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Calculating potential energy curves with fixed-node diffusion Monte Carlo: CO and N₂

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This study reports on the prospect for the routine use of Quantum Monte Carlo (QMC) for the electronic structure problem, applying fixed-node Diffusion Monte Carlo (DMC) to generate highly accurate Born-Oppenheimer potential energy curves (PECs) for small molecular systems. The singlet ground electronic states of CO and N₂ were used as test cases. The PECs obtained by DMC employing multiconfigurational trial wavefunctions were compared with those obtained by conventional high-accuracy electronic structure methods such as multireference configuration interaction and/or the best available empirical spectroscopic curves. The goal was to test whether a straightforward procedure using available QMC codes could be applied robustly and reliably. Results obtained with DMC codes were found to be in close agreement with the benchmark PECs, and the n^3 scaling with the number of electrons (compared with n^7 or worse for conventional high-accuracy quantum chemistry) could be advantageous depending on the system size. Due to a large pre-factor in the scaling, for the small systems tested here, it is currently still much more computationally intensive to compute PECs with QMC. Nevertheless, QMC algorithms are particularly well-suited to large-scale parallelization and are therefore likely to become more relevant for future massively parallel hardware architectures. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4971378>]

I. INTRODUCTION

Quantum Monte Carlo (QMC) methods have shown promise in performance and scalings as an approach to quantum mechanical calculations.¹⁻⁵ These methods have been applied not only to the electronic structure, especially of solids⁶⁻¹⁰ and medium-sized molecules,¹¹ but also to atoms and small molecules¹²⁻²⁸ presenting an alternative to traditional high-accuracy quantum chemistry methods such as configuration interaction (CI)²⁹ and coupled-cluster (CC).^{30,31} Some typical limitations of standard *ab initio* methods are as follows: (1) high-order dynamic electron correlation may be neglected or is prohibitively costly to compute; (2) scaling with the number of electrons is poor;^{32,33} (3) some errors may be introduced by internal contraction;³⁴ and (4) many algorithms are not yet efficient for large scale parallelization.

Key advantages for QMC methods are favorable scaling with the number of electrons and efficient parallelization (scaling with the number of computing cores). CI and CC methods can scale as n^7 (for n electrons) or worse³² and thus rapidly become prohibitively expensive with the increasing system size, whereas QMC methods scale as n^3 making them especially favorable for larger systems. In practice for small systems, despite the impressive n^3 scaling, QMC tends to have a large cost-prefactor making it relatively expensive compared with traditional quantum methods. Nevertheless, the vastly better scaling means that there exists a crossover point in system size beyond which QMC is favored. In addition, QMC algorithms can be very efficiently parallelized, scaling

essentially linearly with the number of cores.³⁵ QMC methods can take full advantage of massively parallel machines, and are thus well-suited for next-generation computer architectures with millions of cores.^{3,5}

During the development of QMC methods over the past few decades, there have been numerous reported studies of first-row atoms and (mostly) homonuclear diatomics^{12-27,36} as well as hydrides.^{37,38} The majority of those studies have focused on a single equilibrium geometry for each species while treating the total binding energy as well as components of the energy as method development benchmarks. It is well established that QMC methods can capture large fractions of both the strong and dynamic correlation energies, illustrated for example, by its impressive performance for the challenging Be₂ system.^{17,25} Methods to compute forces have also been developed³⁹ and estimates of anharmonic force constants based on a few near-equilibrium points have been reported.¹⁵

Some PECs calculated with QMC have been reported⁴⁰⁻⁴² including the most recent work of Giner *et al.*⁴⁰ Those studies focus on technical aspects of the wavefunction construction and sampling as well as accuracy performance, but with less emphasis on assessments of cost and routine feasibility. They did achieve high-accuracy in comparison with reference curves, and reported that the fixed-node error (due to the fixed-node approximation)⁴³ was reduced as an increasing number of determinants were used. Some of the studies did not pursue the highest degree of accuracy, limiting the size of basis set in the trial wavefunction.⁴⁰ The largest bond dissociation distances were the least well converged relative to reference PECs,^{37,40} and this was ascribed to limitations in the number of determinants.

