

Lecture Notes in Chemistry

56

Edited by:

Prof. Dr. Gaston Berthier
Université de Paris

Prof. Dr. Michael J. S. Dewar
The University of Texas

Prof. Dr. Hanns Fischer
Universität Zürich

Prof. Dr. Kenichi Fukui
Kyoto University

Prof. Dr. George G. Hall
University of Nottingham

Prof. Dr. Jürgen Hinze
Universität Bielefeld

Prof. Dr. Hans Jaffé
University of Cincinnati

Prof. Dr. Joshua Jortner
Tel-Aviv University

Prof. Dr. Werner Kutzelnigg
Universität Bochum

Prof. Dr. Klaus Ruedenberg
Iowa State University

Prof. Dr. Jacopo Tomasi
Università di Pisa



D. Heidrich W. Kliesch W. Quapp

Properties of Chemically Interesting Potential Energy Surfaces

Springer-Verlag

Berlin Heidelberg New York

London Paris Tokyo

Hong Kong Barcelona

Budapest

Authors

D. Heidrich
Sektion Chemie

W. Kliesch
W. Quapp
Sektion Mathematik
Universität Leipzig
O-7010 Leipzig

ISBN-13:978-3-540-54286-5 e-ISBN-13:978-3-642-93499-5
DOI: 10.1007/978-3-642-93499-5

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, re-use of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its current version, and a copyright fee must always be paid. Violations fall under the prosecution act of the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1991

2151/3140-543210 - Printed on acid-free paper

PREFACE

The exploration, characterization, and representation of potential energy hypersurfaces (PES) of chemical systems consisting of N interacting atoms is a task of increasing importance especially as a basis for modern reactivity theory.

In Chap. 1 of this book, meaning and problems of the potential surface concept are summarized. The mathematical analysis of the PES is subject of the Chapters 2 and 3. It covers the calculation and characterization of chemically interesting points, curves and global situations on a reaction PES. Since adequate mathematical representations are of increasing importance for the informative processes within the chemical community, the presentation of the mathematical methods in this book also implies educational aspects. Finally, the dependence of PES properties on those approximations is considered which occur in the usual application of quantum chemical theory. This presentation may give the chance to deepen the chemist's PES intuition concerning the handling of reaction PES as a source for microscopic and macroscopic information with and without medium influence (Chap. 4). Thus, we hope to stimulate theoretical understanding and research. Considering the importance of proton transfer reactions in chemistry and biology as well as their advantages in a theoretical treatment, they form the main source for selected examples in Chap. 4. For a full account of experimental and theoretical work in this field, we refer to excellent reviews in the literature.

As soon as Pulay's pioneering work on the problem of quantum chemical geometry optimization was supported by important contributions of McIver and Komornicki in the early seventies, the utilization of the gradient of potential energy has revolutionized the *a priori* calculation of chemical reactivity. The gradient concept was suitable as a basis for a systematic study of chemical reactions and the further development of reaction theory. In 1973, one of the authors (D.H.) published his first quantum chemical program system with some applications using the gradient of the potential energy in semi-empirical methods. The main interest was in the structure and stability of carbocations forming intermediates in important chemical standard reactions.

Later on, we started a cooperation between the Departments of Chemistry and Mathematics at our University to improve the possibilities of PES analysis. At present our work follows three main directions:

- ▶ development of mathematical methods for the analysis of PES,
- ▶ application of quantum chemical ab initio methods on models of chemical standard reactions (exploration of reaction mechanisms),
- ▶ the role of vibrations and intramolecular vibrational redistribution (IVR) during a reaction.

We hope that our experience and results gained in these fields will enrich this book. Dietmar Heidrich is responsible for Chaps. 1 and 4, Wolfgang Kliesch is the leading author for Chap. 2 (up to 2.5), Wolfgang Quapp from 2.6 up to Chap.3.

