QUANTUM-MECHANICAL PREDICTION OF THERMOCHEMICAL DATA

Understanding Chemical Reactivity

Volume 22

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Quantum-Mechanical Prediction of Thermochemical Data

edited by

Jerzy Cioslowski
Florida State University,
Tallahassee, Florida, U.S.A.

KLUWER ACADEMIC PUBLISHERS
NEW YORK, BOSTON, DORDRECHT, LONDON, MOSCOW

eBook ISBN: 0-306-47632-0
Print ISBN: 0-7923-7077-5

Created in the United States of America

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Preface

For the first time in the history of chemical sciences, theoretical predictions have achieved the level of reliability that allows them to rival experimental measurements in accuracy on a routine basis. Only a decade ago, such a statement would be valid only with severe qualifications as high-level quantum-chemical calculations were feasible only for molecules composed of a few atoms. Improvements in both hardware performance and the level of sophistication of electronic structure methods have contributed equally to this impressive progress that has taken place only recently.

The contemporary chemist interested in predicting thermochemical properties such as the standard enthalpy of formation has at his disposal a wide selection of theoretical approaches, differing in the range of applicability, computational cost, and the expected accuracy. Ranging from high-level treatments of electron correlation used in conjunction with extrapolative schemes to semiempirical methods, these approaches have well-known advantages and shortcomings that determine their usefulness in studies of particular types of chemical species. The growing number of published computational schemes and their variants, testing sets, and performance statistics often makes it difficult for a scientist not well versed in the language of quantum theory to identify the method most adequate for his research needs.

In this book, the experts who have developed and tested many of the currently used electronic structure procedures present an authoritative overview of the theoretical tools for the computation of thermochemical properties of atoms and molecules. The first two chapters describe the highly accurate, computationally expensive approaches that combine high-level calculations with sophisticated extrapolation schemes. In chapters 3 and 4, the widely used G3 and CBS families of composite methods are discussed. The applications of the electron propagator theory to the estimation of energy changes that accompany electron detachment and attachment processes follow in chapter 5. The next two sections of the book focus on practical applications of the aforedescribed

methods to free radicals and organometallic compounds. Finally, a brief review of semiempirical methods is given in chapter 8.

Since the science presented here would never materialize without productive interactions between theory and experiment, it is certainly appropriate to dedicate this book to the practitioners of experimental chemistry who do not hesitate to regard electronic structure calculations as an integral part of their investigations and to the vanguards of molecular quantum mechanics who do not shy away from visiting research laboratories where matter rather than its abstract representations is studied.

Jerzy Cioslowski

Tallahassee, April 2001

Contributors

Keld L. Bak, UNI-C, Olof Palmes Allé 38, DK-8200 Århus N, Denmark

Larry A. Curtiss, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL 60439, U.S.A.

O. Dolgounitcheva, Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701

Antonio M. Ferreira, Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701

Gernot Frenking, Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein Strasse, D-35032, Marburg, Germany

Nikolaus Fröhlich, Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein Strasse, D-35032, Marburg, Germany

Asger Halkier, Theoretical Chemistry Group, Debye Institute, Utrecht University, P. O. Box 80052, NL-3508 TB Utrecht, The Netherlands

Trygve Helgaker, Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

David J. Henry, Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Poul Jørgensen, Department of Chemistry, Århus University, DK-8000 Århus C, Denmark

Wim Klopper, Theoretical Chemistry Group, Debye Institute, Utrecht University, P. O. Box 80052, NL-3508 TB Utrecht, The Netherlands

Jan M.L. Martin, Department of Organic Chemistry, Weizmann Institute of Science, Kimmelman Building, IL-76100 Reḥovot, Israel

Jeppe Olsen, Department of Chemistry, Århus University, DK-8000 Århus C, Denmark

J. V. Ortiz, Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701

S. Parthiban, Department of Organic Chemistry, Weizmann Institute of Science, Kimmelman Building, IL-76100 Reḥovot, Israel

George A. Petersson, Hall-Atwater Laboratories of Chemistry, Wesleyan University, Middletown, Connecticut 06459-0180, U.S.A.

Leo Radom, Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Krishnan Raghavachari, Electronic and Photonic Materials Physics Research, Agere Systems, Murray Hill, NJ 07974, U.S.A.

Gustavo Seabra, Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701

Walter Thiel, Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-454 70 Mülheim, Germany

V. G. Zakrzewski, Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701