Bond breaking with auxiliary-field quantum Monte Carlo

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Bond stretching mimics different levels of electron correlation and provides a challenging test bed for approximate many-body computational methods. Using the recently developed phaseless auxiliary-field quantum Monte Carlo (AF QMC) method, we examine bond stretching in the well-studied molecules BH and N_2 and in the H_{50} chain. To control the sign/phase problem, the phaseless AF QMC method constrains the paths in the auxiliary-field path integrals with an approximate phase condition that depends on a trial wave function. With single Slater determinants from unrestricted Hartree-Fock as trial wave function, the phaseless AF QMC method generally gives better overall accuracy and a more uniform behavior than the coupled cluster CCSD(T) method in mapping the potential-energy curve. In both BH and N_2 , we also study the use of multiple-determinant trial wave functions from multiconfiguration self-consistent-field calculations. The increase in computational cost versus the gain in statistical and systematic accuracy are examined. With such trial wave functions, excellent results are obtained across the entire region between equilibrium and the dissociation limit. © 2007 American Institute of Physics. [DOI: 10.1063/1.2770707]

I. INTRODUCTION

Quantum Monte Carlo (QMC) methods are an attractive means to explicitly treat the interacting many fermion system. Their computational cost scales favorably with system size, as a low power. The ground state wave function is obtained stochastically by Monte Carlo (MC) sampling, either in particle coordinate space^{1,2} or in Slater determinant space.^{3,4} Except for a few special cases, however, these methods suffer from the fermion sign problem,^{5,6} which, if uncontrolled, causes an exponential loss of the MC signal and negates the favorable computational scaling. No formal solution has been found for this problem, but approximate methods that control it have been developed. These include the fixed-node method⁷ in real coordinate space and constrained path methods^{3,4,6} in Slater determinant space. The real-space fixed-node diffusion Monte Carlo (DMC) method has long been applied to many of solids and molecules.¹ Recently, the phaseless auxiliary-field (AF) method was introduced providing a framework for ab initio electronic structure calculations by QMC in Slater determinant space, within a Hilbert space defined by any single-particle basis.³

The phaseless AF QMC method controls the phase problem in an approximate way by using an input trial wave function (WF).³ This is a generalization of the constrained path approach⁴ which has been applied to lattice models with Hubbard-type interactions. Compared with previous efforts^{8,9} on realistic electronic systems using the standard auxiliaryfield formalism,^{10,11} the phaseless AF QMC method overcomes the poor (exponential) scaling with system size and projection time and has statistical errors that are well behaved. Compared to fixed-node DMC, this approach provides a different route to control the sign problem. The behavior of the many-body nodes is different,⁴ and the method has shown promise in reducing the dependence of the systematic error on the trial wave function.

The systematic error from the phaseless approximation has been found to be small near equilibrium geometries in a variety of systems. The method was applied using a plane wave basis with pseudopotentials to several sp-bonded atoms, molecules, and solids 3,12,13 and to the transition metal molecules TiO and MnO.¹⁴ It has also been applied, with Gaussian basis sets, to first- and second-row atoms and molecules,¹⁵ to post-*d* elements (Ga–Br and In–I),¹⁶ and to hydrogen bonded systems.¹⁷ The calculated all-electron total energies of first-row atoms and molecules at equilibrium geometries show typical systematic errors of no more than a few millihartrees compared to exact results. This accuracy is roughly comparable to that of CCSD(T), coupled cluster with single- and double-excited clusters plus a noniterative correction to the energy due to triple excited clusters. In post-d systems, our results with several basis sets are in good agreement with CCSD(T) results and, for large basis sets, in excellent agreement with experiment.¹⁶ In almost all of these calculations, we have used independent-electron solutions from Hartree-Fock or density functional theory as trial WF.

Bond stretching provides a difficult test for approximate correlated methods. In the dissociation limit, the unrestricted Hartree-Fock (UHF) solution gives a qualitatively correct description of the system. The intermediate region between the equilibrium and dissociated geometries represents a situation analogous to a metal-insulator transition. Due to quasidegeneracies, there can be more than one important electronic configuration, and a single determinant often cannot adequately describe the system. Multiconfigurational approaches can de-

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scribe to a large degree the static correlations in the system but often miss a large proportion of the dynamic correlations.

