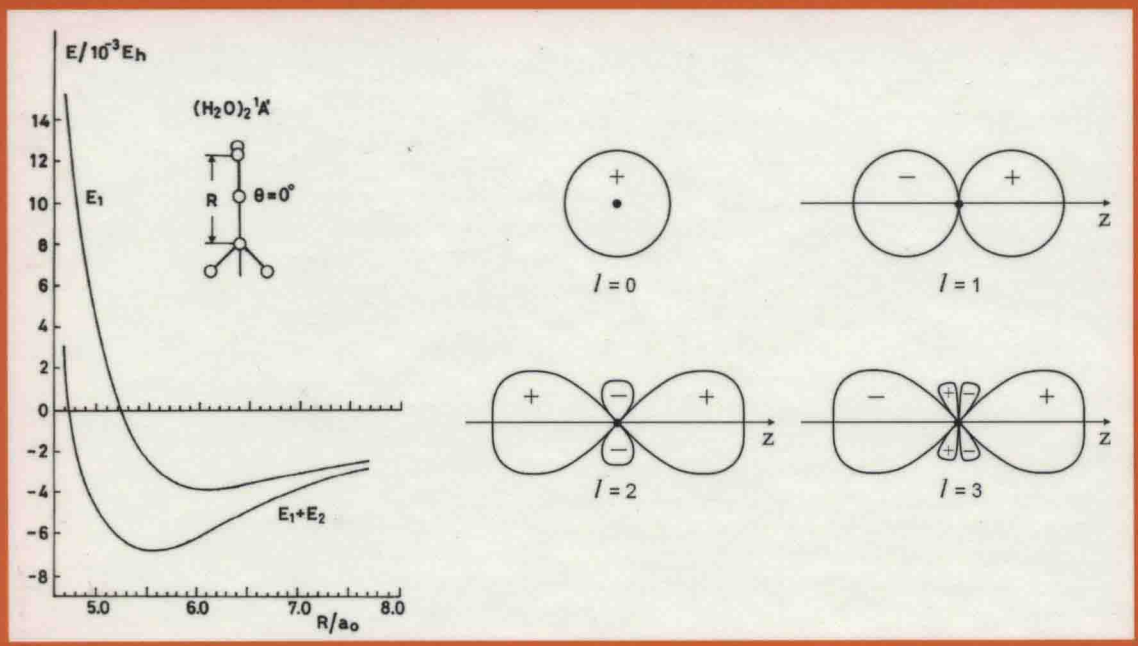
Second Edition

Elementary Molecular Quantum Mechanics

Mathematical Methods and Applications

Valerio Magnasco



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Elementary Molecular Quantum Mechanics: Mathematical Methods and Applications

To Charles Alfred Coulson
To Paola, my wife

To my former Quantum Chemistry students
Giorgio Aliani, Mauro Amelio, Luca Arcesi, Paolo Armanino, Cristina Artini, Roberto Austi, Fiorenza Azzurri, Monica Beggiato, Walter Bellini, Angelo Benazzo, Maurizio Benzo, Anna Berti, Luca Berti, Federico Bianchi, Anja Bijedic Mitranic, Sergio Bisio, Claudio Boffito, Vito Boido, Gabriella Borzone, Carlo Bottero, Andrea Briatore, Stefano Brusco, Santino Bruzzone, Giuseppe Burgisi, Vincenzo Buscaglia, Fabio Canepa, Maria Rosaria Carcassi, Francesca Carosi, Silvio Carrettin, Angela Cartosio, Massimo Casanova, Danilo Cassaglia, Rosana Cavalli, Marino Cervetto, Roberta Cesari, Silvia Ciuffini, Fabrizio Colace, Bianca Cosma, Camilla Costa, Aldo Curti, Marco Delfino, Giovanna Dellepiane, Fabrizio De Melas, Serena De Negri, Maria Grazia Desirello, Silvia De Vito, Ilaria Devoti, Daniele Duce, Roberto Eggenhoffner, Leandro Esposito, Sandro Ferraro, Alessandra Ferretti, Dino Romano Ferro, Giuseppe Figari, Maria Luisa Fornasini, Giuseppe Francese, Ambra Frare, Silvano Fuso, Massimo Gambetta, Silvia Garbarino, Paolo Gatti, Chiara Ghiron, Michele Giardina, Claudia Grandi, Paola Guarnone, Marina Guenza, Roberto La Ferla, Marco Leoncini, Serena Leporatti, Alessandra Leprini, Franco Lichene, Nara Liessi, Andrea Lionello, Romeo Losso, Mattia Lucchini, Costanzo Luzzago, Filippo Maido, Alberto Martinelli, Roberta Martolini, Bruno Matteazzi, Franco Merlo, Valeria Merlo, Giovan Battista Minetto, Tomaso Munari, Riccardo Musenich, Gian Franco Musso, Riccardo Narizzano, Marco Nencioni, Sergio Novelli, Riccardo Olivieri Colombo, Massimo Ottonelli, Donatella Paci, Silvia Palacio Azcona, Andrea Palenzona, Christopoulos Panagiotis, Laura Pardo, Paolo Parodi, Lise Pascale, Stefano Passalacqua, Elisa Pastore, Marta Patrone, Gianfranco Patrucco, Enrica Perrotta, Roberto Peverati, Matteo Piccardo, Giulio Pieretti, Francesca Pin, Arnaldo Rapallo, Marcello Rasparini, Anna Ravina, Renzo Rizzo, Caterina Rocca, Giuseppe Roncallo, Massimiliano Rossi, Marina Rui, Paolo Russo, Paolo Sacco, Carlo Scapolla, Daniele Scavo, Giovanna Schmid, Andrea Sciutto, Andrea Siciliano, Lucia Somma, Giuseppe Tassano, Anton Thumiger, Giuseppe Tonello, Giulio Andrea Tozzi, Riccardo Tubino, Alessandro Valente, Vito Vece, Massimo Vizza, Gilberto Vlaich, Ugo Zanelli, Maria Teresa Zannetti

