

A simplified released-node quantum Monte Carlo calculation of the ground state of LiH

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We report an exact *ab initio* calculation of the ground state of the LiH molecule using a simplified released-node Green's function quantum Monte Carlo method. The energy determined for an internuclear separation of 3.015 bohr is $-8.070\ 21 \pm 0.000\ 05$ hartree, a value lower than that of the lowest-energy variational calculation, more accurate than that of prior quantum Monte Carlo calculations, and in excellent agreement with the nonrelativistic energy of $-8.070\ 21$ hartree determined from experimental measurements. © 1995 American Institute of Physics.

I. INTRODUCTION

Quantum Monte Carlo (QMC) methods have been found to be powerful techniques for solving the Schrödinger equation for atomic and molecular systems. These methods and their successes in providing accurate predictions of energies and structures for molecular systems ranging from simple molecular ions such as the H_3^+ ion¹ to pieces of condensed matter such as N_2 crystals² have been described in recent reviews.³⁻⁵

Several different schemes, some exact and some approximate, have been developed to overcome the "sign problem" and allow the accurate treatment of nodal hypersurfaces in QMC calculations. These include fixed-node methods,^{6,7} released-node methods,^{8,9} and exact cancellation methods.^{10,11}

The released-node method is particularly useful in calculations for molecular systems of 4–15 electrons.^{8,9,12,13} It has given energies of very high accuracy for molecules such as LiH and H_2O . When used with Green's function sampling it is an "exact" method capable, in principle, of giving solutions of the Schrödinger equation without systematic error but with statistical or sampling error. It is a "transient" method in which the desired fermion wave function develops as the difference between two populations, each evolving toward the nodeless boson ground state wave function. The difference disappears in noise as the two populations approach the same distribution. A maximum of information may be extracted from the transient wave function with use of Lanczós¹² and, particularly, Bayesian¹³ methods.

We report here an investigation of a simplified released-node Green's function quantum Monte Carlo method and its application in determining the energy of the LiH molecule. The simplified method allows large step sizes without step-size error, eliminates conditional sampling, and eliminates the use of a guide function. Importance sampling is incorporated by use of variable sample weighting.

II. THEORETICAL BASIS

The time-independent Schrödinger equation for a molecular system of N electrons and an arbitrary number of fixed nuclei is

$$-\frac{\hbar^2}{2m_e} \sum_i^N \nabla_i^2 \Psi(\mathbf{R}) + V(\mathbf{R})\Psi(\mathbf{R}) = E\Psi(\mathbf{R}), \quad (1)$$

where \mathbf{R} is the $3N$ -dimensional coordinate vector of N electrons and

$$V(\mathbf{R}) = \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}}. \quad (2)$$

The equation may be rearranged to obtain

$$-\nabla^2 \Psi(\mathbf{R}) + k^2 \Psi(\mathbf{R}) = k^2 \frac{V(\mathbf{R})}{E} \Psi(\mathbf{R}), \quad (3)$$

where $k^2 = -2m_e E / \hbar^2$. By adjusting the potential energy offset, the energy E can be made negative so that k is real.

In the case of systems with boundary conditions $\Psi(\mathbf{R}) \rightarrow 0$ as $R \rightarrow \infty$, the Green's function corresponding to the left side of Eq. (3) is known and is given by

$$G_0(\mathbf{R}, \mathbf{R}') = (2\pi)^{-3N/2} (k|\mathbf{R} - \mathbf{R}'|)^{-3N/2} \times K_{3N/2-1}(k|\mathbf{R} - \mathbf{R}'|), \quad (4)$$

where K_ν is the modified Bessel function of the second kind. Integrating Eq. (3) and using the Green's function G_0 and energy E , one has

$$\Psi(\mathbf{R}) = \int d\mathbf{R}' G_0(\mathbf{R}, \mathbf{R}') \frac{V(\mathbf{R}')}{E} \Psi(\mathbf{R}'). \quad (5)$$

One can solve the integral equation by iteration, starting with an approximate wave function and generating the sequence

$$\psi_{n+1}(\mathbf{R}) = \int d\mathbf{R}' G_0(\mathbf{R}, \mathbf{R}') \frac{V(\mathbf{R}')}{E} \psi_n(\mathbf{R}'). \quad (6)$$

Equation (6) is the basis for Green's function quantum Monte Carlo calculations. As shown by Kalos¹⁴ the iterations

can be carried out in Monte Carlo fashion using wave function samples or “walkers” with weights multiplied at each generation by $V(\mathbf{R}')/E$ and random steps to new positions \mathbf{R} selected with probabilities proportional to $G_0(\mathbf{R}, \mathbf{R}')$. Successive iterations lead to a distribution of walkers corresponding to the lowest-energy wave function satisfying the Schrödinger equation subject to any restrictions imposed. Further iteration continues the sampling.