No general method has demonstrated the ability to consistently maintain uniformly high accuracy away from equilibrium. Coupled cluster (CC) methods,^{18,19} such as CCSD(T), are remarkably good in describing the equilibrium properties but are less successful in describing systems with quasidegeneracies such as the case in the breaking of chemical bonds.²⁰⁻²³ Higher order clusters have to be fully included in the iterative approach, because the perturbative corrections are based on nondegenerate perturbation theories and usually lead to divergences for stretched nuclear geometries. Since CCSD already scales as N^6 with basis size, going to triple and higher order clusters is computationally expensive. Multireference CC methods could potentially solve some of these problems, but unlike the single reference CC method, these are still not widely established.²⁴ CC-based approaches have been introduced recently to handle bond stretching, and this remains an active field of research; see, for example, Refs. 25-27.

In this paper, we test the phaseless AF QMC method away from Born-Oppenheimer equilibrium configurations. There have been few QMC studies of bond breaking.²⁸ We investigate bond stretching in two well-studied molecules, BH and N₂, and in a hydrogen chain, H₅₀, where exact or very accurate results from full-configuration interaction (FCI) or density-matrix renormalization group^{29–31} (DMRG) methods are available. We first use single Slater determinant trial WFs, obtained by the UHF method. It is shown that AF QMC with UHF as trial WF generally gives better overall accuracy and a more uniform behavior than CCSD(T). The use of multiple-determinant trial WFs from multiconfiguration self-consistent-field (MCSCF) calculations is then examined in the diatomic molecules. With these trial WFs, excellent AF QMC results are achieved across the entire potential-energy surface.

The rest of the paper is organized as follows. The phaseless AF QMC method is first briefly reviewed in the next section. In Sec. III, we present and discuss the potentialenergy curves of the various systems. Finally, in Sec. IV, we conclude with a brief summary.

II. THE PHASELESS AF QMC METHOD

The many-body Born-Oppenheimer Hamiltonian in electronic systems can be written in second quantization, in any single-particle basis, as

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{i,j}^{N} T_{ij} c_i^{\dagger} c_j + \frac{1}{2} \sum_{i,j,k,l}^{N} V_{ijkl} c_i^{\dagger} c_j^{\dagger} c_k c_l,$$
(1)

where N is the size of the chosen one-particle basis and c_i^{\dagger} and c_i are the corresponding creation and annihilation operators. The one-electron, T_{ij} , and two-electron, V_{ijkl} , matrix elements depend on the chosen basis.

The phaseless AF QMC obtains the ground state of the system by projecting from a trial WF $|\Psi_T\rangle$ which has a non-zero overlap with the exact ground state of the system,

$$\Psi_{\rm GS} \rangle = \lim_{M \to \infty} (e^{-\tau \hat{H}})^M |\Psi_T\rangle, \tag{2}$$

where τ is a small time step and $|\Psi_T\rangle$ is assumed to be in the form of a Slater determinant or a linear combination of Slater determinants. Using a second order Trotter decomposition, we can write $e^{-\tau \hat{H}} \doteq e^{-\tau \hat{H}_1/2} e^{-\tau \hat{H}_2} e^{-\tau \hat{H}_1/2}$. The resulting Trotter time-step error decreases with τ and can be eliminated by an extrapolation to $\tau=0$ with multiple calculations.

