

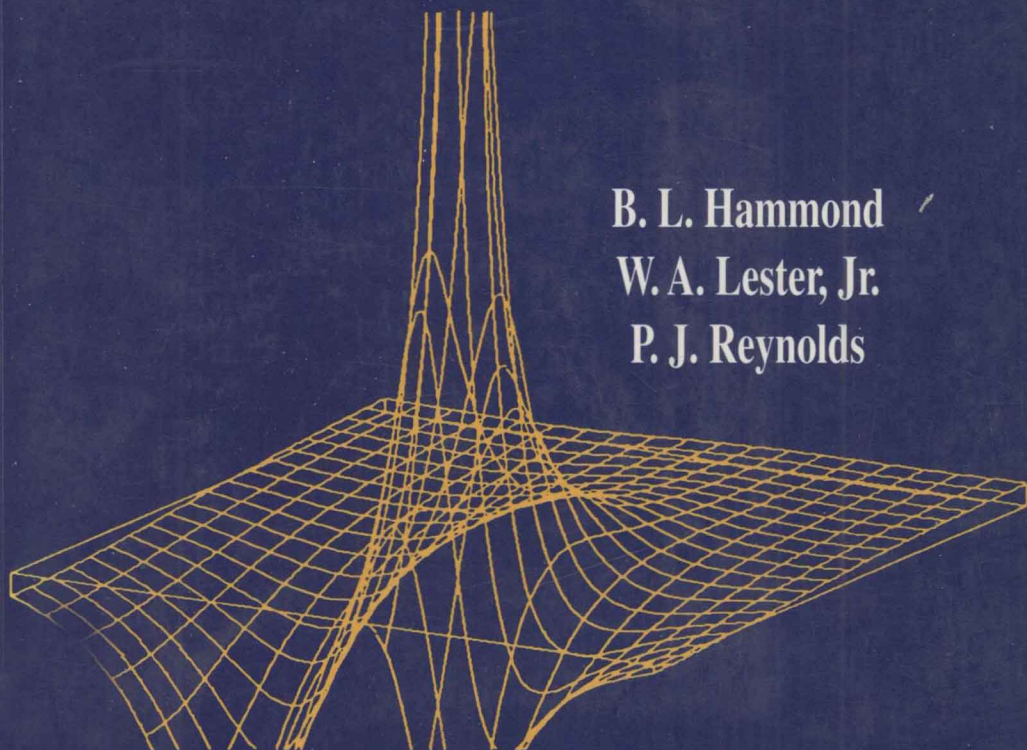
World Scientific Lecture and Course Notes in Chemistry — Vol. 1

Monte Carlo Methods in Ab Initio Quantum Chemistry

B. L. Hammond

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*Monte Carlo Methods in
Ab Initio Quantum Chemistry*

**WORLD SCIENTIFIC LECTURE AND COURSE NOTES
IN CHEMISTRY**

Editor-in-charge: S. H. Lin

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Preface

An accurate and consistent treatment of electron correlation is one of the great challenges currently confronting electronic structure calculations in theoretical chemistry, atomic and molecular physics, and condensed matter theory. Such a treatment is critical for many aspects of the *ab initio* determination of atomic and molecular structure. In these problems, the reference point from which degree of correlation is judged is the Hartree-Fock limit. By convention Hartree-Fock is said to have no correlation since it is a mean field, single particle description. In contrast, the goal of electronic structure theory is the solution of the non-relativistic, Born-Oppenheimer (clamped nuclei) Schrödinger equation. To this end, a number of “post-Hartree-Fock” methods have been developed, i.e. methods that go beyond the mean-field approximation, yet retain the simple molecular-orbital picture. Importantly, these methods add many-body correlation at various levels of approximation. The success of Hartree-Fock and post-Hartree-Fock methods for treating electronic structure benefits considerably from cancellation of errors between two or more computations in the calculation of observables. In many other cases, in particular in the calculation of excited states and classical barrier heights, these errors often do not cancel. Sometimes quantitative accuracy can only be obtained by including vast numbers of terms in various expansions, but such an approach is typically limited in its applicability to small systems.

Post-Hartree-Fock methods fall mainly into two categories: those based on config-

uration interaction, which expand the wave function in primitive basis functions and determinants (configurations), and those based on many-body perturbation theory which treat electron-correlation as a perturbation. In both cases, correlation corrections usually begin from a Hartree-Fock wave function. Other important formalisms that treat the correlation energy are density functional theory and electron propagator methods. The former approach is rapidly gaining momentum and is useful in a variety of applications.