The wave function samples may be used to determine the energy in several different ways, but the most accurate result is usually obtained from importance sampling¹⁵ with the aid of an approximate or trial wave function ψ_0 having the same symmetry as the desired wave function. The expression for the energy is given in integral form by

$$E = \frac{\int d\mathbf{R} \Psi(\mathbf{R}) \psi_0(\mathbf{R}) H \psi_0(\mathbf{R}) / \psi_0(\mathbf{R})}{\int d\mathbf{R} \Psi(\mathbf{R}) \psi_0(\mathbf{R})} \quad (7)$$

and in terms of summations by

$$E = \frac{\sum_i \sigma_i W_i \psi_0(\mathbf{R}) H \psi_0(\mathbf{R}) / \psi_0(\mathbf{R})}{\sum_i \sigma_i W_i \psi_0(\mathbf{R})}, \quad (8)$$

where the summations are for (Ψ based) walkers with weights W_i and signs σ_i .

III. RELEASED-NODE METHOD

Our simplified released-node method is based on a simplified sampling method developed earlier¹⁶ for Green's function QMC calculations of systems without nodes. In a nodeless system the walkers can be maintained positive at all times, but positive and negative walkers are an essential part of released-node calculations.

For a system containing two or more electrons of the same spin the nodal hypersurface of the exact ground-state wave function divides the $3N$ -dimensional configuration space of the electrons into two equivalent regions corresponding to positive and negative values of the wave function. Permutation of any two electrons of the same spin moves a point in one region to an equivalent point in the other region. The trial wave function ψ_0 and its nodal surface have the same characteristics. One can begin a released-node calculation with positive and negative walkers obtained by sampling the trial wave function. This produces a starting distribution with positive walkers in the positive region of the trial function and negative walkers in the negative region of the trial wave function. But since the two regions are geometrically similar, one need not use both regions. One may limit the calculation to the positive region of the trial wave function if walkers crossing into the negative region are returned with an opposite sign to their equivalent points in the positive region. A better starting distribution is obtained by sampling the wave function generated by a fixed-node calculation with the nodal surface specified as that of the trial function.

Thus a calculation is begun with positive walkers from a fixed-node QMC calculation on the positive side of the nodal surface of the trial function and proceeds through successive iterations. A walker crossing to the negative side is returned to the positive side by permuting any two electrons of the

same spin and changing its sign. The sign of a walker may also be changed in the process of multiplication by the term $V(\mathbf{R}')/E$. Of course, there are other procedures which could achieve the same overall result without moving walkers back to the positive side.

For importance sampling to be most effective the individual values of the products $W_i \psi_0(\mathbf{R})$ in the summations of Eq. (8) must be approximately equal. This may be achieved by dividing walkers to produce weights inversely proportional to the values of their associated trial wave functions.

For an initial distribution of walkers at positions \mathbf{R}' in the positive region of the trial function the calculation procedure is as follows:

- (1) Multiply weight W_i by $|V(\mathbf{R}')/E|$ and sign σ_i by sign $[V(\mathbf{R}')/E]$.
- (2) Sample $G_0(\mathbf{R}, \mathbf{R}')$ for a new position \mathbf{R} and move walker from \mathbf{R}' to \mathbf{R} .
- (3) Evaluate $\psi_0(\mathbf{R})$. If $\psi_0(\mathbf{R}) < 0$, permute two electrons of the same spin and reverse sign σ_i . If not already positive the sign of $\psi_0(\mathbf{R})$ becomes positive.
- (4) Multiply weight W_i by $\psi_0(\mathbf{R})/\psi_{\text{avg}}$ to obtain a “value” Y_i . The constant term ψ_{avg} is a long-term weighted average of ψ_0 for walkers in a preliminary run used to aid in choosing values Y_i for splitting such that the number of walkers at each iteration is maintained approximately equal to their total weight and their individual values are unity. The total weight is allowed to change in the course of a run (see next step).
- (5) Divide walker into m walkers of unit value with the same sign. Their number m is given by the integer part of $Y_i + u$, where u is a random number in the interval of $[0, 1]$. For $m > 0$ their weights are given by W_i/m .
- (6) Calculate the local energy. Add the weight–energy product and the weight to the appropriate positive or negative group sums for computing the final averages for different generations.
- (7) Go back to step (1).