The central idea in the AF QMC method is the use of the Hubbard-Stratonovich transformation,³²

$$e^{-\tau \hat{H}_2} = \prod_{\alpha} \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\sigma_{\alpha} e^{-(1/2)\sigma_{\alpha}^2} e^{\sqrt{\tau}\sigma_{\alpha}\sqrt{\zeta_{\alpha}}\hat{v}_{\alpha}} \right).$$
(3)

Equation (3) introduces *one-body operators* \hat{v}_{α} which can be defined generally for any two-body operator by writing the latter in a quadratic form, such as $\hat{H}_2 = -\frac{1}{2} \sum_{\alpha} \zeta_{\alpha} \hat{v}_{\alpha}^2$, with ζ_{α} a real number. The many-body problem as defined by \hat{H}_2 is now mapped onto a linear combination of noninteracting problems defined by \hat{v}_{α} , interacting with external auxiliary fields. Averaging over different auxiliary-field configurations is then performed by MC techniques. Formally, this leads to a representation of $|\Psi_{\text{GS}}\rangle$ as a linear combination of an ensemble of Slater determinants $\{|\phi\rangle\}$. The orbitals of each $|\phi\rangle$ are written in terms of the chosen one-particle basis and stochastically evolve in imaginary time.

Generally, the AF QMC method suffers from the sign or phase problem.^{4,6} The phaseless AF QMC method³ used in this paper controls the phase/sign problem in an approximate manner using a trial WF $|\Psi_T\rangle$. The method recasts the imaginary-time path integral as a branching random walk in Slater determinant space.^{3,4} It uses the overlap $\langle \Psi_T | \phi \rangle$ to construct phaseless random walkers $|\phi\rangle/\langle\Psi_T|\phi\rangle$ which are invariant under a phase gauge transformation. The resulting two-dimensional diffusion process in the complex plane of the overlap $\langle \Psi_T | \phi \rangle$ is then approximated as a diffusion process in one dimension. The ground-state energy computed with the so-called mixed estimate is approximate and not variational in the phaseless method. The error depends on the quality of $|\Psi_T\rangle$, and the method becomes exact as the trial WF approaches the exact ground state of the system. This is the only error in the method that cannot be eliminated systematically.

In most applications to date,^{3,12–17} the trial WF has been a single Slater determinant taken directly from mean-field calculations. Jastrow factors, which have a key role in the trial WF in DMC calculations,¹ are not included. (A Jastrow factor in $|\Psi_T\rangle$ is not straightforward to include⁹ in the AF framework, since it makes the computation of the overlap $\langle \Psi_T | \phi \rangle$ more complicated.) This is possible because our random walkers are full Slater determinants, not real-space particle coordinates. Also, by use of a basis, the singularity (cusp) as two electrons approach each other or an electron approaches a nucleus is integrated out, as in standard quantum chemistry methods. We have found^{15,16} that using the UHF solution leads to better QMC energies than using the restricted Hartree-Fock (RHF) Slater determinant. This was the case even with singlets.

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TABLE I. All-electron total energies of BH vs bond length as calculated by a variety of methods, using a cc-pVDZ basis set. The exact results are given by FCI. AF QMC energies obtained with both the UHF and MCSCF (see text) trial wave functions are shown. All energies are in hartree and statistical errors in QMC (shown in parentheses) are on the last digit. An equilibrium bond length of R_e =1.2344 Å is used.

R/R_e	1	1.5	2	2.5	3	4	5
RHF	-25.125 336	-25.063 683	-24.992 753	-24.940 236	-24.902 882	-24.859 110	-24.840 065
UHF	-25.131 559	-25.065 817	-25.034 695	-25.030 226	-25.029 455	-25.029 262	-25.029 241
MCSCF	-25.199 413	-25.150 182	-25.105 151	-25.086 687	-25.081 836	-25.080 626	-25.080 571
RCCSD	-25.214 360	-25.163 701	-25.112 404	-25.088 577	-25.080 907	-25.078 318	-25.078 097
RCCSD(T)	-25.215 767	-25.165 880	-25.117 034	-25.099 308	-25.100 152	-25.107 421	-25.109 133
UCCSD	-25.214 360	-25.163 498	-25.110 239	-25.091 729	-25.089 185	-25.088 720	-25.088 710
UCCSD(T)	-25.215 767	-25.165 784	-25.114 131	-25.093 105	-25.090 055	-25.089 555	-25.089 545
QMC/UHF	-25.2149(3)	-25.164 0(2)	-25.114 0(1)	-25.093 9(3)	-25.0887(1)	-25.0869(4)	-25.087 1(2)
QMC/MCSCF	-25.215 89(6)	-25.166 51(7)	-25.117 78(8)	-25.097 97(6)	-25.09274(9)	-25.091 58(6)	-25.091 3(2)
FCI	-25.216 249	-25.166 561	-25.117 705	-25.097 084	-25.091 467	-25.089 986	-25.089 912

In this study, we will present, in addition to the singledeterminant trial WF, results based on multideterminant trial WFs obtained from MCSCF calculations. In some cases, such as bond stretching, a multideterminant trial WF can capture some of the static correlation in the system and thus improve the quality of the constraint in the phaseless approximation. A better trial WF will generally reduce the systematic errors of the phaseless AF QMC method.