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For PECs, single-reference methods (with typical levels of truncation of the excitation operators) often do not produce the correct behavior over the entire bond-distance range, because they cannot easily account for the evolution toward other configurations as the bond is stretched toward dissociation. The problem is common when breaking multiple bonds, a well-known example being N_2 .⁴⁴ Even though CCSD(T), i.e., coupled-cluster with single, double, and perturbative triple excitations, is considered the “gold standard” of quantum chemistry, for N_2 it cannot accurately calculate the region of the PEC corresponding to dissociation. CCSD(T) breaks down at about twice the equilibrium bond length r_e and produces an artificial hump.^{44,45}

Multi-reference methods are often preferred as a globally applicable approach with correct dissociative behavior and have been found necessary in previous QMC studies.³⁷ The single determinant fixed-node (FN-DMC) atomization benchmarks reported by Grossman in 2002 found a 2.9 kcal/mol average absolute deviation over a 55 molecule test set, with deviations of 3.0 and 4.1 kcal/mol for CO and N_2 , respectively.¹⁴ The efficient use of multideterminants in QMC codes is not trivial but has been successfully addressed by an algorithm known as the *table method*^{46,47} implemented in the QMCPACK⁴⁸ code package. The work reported here focuses on assessing the accuracy, cost, and routine feasibility of using QMC as implemented in two freely available packages, calculating ground state potential energy curves (PECs) for two test systems (CO and N_2). The multi-determinant trial wave functions used in this study were generated from orbitals and determinants using the multi-configurational self-consistent field (MCSCF) and configuration interaction (CI) methods from GAMESS (U.S.).⁴⁹ The CASINO⁵⁰ package was used for most of the QMC calculations reported here, along with some timing comparisons conducted using the QMCPACK⁴⁸ code.

II. FIXED-NODE QUANTUM MONTE CARLO

Here, we give a brief summary of some important aspects of QMC. For more technical details, the reader is referred to Refs. 50 and 51.

A. Variational Monte Carlo (VMC)

Variational Monte Carlo (VMC), using an approximate trial wave function Ψ_T , calculates the expectation value of a Hamiltonian H , with the integrals being performed by a Monte Carlo method.^{52–54} The variational energy E_{VMC} is an upper bound to the exact ground state energy E_0 and is mathematically defined as

$$E_{VMC} = \frac{\int \Psi_T^*(\mathbf{R}) H \Psi_T(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R}) d\mathbf{R}} \geq E_0, \quad (1)$$

where \mathbf{R} is a $3N$ -dimensional vector of the coordinates ($\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$) of the N particles in the system (in this case electrons).⁵⁰ The expectation value of the Hamiltonian H can be rewritten with respect to the trial wave function Ψ_T as

$$\langle H \rangle = \frac{\int |\Psi_T(\mathbf{R})|^2 E_{loc}(\mathbf{R}) d\mathbf{R}}{\int |\Psi_T(\mathbf{R})|^2 d\mathbf{R}}, \quad (2)$$

with the local energy $E_{loc} = \Psi_T^{-1} H \Psi_T$. By sampling the points \mathbf{R}_i according to the distribution $|\Psi_T|^2$ with M configurations, the variational energy can then be computed from a set of local energies,

$$E_{VMC} = \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{i=1}^M E_{loc}(\mathbf{R}_i). \quad (3)$$

Statistical uncertainty in a Monte Carlo method decreases as $1/\sqrt{M}$, where M is the number of samples. The primary purpose of the VMC method in this application is to optimize the parameters of a trial wave function, such as the Jastrow factor,^{55–59} for subsequent use in the more accurate DMC (Diffusion Monte Carlo) method.

In this work, to help describe dynamic electron correlation, a three-body Jastrow factor was used,⁵² which includes electron-electron u terms, electron-nucleus χ terms, and electron-electron-nucleus f terms. The Jastrow factor makes the trial wave function depend explicitly on particle separations and is symmetric under the interchange of identical particles.⁶⁰ Note that in a similar application to the F_2 molecule, Giner *et al.* justified not employing a Jastrow factor, primarily in order to avoid the costly optimization of parameters.⁴⁰ They state that non-linear optimizations of Jastrow factors may make it more difficult to obtain smooth PECs. The main drawback to lacking a Jastrow factor conceded by Giner *et al.* is a greatly increased variance in the trial wavefunction and corresponding increased simulation times.⁴⁰ For a detailed description of the form of the Jastrow factor that is used in CASINO, see Ref. 54.

B. Diffusion Monte Carlo

The Diffusion Monte Carlo (DMC) method^{61,62} uses the importance-sampled imaginary-time Schrödinger equation to evolve an ensemble of electronic configurations toward the ground state. The Schrödinger equation can be written in integral form as

$$f(\mathbf{R}, t) = \int G(\mathbf{R} \leftarrow \mathbf{R}', t - t') f(\mathbf{R}', t') d\mathbf{R}', \quad (4)$$

where \mathbf{R} is a point in the configuration space of an N -particle system. Here, $f(\mathbf{R}, t)$ is a mixed distribution dependent on some trial wave function Ψ_T , and written mathematically as $f(\mathbf{R}, t) = \Psi(\mathbf{R}, t) \Psi_T(\mathbf{R})$. The Green’s function $G(\mathbf{R} \leftarrow \mathbf{R}', t - t')$ gives the probability of a transition from \mathbf{R} to \mathbf{R}' in the time interval $t - t'$, and satisfies the initial condition $G(\mathbf{R} \leftarrow \mathbf{R}', 0) = \delta(\mathbf{R} - \mathbf{R}')$.

