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0521803918 - Variational Principles and Methods in Theoretical Physics and Chemistry

Robert K. Nesbet

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## VARIATIONAL PRINCIPLES AND METHODS IN THEORETICAL PHYSICS AND CHEMISTRY

This book brings together the essential ideas and methods behind current applications of variational theory in theoretical physics and chemistry. The emphasis is on understanding physical and computational applications of variational methodology rather than on rigorous mathematical formalism.

The text begins with an historical survey of familiar variational principles in classical mechanics and optimization theory, then proceeds to develop the variational principles and formalism behind current computational methodology for bound and continuum quantum states of interacting electrons in atoms, molecules, and condensed matter. It covers multiple scattering theory, as applied to electrons in condensed matter and in large molecules. The specific variational principles developed for electron scattering are then extended to include a detailed presentation of contemporary methodology for electron-impact rotational and vibrational excitation of molecules. The book also provides an introduction to the variational theory of relativistic fields, including a detailed treatment of Lorentz and gauge invariance for the nonabelian gauge field of modern electroweak theory.

Ideal for graduate students and researchers in any field that uses variational methodology, this book is particularly suitable as a backup reference for lecture courses in mathematical methods in physics and theoretical chemistry.

ROBERT K. NESBET obtained his BA in physics from Harvard College in 1951 and his PhD from the University of Cambridge in 1954. He was then a research associate in MIT for two years, before becoming Assistant Professor of Physics at Boston University. He did research at RIAS, Martin Company, Baltimore, the Institut Pasteur, Paris and Brookhaven National Laboratory, before becoming a Staff Member at IBM Almaden Research Center in San Jose in 1962. He acted as an Associate Editor for the *Journal of Computational Physics* and the *Journal of Chemical Physics*, between 1969 and 1974, and was a visiting professor at several universities throughout the world. Professor Nesbet officially retired in 1994, but has continued his research and visiting since then. Over the years he has written more than 270 publications in computational physics, atomic and molecular physics, theoretical chemistry, and solid-state physics.

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*IBM Almaden Research Center*



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To Anne, Susan, and Barbara

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## Preface

As theoretical physics and chemistry have developed since the great quantum revolution of the 1920s, there has been an explosive speciation of subfields, perhaps comparable to the late Precambrian period in biological evolution. The result is that these life-forms not only fail to interbreed, but can fail to find common ground even when placed in proximity on a university campus. And yet, the underlying intellectual DNA remains remarkably similar, in analogy to the findings of recent research in biology. The purpose of this present text is to identify common strands in the substrate of variational theory and to express them in a form that is intelligible to participants in these subfields. The goal is to make hard-won insights from each line of development accessible to others, across the barriers that separate these specialized intellectual niches.

Another great revolution was initiated in the last midcentury, with the introduction of digital computers. In many subfields, there has been a fundamental change in the attitude of practicing theoreticians toward their theory, primarily a change of practical goals. There is no longer a well-defined barrier between theory for the sake of understanding and theory for the sake of predicting quantitative data. Given modern resources of computational power and the coevolving development of efficient algorithms and widely accessible computer program tools, a formal theoretical insight can often be exploited very rapidly, and verified by quantitative implications for experiment. A growing archive records experimental controversies that have been resolved by quantitative computational theory.

It has been said that mathematics is queen of the sciences. The variational branch of mathematics is essential both for understanding and predicting the huge body of observed data in physics and chemistry. Variational principles and methods lie in the bedrock of theory as explanation, and theory as a quantitative computational tool. Quite simply, this is the mathematical foundation of quantum theory, and quantum theory is the foundation of all practical and empirical physics and chemistry, short of a unified theory of gravitation. With this in mind, the present text is

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subdivided into four parts. The first reviews the variational concepts and formalism that developed over a long history prior to the discovery of quantum mechanics, subdivided into chapters on history, on classical mechanics, and on applied mathematics (severely truncated out of respect for the vast literature already devoted to this subject). The second part covers variational formalism and methodology in subfields concerned with bound states in quantum mechanics. There are separate chapters on time-independent quantum mechanics, on independent-electron models, which may at some point be extended to independent-fermion models as the formalism of the Standard Model evolves, and on time-dependent theory and linear response. The third part develops the variational theory of continuum states, including chapters on multiple scattering theory (the essential formalism for electronic structure calculations in condensed matter), on scattering theory relevant to the true continuum state of a quantum target and an external fermion (with emphasis on methodology for electron scattering by atoms and molecules), continuing to a separate chapter on the currently developing theory of electron-impact rotational and vibrational excitation of molecules. The fourth part develops variational theory relevant to relativistic Lagrangian field theories. The single chapter in this part derives the nonquantized field theory that underlies the quantized theory of the current Standard Model of elementary particles.

This book grew out of review articles in specialized subfields, published by the author over nearly fifty years, including a treatise on variational methods in electron–atom scattering published in 1980. Currently relevant topics have been extracted and brought up to date. References that go more deeply into each of the topics treated here are included in the extensive bibliography. The purpose is to set out the common basis of variational formalism, then to open up channels for further exploration by any reader with specialized interests. The most recent source of this text is a course of lectures given at the Scuola Normale Superiore, Pisa, Italy in 1999. These lectures were presented under the present title, but concentrated on the material in Parts I and II here. The author is indebted to Professor Renato Colle, of Bologna and the Scuola Normale, for making arrangements that made these lectures possible, and to the Scuola Normale Superiore for sponsoring the lecture series.