In addition, a better trial WF will typically also lead to better statistics in the AF QMC method, for a fixed number of independent MC samples. A simple measure of the efficiency of the multideterminant MCSCF trial WF relative to a single-determinant UHF trial WF is the following ratio, η :

$$\eta = \frac{(N_{\text{sample}}\epsilon^2)_{\text{MCSCF}}}{(N_{\text{sample}}\epsilon^2)_{\text{UHF}}},\tag{4}$$

where ϵ is the final statistical error and N_{sample} is the total number of MC samples used in the calculation. (A more precise but closely related measure is the ratio of the variances of the local energy. For its purpose here as a rough indicator, however, the difference between them is not significant.) We expect $\eta < 1$ for a reasonable number of determinants in the MCSCF; in general, the better $|\Psi_T\rangle$, the smaller η . Since the computational cost of the phaseless AF QMC method increases linearly with the number of determinants in $|\Psi_T\rangle$, the overall computational cost of the QMC calculation with respect to the single-determinant trial WF is η times the number of determinants in $|\Psi_T\rangle$.

III. RESULTS AND DISCUSSION

To examine the performance of the phaseless AF QMC method in bond stretching, the potential-energy curves of the diatomic molecules BH and N₂ are first studied and compared to exact FCI, near-exact DMRG, and several levels of CC methods. In addition, the symmetric and asymmetric bond stretching of an H₅₀ linear chain is examined and compared to DMRG results. For the diatomic molecules, both single-determinant UHF (QMC/UHF) and multideterminant MCSCF (QMC/MCSCF) trial WFs were used. AF QMC calculations for the H₅₀ chain used single-determinant Hartree-Fock trial wave functions.

In our calculations, all the electrons are correlated and the spherical harmonic (as opposed to Cartesian) form of the Gaussian basis functions was used. For the molecules, ccpVDZ basis sets were used, except in the challenging case of the (triple) bond stretching of N₂, where calculations were also performed with the cc-pVTZ basis set.³³ For the H₅₀ chain, the minimal STO-6G basis set was used.

All of the Hartree-Fock, MCSCF, and CC calculations were carried out using NWCHEM (Ref. 34) within C_{2v} symmetry. Some of these calculations were also verified using GAUSSIAN 98 (Ref. 35) and MOLPRO.³⁶ The MCSCF energies were obtained from a complete-active-space SCF (CASSCF) (Ref. 37) calculations. In most of the molecules, we used the RHF and UHF reference states for the CC calculations [e.g., labeled RCCSD(T) and UCCSD(T), respectively]. FCI calculations were performed using MOLPRO.^{36,38}

A. BH

Table I summarizes the cc-pVDZ basis set energies (in hartrees) obtained with a variety of methods for seven BH geometries over a range $R/R_e=1-5$, where $R_e=1.2344$ Å. The MCSCF energy was obtained by a CASSCF calculation, performed with four active electrons and eight active orbitals. Figure 1 shows the potential-energy curves from selected methods.

Near the equilibrium geometry, the RCCSD(T) energies are in good agreement with the FCI energy. However, this agreement deteriorates for larger nuclear separation, and RCCSD(T) shows an unphysical dip for $R \ge 2.5R_e$ which increases for larger bond length R. The failure of RCCSD(T) to describe the molecule for larger bond lengths is attributed to the poor quality of the RHF WF in describing bond breaking. In the large bond length limit, the UHF solution is better than the RHF solution. This is reflected also in CC results based on the UHF solution; the UCCSD(T) energies are in very good agreement with the FCI energy for large R. The UCCSD(T) energies are in less good agreement with FCI in the intermediate region. Overall, UCCSD(T) does quite well in BH, which has a relatively small number of excitations.

