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Excitation Energies and Properties of Open-Shell Singlet Molecules

Applications to a New Class of Molecules
for Nonlinear Optics and Singlet Fission

 Springer

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ISSN 2191-5407

ISSN 2191-5415 (electronic)

ISBN 978-3-319-08119-9

ISBN 978-3-319-08120-5 (eBook)

DOI 10.1007/978-3-319-08120-5

Library of Congress Control Number: 2014944342

Springer Cham Heidelberg New York Dordrecht London

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*To
My Wife Satomi, Daughter Makiko,
and Son Yoshiyuki*

Preface

This book presents a novel viewpoint, “open-shell character,” which is a quantum-chemically defined chemical index for bond nature, for excitation energies, and properties of open-shell singlet molecules, as well as its application to molecular design for two functionalities, i.e., nonlinear optics (NLO) and singlet fission.

Excitation energies and transition properties, e.g., transition moments and dipole moment differences, between two electronic states of a molecule are known to be understood by analyzing the primary configurations describing the two electronic states in the configuration interaction (CI) scheme. In the case of single excitation CI scheme, the ground state is unchanged, e.g., the Hartree–Fock ground state, while the excited states are usually described by a few singly excited configurations, e.g., HOMO (the highest occupied molecular orbital) \rightarrow LUMO (the lowest unoccupied molecular orbital), which implies the ground-state Slater determinant with a substitution of HOMO by LUMO. In such a case, the excitation energies and transition properties are understood by the orbital energy gap and one-electron transition moment between the corresponding occupied and unoccupied MOs, respectively. Thus, various optical spectra and response phenomena can be described by using the single excitation picture. Although such a simple one-electron picture is preserved for weak electron-correlated systems, it is broken down for intermediate/strong electron-correlated systems, which are characterized by the nonzero open-shell character as explained later. The target systems in this book—open-shell singlet molecules—really belong to the class of intermediate/strong electron-correlated systems. The simplest model for such systems is a two-site diradical model with two electrons in two active orbitals [bonding (g) and antibonding (u) orbitals], where the open-shell (diradical) nature is, for instance, controlled by varying the interatomic distance. In the equilibrium bond length region, the system is regarded as a closed-shell system, while the diradical nature gradually increases by increasing the bond length, and finally the bond of two-site system is completely broken. Such a bond breaking is described by the doubly excited configuration from g to u , which becomes more significant with increasing the bond distance due to the decrease in the g – u gap. Namely, the weight of double excitation configurations in the ground-state wave function is a measure of

“*electron correlation*,” i.e., the degree of localization of each site, and thus represents the “*diradical character*.” As expected from the correlation between these configurations in the two-site model, the excitation energies and properties are described as functions of diradical character in the ground state. This implies that the excitation energies and properties have the possibility of being controlled through tuning the diradical character in the ground state. In addition, the diradical character is closely related to the molecular architecture, MO picture (one-electron picture), aromaticity and so on since it is a chemical index of a bond nature. Namely, tuning diradical character in molecules is expected to be relatively easy because of the close relationships between the diradical character and the conventional chemical indices, which many chemists are familiar with. This fact describes a fundamental concept in this book, i.e., “diradical character view of various physico-chemical phenomena,” which is thus useful for designing functional molecular systems. In this book, we present several molecular design principles for efficient NLO molecules as well as for singlet fission molecules based on the open-shell singlet molecules, where the intermediate open-shell character is revealed to be a key factor. The performances of these functionalities in intermediate open-shell singlet systems are demonstrated to surpass those in conventional closed-shell systems. In conclusion, the open-shell character viewpoint provides a new basis for comprehensive understanding of excitation energies and properties for a wide range of molecular systems including intermediate/strong electron-correlated systems as well as for constructing novel molecular design principles for highly efficient functional molecular systems.

First of all, I would like to thank Professor Dr. Kizashi Yamaguchi (Osaka University) for his introducing me to the wonderful field of open-shell systems during my doctoral studies in Graduate School of Engineering Science, Osaka University. I am also thankful to Prof. Dr. George Maroulis (University of Patras) for inviting me to give several lectures on the first part of this book in International Conference of Computational Methods in Sciences and Engineering (ICCMSE 2004–2011) held in Greece. I would like to thank Assistant Professor Dr. Ryohei Kishi, Associate Prof. Dr. Yasuteru Shigeta (Professor in University of Tsukuba, at present), Associate Prof. Dr. Hideaki Takahashi (Associate Professor in Tohoku University, at present), and JSPS postdoctoral fellow Dr. Shabbir Muhammad (Assistant Professor in King Khalid University, at present) in our laboratory for many valuable discussions and suggestions, and for supplying numerical calculation data. Furthermore, it is a pleasure to thank Dr. Takuya Minami (Showa Denko K.K.), Dr. Hitoshi Fukui (Sumitomo Chemical Company, Limited), and Dr. Kyohei Yoneda (Assistant Professor in Nara National College of Technology, at present), who worked as graduate students in our laboratory, for making numerical analysis, preparing many of the figures, and for valuable discussions. In particular, Dr. Takuya Minami has been an invaluable help with the work on singlet fission discussed in the latter part of this book. I would also like to acknowledge Prof. Dr. Benoît Champagne (University of Namur), Prof. Dr. Takashi Kubo (Osaka University), Dr. Kenji Kamada (AIST), Prof. Dr. Koji Ohta (Kyoto University), and Associate Prof. Dr. Frédéric Castet (Université Bordeaux 1), who are collaborators

sharing the common interests in the open-shell singlet NLO and singlet fission molecules, for many comments, suggestions, and discussions on the subjects included in this book. In addition, we would like to thank Prof. Dr. Yoshito Tobe (Osaka University), Assistant Prof. Dr. Akihiro Shimizu (Kyoto University), Prof. Dr. Hiroshi Miyasaka (Osaka University), Prof. Dr. Yosuke Yamamoto (Hiroshima University), Prof. Dr. Manabu Abe (Hiroshima University), Prof. Dr. Akira Sekiguchi (University of Tsukuba), Prof. Dr. Hiroshi Ikeda (Osaka Prefecture University), and Prof. Dr. Takeaki Iwamoto (Tohoku University) for sharing with me their excellent idea and wonderful experimental results on various unique molecules. I also wish to thank Mr. Kotato Fukuda (a Doctor course student at Osaka University) for his careful checking of the manuscript, formulas, and so on. Finally, numerous students and colleagues have helped me by preparing many numerical data and analysis and by making useful suggestions. Although I will not recall everyone, this book could not have seen the light of day without his/her contribution.

Toyonaka, Osaka, March 2014

Masayoshi Nakano

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