

# Lecture Notes in Chemistry

Edited by G. Berthier, M. J. S. Dewar, H. Fischer,  
K. Fukui, H. Hartmann, H. H. Jaffé, J. Jortner,  
W. Kutzelnigg, K. Ruedenberg, E. Scrocco, W. Zeil

3

---

Svetozar R. Niketić  
Kjeld Rasmussen

The Consistent Force Field:  
A Documentation

---



Springer-Verlag  
Berlin · Heidelberg · New York 1977

## Authors

Svetozar R. Niketić  
Department of Chemistry  
Faculty of Science  
University of Beograd  
P.O. Box 550  
YU-11001 Beograd

Kjeld Rasmussen  
Chemistry Department A  
Building 207  
The Technical University of Denmark  
DK-2800 Lyngby

### Library of Congress Cataloging in Publication Data

Niketic, Svetozar R. 1944-  
The consistent force field.  
  
(Lecture notes in chemistry ; 3)  
Bibliography: p.  
Includes index.  
1. Chemical equilibrium. 2. Matter--Properties.  
3. Field theory (Physics) I. Rasmussen, Kjeld,  
1936- joint author. II. Title.  
OD505.N54 541'.042 77-24235

ISBN-13: 978-3-540-08344-3 e-ISBN-13: 978-3-642-93063-8  
DOI: 10.1007/978-3-642-93063-8

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically those of translation, re-printing, re-use of illustrations, broadcasting, reproduction by photocopying machine or similar means, and storage in data banks.

Under § 54 of the German Copyright Law where copies are made for other than private use, a fee is payable to the publisher, the amount of the fee to be determined by agreement with the publisher.

© by Springer-Verlag Berlin · Heidelberg 1977

Softcover reprint of the hardcover 1st edition 1977

2152/3140-543210

## **PREFACE**

The preface of a book is probably the pleasantest part to write, as it gives the authors an opportunity to express their gratitudes towards all those who have helped.

This book has grown out of two dissertations and two series of seminar notes. We are grateful to those students and colleagues who contributed valuable criticism. Two former students appear as co-authors of individual chapters.

One author (KjR) has spent, over the years 1969-74, several months at Chemical Physics Department, The Weizmann Institute of Science, Israel, studying and developing the CFF. Without the generous hospitality of Professor Shneior Lifson, the Department and the Institute the whole project would not have been.

The other author (SRN) has spent a total of three years at Chemistry Department A, The Technical University of Denmark, as a graduate student of KjR and Professor Flemming Woldbye. He was supported for the greater part of his stay by the Danish Natural Science Research Council. During that period the CFF version described in the book took shape. When Danish computer centres had to charge users for their services, all costs were met through grants from the same Council.

Travel grants were donated by two private funds, Tribute to the Danes through Scholarships in Israel (to Klavs Kildeby) and Berg's Fund for the Advancement of Danish Engineering Science (to KjR).

IV

Mrs. Birgit Rasmussen composed the manuscript, using a text editing programme written at the Danish Data Archives and maintained by the Technical University Computing Centre.

A grant towards part of the cost of the machine editing of the manuscript was provided by G. A. Hagemann's Memorial Fund.

We wish to acknowledge the good service of the academic and technical staff of the Computing Centre throughout the years.

Dr. Ivan Gutman is thanked for valuable comments on the terminology of graph theory.

All drawings were made by Mrs. Rita Bloch Hansen.

Professor Flemming Woldbye is to be thanked for having fostered conformational calculations at Chemistry Department A, and for having established the contact between Professor Shneior Lifson and KJR, as well as between the two authors.

The Board of Chemistry Department A, through the Director, Professor N. Hofman-Bang, are thanked for having given us sufficient everyday facilities to carry out our project.

Last, but not least, we want to thank our wives for constant encouragement and prodding throughout the years.

Beograd and Copenhagen

in April 1977

Svetozar R. Niketić      Kjeld Rasmussen

## CONTENTS

PREFACE	III
1 INTRODUCTION	1
1.1 What the CFF is	2
1.2 Background	6
1.3 Pre-CFF	7
1.4 The ascent of CFF	7
1.5 In the wake of CFF	8
2 THE PROGRAMMING SYSTEM	10
2.1 Introduction	10
2.2 Outline of the programming system	11
2.2.1 Section I	11
2.2.2 Section II	11
2.2.3 Section III	13
2.2.4 Section IV	14
2.2.5 Section V	16
2.2.6 Section VI	17
2.2.7 Section VII	17
2.3 Other programmes	18
2.3.1 Utilities	18
2.3.2 CFFPLOT	18
2.3.3 CRYSTAL	18
2.3.4 EDITOR	19
2.3.5 ORTEP	19
2.3.6 MCNSTER	19
2.4 Organisation of the system	20
2.4.1 Overlay structure	20
2.4.2 JCL procedures	22
2.4.2.1 CFFCLIB	27
2.4.2.2 CFFG	27

