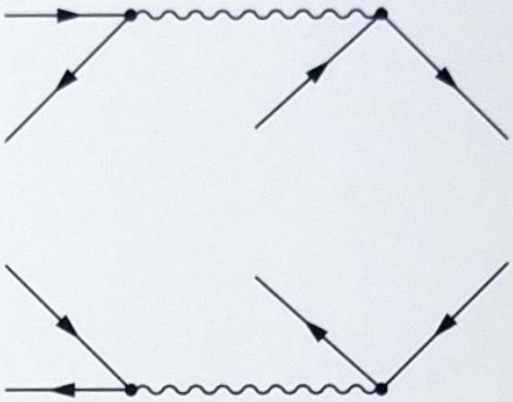
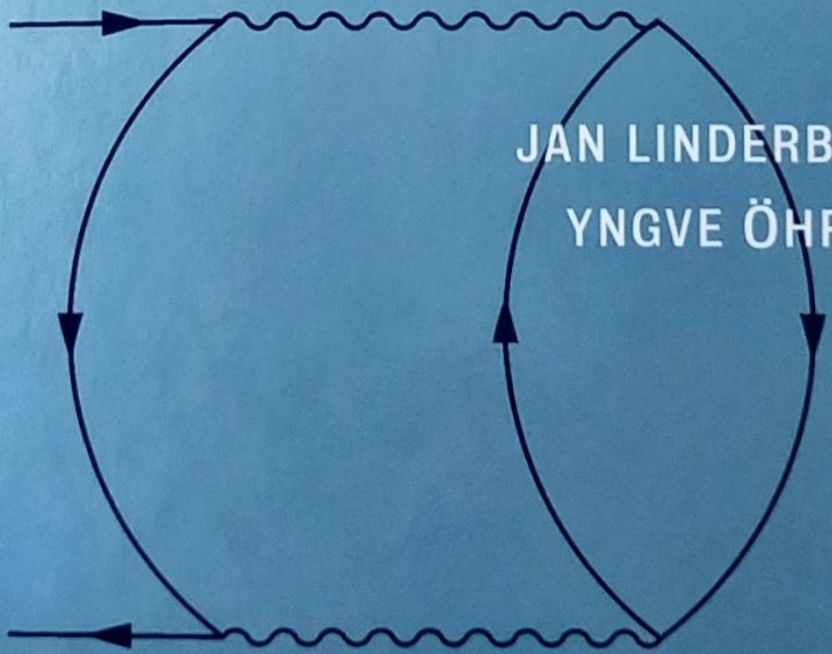


PROPAGATORS IN QUANTUM CHEMISTRY

SECOND EDITION



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PROPAGATORS IN QUANTUM CHEMISTRY

Second Edition

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Contents

Chapter 1

Introduction

This text has grown out of the monograph *"Propagators in Quantum Chemistry"* by J. Linderberg and Y. Öhrn, Academic Press, London, 1973, which has been out of print for some time. The content is revised to take into account some of the considerable literature in the intervening years by many workers in the field. However, this is not intended as a review of the theory and application of propagators, but rather an attempt to present the theory and the basic approximations in a unified manner with some illustrative applications. The material is presented from our own perspective, and we apologize for any omissions of references to important work in the field.

Propagators gained early prominence in formal many-body theory of fermion systems[1]. Concerns about the elimination of unlinked terms in the perturbation expansions and the associated correct scaling with systems size naturally led to the propagator concept. Treatment of double-time Green's functions (propagators)[2] established that they provide an important and useful link between pure state quantum mechanics at the absolute zero of temperature and quantum statistical mechanics employing ensembles at finite temperature. Condensed matter theory employed the propagator concept to great advantage[3]. Recent advances in computational techniques and power of electronic computers have led to numerous successful applications of approximate propagator theory for so-called quasiparticle calculations in solids [4]. Propagator theory for finite systems led to new ideas in the theory of molecular electronic spectra[5].

