Preface

For some years we have worked on creating a set of user-friendly programs for real-time electronic structure analysis using the extended Hückel method. As shown by numerous studies in the past three and a half decades, electronic structure calculations based on this semi-empirical method are practical and useful in understanding how physical properties of molecules, solids and surfaces are related to their geometrical structures. Studies of structure-property correlations based on any electronic structure calculations require a detailed analysis of the geometrical structures of a molecule, solid or surface under examination. Thus we have also worked on producing a user-friendly program for real-time crystal structure analysis and editing. The program package *CAESAR*, written for Personal Computers (PC's), is a result of these efforts. At present, this package consists of five groups of programs to carry out the following tasks:

- Crystal structure analysis and editing
- Electronic structure calculation and analysis for molecules
- Electronic structure calculation and analysis for solids
- Fermi surface calculation and analysis for normal metals
- Electron density calculation for STM and AFM image analysis

The primary objective of creating the *CAESAR* package was to make its programs menu-driven to such an extent that one can use the package to generate useful results even without extensive knowledge in crystallography, electronic structure theory and computer programming. Another objective was to make the running of its programs as real-time as possible. The *CAESAR* package can be a useful research tool for those who look for qualitative structure-property relationships to be tested and refined by further experiments. It can also be a useful teaching tool for undergraduate and graduate courses on molecular orbital theory, inorganic chemistry and solid state chemistry.

We discuss the strengths and weaknesses of extended Hückel electronic structure calculations in Chapter 1, and how to install and run the *CAESAR* package in Chapter 2. The use of the crystal structure analysis and editing program is described in Chapter 3. We summarize essential aspects of molecular and solid state electronic structure theories in Chapter 4 to provide the users with a clear picture about the kinds of computational results the programs of the *CAESAR* package produce. The use of the molecular orbital calculation and analysis programs is presented in Chapter 5, that of the electronic band structure calculation and analysis programs in Chapters 6 and 7, that of the Fermi surface calculation and analysis programs in Chapter 8, and that of the electron density calculation and analysis programs in Chapter 9. A number of examples are included in Chapter 3 and 5-9 to help the users acquire some feel as to how the *CAESAR* package can be employed in solving their own research problems. It is hoped that this book will serve as a manual for the *CAESAR* package as well as a hands-on guide for learning how to think about structures and properties of molecules, solids and surfaces.

We would like to acknowledge those whose work we incorporated in producing the current *CAESAR* package by briefly tracing the important developments leading to the package. R. Hoffmann devised the extended Hückel method for molecular electronic structure calculations [1] and wrote the first program for such calculations.[2] This program was improved by J. Howell, A. Rossi, D. Wallace and K. Haraki in R. Hoffmann's laboratory.[3] Based on this work, M.-H. Whangbo wrote the first extended Hückel program for electronic band structure calculations for solids at R. Hoffmann's laboratory in 1976.[4,5] This program was improved by T. Hughbanks, M. Kertesz, S. Wijeyesekera, C. Wilker and C. Zheng at R. Hoffmann's laboratory.[6-9] At M.-H. Whangbo's laboratory M. Evain revised and reorganized the program further and added crystal structure analysis and Fermi surface

calculation programs in 1987. A few of the programs revised by M. Evain were released to QCPE.[10] His crystal structure analysis program was improved by W. Liang, and an electron density calculation program designed to help interpret STM and AFM images was written by J. Ren, both at M.-H. Whangbo's laboratory. Thus, by summer 1993, the predecessors of the main parts of the *CAESAR* package were completed, although they were written for VAX Workstation computers. J. Ren began the project of converting these programs for PC's in summer 1993. He produced the first MS-DOS version around summer 1994, and the first Windows version a year later. W. Liang started writing a real-time crystal structure analysis program in summer 1995, and produced its first PC Windows version a year later. By summer 1996 the main parts of the PC Windows version of the *CAESAR* package were completed. For the past two years the authors worked on improving and debugging the package to obtain its current version.

The authors are grateful to Professor Kwang-Soon Lee, Professor Dongwoon Jung, Dr. Dong-Kyun Seo, Dr. Hyun-Joo Koo, and Peter Schmidt for their testing the earlier Windows versions of the *CAESAR* package. They found a large number of bugs to correct and improvements to make.

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August 1998

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