As shown in Table I, QMC/UHF energies are comparable to RCCSD(T) and in good agreement with FCI near the equilibrium geometry. As the bond is stretched, QMC/UHF



FIG. 1. (Color online) Potential-energy curves of the BH molecule from FCI, coupled cluster, and QMC methods, using the cc-pVDZ basis. The QMC/UHF and QMC/MCSCF curves are obtained, respectively, with single-determinant UHF and multideterminant truncated MCSCF trial wave functions. The inset shows the deviations (in mhartree) of the various methods from the FCI results.

energies become less accurate. The discrepancy with FCI energies is ≈ 3 mhartrees for $R > 2R_e$. In the QMC/MCSCF calculations, the multideterminant trial WF included determinants from MCSCF with a coefficient cutoff of 0.01. Thus the variational energy of our MCSCF WF is higher than the corresponding MCSCF result listed in the tables. The average value of η , as defined in Eq. (4), is 0.04, and the largest value is 0.08, at the largest bond length. The QMC/MCSCF energies are in excellent agreement with the FCI energies, to within ≈ 1 mhartree for all studied bond lengths.

The optimum value of determinant coefficient cutoff in the MCSCF trial WF is, of course, system dependent. The accuracy of the QMC calculation generally improves as the cutoff is lowered, while the computational cost increases. For a small system such as BH, a relatively low cutoff leads to excellent trial WFs with large efficiency gain, as the η values show. Figure 2 shows the QMC errors as a function of the number of determinants included in the trial WF for three geometries of BH. For $2R_e$, the QMC results with MCSCF trial WFs containing determinants with coefficient cutoffs of 0.02 (29 determinants) and of 0.01 (52 determinants) are equivalent within statistical errors. Similarly, for $2.5R_e$, the QMC results obtained with trial WFs of 24 and 44 determinants are indistinguishable within the statistical errors. Indeed, in both of these cases, eight determinants in the trial WF give systematic errors less than 2 mhartrees. By contrast, for $5R_e$, considerably more determinants are required to achieve converged QMC systematic errors. Note that, because the MCSCF WF is in a spin restricted form, more than one determinant (many more in the case of $5R_e$) is required to surpass the accuracy of QMC/UHF.

B. N₂

Bond stretching in N_2 is particularly challenging, because it involves the breaking of a triple bond. As a result, N_2 has been extensively studied.^{22,23,39–41} Table II summarizes the calculated total energies, using cc-pVDZ and cc-pVTZ basis sets. Figure 3 plots a selected subset of these potentialenergy curves. With the cc-pVDZ basis set, CC results are based on the UHF reference state, and the near-exact DMRG energies are from Ref. 39. We have also verified the UCCSD and UCCSD(T) energies. For both basis sets, the CASSCF calculations are performed with 6 active electrons and 12 active orbitals.

The main features of the CC potential-energy curves of N_2 are similar to those of BH. In contrast with the BH molecule, however, the effects beyond double excitations are substantial in N_2 , even at the equilibrium geometry. CC results based on a RHF reference show an unphysical dip for



FIG. 2. (Color online) Phaseless AF QMC systematic errors vs the number of determinants included in the trial WF from MCSCF. The discrepancy between QMC and FCI energies in BH/cc-pVDZ is shown for geometries of $2R_e$, $2.5R_e$, and $5R_e$ (in mhartree). The corresponding errors from the single-determinant UHF trial WF are also shown, as symbols on the left.

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TABLE II. All-electron energies of N_2 vs bond length (in bohr) as calculated by a variety of methods, using cc-pVDZ and cc-pVTZ basis sets. With the cc-pVDZ basis, DMRG energies and CC results based on a UHF reference are taken from Ref. 39. QMC/UHF energies are obtained with the UHF trial WF, and QMC/MCSCF are obtained with a multideterminant trial WF from a MCSCF calculation (see text). All energies are in hartree, and QMC statistical errors (shown in parentheses) are on the last digit.

