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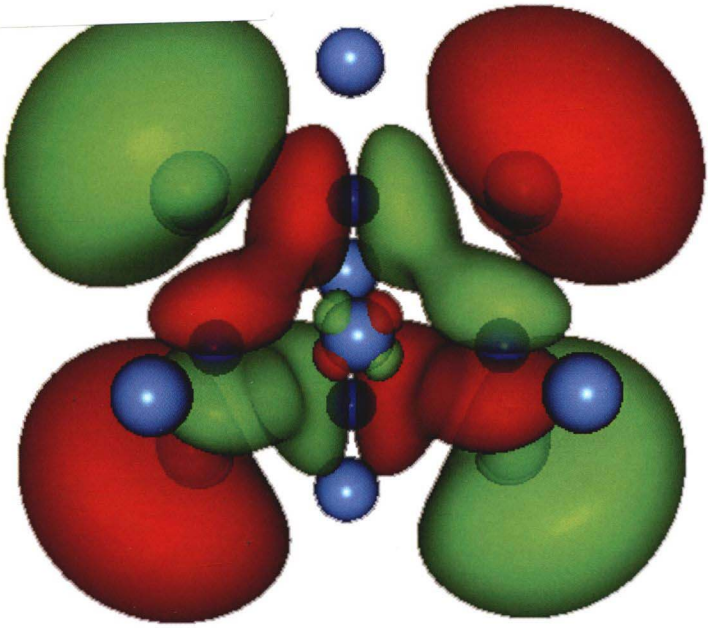

VIRTUAL SYNTHESIS OF NANOSYSTEMS BY DESIGN

FROM FIRST PRINCIPLES TO APPLICATIONS

LIUDMILA A. POZHAR

Virtual Synthesis of Nanosystems by Design

From First Principles to Applications

by

Liudmila A. Pozhar

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Virtual Synthesis of Nanosystems by Design

Preface

A fundamental role of quantum many-body theory, quantum statistical mechanics and quantum chemistry methods in advanced nanomaterials and media design, and in particular, in the development of novel approaches to electronic structure engineering, makes it highly desirable for graduate students and researchers working in physics, chemistry, various fields of engineering, applied mathematics and computer science to understand major ideas and practical applications of such methods. This book has been written with a goal to help readers familiar with foundations of quantum theory at least at a graduate level link their theoretical background to the state of the art in the field of virtual (that is, quantum many-body theory-based, computational) synthesis of materials and media by design, its numerical methods and its software, to be able to apply their theoretical knowledge to solve practical problems.

Material included in this book is not intended as a review in the fields of science and engineering concerning synthesis of materials and media by design. Instead, the book provides only necessary conceptual, methodological, and software information to enable a reader to use the virtual synthesis method in practice. Part One of the book is devoted to theoretical foundations and consists of two chapters. Rigorous quantum statistical mechanical methods allow calculation of measurable properties of quantum systems using information on their structure, composition and conditions of their synthesis (such as the presence of quantum confinement). Descriptions of such methods and their results can be found in extensive literature accumulated since the late 19^{th} century. Unfortunately, the majority of these methods has been derived to address spatially uniform systems, and thus is not applicable without the use of additional *ad hoc* assumptions to the case of small and/or strongly inhomogeneous systems, such as small quantum dots or wires, where a characteristic size of the system is of the same order as that of its constitutive units. This makes results obtained by applications of the standard quantum statistical methods to spatially non-uniform systems ambiguous and inconclusive. The only existing family of quantum statistical mechanical methods capable of providing reliable description of strongly spatially non-uniform systems is the first-principle projection operator methods. These methods and their results are discussed in Chapter 1. The chapter is unique in that that it links two of the first-principle projection operator methods and discusses their results from a standpoint of their use in quantum system design.

Notably, applications of all quantum statistical mechanical methods (projection operator-based, or otherwise) for purposes of (nano)materials synthesis by design rely on quantum many-body theoretical methods that provide information on the structure factors (such as electronic energies, correlation functions, Green's functions, etc.) of studied systems. The latter are used in quantum statistical mechanical formulae (derived using projection operator or other methods) to calculate measurable properties of

many-body systems. Quantum chemistry codes realize some of such quantum many-body theoretical methods and implement them in the form of so-called first-principle quantum chemistry software. Chapter 2 of this book contains an overview of quantum many-body theoretical methods used in quantum chemistry, and their corresponding implementation. It also briefly outlines the existing first-principle quantum chemistry software. Quantum many-body theoretical methods of Chapter 2 can also be used on their own, if only the basic electronic and structural information on a system of interest is needed.