Due to the fermion sign problem,⁵¹ the DMC method in CASINO adopts the fixed-node approximation, in which the nodes of f are constrained to be the same as those of the trial wave function Ψ_T . The DMC method then produces the lowest energy possible for this nodal surface and can be considered variational with respect to it.⁴¹ Interestingly, for both atoms and diatomic molecules, Giner *et al.* reported a systematic decrease in the fixed-node error with respect to both the number of determinants retained and the size of the one-particle basis.⁴⁰

III. COMPUTATIONAL METHOD

For all of the QMC calculations, multi-determinant Slater-Jastrow (MD-SJ) trial wave functions were used, which can be written mathematically as

$$\Psi_T(\mathbf{R}) = e^J(\mathbf{R}) \sum_{k=1}^{N_D} c_k D_k^\uparrow D_k^\downarrow, \quad (5)$$

where Ψ_T is the trial wave function, e^J is the Jastrow factor, c_k are the determinant coefficients for the multi-determinant expansion describing static correlation,⁵¹ and D_k^\uparrow and D_k^\downarrow are the spin-up and spin-down Slater determinants, respectively. For both CO and N₂, the aug-cc-pwCV5Z basis sets⁶³ were truncated to 11s10p8d, i.e., angular momentum functions $\geq f$ were removed. The orbitals in the trial wave functions were cusp corrected using the scheme of Ma *et al.*⁶⁰

All DMC calculations were performed with the electrons moving one at a time (electron-by-electron). The time steps for all the systems were chosen so that the acceptance ratio of the proposed moves would be $\sim 99.5\%$.

A. Applications

For both systems, the Jastrow factor was defined using an expansion of order 8 for the u terms ($N_u = 8$), an expansion also of order 8 for the χ terms ($N_\chi = 8$), and an order of 4 for the f terms ($N_f^{en} = N_f^{ee} = 4$), resulting in a total of 149 variable parameters for N₂ and 281 parameters for CO in the two respective Jastrow factors. For all trial wave functions, the truncation order-parameter C , which determines the behavior at the cutoff lengths, was set to a value of 3, providing a local energy that is continuous in configuration space.⁶⁰ For the electron-electron u terms and electron-electron-nucleus f terms, different parameter values were used for the parallel and the antiparallel-spin electron-pairs, and, for the electron-nucleus χ terms, different parameters were used for spin-up and spin-down electrons.

The parameters of the Jastrow factor were optimized with un-reweighted variance minimization. For each initial optimization cycle, the default cutoff lengths for the u , χ , and f terms were used and the initial Jastrow parameters were set to zero. To see how uncertainties in the optimized Jastrow factors would carry over to the subsequent DMC calculations, two procedures with vastly different costs were tested. *Procedure 1* is designed to seek high precision during the optimization stage, thus incurring a high computational cost. *Procedure 2* explores what compromises in accuracy are suffered when a less rigorous and time consuming optimization is performed. In *Procedure 1*, the Jastrow parameters were optimized using 5.0×10^5 configurations for one initial cycle, followed by a system-dependent number of additional optimization cycles. For N₂, the number of additional cycles was 6 and, for CO, the number of additional cycles was 9. In *Procedure 2*, the Jastrow parameters were optimized using 1.0×10^5 configurations (five times fewer than procedure 1) for 10 cycles with the cost of the optimizations being roughly an order of magnitude fewer CPU-hours than *Procedure 1*. It is common in studies using multiconfigurational trial wavefunctions to also re-optimize the CI coefficients.²⁵ In this study, this was

tested for each system at a few points. Following Jastrow optimization using the VMC *variance minimization* procedure, additional cycles were performed to re-optimize both the Jastrow parameters and the CI coefficients, using the VMC *energy minimization* method. For these systems, further optimization using energy minimization did not yield significantly lower VMC energies and also resulted in larger variances and uncertainties. The energy minimization optimizations were less robust (particularly at stretched geometries), requiring additional sampling, thus making the procedure less straightforward and further increasing costs. We therefore elected to use the variance minimized Jastrow parameters and not re-optimize the CI coefficients. In both procedures, the subsequent DMC calculations were performed with target populations of 2500, a minimum of 1.5×10^5 sample points, and time steps of 0.002 a.u. for all geometries. For comparison with DMC, multireference configuration interaction (MRCI) calculations were also done using the MOLPRO⁶⁴ package.