R	2.118	2.4	2.7	3.0	3.6	4.2
cc-pVDZ						
RHF	-108.949 378	-108.866 811	-108.737 400	-108.606 226	-108.384 757	-108.222 897
UHF	-108.949 378	-108.891 623	-108.833 687	-108.790 272	-108.767 549	-108.775 057
MCSCF	-109.116 455	-109.074 562	-108.989 741	-108.916 484	-108.829 340	-108.804 720
RCCSD	-109.267 626	-109.220 331	-109.131 665	-109.044 031	-108.925 318	-108.927 983
RCCSD(T)	-109.280 305	-109.238 814	-109.158 401	-109.081 661	-109.003 754	-109.133 852
RCCSDT	-109.280 323	-109.238 264	-109.156 751	-109.079 080	-109.014088	-109.083 378
UCCSD	-109.267 626	-109.219 794	-109.131 491	-109.052 879	-108.975 885	-108.960 244
UCCSD(T)	-109.280 305	-109.235 575	-109.150 645	-109.068 864	-108.982 836	-108.962 985
UCCSDT	-109.280 323	-109.238 03	-109.156 703	-109.079 437	-108.990 518	-108.966 852
QMC/UHF	-109.282 2(4)	-109.242 0(6)	-109.163 2(3)	-109.092 5(3)	-109.007 2(2)	-108.975 4(5)
QMC/MCSCF	-109.282 3(4)	-109.241 8(7)	-109.161 9(9)	-109.088 4(7)	-108.9964(6)	-108.967 3(5)
DMRG	-109.282 157	-109.241 886	-109.163 572	-109.089 375	-108.998 052	-108.970 09
cc-pVTZ						
RHF	-108.977 514	-108.891 508	-108.762 233	-108.631 934	-108.411 469	-108.250 458
UHF	-108.977 514	-108.916 523	-108.857 825	-108.813 255	-108.787 344	-108.793 604
MCSCF	-109.151 345	-109.099 960	-109.015 398	-108.939 652	-108.851 892	-108.825 313
RCCSD	-109.379 102	-109.322 25	-109.228 642	-109.137 174	-109.003 895	-108.970 265
RCCSD(T)	-109.398 869	-109.348 885	-109.264 650	-109.184 927	-109.089 492	-109.164 999
RCCSDT	-109.398 507	-109.347 742	-109.262 165	-109.181 288	-109.101 356	-109.163 254
UCCSD	-109.379 102	-109.321 028	-109.227 910	-109.147 555	-109.066 293	-109.047 706
UCCSD(T)	-109.398 869	-109.345 265	-109.255 538	-109.170 421	-109.078 448	-109.054 423
UCCSDT	-109.398 507	-109.347 636	-109.262 449	-109.182 439	-109.086 9	-109.058 5
QMC/UHF	-109.401 6(7)	-109.352 2(8)	-109.270 6(5)	-109.197 5(6)	-109.108 6(6)	-109.076 0(4)
QMC/MCSCF	-109.402 4(7)	-109.353 4(7)	-109.2707(9)	-109.192 8(9)	-109.096 0(8)	-109.0629(7)

 $R \ge 3.6$ bohrs $(R/R_e \ge 1.75$ in Fig. 3). For the cc-pVDZ basis at the larger R=3.6 and 4.2 bohr bond lengths, UCCSD(T) based on the UHF reference is in better agreement with DMRG than RCCSD(T). Fully including triple excitations with UCCSDT leads to a significant improvement over UCCSD(T) for all geometries except R_e , while RCCSDT seems to be slightly worse than RCCSD(T), except at the last geometry.

QMC with an UHF trial wave function gives a better overall accuracy and a more uniform behavior than CCSD(T) in mapping the potential-energy curve in the ccpVDZ basis. The largest difference of the QMC/UHF energies compared to DMRG is at the second to last nuclear separation and is approximately 9 mhartrees. With QMC/ MCSCF, we included in the multideterminant trial WF all determinants whose coefficient (abs) are larger than 0.01. This gives 65, 66, 76, 97, 82, and 58 determinants for the six bond lengths (in ascending order), respectively. As can be seen from Table II and the inset of Fig. 3, the agreement between the QMC/MCSCF and DMRG values is more uniform and the discrepancy is less than 2–3 mhartrees for all geometries.