Part Two of this book is devoted to applications of the first-principle methods discussed in Part One to design virtually about 40 small systems composed of semiconductor compound and transition metal atoms, and Ni- and Co- oxides. The equilibrium structure, electronic energy level structure (ELS), molecular orbits, the charge and spin density distributions (CDDs and SDDs) of the nanostructures [or molecules, from a chemical point of view] of about 1 to 6 nm in linear dimensions virtually synthesized in model quantum confinement or in "vacuum" (*i.e.*, in the absence of any external fields or foreign atoms) are discussed in detail. Each of Chapters 3 to 8 included into Part Two can be worked with independently of the rest of the book content. However, an inexperienced reader is strongly advised to familiarize him/herself at least with Chapter 2 of Part One, to understand physical and chemical meaning of the results discussed in Chapters 3 to 8. Readers who are well familiar with quantum statistical mechanical, many-body theoretical and computational quantum chemistry methods will benefit from a unique description of projection operator-based quantum statistical methods outlined in Chapter 1, overview of computational methods in Chapter 2, and their applications described in Part Two of the book.

The book website booksite.elsevier.com/9780123969842/ and the corresponding webpage of the website www.PermaNature.com contain an additional Chapter 9 available only electronically for a free download. This chapter describes results of virtual synthesis by design of small cobalt oxide quantum dots. Chapter 9 also is independent of other chapters included in Part Two. The website www.PermaNature.com has a forum page and contact pages that can be used to communicate with the author. Moreover, both websites include free downloads containing 14 files (a brief description of these files can be found in Appendix "Examples of Virtual Templates of Small Quantum Dots and Wires of Semiconductor Compound Elements" at the end of the book) that can be used to configure input files for GAMESS software modules. Readers are encouraged to use such input files to (1) repeat some results of the author, (2) attempt higher-order approximations as applied to the systems investigated by the author, and (3) modify author's setups and attempt virtual design of other systems of interest.

My research discussed in this book significantly benefitted from advice and encouragement of outstanding physicists and chemists whom I had a privilege to collaborate with. In particular, the content of Chapter 1 has been refined in enlightening discussions with my teacher Yu. A. Tserkovnikov (Steklov Institute of Mathematics, Russian Academy of Sciences, Moscow, Russia) who was one of the brightest students of Nikolai N. Bogoliubov, and one of the greatest scientists ever worked in the fields of quantum statistical mechanics and its mathematical foundations. My interest in applications of the quantum many-body theoretical methods to semiconductor compound

systems has been stimulated by F. Szmulowicz (University of Dayton Research Institute, Dayton, OH) and W. C. Mitchel (Air Force Research Laboratory, Dayton, OH). Enthusiasm and support of A. T. Yeates and D. Dudis of the Air Force Research Laboratory in Dayton, OH, encouraged my involvement with quantum chemistry, and my appreciation of its virtues and exquisite charms. The virtual synthesis method has been developed and realized in close collaboration with these esteemed colleagues. I had many insightful discussions of magnetic properties of nanosystems with Y. Qiang, and mathematical methods of many-body quantum theory with R. Machleidt and F. Sammarruca-Machleidt during my years with the University of Idaho in Moscow, ID. Several of my students, notably C. Mavromichalis (BoiseLAN, Boise, ID), contributed to research described in Chapters 7 and 9. Encouragement and understanding of my husband G. M. Tsoy (University of Alabama at Birmingham and IPG Photonics, Birmingham, AL) have made my work on this book, and our joint life in physics in general, an exciting and unforgettable experience. My heartfelt gratitude goes to these great scientists, colleagues and friends.

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Contents

Part One

Quantum Statistical Mechanics Fundamentals

Transport Properties of Spatially Inhomogeneous Quantum Systems From the First Principles