Our aim in this volume is to present the fundamental background and current status of the application of Monte Carlo to the determination of correlation in electronic structure. We shall use the term *quantum Monte Carlo* (QMC) to refer to methods that directly solve the Schrödinger equation, as contrasted with *variational Monte Carlo* (VMC) methods that evaluate quantum mechanical expectation values by Monte Carlo procedures. QMC differs from post-Hartree-Fock approaches in that it is a fully correlated method from the outset, rather than building on a mean-field approach. We also distinguish QMC here from a large class of other Monte Carlo methods used in the treatment of quantum problems, often also referred to as QMC in the literature. The distinguishing feature of all these QMC methods is their essentially exact nature, and the lack of any special attention that needs to be paid to correlation *per se*. Their differences lie in the class of problems they were designed to treat. Among these other methods we mention Hubbard-Stratanovich approaches designed for lattice models of strongly interacting electrons, and path integral Monte Carlo which is most often encountered in simulations of condensed matter. Both of these latter methods are finite-temperature approaches, important for treating macroscopic systems.

Though the QMC we discuss here also has its roots in condensed matter physics and statistical mechanics, it is a zero-temperature or ground-state approach. As such

it is the most appropriate starting point for treating electronic structure by Monte Carlo. Nevertheless, work on adapting other QMC approaches to electronic structure, as well as to adapting the kinds of QMC we discuss here to other realms are currently in progress.

All QMC methods are presently computationally demanding. Nevertheless, as experimental advances push the limits of accuracy required of computational approaches, and as computers continue to achieve greater speed, emphasis must increasingly be placed on the simplicity, consistency and accuracy of a method. QMC holds high promise here. Moreover, Monte Carlo methods are the most natural for massively parallel computation, ultimately providing a great advantage.

The subject matter of this book is divided conceptually into two parts. The first five chapters present the basic concepts in detail. The latter part of the book, chapters 6–9, covers important extensions of these basic methods. Chapter 1 provides background on random numbers, probability distributions, integral estimation, and simulation of simple differential equations. Those readers already familiar with statistics and the use of random numbers may wish to skip this chapter. Chapter 2 treats VMC, describing methods to evaluate the energy and expectation values derived from variational trial wave functions. The power of VMC is that Monte Carlo integration methods enable one to exploit functional forms that are not analytically integrable for many-electron systems. Such forms include those due to Hylleraas as well as more recent forms, all of which depend explicitly on interelectronic distances. In addition, concepts central to both VMC and QMC, such as importance sampling and optimization are introduced here. QMC solution of the Schrödinger equation is the topic of Ch. 3. The focus is on the use of Green's functions to sample the exact ground state energy. Chapter 4 continues the discussion of QMC with consideration of aspects that must be addressed to treat Fermion systems. In Ch. 5 we discuss the

important issue of the choice of trial function. Though QMC methods are not based on trial functions or basis set expansions, unlike many other *ab initio* approaches, these functions do play a central role in importance sampling and in the fixed-node method.

These chapters provide the necessary information and methods to evaluate ground state energies of atoms and molecules. The remainder of the book is dedicated to a number of extensions that are necessary for important chemical applications. The determination of excited-states is treated in Ch. 6, while Ch. 7 describes how to evaluate single-state properties, e.g., dipole and quadrupole moments, and multistate properties, such as the transition dipole moment. Chapter 8 discusses the determination of equilibrium geometries and interaction potentials by means of explicit energy differences and through calculation of energy gradients. Finally, in Ch. 9 we explore new directions being developed which allow QMC to more easily treat systems containing heavy atoms.

We have organized the subject matter with the intent that it may be understood at the entering graduate student level while also being of interest to researchers familiar with the topic. A knowledge of quantum mechanics is required, and some knowledge of molecular electronic structure theory is helpful. For senior undergraduate and graduate level courses, the material in the first four chapters is fundamental. If computational projects are to be undertaken, then Ch. 5 should also prove especially useful. The final chapters may be treated as special topics on the basis of time and interest. For those already familiar with electronic structure theory and Monte Carlo methods in general, chapters 2 through 5 will provide background and breadth, whereas the final chapters will be of more topical interest. To facilitate course work and research projects, we have provided explicit algorithms, exercises, suggested reading, and references at the end of each chapter. The algorithms are writ-

ten using FORTRAN-like syntax; however we have often deviated from FORTRAN in the interests of readability and brevity. In addition, a number of supplementary topics are addressed in the appendices. Conversion factors to and from atomic units are given in Appendix A. Details of the evaluation of determinantal trial functions are discussed in Appendix B. In Appendix C we provide a listing of a FORTRAN77 implementation of diffusion Monte Carlo without importance sampling, which can be used to treat one-dimensional potentials. For those wishing to continue the study of QMC, the electronic structure program QuantumMagiC, developed at the University of California at Berkeley, may be obtained from the Quantum Chemistry Program Exchange (QCPE) at Indiana University, Bloomington, IN 47405 USA. Finally, a comprehensive topical listing of all references used in the text is given in Appendix D.

