Quantum Monte Carlo

Origins, Development, Applications

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Quantum Monte Carlo

To Nancy

. . . many shall run to and fro,
and knowledge shall be increased.
Daniel 12:4

PREFACE

In studying quantum mechanics and especially quantum chemistry I found a little book written by Henry F. Schaefer III to be especially useful in providing an overview of the subject, a guide to its trends, and an easily researched compendium of important papers in the area. In writing this new book in the area of quantum Monte Carlo (QMC) I hope to have provided the same sorts of services to those studying and working in the area of quantum Monte Carlo methods.

Schaefer's book is titled *Quantum Chemistry* and subtitled *The development of ab initio methods in molecular electronic structure theory* [Oxford University Press, 1984]. In adopting a similar approach to a review of QMC I hope that Professor Schaefer considers my following his example as flattery.

The term "Monte Carlo" was first used to describe calculational methods based on chance in the 1940s, but the methods themselves preceded the term by as much as a century. The combination of "quantum" and "Monte Carlo" first appeared in 1981 and, similarly, was preceded by early developments of the methods.

In this book I have attempted to collect summaries of some of the most important papers in the quantum Monte Carlo literature. In doing so I have chosen those papers which describe the bases for the many different methods within QMC, provide samples of the works of many of those responsible for the development of QMC, and illustrate the breadth of applications of QMC. The selection is, of course, somewhat random, somewhat arbitrary, and surely arguable. I express my apologies to those authors whose papers may be underrepresented.

The success of QMC methods over the past few decades has been remarkable, and the papers described in this book clearly

demonstrate that success. For isolated molecules, the basic material of chemistry, QMC methods have produced "exact" solutions of the Schrödinger equation for very small systems and the most accurate solutions available for very large systems. The range of applications is impressive for other types of problems: folding of protein molecules, interactions in liquids, band structures in crystals, quantum dots, enzyme structure, energetics of light harvesting materials, potential energy surfaces for reactions of all types, transition dipole moments, structure of a water droplet, frequency shifts in heteroclusters, energetics of excitons, binding in nuclei, and interdimensional degeneracies. Many of these are new problems, approached successfully for the first time using QMC methods.

One may certainly expect the further development of QMC methods and many more applications. It is my hope that this book will in some small way provide assistance to those engaged in the effort.

I am happy to acknowledge the assistance of Dr. Nathan M. Urban in producing the manuscript and of Professor Stuart M. Rothstein and Professor Arne Lüchow for their suggestions and corrections.

An Incomplete List of Important Papers in Quantum Monte Carlo

1
E. Schrödinger
Über die Umkehrung der Naturgesetze
Sitzber. Preuss. Akad. Wiss. Phys.-math. Kl., 144–153 (1931)

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N. Metropolis & S. Ulam
The Monte Carlo method
J. Am. Stat. Assoc. **44**, 335–341 (1949)

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M. H. Kalos
Monte Carlo calculations of the ground state of three- and four-body nuclei
Phys. Rev. **128**, 1791–1795 (1962)

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H. Conroy
Molecular Schrödinger equation. II. Monte Carlo evaluation of integrals
J. Chem. Phys. **41**, 1331–1335 (1964)

5
W. L. McMillan
Ground state of liquid ^{4}He
Phys. Rev. **138**, A442–A451 (1965)

6
M. H. Kalos
Stochastic wave function for atomic helium
J. Comput. Phys. **1**, 257–276 (1967)

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R. C. Grimm & R. G. Storer
Monte-Carlo solution of Schrödinger's equation
J. Comput. Phys. **7**, 134–156 (1971)

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M. H. Kalos, D. Levesque, & L. Verlet
Helium at zero temperature with hard-sphere and other forces
Phys. Rev. A **9**, 2178–2195 (1974)

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K. S. Liu, M. H. Kalos, & G. V. Chester
Quantum hard spheres in a channel
Phys. Rev. A **10**, 303–308 (1974)

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J. B. Anderson
A random-walk simulation of the Schrödinger equation: H_3^+
J. Chem. Phys. **63**, 1499–1503 (1975)

11
D. J. Klein & H. M. Pickett
Nodal hypersurfaces and Anderson's random-walk simulation of the Schrödinger equation
J. Chem. Phys. **64**, 4811–4812 (1976)

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J. B. Anderson
Quantum chemistry by random walk. H ^2P, H_3^+ D_{3h} $^1A_1'$, H_2 $^3\Sigma_u^+$, H_4 $^1\Sigma_g^+$, Be ^1S
J. Chem. Phys. **65**, 4121–4127 (1976)