In the QMC/MCSCF calculations for the cc-pVDZ basis set, the average value of η of Eq. (4) is 0.42, and the largest value is 0.80 at the equilibrium geometry. The coefficient cutoff choice of 0.01 in selecting the determinants to include from the MCSCF WF was the same as in the BH calculations. This was likely too conservative as in BH. For ex-

ample, for R=2.118 bohrs, the QMC results were within statistical errors for a trial WF that included determinants with coefficient cutoffs >0.035.

The cc-pVTZ results from the various methods parallel very well the cc-pVDZ results, as can be seen from Fig. 3 and Table II. Both the QMC/UHF and QMC/MCSCF, for example, mirror each other in the two basis sets. We thus expect the accuracy of the different QMC and CC methods using the cc-pVTZ basis to be comparable to that using the cc-pVDZ basis, where DMRG results are available. For the cc-pVTZ basis set, the QMC/MCSCF calculations included determinants with coefficient cutoffs >0.02. The average value of η is 0.16 and the largest value is 0.41 for R =2.7 bohrs. Additional QMC/MCSCF calculations were performed for R=4.2, 3.6, and 2.7 bohrs, including determinants with coefficient cutoffs >0.01, and the same energies were obtained as those in Table II within statistical errors.

C. Hydrogen chain: H₅₀

The hydrogen linear chain exhibits characteristic signatures of a metal-insulator transition as the interatomic distances are varied. It also provides a simple but challenging model for extended systems, where the favorable scaling of QMC will be especially valuable. Bond stretching in a linear chain of hydrogen atoms H_{50} was recently benchmarked with DMRG.⁴² This 50-electron system was treated using a minimal STO-6G basis set of 50 orbitals. Both symmetric and



FIG. 3. (Color online) Potential-energy curves of N_2 , using cc-pVDZ and cc-pVTZ basis sets. QMC/UHF energies are obtained with a UHF trial WF, and QMC/MCSCF with a truncated multideterminant trial WF taken from a MCSCF calculation. CC results at several levels are shown for both RHF and UHF reference states. For the cc-pVDZ basis set, DMRG results from Ref. 39 are also shown, and the inset shows the deviations (in mhartree) of the various methods from the DMRG potential-energy curve.



asymmetric bond stretchings were considered. In the case of symmetric bond stretching, the bond between consecutive hydrogen atoms is stretched over the range R=1.0-4.2 bohrs, and the final structure consists of 50 equidistant, nearly independent H atoms. In the case of asymmetric bond stretching, 25 equivalent H₂ molecules are considered, each with a fixed bondlength of 1.4 bohrs, where two consecutive hydrogen atoms belonging to two different H₂ molecules are separated over a range of R=1.4-4.2 bohrs, and the final structure consists of 25 equidistant, nearly independent H₂ molecules, each at its equilibrium bond length. Figure 4 and Table III shows the results for both symmetric and asymmetric bond stretchings. The RHF and UHF energies, as well as our QMC results obtained using the UHF trial wave function (or RHF when there is no UHF solution) are shown. The RCCSD(T) and DMRG energies as reported in Ref. 42 are also shown for comparison.

For symmetric stretching, the QMC/UHF total energies are in good agreement with the DMRG results, with the largest discrepancy being about 5 mhartrees for R=3.2 and R=3.6 bohrs. As the bond length is stretched, the correlation energy of the system increases. In view of the above results for bond stretching in diatomic molecules, it is not surprising that the discrepancy between RCCSD(T) and DMRG increases as *R* is increased, and for R > 2.4, RCCSD(T) fails to converge as reported in Ref. 42.

For asymmetric bond stretching, the QMC energies are again in good agreement with the DMRG values. The difference between the QMC and DMRG total energies is less than $\approx 2-3$ mhartrees for all bond lengths. Here no distinct UHF solution was found, so the RHF Slater determinant was used as the trial WF. The RHF trial WF dissociates properly as *R* is increased in this case, so, not surprisingly, RCCSD(T) is in good agreement with DMRG.