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Contents

Preface	v
1 Introduction to Monte Carlo Methods	1
1.1 Random Numbers and Statistical Analysis	2
1.1.1 Probability density and distribution functions	3
1.1.2 Characterization of probability density functions	8
1.1.3 Functions of random variates and the central limit theorem . .	14
1.2 Generation of Pseudorandom Numbers	16
1.2.1 Generation of uniform variates	16
1.2.2 Generation of non-uniform random variates	20
1.3 Random Walks and Metropolis Sampling	23
1.3.1 Markov chains	24
1.3.2 Random walks in state space	28
1.3.3 The Metropolis method	29
1.3.4 The generalized Metropolis method	34
1.4 Monte Carlo Integration	37
1.4.1 Uniform sampling	38
1.4.2 Importance sampling	39
1.4.3 Expected values using importance sampling	41
2 Variational Methods	45
2.1 Review of the Variational Method	47
2.2 Monte Carlo Evaluation of Expectation Values	49
2.2.1 Simple Metropolis sampling	49
2.2.2 Importance sampling: Fokker-Planck formalism	52
2.2.3 Importance sampling: Metropolis formalism	54
2.2.4 Electronic properties	57
2.2.5 Evaluation of the variance	58
2.3 Other Sampling Methods	61
2.3.1 Guiding functions	62
2.3.2 Correlated sampling	65
2.4 Monte Carlo Optimization	66

2.4.1	Optimization criteria	68
2.4.2	Energy optimization	69
2.4.3	Variance optimization	70
3	Green's Function Methods	77
3.1	Integral Form of Schrödinger's Equation	78
3.1.1	Green's function formalism	79
3.1.2	Time-dependent Green's functions	83
3.2	Diffusion Monte Carlo	87
3.2.1	Short time approximation	88
3.2.2	Importance sampling	92
3.2.3	Estimating the ground state energy	98
3.2.4	"Pure" diffusion Monte Carlo	100
3.3	Exact Green's Function Methods	102
3.3.1	Green's function Monte Carlo for a bounded potential	103
3.3.2	Domain Green's function Monte Carlo	107
3.3.3	Coulomb Green's function Monte Carlo	112
3.3.4	Feynman-Kac Coulomb correction	114
3.3.5	Explicit sampling of the Coulomb singularity	116
3.4	Comparison of QMC Methods	119
4	Treating Fermions	131
4.1	Nodal Methods	132
4.1.1	Fixed-node approximation	132
4.1.2	Understanding the nodes	137
4.1.3	Releasing the nodes	139
4.1.4	Adaptive nodes	144
4.2	Interacting Walker Methods	145
4.2.1	Pairing methods	146
4.2.2	Fully interacting ensembles	148
5	Variational Trial Functions	155
5.1	Properties of the Exact Wave Function	156
5.2	General Trial Function Forms	159
5.3	Hartree-Fock and Beyond	161
5.3.1	Hartree-Fock and correlation energies	162
5.3.2	Linear combination of atomic orbitals and the self-consistent field equations	163
5.3.3	Cusp conditions	165
5.3.4	Some Hartree-Fock trial function properties	167
5.3.5	Post Hartree-Fock methods	168
5.4	Correlated Molecular Orbital Functions	171

6	Excited States	181
6.1	Transforming Energy Decay Curves	182
6.2	Explicit Orthogonalization	184
6.3	Fixed-Node Method	185
6.4	Concurrent Evaluation of Many States	189
7	Electronic Properties	199
7.1	VMC Properties	200
7.2	Approximate Φ_0^2 Estimators	201
7.3	Rigorous Sampling of Φ_0^2	203
7.3.1	Future walking	203
7.3.2	Time correlation methods	207
7.3.3	Discussion of Φ_0^2 methods	209
7.4	Excited State Properties	212
7.5	Static and Dynamic QMC Polarizabilities	215
8	Derivatives and Finite Differences	221
8.1	Finite Differences and Correlated Sampling	223
8.2	Virial and Hellmann-Feynman Theorems	226
8.2.1	The virial theorem	227
8.2.2	The Hellmann-Feynman theorem	228
8.3	Analytic Energy Derivatives	232
8.3.1	Analytic energy gradients	233
8.3.2	Higher derivatives and derivative properties	236
9	Heavy Atoms	241
9.1	Valence Only Methods	244
9.1.1	Effective core potentials	245
9.1.2	Model potentials	248
9.1.3	Pseudo Hamiltonians	251
9.2	Approximate All-Electron Methods	254
9.2.1	All-electron damped-core QMC	254
9.2.2	Effective two-electron potentials	258
9.3	Acceleration Methods	259
9.3.1	Metropolis acceleration	260
9.3.2	Langevin-based acceleration	263
A	Atomic Units	271
B	Evaluating the Trial Function	273
B.1	Efficient Evaluation of the Trial Function	275
B.2	Computing the Inverse Slater Matrix	277
B.3	Molecular Orbitals and Correlation Functions	279

