Lawrence Berkeley National Laboratory
Recent Work

Title
EXACT MONTE CARLO FOR MOLECULES

Permalink
https://escholarship.org/uc/item/5x30k4bm

Authors
Lester, W.A.
Reynolds, P.J.

Publication Date
1985-03-01

eScholarship.org Powered by the California Digital Library
University of California

UC-4
LBL-20752 c1

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY
FEB 18 1986
LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular
Research Division

Presented at the Tenth Spring Science Seminars,
Tallahassee, FL, March 28-29, 1985

EXACT MONTE CARLO FOR MOLECULES

W.A. Lester, Jr. and P.J. Reynolds

March 1985

For Reference
Not to be taken from this room

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-20752 c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-20752

EXACT MONTE CARLO FOR MOLECULES

William A. Lester, Jr.[+] and Peter J. Reynolds

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

[+]Also, Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720

March 1985

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76-SF00098.

EXACT MONTE CARLO FOR MOLECULES*

William A. Lester, Jr.+ and Peter J. Reynolds
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

A brief summary of the fixed-node quantum Monte Carlo method is presented. Results obtained for binding energies, the classical barrier height for $H + H_2$, and the singlet-triplet splitting in methylene are presented and discussed.

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76-SF00098.

+Also, Department of Chemistry, University of California, Berkeley.

Introduction to Quantum Monte Carlo

Monte Carlo approaches to solving problems with many degrees of freedom are a class of statistical methods having in common the generation of "random" numbers. In the past few years, Monte Carlo approaches have seen increased application in a number of diverse fields. In particular, quantum mechanical Monte Carlo (QMC) methods[1-13] have been successfully used for the treatment of molecular problems.[3,5,8-12] What we mean here by QMC is a Monte Carlo procedure which solves the Schroedinger equation. This is to be distinguished from so-called variational Monte Carlo, in which one obtains expectation values for a *given* trial wavefunction.

This ability to stochastically solve the Schroedinger equation provides an alternative to conventional techniques of quantum chemistry. Early work[8] has shown that highly accurate total energies and correlation energies can be obtained by QMC. In fact, in a procedurally simple manner, accuracies exceeding those of the best *ab initio* configuration interaction calculations have been obtained.

Much of chemistry takes place predominantly in the valence electrons of a system. Thus, the quantities of interest are usually small differences of large total energies. If QMC is to be useful in calculating binding energies, electron affinities, reaction barriers, etc., it must be able to calculate not only accurate *total* energies, but also these more relevant energy differences. This is a far more difficult task for Monte Carlo, since a statistical uncertainty of as little as 0.1% in the separate total energies can mask the sought-after energy difference.

Nevertheless, we have successfully calculated the reaction barrier for the H + H_2 exchange reaction, the singlet-triplet splitting in methylene, and the binding energy of N_2. Furthermore, algorithmic developments, such as differential QMC[14a] and direct calculation of QMC derivatives,[14b] hold promise for reductions in variance, particularly for potential energy surface calculations. In the next section we briefly describe the method and discuss our previous work. We note that among the results discussed is the first calculation of an excited state energy by Monte Carlo.

Quantum Monte Carlo Approach for Molecules

Here we give an overview of the method; a complete description can be found in Ref. 8. The essence of the procedure is to simulate a quantum system by allowing it (and an ensemble of differently prepared systems) to evolve under the time-dependent Schroedinger equation in imaginary time. It is easy to show[8] that the use of imaginary time causes the ensemble to approach a stationary state which is the lowest state of a given symmetry. Properties may then be "measured" as averages over the resulting equilibrium distribution.

Until recently only ground-state properties have been obtained by this approach. However, we have now calculated the singlet-triplet splitting in methylene (CH_2) very accurately, and begun calculations on $H_2(B\ {}^1\Sigma_u^+)$. Thus, excited-state calculations are a new realm for the application of molecular QMC, and hold much promise.