1. CO: $C(^3P_g) + O(^3P_g) \rightarrow CO(X^1\Sigma^+)$

When the ground states of carbon and oxygen atoms combine, the number of molecular states of CO, resolved into C_{2v} symmetry, is⁶⁵

$$^{5,3,1}(3A_1 + 2B_1 + 2B_2 + 2A_2), \quad (6)$$

which represents a total of nine states of each of three spin-multiplicities (singlet, triplet, and quintet). Since there are nine singlet-states, dynamic weighting⁶⁶ was used to facilitate robust convergence near the asymptote for the full-valence (10e,8o), state-averaged multi-configurational self-consistent field (SA-MCSCF) calculations. As in the case of N₂, a high-spin (quintet) restricted-open Hartree-Fock (ROHF) calculation was performed before the subsequent singlet DW-SA-MCSCF calculations.

To control the cost of the QMC calculations, only a limited number of determinants were retained (specified by two contending criteria). First, a coefficient cutoff of 0.002 was used at each point, such that all determinants with an absolute weight coefficient value >0.002 were retained. This resulted in a varying number of retained determinants at each r_{CO} distance. Second, for comparison, a fixed number of 250 determinants (those with the largest coefficients) were retained throughout the coordinate range.

To assess the quality of the QMC results for CO in comparison to typical high-level conventional electronic structure methods, an accurate MRCI-based reference PEC by Dawes *et al.*⁶⁷ was used. It was constructed from Davidson-corrected MRCI data, based on a dynamically weighted state-averaged CASSCF reference (DW-SA-CASSCF), with a full-valence active space. The MRCI(Q) data were extrapolated to the complete basis set (CBS) limit with the aug-cc-pwCVnZ ($n = 3-5$) bases and all electrons correlated. The vibrational levels on the PEC are of spectroscopic accuracy. The MRCI-based PEC also includes small spin-orbit (SO) and scalar-relativistic (SR) corrections. The small SO and SR correction terms were removed from the MRCI-based PES for the

comparisons with DMC presented here. This permits a more direct comparison since the DMC Hamiltonian does not include those terms.

2. $N_2: N(^4S_u) + N(^4S_u) \rightarrow N_2(X^1\Sigma_g^+)$

When two ground state $N(^4S_u)$ nitrogen atoms combine, the total number of molecular states of N_2 , resolved into D_{2h} symmetry, is $7,5,3,1A_g$ (one state of each of four spin-multiplicities).⁶⁵

For the calculations in GAMESS, to ensure convergence to the ground state of N_2 , a high-spin (in this case septet) restricted-open Hartree-Fock (ROHF) calculation was performed at the largest N–N distance, followed by a 1-state MCSCF calculation for the desired singlet ground state with the full-valence (10e,8o) active space. In the QMC calculations, based on the results for CO discussed above, the strategy of retaining a variable number of determinants based on a coefficient threshold was abandoned, and a fixed (generous) number of 396 determinants were retained. The QMC data obtained along the coordinate range were assessed by comparison with an empirical spectroscopic PEC by Le Roy *et al.*⁶⁸

IV. RESULTS AND DISCUSSION

For CO, initially a coefficient weight cutoff of 0.002 was used to restrict the number of determinants retained in the trial wavefunctions, generally resulting in a different number of determinants employed at each CO bond distance. The DMC energy data and the number of determinants are given in Tables I and II for *Procedure 1* and *Procedure 2* (respectively), which differ by roughly an order of magnitude in the computational expense devoted to optimizing the Jastrow factor (the parameters are better converged by *Procedure 1*). The DMC energy data were overlaid with the reference PEC using weighted least-squares to account for the different uncertainties at each data point. The root mean-squared deviation (RMSD) of the DMC energy data with respect to the reference PEC is 315 cm^{-1} . As shown in Figure 1, the points obtained via both (Jastrow optimization) procedures follow the reference PEC quite well near the equilibrium geometry. At bond distances $>2.0\text{ \AA}$, where fewer determinants are retained, the DMC points tend to deviate

TABLE I. DMC energies for CO following *Procedure 1* (see text) for Jastrow factor optimization (data plotted in Figure 1).

Bond distance (Å)	Number of determinants	DMC (a.u.)	Uncertainty (\pm) (a.u.)
0.90	107	-113.095 117 4	0.000 413 133
1.00	133	-113.248 941 4	0.000 380 672
1.10	153	-113.295 985 9	0.000 415 229
1.30	229	-113.252 781 4	0.000 348 658
2.60	204	-112.900 792 8	0.000 193 650
3.00	113	-112.888 233 2	0.000 321 403
3.30	95	-112.884 669 0	0.000 296 271
3.50	87	-112.884 567 8	0.000 310 887

TABLE II. DMC energies for CO following *Procedure 2* (see text) for Jastrow factor optimization (data plotted in Figure 1).