Computer codes were developed, and *ab initio* calculations were carried out primarily for a great variety of electronic spectra and properties of molecular systems, in particular, implementing the theory of the electron and the po-

[1] see P. Nozière, *Theory of Interacting Fermion Systems*, W. A. Benjamin Inc., New York, 1964

[2] see D. N. Zubarev, *Soviet Physics Uspekhi* **3**, 320 (1960)

[3] see L. Hedin and S. Lundqvist, *Solid State Physics* **23**, 1 (1969) and references therein

[4] see W. G. Aulbur, L. Jönsson, and J. W. Wilkins, *Solid State Physics* **54**, 1 (2000)

[5] see Y. Öhrn and J. Linderberg, *Phys Rev.* **139**, A1063 (1965), and J. Linderberg and Y. Öhrn, *Proc. Roy. Soc.* (London) **A285**, 445 (1965); *Chem. Phys. Letters* **1**, 295 (1967)

larization propagators[6]. Also, reviews were written[7], as well as an important monograph by P. Jørgensen and J. Simons[8].

In recent years there has been many applications of the electron and the polarization propagators to a great variety of problems concerned with molecular properties and spectra, demonstrating the importance and usefulness of propagators to the understanding of experimental results. Stationary states, which is the focus of traditional electronic structure theory cannot, strictly speaking, be observed as such through experiments, since every observation involves a probing of the system with some external perturbation. The response of the molecular system to such probing and the associated influence on the probe are directly involved in the measuring process. A theoretical analysis, which focuses on the determination of observable quantities, naturally leads to the study of propagators as a key concept. This view was pioneered by Richard P. Feynman in his path integral approach to quantum mechanics, and propagators are theoretical tools commonly used in physics.

In spite of their demonstrated power and success, propagators are not yet widely accepted tools in theoretical chemistry. This may have to do with the tendency on the part of all but a few quantum chemists to focus almost exclusively on the running of generally available computer codes, which employs traditional and well-worn concepts, and applying them to new chemistry problems. There is also a certain reluctance to struggle with new theoretical concepts, no matter how powerful they may be. There are notable exceptions, however, and particularly the work of J. V. Ortiz shows great promise [9]. He uses the electron propagator to achieve correlated treatments of molecular electronic structure and spectra while still preserving the chemically useful orbital concept. This approach is available for applications through the ubiquitous Gaussian program system.

This text is written with the graduate student or researcher in mind, who is already familiar with atomic and molecular quantum theory and with elementary statistical physics. The choice of topics reflects the personal tastes of the authors. Problems are introduced throughout the text to give the reader an opportunity to work out further details and applications of the theory.

Special thanks go to Dr. Remigio Cabrera-Trujillo who has provided the expertise and help to convert text files from outdated formats to .tex files that can be easily edited and merged into a book format.

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[6]see *e.g.* G. D. Purvis and Y. Öhrn, *J. Chem Phys.* **60**, 4063 (1974); *J. Chem Phys.* **62**, 2045 (1974); L. S. Cederbaum, *Theor. Chim. Acta* **31**, 239 (1973); *Mol. Phys.* **26**, 1405 (1973); J. Simons and W. D. Smith, *J. Chem. Phys.* **58**, 4899 (1973)

[7]see G. Csanak, H. S. Taylor, and R. Yaris, in *Advances in Atomic and Molecular Physics* **7**, 287 (1971), Editors D. R. Bates and I. Esterman; P. Jørgensen, *Annual Reviews of Physical Chemistry*, **26**, 359 (1975); L. S. Cederbaum and W. Domcke, in *Advances in Chemical Physics* **36**, 205 (1977), Editors I. Prigogine and S. A. Rice; J. Oddershede, *Advances in Quantum Chemistry* **11**, 275 (1978); Y. Öhrn and G. Born, *Advances in Quantum Chemistry* **13**, 1 (1981)

[8]P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry*, Academic Press, New York, 1981

[9]see, for instance, J. V. Ortiz,*J. Phys. Chem. A* **106**, 5924 (2002), and references therein