C Sample Diffusion Monte Carlo Program	281
D Bibliography	287

Chapter 1

Introduction to Monte Carlo Methods

Monte Carlo methods are a class of techniques that can be used to *simulate* the behavior of a physical or mathematical system. They are distinguished from other simulation methods such as molecular dynamics, by being *stochastic*, that is, *non-deterministic* in some manner. This stochastic behavior in Monte Carlo methods generally results from the use of random number sequences. Although it might not be surprising that such an analysis can be used to model random processes, Monte Carlo methods are capable of much more. A classic use is for the evaluation of definite integrals, particularly multidimensional integrals with complicated boundary conditions. The use to which we will apply Monte Carlo is the solution of the well-known partial differential equation, the Schrödinger equation.

Monte Carlo methods are frequently applied in the study of systems with a large number of strongly coupled degrees of freedom. Examples include liquids, disordered materials, and strongly coupled solids. Unlike ideal gases or perfectly ordered crystals, these systems do not simplify readily. The many degrees of freedom present are not separable, making a simulation method, such molecular dynamics or Monte Carlo, a wise choice. Furthermore, use of Monte Carlo is advantageous for evaluating high

dimensional integrals, where grid methods become inefficient due to the rapid increase of the number of grid points with dimensionality. Monte Carlo also can be used to simulate many classes of equations that are difficult to solve by standard analytical and numerical methods.

In this chapter we introduce various aspects of statistics and simulation germane to the Monte Carlo solution of the Schrödinger equation. We begin with a discussion of random and pseudorandom numbers in Sec. 1.1. We then present the essentials of Monte Carlo sampling (in Sec. 1.2), integration (in Sec. 1.3), and simulation (in Sec. 1.4). We attempt to discuss only those concepts needed later in the book. Further details may be found in standard statistics texts.¹

1.1 Random Numbers and Statistical Analysis

A loose definition of a random number is a numerical value resulting from a process or experiment whose value cannot be predetermined by the initial conditions. It is important to note that the term “random number” is somewhat misleading; a number is not random, rather it is the relationship between numbers in a set which is random. Many natural processes display randomness -- from the decay of subatomic particles to the trajectories of dust particles across the surface of a liquid.

We need to start by defining the concepts and notation used to discuss random numbers and events. An *experiment* is the process of observing one or a set of physical properties in a system of interest. The result of an experiment is limited to certain values or ranges of values of the physical properties. A *state* is an allowed value of the set of physical properties of the system. The set of all possible states is the *sample space*. A *discrete* sample space contains either a finite or infinite number of distinct values. A *continuous* sample space contains an infinite number of continuous values (such as the positions of particles). A *sample point* is a single point in sample space.

A *random variable*, or *variate*, is a variable whose value lies within the sample space with a certain probability distribution. To avoid confusion, we will use upper case (X, Y, Z) to denote sample points and lower case (x, y, z) to denote variables. This distinction will become clear with usage. A *sequence* is a series, in order of occurrence, of sample points resulting from an experiment. We often will use the set notation $\{X_i\}$ to denote all the members of a sequence.

1.1.1 Probability density and distribution functions

The most familiar uses of random numbers occur in games of chance. This connection gives the Monte Carlo method its name. Consider a standard six-sided die. If one tosses an ideal, unbiased die, and records the outcome for a sufficiently large number of tosses (in principle, an infinite number), each of the six outcomes will occur exactly one sixth of the time. Even though the outcome of a single toss is random, and thus unknown beforehand, the probability of each outcome is $1/6$. The *probability density function* is the function that describes the probabilities of all possible events. The sum or integral of the probabilities must be unity to insure the proper normalization of the density function. For a discrete distribution the normalized probability function p must satisfy,

$$\sum_{i=1}^N p(x_i) = 1, \quad (1.1)$$

where the sum is over all states, x_i . In the case of the die, the normalized probability density function is $p(x_i) = 1/6$, for each $x_i = 1, 2, 3, 4, 5, 6$. For the general one-dimensional case, the discrete density function can be represented by a histogram as in Fig. 1.1. This figure illustrates the probabilities of the various sums of two dice. A simple discrete probability density function, such as the one shown in Fig. 1.1, can be determined combinatorially by counting the occurrence of each possible event. In many physical situations, however, the probability density function must be deter-