Bond distance (Å)	Number of determinants	DMC (a.u.)	Uncertainty (\pm) (a.u.)
0.90	107	-113.094 438 0	0.000 389 325
0.95	127	-113.189 637 8	0.000 436 312
1.00	133	-113.249 445 7	0.000 436 334
1.10	153	-113.296 637 3	0.000 396 878
1.20	202	-113.288 083 3	0.000 415 661
1.30	229	-113.253 058 1	0.000 446 796
1.50	317	-113.161 942 5	0.000 352 915
2.10	276	-112.959 646 9	0.000 301 529
2.50	229	-112.907 849 8	0.000 321 865
3.00	113	-112.888 736 5	0.000 296 142
3.30	95	-112.885 660 1	0.000 307 478
3.50	87	-112.884 845 8	0.000 329 048

slightly from the reference PEC (to higher energies). To see if this behavior might be related to the reduced numbers of determinants, trial wave functions with a fixed number of determinants (250) were optimized via both procedures and then recalculated with DMC. The results are given in Tables III and IV and in Figure 2. The RMSD of the DMC energy data computed using a fixed number of determinants with respect to the reference PEC is 292 cm^{-1} . This is only slightly less than that of the variable determinants data. Note that corresponding to the number of DMC samples, the uncertainties at each data point are in the range of $40\text{--}90\text{ cm}^{-1}$ (see tables). It is not clear from these results that retaining a fixed number of determinants produces significantly more consistent results than the lower-cost coefficient weight cutoff strategy (which results in a variable number of retained determinants). Regarding the Jastrow optimization, since the results obtained by procedures 1 and 2 are of similar quality and are essentially interchangeable, it appears that the investment of considerably more CPU time in *Procedure 1* was not warranted.

To test whether sensible spectroscopic parameters could be obtained from the data, a fit to the Morse function was performed (it is straightforward to convert Morse parameters into anharmonic parameters).¹⁵ First, since the most accurate PEC will not be precisely Morse-like, parameters obtained by fitting the reference PEC were compared to the experimental CO parameters of $r_e = 1.128\text{ \AA}$, $\omega_e = 2170.2\text{ cm}^{-1}$, and $\omega_e x_e = 13.46\text{ cm}^{-1}$.⁶⁵ The Morse form could not accurately accommodate the entire coordinate range of the reference PEC and produced a fitted value for the harmonic constant that is significantly too high ($\omega_e = 2215.1\text{ cm}^{-1}$). Fitting data in a more limited range of $r_{CO} = [0.9, 1.6]\text{ \AA}$ produced more reasonable values of $r_e = 1.128\text{ \AA}$, $\omega_e = 2174.9\text{ cm}^{-1}$, and $\omega_e x_e = 13.05\text{ cm}^{-1}$. Fitting the DMC data over the same coordinate range yields parameters of $r_e = 1.129\text{ \AA}$, $\omega_e = 2187.0\text{ cm}^{-1}$, and $\omega_e x_e = 13.28\text{ cm}^{-1}$, all of which are quite useful estimates. Since the spectroscopically accurate reference PEC and the DMC data are globally consistent, it seems likely that further reducing the DMC uncertainties (through additional sampling) and a denser grid would yield even better constants.

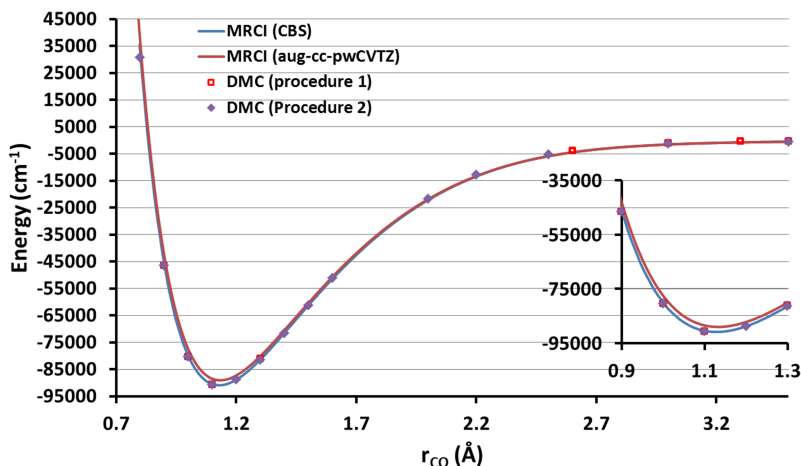


FIG. 1. DMC calculations for CO with variable numbers of determinants are compared with two MRCI reference curves (see text).

