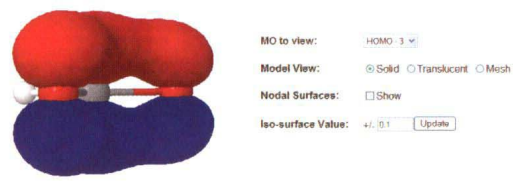
Online resources are indicated by boxes like this one, located in the margin.

The material on the web is not simply a repeat of a diagram in the text. Rather, it is an interactive resource in which you can alter the view of some three-dimensional object, or see how a graph changes in real time when you alter the parameters. There are four main kinds web resources

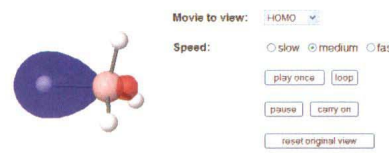
- Three-dimensional representations of molecules and lattices which you can rotate, zoom and view in different ways.



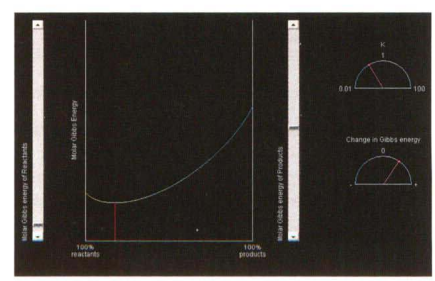

- Three-dimensional representations of orbitals which you can also rotate and zoom so that you can get a real feel for their shape.




- 'Movies' showing how orbitals change during reactions.




- Graphs or plots in which you can change the parameters (usually with real-time sliders), so that you can get a real feel for how the graph responds.




## For teachers

Detailed worked solutions to all of the questions are available to *bona fide* teachers; the resource centre gives details of how to request the solutions manual. Registered adopters of this book will also have access to all the figures, in a high-resolution digital format.

The *Weblink* resources can also be projected during lectures, and provide both excellent illustrations of the topics as well as helping to vary the presentation during the lecture.

# Brief contents

## **Part I** The fundamentals



## **Part II** Going further

## Part III Reference material

# Full contents

## **Part I** The fundamentals