Preface

The idea of a book presenting in a simple way most of the essential mathematical tools beyond elementary calculus, and possibly entitled *Mathematical Methods in Molecular Quantum Mechanics*, grew for some time in the author's mind during the many years of teaching and research at the University of Genoa. In 2007, Elsevier published a teaching book by the author for graduate university students of chemistry and physics entitled *Elementary Methods of Molecular Quantum Mechanics*, the book being intended as a bridge between the classic elementary Coulson's *Valence* and the more advanced McWeeny's *Methods of Molecular Quantum Mechanics*. After 5 years, this book necessarily needed some revision and restyling to eliminate various misprints.

After an intense correspondence with the Elsevier's editorial board, to avoid the narrowness of a single mathematical text, it was decided to merge the two books into the present single book, entitled *Elementary Molecular Quantum Mechanics: Mathematical Methods and Applications*. The new book is mostly based on the content of the old one, of which it maintains the interesting elementary approach to quantum chemical applications, and contains a new introductory part more specifically devoted to mathematical methods. So, the new book can be considered as a deeply revised edition of the former Elsevier's book with a sensibly enlarged mathematical part. It is hoped that, in this way, the new book can meet better the students' needs, enlarging its usability even for university students of applied maths, at least in their first years.

The first part of the book is not intended to cover all mathematical topics, rather it is intended to offer the reader in a plane way and more in detail many of the building stones of the advanced mathematics needed in working applications of Quantum Mechanics to Quantum Chemistry. For the same reason, some important topics are omitted, such as functional, numerical, and computational analysis, but these arguments are so wide that they would imply separate books in themselves. For them, the reader should be addressed to specific treatises or to internet resources. The required background for students of physics and chemistry is still that of a few semester courses in mathematical analysis and physics.

The book might help as an auxiliary advanced mathematical and physical text of about 60 h for university students of chemistry, physics, and applied maths.

The main differences with the former Elsevier's book are the following. (1) The shifting to the new Chapter 1 of both the fundamental approximation methods of Quantum Mechanics, the variational method and the various perturbative approaches (formerly partly given in Chapters 5 and 11), (2) the introduction of three new mathematical chapters devoted to the solution of the partial differential equations of Quantum Mechanics (Chapter 3), to the theory of special functions, including Fourier and Laplace transforms and Green's functions (Chapter 4), to the functions of a complex variable and the evaluation of integrals of a real variable by the method of residues (Chapter 5), (3) the subdivision of the former unusually large Chapter 7 into the two new Chapters 14 and 16, the first devoted to the theory of model Hamiltonians (Hartree–Fock, Hückel and approximate MO methods), the second to the correlation problem and to the Post-Hartree–Fock methods, (4) the accurate revision of the old Chapter 12 on atomic and molecular interactions, which was completely re-written and updated in the new Chapter 17, (5) the addition of the Gaussian GTO approach besides the prevalent STO approach in the evaluation of multicentre molecular integrals in the new Chapter 18, (6) the addition of Chapter 19,

which introduces the reader to the still actually growing field of relativistic molecular quantum mechanics, starting from the Dirac's equation for the relativistic electron up to its major applications to atomic and molecular systems, and, lastly, (7) a short outlook to the problem of molecular vibrations (Chapter 20) with particular emphasis to the vibronic interactions, a topic which was completely omitted in the former book. The original feature of the former book which completed each chapter with *problems* and *solved problems* was maintained and enlarged in the new book.

The contents of the new book are given in the introductory section *Contents*, where all items in each chapter are specified in detail, so that they will be omitted here.

A wide list of alphabetically ordered references, mostly taken from original research papers, and author and subject indices complete the book.

Thanks are due to my son Mario and his daughter Laura, who prepared the drawings at the computer, to Professor Giuseppe Figari, who helped much during the many years of research at the Department of Chemistry of the University of Genoa, to Dr Michele Battezzati for useful suggestions and discussions on specific points, to Dr Tomas Martišius of Vilnius (Lithuania), who provided the software for translating from Latex to Word, which made this work possible, and to Dr Camilla Costa, who helped in the translation of the former published text from Latex to Word. Particularly warm thanks are due to the Elsevier' Senior Acquisition Editor, Mr Adrian Shell, PhD, for his patience in discussing the best structure of the new book, and to Dr Egbert van Wezenbeek for his constant encouragement and support. Finally, I acknowledge the Italian Ministry for Education University and Research (MIUR) and the University of Genoa for their financial support during the many years of scientific research of the Genoa group.

My last thanks are for my wife Paola, who supported me strongly during the long time this work was in progress.

Valerio Magnasco
Genoa, 30th November 2012

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