2.4.2.3 CFFCLG	29
2.4.2.4 CFFECLG	30
2.4.2.5 Listing of CFFECLG	31
2.4.3 Input-output	35
2.5 Input manual	35
3 MOLECULAR TOPOLOGY AND GEOMETRY	42
3.1 Molecular topology	42
3.1.1 Topological representation of chemical structures	43
3.1.2 From structural formula to linear notation	44
3.1.3 Coding of formulae	47
3.1.3.1 Rules for coding line formulae	48
3.1.3.2 Limitations	50
3.1.3.3 Examples	51
3.1.4 Coordination compounds	52
3.1.5 Output from the programmes	55
3.1.5.1 Programme PRACK	56
3.1.5.2 Programme CODER	56
3.2 Lists of interactions	57
3.2.1 Programme MKLIST	57
3.2.2 Interaction codes	57
3.2.3 Coding and decoding of integer words of interaction	59
3.3 Molecular geometry	60
3.3.1 Construction of molecular geometry	60
3.3.2 Coordination compounds	68
3.3.3 Incomplete structures	70
3.3.4 Sideatom positions	72
3.3.5 Torsional angle specification	76
4 THE CONFORMATIONAL ENERGY AND ITS DERIVATIVES	78
4.1 Introduction	78
4.2 Intermolecular forces	79

4.2.1 Non-bonded interactions	80
4.2.2 Electrostatic interactions	84
4.2.3 Hydrogen bonding	85
4.3 Intramolecular forces	86
4.3.1 Bond stretching	86
4.3.2 Bond torsion	87
4.3.3 Angle bending	91
4.3.4 Urey-Bradley potential	91
4.4 Force field parametrisation	92
4.4.1 Parameters and variables	92
4.4.2 Specification of energy functions and parameters	95
4.4.2.1 Global control parameters	95
4.4.2.2 Function subroutines	97
4.4.2.3 Energy parameter input	98
4.5 Energy calculations	101
4.5.1 Expansion of $V$ in a Taylor Series	101
4.5.2 Energy processing subprogrammes	103
4.5.3 First- and second-order derivative calculation	107
4.5.3.1 Derivatives of interatomic distances	110
4.5.3.2 Derivatives of valence angles	113
4.5.4 Derivatives of torsional angles	118
4.6 Numerical calculation of derivatives	121
5 ENERGY MINIMISATION	124
5.1 Statement of the problems	124
5.2 Minimisation algorithms	126
5.2.1 Direct search methods	137
5.2.2 Descent methods	138
5.3 Unified approach to gradient algorithms	139
5.4 Evaluation of minimisation methods	142
5.4.1 The method of steepest descent	145

5.4.2 The Davidon-Fletcher-Powell method	148
5.4.3 The modified Newton method	151
5.5 The minimisation programme	155
5.6 Concluding remarks	158
5.6.1 Minimisation methods in conformational analysis	158
5.6.2 Local versus global minimum	159
5.6.3 False minima	161
6 VIBRATIONAL CALCULATIONS	162
6.1 The vibrational problem	162
6.2 Normal coordinates	165
6.3 Programme VIBRAT	166
6.4 Practical considerations	168
7 OPTIMISATION OF ENERGY PARAMETERS	169
7.1 The basic algorithm	169
7.2 The partial derivatives	174
7.2.1 Internal coordinates	174
7.2.2 Internal frequencies	177
7.3 Implementation of the optimisation	178
7.3.1 Reading of experimental data	178
7.3.2 Organisation of the optimisation	179
8 DEVELOPING A FORCE FIELD	180
8.1 The concept of energy functions	181
8.1.1 Bonded interactions	182
8.1.1.1 Bonds	182
8.1.1.2 Torsions	183
8.1.2 Non-bonded interactions	183
8.1.2.1 Atom-atom interactions	183
8.1.2.2 Geminal interactions	185
8.2 Examples	185
8.2.1 Pre-CFF, cycloalkanes	185



8.2.2 Original CFF, n- and cycloalkanes	186
8.2.3 CFF, alkane crystals	187
8.2.4 CFF, amides and lactams	189
8.2.5 CFF, amides	191
8.2.6 Flexible amino acids	192
8.2.7 Coordination compounds	193
8.2.8 Saccharides	196
9 REFERENCES	198
SUBJECT INDEX	207