1

1.1 Introduction

Since Gibbs and Boltzmann, statistical mechanics has been focused on the first-principle prediction of thermodynamic and transport properties of many particle systems. The majority of models and mathematical methods of statistical mechanics are designed to work in so-called thermodynamic limit where the number of particles (N) and the system volume (V) simultaneously tend to infinity, while their ratio remains finite. Another important concept concerns the initial state of a many-particle system that is assumed to be the thermodynamic equilibrium corresponding to the *minimum minimorum* of the total energy of the system. These two concepts validate rigorously the use of theory of stochastic processes and mathematical statistics methods to reduce a system of 6N coupled equations of motion (in the simplest case) for the system particles to one equation of motion of the entire system formulated with respect to the N-particle distribution function of the system (classical Liouville equation) or the N-particle density matrix (the von Neumann, or quantum Liouville equation), respectively. At the next step, perturbation theory, DFT or projection operator methods are used to reduce the Liouville, or von Neumann (in the quantum case) equations to the so-called master equation for collective dynamical variables or observables, respectively, that can be further reduced to a manageable system of coupled equations for correlation functions or Green's functions (GFs). Further on, the equations for conserved collective dynamical variables (observables) are derived, and the thermodynamic and/or transport properties are identified in terms of the correlation functions and/or GFs. Thus, once the correlation functions or GFs are determined, the thermodynamic and transport properties of the N-particle system can be calculated directly.

With advent of novel technologies of materials and media synthesis there is a growing demand for updating the fundamental basis of statistical mechanics to account for small and/or strongly spatially inhomogeneous systems. Such first-principle statistical mechanical foundation is especially important to design novel materials for quantum electronics, spinstronics, quantum computing, communication, information processing and storage technologies. In particular, fundamental understanding of coherent, polarized, and entangled charge and spin states of quantum particles, their dynamics, and their contributions to quantum spin/charge transport properties at realistic materials synthesis conditions, such as quantum confinement, is paramount [1–5] to establish novel electronic materials technologies. In other words, relations between the structure, and thermodynamic and transport properties of materials and media, must be established using first principle quantum statistical mechanical methods.

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At present, solid state electronic structure theory [6–10] largely employs somewhat modified statistical mechanical foundation specific to bulk solid lattices and various half-heuristic methods [11] to identify systems exhibiting new electronic properties, such as quantum wells, large quantum wires [12] and quantum dots (QDs) [13]. In the case of small structures, such as small QDs, where statistical mechanical approaches so modified do not work, computational methods, such as DFT- and Hartree-Fock-based (HF) methods, self-consistent field (SCF) approximations, configuration interaction (CI) methods, complete active space SCF (CASSCF), multi configuration SCF (MCSCF), Møller-Plesset - and coupled-clusters approximations are used to calculate the electronic energy level structure directly solving the Schrödinger equation numerically. [These methods will be briefly discussed in Chapter 2.] At present, the corresponding software packages, such as GAMESS, NWChem [14], GAUSSIAN or Molpro, allow the electronic structure calculations for systems in equilibrium at zero temperature. In addition, equilibrium and non-equilibrium molecular dynamics (MD) simulations are widely used to study structure-property relations at non-zero temperature. In particular, the spin/charge transport processes are simulated using MD or Monte-Carlo means in the Born-Oppenheimer approximation. In the case of numerical calculations and MD simulations, correlations between the electronic structure and the transport properties are introduced heuristically, adjusting the statistical mechanical and semi-phenomenological approaches developed for large systems. Such computations, on their own, do not permit first-principle predictions of the spin/charge transport properties of small QDs and molecules. Yet accurate first-principle predictions are crucial to manipulate with electron spins and quantum states of energy and information carriers in small QD/QW systems.

In their turn, existing *semi-heuristic* modifications [15–23] of various theoretical models developed originally for much larger systems at low temperature conditions and applied to characterize charge and spin transport in small systems often lead to physically incorrect predictions even for mesoscopic tunneling junctions [24]. Even the best of such models do not include adequate description of system-to-confinement coupling, such as quantum confinement effects. At the same time, such coupling is one of the major sources of both decoherence and coherence [25,26] of states of quantum particles, such as the electron charge and spin states [27–29]. Thus, the nature of such models does not allow, in principle, first-principle predictions of electronic and spin/charge transport properties of small and strongly spatially inhomogeneous systems.

As already mentioned in the beginning of this section, first-principle predictions of electronic transport properties imply the use of specifically tailored quantum statistical mechanical methods to derive self-consistently the spin/charge transport theory from the quantum Liouville (von Neumann) equation. Thus far, this formidable task has been properly addressed only for mesoscale systems where non-equilibrium GF (NGF)-based methods [such as Keldysh's two-time NGF [30–32] and more recent DFT-NGF approaches [33]] are among the most adequate statistical mechanical techniques used. Unfortunately, these methods have several major disadvantages. In particular, the field-theoretical NGFs used in the majority of these approaches are not directly related to the transport coefficients. Thus, despite the availability of a system