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PREFACE

In recent years quantum Monte Carlo (QMC), a stochastic method for solving the Schroedinger equation, has become a subject of increased interest in chemistry and physics. As one of the newer approaches in the arsenal of theoretical methods, with only a relatively modest history of development compared to basis set expansion approaches, the method has sprung to the fore because of its capability of yielding computational results of high accuracy.

Formulations of QMC can take on different forms depending on the particular area of application. Emphasis in the present volume is on the electronic structure of atoms and molecules. Also of major interest generally is the application of QMC to the determination of nuclear motion in molecular systems and to statistical mechanics. These latter areas are touched on only briefly in this volume.

The contributions contained herein cover a broad range of topics. In Chapter 1, Dario Bressanini, Pietro Cremaschi, Massimo Mella, and Gabriele Morosi show how information on the exact wave function can be extracted in a QMC simulation and stored in an approximate analytical wave function whose linear and nonlinear parameters are optimized by a least squares criterion. In a related but independent study in Chapter 2, James Anderson, Arne Luechow, and Massimo Mella present a method for direct determination of the difference between the exact wave function and an approximate wave function. They indicate how the difference can be used to correct the trial function to obtain a wave function of higher accuracy.

In Chapter 3, Steven Alexander and Robert Coldwell review a variational Monte Carlo (VMC) method for the computation of atomic energies and present very detailed results for He-Ne. A hybrid method, one that combines in a novel way both VMC (for nuclear motion) and QMC (for electronic motion), is presented in Chapter 4 by Dario Bressanini and Peter Reynolds and applied to HD^+ . In Chapter 5 Heinz-Juergen Flad, Michel Caffarel, and Andreas Savin investigate the use of multi-configuration self-consistent field trial wave functions for a class of QMC calculations, fixed node, to ascertain the effect of the addition of various types of configurations on the nodal structure and the energy of the atoms B - F.

In Chapter 6, Kaoru Iguchi summarizes various QMC approaches with representative examples. He extends work on molecules with comments on applications to systems containing a positron. For many molecular studies,

the most inner-shell electrons play a minor role and can be addressed with the use of effective core potentials. This approach is discussed in Chapter 7 by Carl Greeff, Brian Hammond, and William Lester, Jr. and exemplified by their recent work. In Chapter 8, Lubos Mitras and Jeffrey Grossman also address this approach and present a summary of these recent studies of silicon and carbon systems. They argue persuasively for the promise of QMC for the study of systems containing up to 100-200 valence electrons with energies consistent with experiment to within a few percent.

The applicability of QMC to positron-containing molecules is the focus in Chapter 9 of David Schrader's presentation. He provides evidence for the thesis that QMC is superior to expansion variational methods for treating positronic systems. Systems of large atomic number present serious sampling problems. In Chapter 10, Stuart Rothstein briefly reviews the various approaches that have been introduced to address this problem including an all-electron partitioning scheme. He also mentions his work with collaborators on the infinitesimal differential diffusion QMC method.

In addition to the use of effective core potentials to eliminate the sampling problem of the innermost core electrons, model potentials have also been introduced for this purpose. In Chapter 11, Takashi Yoshida reviews this area with particular attention to alkaline earth atoms.

Optimization of many-parameter wave functions, which pervades many approaches to VMC and QMC computations, is examined in Chapter 12 by Peter Nightingale and Cyrus Umrigar. These authors review selected applications to atoms, molecules and van der Waals clusters.

I am indebted to the contributing authors for their cooperation in bringing this volume to fruition. I thank Delano Chong, Series Editor, for the opportunity to make this project a reality.

William A Lester, Jr.
Berkeley, California
November 1996

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