For N_2 , a fixed number of 396 determinants were employed for all geometries. The data for Jastrow optimizations via *Procedure 1* and *Procedure 2* are given in Tables V and VI, respectively, and are plotted in Figure 3. The data are compared with an empirical spectroscopic PEC by Le Roy *et al.*⁶⁸ The DMC data are generally consistent with the empirical PEC and are much closer to it than moderately high-level MRCI/AVTZ data shown for additional comparison. The RMSD of the DMC data with respect to the empirical PEC is 598 cm^{-1} , which is significantly larger than was found for CO discussed above. Since the empirical PEC for N_2 was obtained via direct fit to spectroscopic data, it implicitly includes small effects such as relativistic corrections not included in the DMC Hamiltonian (that were removed for this reason from the CO PEC for the previous comparison discussed above). However, this is not likely to be a significant source of discrepancy as these sorts of corrections are relatively small for N_2 . It is noteworthy that the DMC data point at $r_{\text{NN}} = 0.8 \text{ \AA}$ (listed in Tables V and VI) was excluded from the comparison as it is an outlier roughly 5000 cm^{-1} more stable than the value given by the reference PEC. The empirical PEC is expected to be unreliable for repulsive geometries far beyond the turning points of the contributing spectroscopic data. Indeed, the empirical PEC was confirmed to be much more repulsive at short range than a high quality *ab initio* PEC by Gdanitz which is consistent with the DMC value.⁶⁹ Again, as was found for CO, the additional cost of a stricter Jastrow optimization procedure did not yield obviously improved results.

As was done for CO, the reference and DMC-based PECs were each fit to a Morse function to extract spectroscopic

TABLE III. DMC energies for CO following *Procedure 1* for Jastrow optimization with a fixed number of determinants.

Bond distance (Å)	Number of determinants	DMC (a.u.)	Uncertainty (\pm) (a.u.)
1.10	250	-113.296 209 2	0.000 430 335
1.20	250	-113.287 484 7	0.000 453 569
1.60	250	-113.115 708 7	0.000 396 781
2.20	250	-112.941 968 1	0.000 350 373
3.50	250	-112.884 136 9	0.000 288 665

parameters. The experimental values used for comparison are $r_e = 1.094 \text{ \AA}$, $\omega_e = 2359.6 \text{ cm}^{-1}$, and $\omega_e x_e = 14.46 \text{ cm}^{-1}$.⁶⁵ Fitting the reference PEC over the range $r_{\text{NN}} = [0.9, 1.3] \text{ \AA}$ produced values of $r_e = 1.098 \text{ \AA}$, $\omega_e = 2360.6 \text{ cm}^{-1}$, and $\omega_e x_e = 14.70 \text{ cm}^{-1}$. Fitting the DMC data over the same coordinate range yields parameters of $r_e = 1.097 \text{ \AA}$, $\omega_e = 2373.4 \text{ cm}^{-1}$, and $\omega_e x_e = 14.45 \text{ cm}^{-1}$, all of which are again quite accurate.

The cost of generating high quality energies via DMC for the two 14-electron systems (CO and N_2) was assessed. A significant fraction of the total cost relates to the optimization of a Jastrow factor that was employed in this study. As mentioned previously, some advantages and disadvantages of using a Jastrow have been noted by Giner *et al.*⁴⁰ The initial Jastrow optimizations for N_2 with a fixed number of determinants using cheaper *Procedure 2* took ~ 800 -1300 CPU-h per point. With CO, for Jastrow optimizations via *Procedure 2* with a varying number of determinants (using a coefficient cutoff strategy), the CPU-hours depend significantly on the number of retained determinants. The lowest cost was the bond distance of 3.5 \AA , which includes 87 determinants and took about 300 CPU-h. The highest cost was 1.5 \AA , which includes 317

TABLE IV. DMC energies for CO following *Procedure 2* for Jastrow optimization with a fixed number of determinants.

Bond distance (Å)	Number of determinants	DMC (a.u.)	Uncertainty (\pm) (a.u.)
0.80	250	-112.742 692 4	0.000 170 137
0.90	250	-113.094 621 5	0.000 182 671
1.00	250	-113.248 980 0	0.000 158 881
1.10	250	-113.296 145 5	0.000 167 728
1.20	250	-113.287 490 1	0.000 149 456
1.30	250	-113.253 788 0	0.000 168 859
1.40	250	-113.209 066 1	0.000 158 616
1.50	250	-113.162 305 9	0.000 164 298
1.60	250	-113.116 031 3	0.000 144 766
2.00	250	-112.981 497 0	0.000 139 589
2.20	250	-112.941 313 8	0.000 137 728
2.50	250	-112.907 113 6	0.000 138 389
3.00	250	-112.888 779 5	0.000 121 424
3.50	250	-112.885 223 1	0.000 126 156