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R. L. Coldwell & R. E. Lowther
Monte Carlo calculation of the Born-Oppenheimer potential between two helium atoms using Hylleraas-type electronic wave functions
Int. J. Quantum Chem., Symp. Ser. **12**, 329–341 (1978)

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J. B. Anderson
Quantum chemistry by random walk: H_4 square
Int. J. Quantum Chem. **15**, 109–120 (1979)

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J. B. Anderson & B. H. Freihaut
Quantum chemistry by random walk: Method of successive corrections
J. Comput. Phys. **31**, 425–437 (1979)

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Y. Tomashima & J. Ozaki
Monte Carlo solution of Schrödinger's equation for the hydrogen atom in a magnetic field
J. Comput. Phys. **33**, 382–396 (1979)

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J. B. Anderson
Quantum chemistry by random walk: Higher accuracy
J. Chem. Phys. **73**, 3897–3899 (1980)

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D. M. Ceperley & B. J. Alder
Ground state of the electron gas by a stochastic method
Phys. Rev. Lett. **45**, 566–569 (1980)

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F. Mentch & J. B. Anderson
Quantum chemistry by random walk: Importance sampling for H_3^+
J. Chem. Phys. **74**, 6307–6311 (1981)

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K. McDowell & J. D. Doll
Quantum Monte Carlo and the hydride ion
Chem. Phys. Lett. **81**, 335–338 (1981)

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K. McDowell
Assessing the quality of a wavefunction using quantum Monte Carlo
Int. J. Quantum Chem., Symp. Ser. **15**, 177–181 (1981)

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J. G. Zabolitzky & M. H. Kalos
Solution of the four-nucleon Schrödinger equation
Nuc. Phys. A **356**, 114–128 (1981)

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D. M. Arnow, M. H. Kalos, M. A. Lee, & K. E. Schmidt
Green's function Monte Carlo for few fermion problems
J. Chem. Phys. **77**, 5562–5572 (1982)

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J. W. Moskowitz, K. E. Schmidt, M. A. Lee, & M. H. Kalos
Monte Carlo variational study of Be: A survey of correlated wavefunctions
J. Chem. Phys. **76**, 1064–1067 (1982)

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A new look at correlation energy in atomic and molecular systems. II. The application of the Green's function Monte Carlo method to LiH
J. Chem. Phys. **77**, 349–355 (1982)

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Fixed-node quantum Monte Carlo for molecules
J. Chem. Phys. **77**, 5593–5603 (1982)

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Application of the Green's-function Monte Carlo method to the compact Abelian lattice gauge theory
Phys. Rev. D **28**, 2067–2075 (1983)

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V. R. Pandharipande, J. G. Zabolitzky, S. C. Pieper, R. B. Wiringa, & U. Helmbrecht
Calculations of ground-state properties of liquid ^{4}He droplets
Phys. Rev. Lett. **50**, 1676–1679 (1983)

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Ground state of excitonic molecules by the Green's-function Monte Carlo method
Phys. Rev. Lett. **51**, 2422–2425 (1983)

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Quantum chemistry by random walk: Linear H_3
J. Chem. Phys. **80**, 2675–2680 (1984)

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Quantum Monte Carlo for molecules: Green's function and nodal release
J. Chem. Phys. **81**, 5833–5844 (1984)

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Quantum Monte Carlo study of the classical barrier height for the H + H_2 exchange reaction: restricted versus unrestricted trial functions
Int. J. Quantum Chem., Symp. Ser. **18**, 709–717 (1984)

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Binding energy of positively charged acceptors in germanium — A Green's function Monte Carlo calculation
Solid State Comm. **52**, 873–876 (1984)

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Quantum Monte Carlo calculation of the singlet-triplet splitting in methylene
J. Chem. Phys. **82**, 1983–1990 (1985)

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Quantum chemistry by random walk: A faster algorithm
J. Chem. Phys. **82**, 2662–2663 (1985)

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The infrared predissociation spectra of water clusters
J. Chem. Phys. **82**, 3554–3562 (1985)

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Muon–alpha-particle sticking probability in muon-catalyzed fusion
Phys. Rev. A **31**, 1999–2004 (1985)

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Quantum Monte Carlo calculations on Be and LiH
Chem. Phys. Lett. **113**, 257–263 (1985)

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The differential Green's function Monte Carlo method.
The dipole moment of LiH
Chem. Phys. Lett. **115**, 89–94 (1985)

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The domain Green's function method
J. Chem. Phys. **85**, 2868–2874 (1986)

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J. Chem. Phys. **88**, 1032–1034 (1988)

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Quantum Monte Carlo method for some model and realistic coupled anharmonic oscillators
J. Chem. Phys. **90**, 990–1002 (1989)

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J. Chem. Phys. **90**, 1003–1006 (1989)