By writing the imaginary-time Schroedinger equation with a shift in the zero of energy as

$$\frac{\partial\Psi(\tilde{R},t)}{\partial t} = D\nabla^2\Psi(\tilde{R},t) + [E_T - V(\tilde{R})]\Psi(\tilde{R},t), \qquad (1)$$

we see that it may be interpreted as a generalized diffusion equation. The first term on the right-hand-side is the ordinary diffusion terms, while the second term is a position-dependent rate (or branching) term. For an electronic system, $D = \hbar^2/2m_e$, $\tilde{R}$ is the three-N dimensional coordinate vector of the N electrons, and $V(\tilde{R})$ is the Coulomb potential. Since diffusion is the continuum limit of a random walk, one may simulate Eq. (1) with the function Ψ(note not Ψ^2) as the density of "walks." The walks undergo an exponential birth and death as given by the rate term. This connection between a quantum system and a random walk was first noted by Metropolis, who attributes it to Fermi.[15]

The steady-state solution to Eq. (1) is the time-independent Schroedinger equation. Thus, we have $\Psi(\tilde{R},t) \rightarrow \phi(\tilde{R})$, where ϕ is an energy eigenstate. The value of E_T at which the population of walkers is asymptotically constant gives the energy eigenvalue. Early calculations employing Eq. (1) in the way were done by Anderson on a number of one- to four-electron systems.[3]

In order to treat systems larger than two electrons, the Fermi nature of the electrons must be taken into account. The antisymmetry of the eigenfunction implies that Ψ must change sign; however, a density (e.g., of walkers) cannot be negative. To handle this, Anderson made simplifying assumptions about the positions of the nodes. Another method which imposes the antisymmetry, and at the same time provides more efficient sampling (thereby reducing the statistical "noise"), is importance sampling with an antisymmetric trial function Ψ_T (see e.g., Ref. 8). The zeros (nodes) of Ψ_T become absorbing boundaries for the diffusion process, which maintans the antisymmetry. The additional boundary condition that Ψ vanish at the nodes of Ψ_T is the fixed-node approximation. The magnitude of the error thus introduced depends on the accuracy of the nodes of $\Psi_T(R)$, and vanishes as Ψ_T approaches the true eigenfunction. To the extend that Ψ_T is a good approximation of the wavefunction, the true eigenfunction is almost certainly quite small near the nodes of Ψ_T. Thus, one expects the fixed-node error to be small for reasonable choices of Ψ_T. Work on a number of systems has borne this out.[9,10,12] In addition, this error is variationally bounded.

To implement importance sampling and the fixed-node approximation, Eq. (1) is multiplied on both sides by Ψ_T, and rewritten in terms of the new probability density $f(\tilde{R},t) = \Psi_T(\tilde{R})\Psi(\tilde{R},t)$. The resultant for $f(\tilde{R},t)$ may be written

$$\frac{\partial f}{\partial t} = D\nabla^2 f + [E_T - E_L(\tilde{R})]\, f - D\nabla\cdot[fF_Q(\tilde{R})]. \tag{2}$$

The local energy $E_L(\tilde{R})$, and the "quantum force" $F_Q(\tilde{R})$ are simple functions of Ψ_T given by

$$E_L(\tilde{R}) \equiv H\Psi_T(\tilde{R})/\Psi_T(\tilde{R}), \tag{3a}$$

and

$$F_Q(\tilde{R}) \equiv 2\nabla\Psi_T(\tilde{R})/\Psi_T(\tilde{R}), \qquad (3b)$$

Equation (2), like Eq. (1) is a generalized diffusion equation, though now with the addition of a drift term due to the presence of F_Q.

In order to perform the random walk implied by Eq. (2) we use a short-time approximation to the Green's function which is used to evolve $f(\tilde{R},t) \rightarrow f(\tilde{R}', t+\tau)$. This evolution process is iterated to large t. The Green's function becomes exact in the limit of vanishing time-step size, τ.

Summary of Previous Results

We have found[8,11] that a single determinant Ψ_T with only a double-zeta basis set places the nodes extremely well as determined by the quality of the computed total energies. Increasing the basis set beyond double zeta appears to offer insignificant gain in either accuracy (i.e., the fixed-node error does not noticeably decrease) or precision (the statistical uncertainty, for equal computing time, remains essentially unchanged). In practice we have included an electron-electron Jastrow factor in the functions Ψ_T in order to reduce statistical fluctuations, and in some cases we have also included an electron-nuclear factor. Neither factor affects the positioning of the nodes, and hence the fixed-node energies. For a number of 2-14 electron molecules we have obtained total energies which are lower than those obtained by CI in every case.