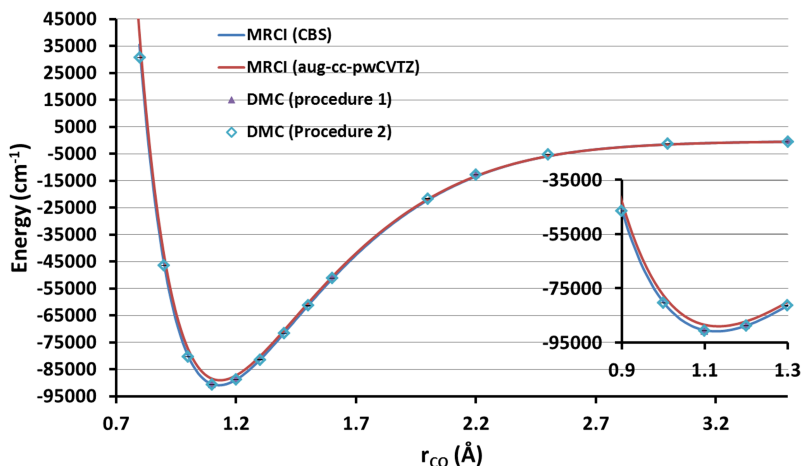


FIG. 2. DMC calculations for CO with a fixed number (250) of determinants are compared with two MRCI reference curves (see text).

determinants and took about 1860 CPU-h. For *Procedure 1*, the cost for CO increased to ~ 5000 - $15\,000$ CPU-h per point, and the cost for N_2 increased to $\sim 18\,000$ - $25\,000$ CPU-h per point.

Once the Jastrow has been optimized by VMC via either *Procedure 1* or *Procedure 2*, the subsequent DMC energy calculations add a significant additional cost which depends on the number of DMC samples which in turn determines the final uncertainties (related as $1/\sqrt{M}$, where M is the number of samples). For N_2 , to reach uncertainties on the order of 100 cm^{-1} (see Tables V and VI), the DMC cost was ~ 1800 - 2200 CPU-h per point. Specifically, after Jastrow optimization via *Procedure 1*, the cost of the DMC sampling for the N_2 points located at $r_{NN} = 0.8\text{ \AA}$, 1.1 \AA , and 2.5 \AA took 2170 CPU-h, 1850 CPU-h, and 2010 CPU-h, respectively, to reach an average uncertainty in the three points of $\sim 86\text{ cm}^{-1}$. Similarly, after *Procedure 2* optimization, the DMC cost for the same points was about 1880 CPU-h, 2035 CPU-h, and 2030 CPU-h, respectively, for an average uncertainty of $\sim 93\text{ cm}^{-1}$.

For CO, the DMC sampling cost after Jastrow optimization was ~ 775 - 1900 CPU-h per point to reach similar uncertainties. The cost of the DMC calculations for CO and N_2 (both 14-electron systems) was approximately the same, but the Jastrow optimizations via *Procedure 1* took about an order of magnitude longer than those of *Procedure 2*. The quality of the final energies is similar for the two procedures, indicating that a more conservative Jastrow optimization is reasonable since it appears that diminishing returns are realized

TABLE V. DMC energies for N_2 following *Procedure 1* (see text) for Jastrow factor optimization (data plotted in Figure 3).

Bond distance (Å)	Number of determinants	DMC energy (a.u.)	Uncertainty (\pm) (a.u.)
0.80	396	-109.016 719 2	0.000 434 940
1.10	396	-109.515 594 9	0.000 434 508
1.20	396	-109.494 409 1	0.000 447 115
1.60	396	-109.293 648 4	0.000 367 967
1.80	396	-109.222 031 5	0.000 335 620
2.00	396	-109.181 161 3	0.000 554 249
2.50	396	-109.154 345 7	0.000 308 338

with respect to further optimization. Trial wave functions for CO with 250 (fixed) determinants were also optimized using *Procedure 2* with a cost of ~ 1000 - 1500 CPU-h per point. To achieve an average uncertainty $\sim 33\text{ cm}^{-1}$ in the DMC, an additional cost of ~ 7000 - $10\,000$ CPU-h per point was required.

The QMCPACK code was used to test the improved efficiency that is expected by the use of the *table method* algorithm for multideterminant calculations.^{46,47} For these comparisons, the same numbers of determinants were retained and the same Jastrow factors were employed. The QMCPACK code was found to reach similar uncertainties for our two test systems in about 30% fewer CPU-hours. For much larger numbers of determinants (up to 16 000), Clark *et al.* reported much more significant speedups in the range of factors of 15-40.⁴⁷ They noted smaller speedup factors for smaller numbers of determinants. The speedup that one might expect from the QMCPACK algorithm will depend on the size of the system and the number of determinants as well as hardware limitations such as memory and cache.⁷⁰ In our study of two small systems with only 14 electrons and modest numbers of determinants, the speedup is already significant indicating that this method should be preferred in future larger scale multideterminant applications.