We would like to thank some colleagues for their help and support to overcome problems and to finish this book:

Dr.S.Ackermann (Leipzig, Germany),
Dr.J.Pancíř (Prague, Czechoslovakia),
Dr.J.Reinhold (Leipzig, Germany),
Prof.Dr.P.v.R.Schleyer (Erlangen, Germany),
Prof.Dr.Z.Slanina (Prague, Czechoslovakia),
Prof.Dr.C.Weiss (Leipzig, Germany),
Prof.Dr.M. and Dr.B.Winnewisser (Gießen, Germany),
Prof.Dr.R.Zahradník (Prague, Czechoslovakia).

Special thanks should be given to

Doz.Dr.H.-J.Hofmann (Leipzig, Germany),
Prof.Dr.J.Tomasi (Pisa, Italy)

who have substantially contributed to this work.

Wolfgang Quapp would like to express his appreciation to the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for supporting in part this work.

Leipzig, April 1991

D.H., W.K and W.Q.

CONTENTS

1	GUIDELINES IN THE DEVELOPMENT OF THE THEORY OF CHEMICAL REACTIVITY USING THE POTENTIAL ENERGY SURFACE (PES) CONCEPT	1
1.1	The Potential Energy Surface (PES) Concept	2
1.2	The Dimensionality Problem	3
1.3	On the Definition of a Reaction Path (RP)	4
1.4	The Hierarchy and Competition of Reaction Theories	11
1.5	What about the Calculation of Absolute Reaction Rates?	17
1.6	Potential Energy Calculation and Gradient Revolution	19
1.7	The "State of the Art" in Everyday Study of Chemical Reactivity	23
	References	26
2	ANALYSIS OF MULTIDIMENSIONAL POTENTIAL ENERGY SURFACES - STATIONARY AND CRITICAL POINTS	31
2.1	Basic Definitions and Notations	31
2.2	Geometrical Properties of PES	33
2.3	Stationary Points	35
2.4	Location of Stationary Points	38
2.4.1	The Newton Process and its Modifications	41
2.4.2	Update Methods	48
2.4.3	Quasi-Newton Methods	60
2.4.4	Descent Methods	66
2.4.5	A Global Newton-like Method	71
2.5	Testing of Numerical Procedures	76
2.6	Zero Eigenvalues of the Hessian	78
2.6.1	Translational and Rotational Invariance	78
2.6.2	"True" Zero Eigenvalues: Catastrophe Points	86
2.6.3	Flat Bottoms and Double Minimum Potentials	95
	References	97
3	ANALYSIS OF MULTIDIMENSIONAL POTENTIAL ENERGY SURFACES - PATHS -	101
3.1	the Simple Valley Floor Line	101
3.2	Mathematics of Valley Floors	107
3.2.1	Gradient Extremals (GE)	107
3.2.2	GE and Bifurcation Points	111
3.2.3	GE for Higher-Dimensional Cases	121
3.3	Steepest Descent Paths	122
3.4	The Independence of Steepest Descent Paths from Parameterization and Coordinate System	126
3.4.1	Parameterization	126
3.4.2	Invariance from Coordinate System	128
3.4.3	Mass-Weighted Cartesian Coordinates	132
	References	136
4	QUANTUM CHEMICAL PES CALCULATIONS: THE PROTON TRANSFER REACTIONS	138
4.1	The Problem in Visualization of PES Properties	139
4.1.1	RP Energy Profiles and Surfaces Derived from Usual PES Sections	139
4.1.2	Graphical Presentation of Three-center Problems	144

VIII

4.1.3	Interaction Surface of an Attacking Species with a Fixed Valence System	144
4.1.4	Empirically Derived Diagrams of more Complex Reactions PES	147
4.1.5	Energy Profiles from Mathematically Defined RP Calculations	148
4.1.6	Summary	150
References		150
4.2	PES Properties Along the Bimolecular Single Proton Transfer	152
4.2.1	Formulation of the Reaction Mechanisms	152
4.2.2	The Proton Transfer Energy	154
4.2.3	Discussion of most Recent PES Data of Bimolecular Single Proton Transfer	155
4.2.4	Gas-Phase Results and Medium Influenced Experimental Data	162
4.2.5	Theoretical Approach to Medium Influence and the PES Concept	167
4.2.6	Proton Transfer, Transition State Theory, and Quantum Chemistry	173
References		176
Index		180