Recently, we have calculated the energy of the first excited state of methylene[16] in order to obtain the (until recently) elusive singlet-triplet splitting. This is the first QMC calculation of an excited state. Our results are in excellent agreement with the most recent experiments. For the best trial function used, the *total energy* is correct to better than 0.008 hartrees (5 kcal/mole) of experiment, or to 1 part in 5000. The statistical uncertainty is roughly half this value (2-2.5 kcal/mole). The remaining error may be attributed to the fixed-node and the short-time approximations. This translates to a Monte Carlo accuracy of 99.98% of the total energy and 96-98% of the correlation energy.

In other work, we have calculated points along the reaction path of the $H + H_2$ exchange reaction. Particular emphasis has been placed on the saddle point, for which Liu[17] has performed the most extensive CI calculation to date. Nevertheless, the bound for the barrier height which we obtained[11c] by QMC is 0.16 kcal/mole below Liu's bound and probably lies within 0.1 kcal/mole of the exact answer. In addition, we were able to obtain these results with only single-determinant trial functions, and a basis set expansion at only the double-zeta level. The nodes, which are so important in determining the correct energy, have to this point proved to be quite insensitive to basis set beyond the double-zeta level. A single-zeta basis set gives a very poor nodal description (see Ref. 11c).

Accurate calculation of the binding energy of N_2 has been a classically difficult problem using traditional *ab initio* quantum chemical approaches. Since the quantity of interest, $E_{binding}$, is desired to better than 5 kcal/mole out of a total energy of over 68,000 kcal/mole, this is an example where QMC requires very high precision. In preliminary calculations we have determined the N_2 binding energy to be 233 ± 5 kcal/mole. To within the statistical uncertainty, this result agrees with experiment.

References

1. M. H. Kalos, Phys. Rev. 128, 1791 (1962); J. Comp. Phys. 1, 257 (1967).
2. M. H. Kalos, D. Levesque, and L. Verlet, Phys. Rev. A 9, 2178 (1974).
3. J. B. Anderson, J. Chem. Phys. 63, 1499 (1975); 65, 4121 (1976).
4. D. M. Ceperley and M. H. Kalos, in Monte Carlo Methods in Statistical Physics, edited by K. Binder (Springer-Verlag, Berlin, 1979).
5. J. B. Anderson, J. Chem. Phys. 73, 3897 (1980); F. Mentch and J. B. Anderson, J. Chem. Phys. 74, 6307 (1981).
6. D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
7. D. M. Ceperley in Recent Progress in Many-Body Theories, edited by J. G. Zabolitzky, M. de Llano, M. Fortes, and J. W. Clark (Springer-Verlag, Berlin, 1981).
8. P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, Jr., J. Chem Phys. 77, 5593 (1982).

9. J. W. Moskowitz, K. E. Schmidt, M. A. Lee, and M. H. Kalos, J. Chem. Phys. 7, 349 (1982).
10. D. M. Ceperley, J. Comp. Phys. 51, 404 (1983).
11. (a) P. J. Reynolds, R. N. Barnett, and W. A. Lester, Jr., "Quantum Monte Carlo Study of the Classical Barrier Height for the H + H_2 Exchange Reaction: Restricted *versus* Unrestricted Trial Functions," Int. J. Quant. Chem. Symp. 18, 709 (1984); (b) F. Mentch and J. Anderson, J. Chem. Phys. 80, 2675 (1984); (c) R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., "Fixed-node Quantum Monte Carlo Study of the Classical Barrier Height for the H + H_2 Exchange Reaction," J. Chem. Phys., 82, 2700 (1985).
12. D. M. Ceperley and B. J. Alder, J. Chem. Phys., in press.
13. K. E. Schmidt and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics, II*, edited by K. Binder, in press.
14. (a) B. Holmer and D. M. Ceperley private communication; B. Wells, P. J. Reynolds, and W. A. Lester, Jr., unpublished; (b) B. Hammond P. J. Reynolds, and W. A. Lester, Jr., unpublished.
15. N. Metropolis and S. M. Ulam, J. Am. Stat. Assoc. 44, 335 (1949).
16. P. J. Reynolds, M. Dupuis, and W. A. Lester Jr., J. Chem. Phys. 82, 1983 (1985).
17. B. Liu, J. Chem. Phys. 80, 581 (1984).

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720