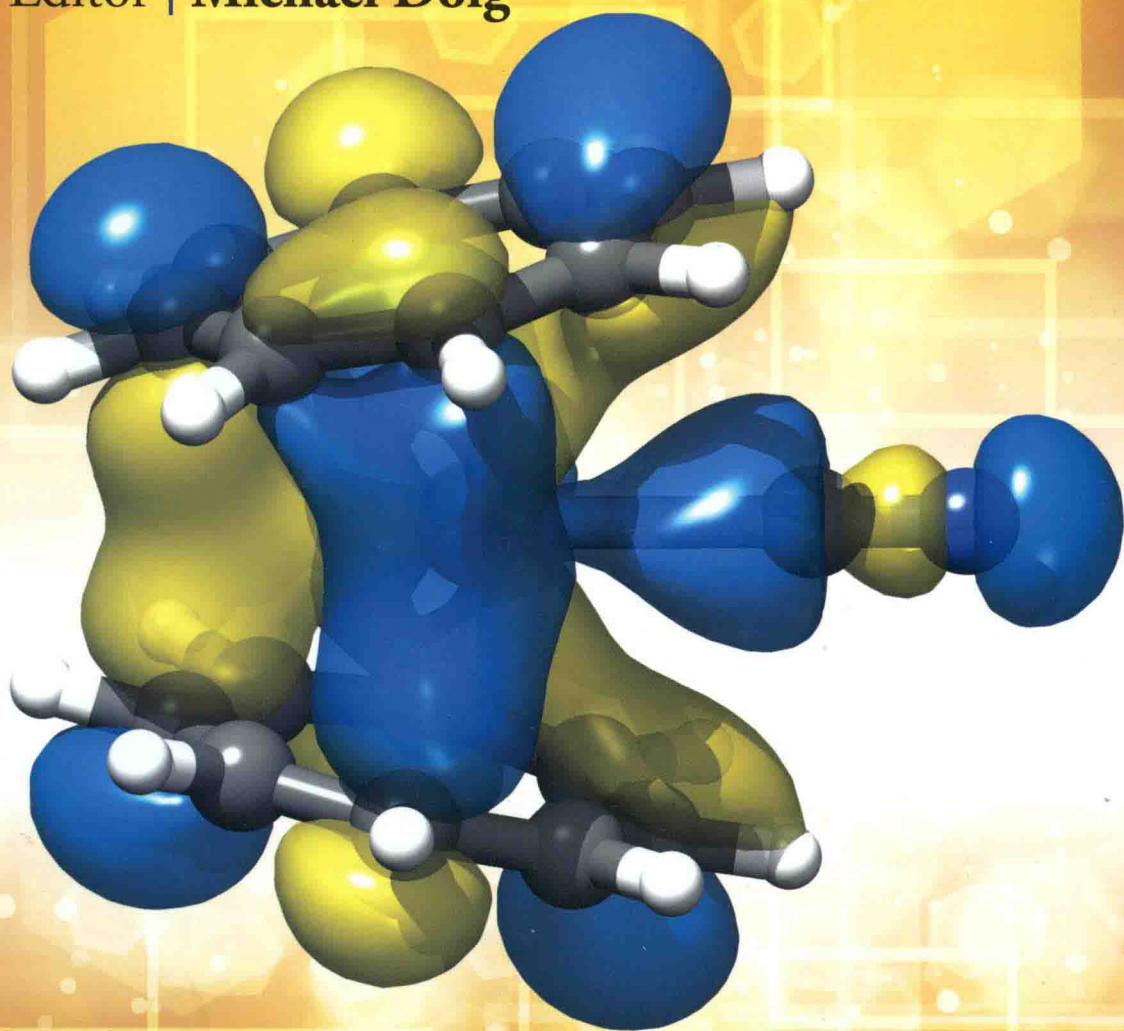# Computational Methods in
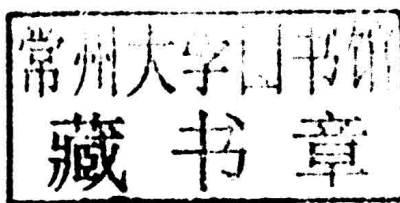# LANTHANIDE AND ACTINIDE CHEMISTRY

Editor | **Michael Dolg**

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Computational Methods in Lanthanide and Actinide Chemistry

Edited by

MICHAEL DOLG

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Computational Methods in Lanthanide
and Actinide Chemistry

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Preface

Lanthanides and actinides comprise about one-quarter of the known chemical elements collected in the periodic table. Because of their complex electronic structure, the significant electron correlation effects, and the large relativistic contributions, the f-block elements are probably the most challenging group of elements for electronic structure theory. In 1987 Pyykkö reviewed the available relativistic electronic structure calculations for f-element molecules (Inorganica Chimica Acta 139, 243–245, 1987). Of the 59 listed studies, 53 dealt with actinides and only 10 with lanthanides. The applied computational methods comprised *ab initio* Dirac-Hartree-Fock one-center expansion and Dirac-Hartree-Fock-Slater calculations, quasirelativistic all-electron X_α-studies, and semiempirical valence-only approaches like relativistic extended Hückel theory. None of these studies took into account static electron correlation explicitly using a multi-configurational wavefunction or included at an *ab initio* level the effects of dynamic electron correlation. No applications of modern density functional theory to f-element molecules were reported either. The treatment of relativity included the Dirac one-particle relativity in a few cases explicitly, but mostly in some approximate form, whereas corrections due to the Breit two-particle interaction or arising from quantum electrodynamics were entirely neglected. Relativistic effective core potentials were only available for a few actinides, which certainly also hampered a routine exploration of lanthanide and actinide chemistry with quantum chemical approaches.

Tremendous progress was made in dealing with lanthanide and actinide systems since the 1987 review of Pyykkö appeared, and the field continues to develop quickly. The current book aims to provide the reader an overview of those state-of-the-art electronic structure theory approaches that have been successfully used for f-element systems so far and summarizes examples of their application. The 16 chapters were written by leading experts involved in the development of these methods as well as their application to various aspects of f-element chemistry. From the results of several studies discussed in these contributions it becomes apparent that quantum chemists successfully conquered the field of lanthanide and actinide chemistry and can provide very valuable contributions not merely supplementing experimental studies, but also frequently guiding their setup and explaining their outcome. Moreover, with largely improved theoretical methods and computational resources at hand, it also became possible to obtain new insights with respect to the interpretation of the electronic structure of f-element compounds.

Despite these many encouraging developments, it is appropriate to say that when it comes to lanthanides and actinides modern electronic structure theory currently can accomplish many things, but certainly not all. It is also clear that this book can only provide a snapshot of the current state of affairs. A number of promising computational approaches, e.g., local electron correlation schemes or F12-dependent wavefunctions, are currently developed and already successfully applied to non-f-element systems. They will during the next years most

likely significantly extend the array of available methods for quantum chemical studies of lanthanides and actinides. Thus more exciting developments can be anticipated.

Finally I would like to thank all authors of the chapters for their excellent contributions. My thanks also go to the staff at Wiley, i.e., Sarah Higginbotham, Sarah Keegan, and Rebecca Ralf, for their guidance and support during this book project. Last but not least, I'm grateful to Mrs. Peggy Hazelwood for copy-editing and to Mr. Yassar Arafat at SPi for final handling of the proofs.

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