The iterations are continued until the difference in populations of positive and negative walkers becomes too small to allow a satisfactory determination of the energy.

IV. CALCULATIONS FOR LiH

The method was applied in the determination of the energy of the ground state of the LiH molecule with fixed nuclei at an internuclear distance of 3.015 bohr. The trial wave function used is the function ψ_{III} of Reynolds *et al.*¹⁷ in the form

$$\psi_0 = \det|D_{kl}^\alpha| \det|D_{kl}^\beta| \exp \left[\sum_{i>j} \frac{a_{ij} r_{ij}}{1 + b r_{ij}} - \sum_{i,\alpha} \frac{Z_\alpha a_{i\alpha} r_{i\alpha}}{1 + b r_{i\alpha}} \right], \quad (9)$$

where $D_{kl}^s = \psi_k(r_l; s)$, s is the spin state, and ψ_k is the k th molecular orbital. The constants a_{ij} for like and unlike electron pairs and $a_{i\alpha}$ for electron–nucleus pairs are selected to give the correct cusp conditions for small separations. The molecular orbitals in the determinants are each localized

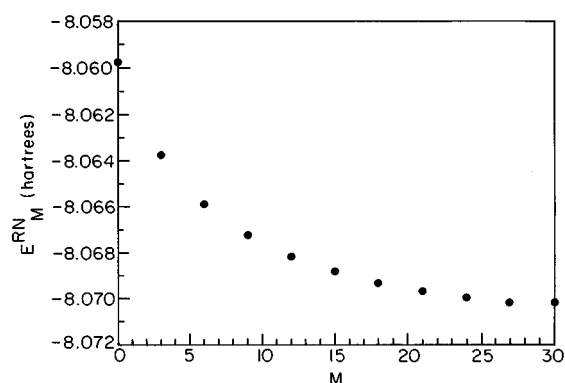


FIG. 1. Variation of calculated energy with released-node generation.

about a single center and have a flexible form. The standard deviation from the mean for individual local energies calculated with the trial function is about 1.0 hartree.

The computations were carried out using IBM SP1 and SP2 machines at the Maui High Performance Computing Center and the Penn State Center for Academic Computation. The calculation was divided into about 500 independent runs, each in about 120 blocks of 2000 iterations. The fixed-node population was normalized every 60 iterations and the number of random walkers was controlled at approximately 750 by random duplication or elimination. The data from the first three iterations after each normalization were discarded in order to avoid any bias due to the fixed-node population normalization. The released-node population was not normalized and thus was free from normalization bias. The released-node calculations were carried out for 30 iterations after node release and then terminated. The results from the independent runs were combined to average energies for each generation group. The statistical error in these average energies was estimated from the variance in the energies of the independent runs.

V. RESULTS AND DISCUSSION

The variation in the average energies with generation is shown in Fig. 1 and the differences in average energies for successive generations are shown in Fig. 2. Convergence to a constant value of the energy may be seen to occur in 24–27 generations. This is also indicated in Fig. 2 by a slope of zero in 24–27 generations. The computed average energy at the 27th generation is -8.07022 ± 0.00005 hartree. To be sure of the convergence we later ran a smaller set of independent calculations to the 30th generation and obtained a converged energy of -8.07020 ± 0.00012 hartree. The combined result for the energy, taken as the weighted average for the last generation in each set, is -8.07021 ± 0.00005 hartree.

A comparison with the results of prior calculations is given in Table I. Included are the energies from several fixed-node QMC calculations, released-node QMC calculations, and analytic variational calculations. The most accurate previous QMC result is that from a released-node calculation, with a Bayesian analysis to reduce statistical error, by Caffarel and Ceperley,¹³ giving -8.0700 ± 0.0002 hartree.

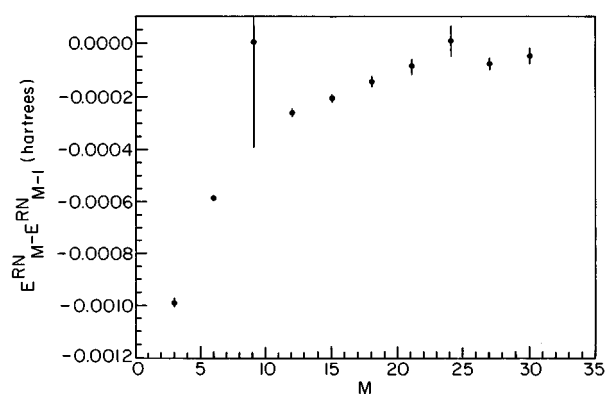


FIG. 2. Change in calculated energy for succeeding released-node generations.