IV. SUMMARY

Bond stretching in chemistry is a nontrivial challenge for all approximate correlated methods. In this paper, we applied the recently introduced phaseless auxiliary-field QMC

FIG. 4. (Color online) Potential-energy curves of H_{50} for the symmetric (S) and asymmetric (A) bond stretchings using STO-6G basis set. The DMRG and CCSD(T) results are from Ref. 42. QMC energies are obtained with a UHF trial WF in the symmetric case and RHF trial WF in the asymmetric case (there is no UHF instability). The inset shows the deviations (in mhartree) from the DMRG potential-energy curve.

TABLE III. Symmetric and asymmetric bond stretchings in a H_{50} linear chain, using a minimal STO-6G basis set. Total energies versus geometry are shown for different methods. DMRG and RCCSD(T) values are from Ref. 42. Bond lengths are in bohr and energies are in hartree. QMC statistical errors (shown in parentheses) are on the last digit.

R	RHF	UHF	RCCSD(T)	DMRG	QMC
Symmetric					
1.0	-16.864 88	-16.864 88	-17.282 27	-17.284 07	-17.2852(1)
1.2	-22.461 27	-22.468 05	-22.944 57	-22.947 65	-22.9475(7)
1.4	-25.02976	-25.058 91	-25.589 12	-25.593 78	-25.5933(3)
1.6	-26.062 25	-26.130 19	-26.713 14	-26.719 44	-26.7188(5)
1.8	-26.265 98	-26.396 69	-27.031 45	-27.038 65	-27.0388(3)
2.0	-26.008 20	-26.237 77	-26.920 90	-26.926 09	-26.9256(9)
2.4	-24.835 76	-25.434 02		-26.160 57	-26.1594(5)
2.8	-23.360 81	-24.634 19		-25.274 80	-25.2765(7)
3.2	-21.896 33	-24.108 60		-24.568 28	-24.5733(5)
3.6	-20.574 29	-23.823 26		-24.10277	-24.1084(7)
4.2	-18.955 95	-23.634 41		-23.749 71	-23.7489(4)
Asymmetric					
1.6	-25.963 71		-26.486 01	-26.487 38	-26.4867(7)
1.8	-26.617 68		-27.126 41	-27.127 16	-27.1264(9)
2.0	-27.071 82		-27.57679	-27.577 32	-27.5769(3)
2.4	-27.609 24		-28.117 27	-28.117 61	-28.1163(7)
2.8	-27.873 62		-28.386 84	-28.387 07	-28.3842(5)
3.2	-28.004 68		-28.521 10	-28.521 24	-28.5189(7)
3.6	-28.069 65		-28.587 28	-28.587 36	-28.5844(5)
4.2	-28.111 00		-28.628 54	-28.628 58	-28.6265(5)

method to study bond stretching in BH and N_2 and in the H_{50} chain. The quality of the phaseless AF QMC method depends on the trial wave function that is used to control the sign/ phase problem. With a single UHF Slater determinant as trial wave function, AF QMC has performed very well for molecular geometries near the equilibrium configuration, as shown by comparisons with exact values, CCSD(T) calculations, and experimental results. The results in this paper are consistent with this and extend the reach of phaseless AF QMC method beyond Born-Oppenheimer equilibrium structures to bond stretching and bond breaking. For larger nuclear separations, we find that AF QMC with a singledeterminant UHF solution in general gives better overall accuracy and a more uniform behavior than coupled cluster CCSD(T). In some stretched bond situations, however, QMC/UHF errors are seen to be significant. In these cases, we find that a trial wave function with a modest number of determinants usually reduces the QMC error to a few millihartrees. The QMC computational cost of the multideterminant trial wave function scales linearly with the number of determinants, but a better trial wave function can reduce both systematic and statistical errors. Using multideterminant trial wave functions taken directly from MCSCF calculations, the AF QMC results are in very good agreement with exact energies, and uniform behavior is seen across the entire potential-energy curve.

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