TABLE VI. DMC energies for N_2 following *Procedure 2* (see text) for Jastrow factor optimization (data plotted in Figure 3).

Bond distance (Å)	Number of determinants	DMC (a.u.)	Uncertainty (\pm) (a.u.)
0.80	396	-109.016 277 8	0.000 501 235
0.90	396	-109.344 800 2	0.000 453 625
0.95	396	-109.432 559 5	0.000 506 966
1.10	396	-109.515 532 7	0.000 455 739
1.20	396	-109.493 794 5	0.000 427 817
1.30	396	-109.447 839 0	0.000 430 446
1.40	396	-109.393 779 5	0.000 361 739
1.50	396	-109.340 537 4	0.000 365 678
1.60	396	-109.293 422 1	0.000 408 069
2.00	396	-109.180 624 2	0.000 341 908
2.20	396	-109.163 490 8	0.000 323 882
2.50	396	-109.154 808 3	0.000 323 347

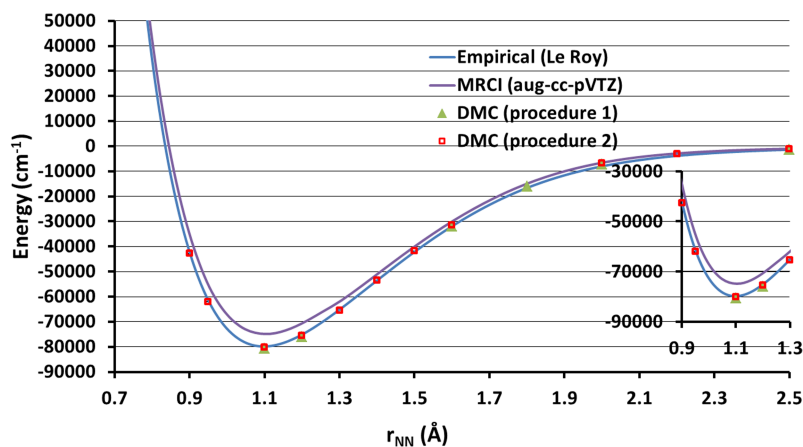


FIG. 3. DMC calculations for N_2 compared with an MRCI curve and an empirical curve from the work of Le Roy *et al.*⁶⁸

V. CONCLUSION

It was determined that straightforward application of QMC methods implemented in two freely available codes (CASINO and QMCPACK) could robustly compute electronic energies along dissociation coordinates of small molecules that are comparable in accuracy to high level traditional quantum chemistry. A QMC tutorial aimed at graduate students who have some familiarity with traditional quantum chemistry, but no experience with QMC, is provided as [supplementary material](#).

Points along the potential energy curves of the ground states of CO and N_2 were generated with multideterminant fixed-node diffusion Monte Carlo methods and were found to be in close agreement with spectroscopically accurate curves. The spectroscopic constants obtained by fitting the data are in close agreement with the experiment. In particular, the equilibrium bond distance parameters obtained by fitting to only a few points are within 1-3 pm of experiment.

For the two 14-electron test systems, generating comparably high-quality electronic structure data by conventional methods such as MRCI takes less than 0.5 CPU-h per point, compared with at least 4000 CPU-h for the employed DMC method, as implemented in CASINO, depending on the desired final uncertainty. The QMCPACK code is known to be more efficient for multideterminant trial wavefunctions. For the small test systems and modest numbers of determinants employed in this study, the QMCPACK code was only slightly faster ($\sim 30\%$), but is indicated for larger scale applications where more significant speedups have been reported.⁴⁷ The favorable n^3 scaling of DMC does ensure a crossover point in system size beyond which it becomes cheaper than conventional high-accuracy electronic structure methods (scaling as n^7 or worse). The large cost pre-factor of DMC seems to preclude it from the routine use in the construction of global PESs (which for 3-5 atom systems typically require thousands of points) at this time. However, in addition to the favorable scaling with system size, QMC methods scale nearly linearly with the number of cores, which could lead to short time-to-solution using next generation architectures with millions of cores.

Even now, given the high accuracy that is achievable via QMC methods, we also see it as a possible arbiter in difficult cases where high-level conventional methods might disagree

about the presence or height of a rate determining reaction barrier.^{71,72}

It is anticipated that QMC methods will become increasingly relevant in the near future.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for a guide illustrating the use of CASINO to perform VMC and DMC calculations with trial wavefunctions generated in GAMESS. The guide is intended to be accessible to readers with some experience in traditional quantum chemistry.

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