The lowest-energy analytic variational calculation to date is that by Cencek and Rychlewski²² giving -8.069221 hartree. Our current result is more accurate than the earlier QMC result and is in agreement with that result within the combined uncertainties. Our current result is lower in energy than the lowest-energy analytic variational result.

The gain in accuracy relative to that of earlier Monte Carlo calculations of the energy for LiH is the result of (a) a simpler faster algorithm and (b) a greater computational effort. The importance sampling trial function used is essentially the same as that used in earlier calculations. We estimate that the simpler algorithm reduces the computational

TABLE I. List of ground state energies of LiH obtained from QMC calculations, analytic variational calculations, and experimental measurements. The energies are nonrelativistic, clamped-nucleus values for an internuclear distance of $R = 3.015$ bohr. Additional values are given in Refs. 4 and 18.

Authors (date) notes	Energy (hartree)	
Ceperley and Alder ^a (1984)		
fixed-node GFQMC	-8.067	± 0.001
released-node GFQMC	-8.071	± 0.001
Harrison and Handy (1985) ^b		
fixed-node DQMC	-8.069 7	$\pm 0.000 3$
Barnett, Reynolds, and Lester (1987) ^c		
fixed-node DQMC	-8.070 0	$\pm 0.000 4$
Caffarel, Gaeda, and Ceperley (1991) ^d		
fixed-node DQMC	-8.069 1	$\pm 0.000 6$
released-node DQMC	-8.070	± 0.001
Caffarel and Ceperley (1992) ^e		
fixed-node DQMC	-8.068 0	$\pm 0.000 6$
released-node DQMC	-8.070 0	$\pm 0.000 2$
Subramaniam, Lee, Schmidt, and Moskowitz (1992) ^f		
fixed-node GFQMC	-8.069 9	$\pm 0.001 0$
Chen and Anderson (This work) (1994)		
released-node GFQMC	-8.070 21	$\pm 0.000 05$
Cencek and Rychlewski (1993) ^g		
lowest-energy analytic variational	-8.069 221	
Experimental value (from Table II)	-8.070 21	

^aReference 9.^cReference 13.^bReference 19.^fReference 21.^eReference 20.^gReference 22.^dReference 12.

TABLE II. Calculation of experimental clamped-nucleus, nonrelativistic energy of LiH at 3.015 bohr (energies in hartree).

Energy of Li atom with infinite-mass nucleus ^a	-7.478 07
Energy of H atom with infinite-mass nucleus	-0.500 00
Energy of Li atom with finite-mass nucleus	-7.477 49
Energy of H atom with finite-mass nucleus	-0.499 73
Experimental dissociation energy D_e^b	+0.092 43
Total energy of LiH with finite-mass nuclei	-8.069 65
Total energy of LiH with infinite-mass nuclei	-8.070 20
Relativistic correction for D_e^c	+0.000 01
Calculated experimental energy for LiH	-8.070 21

^aReference 24.^bReference 25.^cReference 26.

effort for walker moves by about 50% relative to the earlier calculations of Ceperley and Alder.⁹ This represents a significant improvement, but the major contributor to the higher precision is a greater total number of walker moves made possible by faster computers.

The clamped-nucleus energy of LiH may be determined from a combination of experimental measurements with "corrections" to eliminate various real effects not accounted for by the Schrödinger equation. A calculation of the experimental clamped-nucleus, nonrelativistic energy for LiH at a separation of 3.015 bohr is shown in Table II. The lowest-energy variational calculation²³ for the Li atom gives an energy of -7.478 059 hartree for infinite-mass, nonrelativistic Li and the corresponding experimental value²⁴ is -7.478 073 hartree, so that -7.478 07 hartree is a reasonable choice. The finite-mass energy of LiH is derived from the finite-mass energies of Li and H and the experimental dissociation energy of LiH.²⁵ This is converted to the clamped-nucleus energy for LiH. Taking into account the net relativistic correction for the dissociation energy of 0.000 012 hartree as determined by Wallmeier,²⁶ we obtain a clamped-nucleus, nonrelativistic experimental energy of -8.070 21 hartree. The uncertainty is estimated to be less than 0.000 10 hartree. Our calculated energy is in excellent agreement with this value.

Although we find the released-node Green's function QMC calculation described here to be computationally very efficient, we note that incorporating the Lanczós or Bayesian approaches in treating the results is quite likely to improve its efficiency.

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