On the accuracy of the fixed-node diffusion quantum Monte Carlo method

Sebastian Manten and Arne Lüchow

Articles you may be interested in

Fixed-node diffusion Monte Carlo potential energy curve of the fluorine molecule F2 using selected configuration interaction trial wavefunctions
J. Chem. Phys. 142, 044115 (2015); 10.1063/1.4905528

Fixed-node diffusion Monte Carlo study of the structures of m -benzyne
J. Chem. Phys. 128, 154324 (2008); 10.1063/1.2902979

Theoretical study of transition state structure and reaction enthalpy of the F + H 2 → HF + H reaction by a diffusion quantum Monte Carlo approach
J. Chem. Phys. 122, 194323 (2005); 10.1063/1.1899125

Intermolecular forces and fixed-node diffusion Monte Carlo: A brute force test of accuracies for He 2 and He–LiH
J. Chem. Phys. 119, 8225 (2003); 10.1063/1.1612479

Accuracy of electronic wave functions in quantum Monte Carlo: The effect of high-order correlations
J. Chem. Phys. 107, 3007 (1997); 10.1063/1.474658

On the accuracy of the fixed-node diffusion quantum Monte Carlo method

Sebastian Manten and Arne Lüchow[a]
*Institut für Physikalische Chemie und Elektrochemie I, Heinrich-Heine-Universität Düsseldorf,
40225 Düsseldorf, Germany*

The accuracy of the fixed-node diffusion quantum Monte Carlo (FN-DQMC) method is compared to the coupled cluster method CCSD(T). For a test set of 20 small molecules and 17 reactions the electronic contribution to the reaction enthalpy is calculated with the FN-DQMC method using the nodes of a Slater determinant calculated at the HF/cc-pVTZ level. By comparison with reference reaction enthalpies the FN-DQMC method is shown to be more accurate than the CCSD(T)/cc-pVDZ method and almost as accurate as CCSD(T)/cc-pVTZ. The deviation from the reference data is comparable to the CCSD(T)/cc-pVTZ deviation, but, with only two exceptions, of opposite sign. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1394757]

I. INTRODUCTION

In most *ab initio* electron structure methods, the electronic wave function is constructed from determinants of orbitals, whereas in the diffusion quantum Monte Carlo method (DQMC) it is sampled with a stochastic process. This quantum simulation allows an evaluation of the electron correlation because the fully dimensional Schrödinger equation is treated directly. In this respect, the DQMC method is an explicitly correlated electron structure method, and, indeed, more than 90% of the electron correlation energy are easily obtained with this method. Since DQMC scales favorably with the system size like most Monte Carlo methods, the method is promising for accurate correlated calculations of larger molecules.

There are many variants of the quantum Monte Carlo method.[1–5] The fixed-node diffusion quantum Monte Carlo method (FN-DQMC), which is employed in this article, offers a trade-off between efficiency and accuracy. While it is more accurate than the variational quantum Monte Carlo method it is less accurate, but considerably more efficient than released-node variants of QMC.[6,7,8] FN-DQMC achieves its efficiency through the fixed-node approximation[9] which leads to a systematic error, the node location error. Since the correlation treatment is exact, i.e., the full CI, complete basis set limit is calculated, the node location error results from an additional boundary condition for the electronic Hamiltonian; the nodes of a *guide function* Ψ_G are imposed on the DQMC random walk. Although the node location error is small compared to the correlation energy it is not insignificant in terms of chemical accuracy. In a previous paper,[10] one of the authors found node location errors of about 15 mE_h for the first-row atoms and hydrides when using the nodes of HF wave functions. It was also found that node location errors cancel to a large extent when energy differences such as dissociation energies were calculated. Due to this cancellation the dissociation energies for the

first-row hydrides could be calculated in agreement with experimental data.[10] Similarly, Morosi, Mella, and Bressanini were able to obtain excellent electron affinities.[11] This cancellation is the basis of the recent success of the FN-DQMC method for larger molecules and clusters.[12–17]

In this article, we assess the accuracy of the DQMC method with Hartree–Fock nodes (DQMC/HF) based on the correlation consistent cc-pVTZ basis set by Dunning[18] using a test set of reactions where the electronic contribution to the reaction enthalpies have been calculated previously for a range of *ab initio* methods.[19] Most previous DQMC calculations have either employed pseudopotentials, even for first-row atoms, or basis sets with Slater-type orbitals. In an all-electron DQMC calculation, the missing electron-nucleus-cusp of contracted Gaussian basis functions leads to a strong increase of the variance. We propose a method to modify the contracted Gaussian basis function close to the nucleus in order to introduce a proper electron–nucleus cusp. With this slight modification, we are able to use directly HF or MC-SCF wave functions with standard basis sets in FN-DQMC calculations. Since the node location error is completely determined by the *ab initio* wave function we use the abbreviation DQMC/HF/cc-pVTZ for a fixed-node DQMC calculation with nodes of a HF/cc-pVTZ Slater determinant imposed on the random walk.

II. METHOD

The diffusion quantum Monte Carlo method[20] is used as in previous work[10,8,2] and will be discussed here only briefly. The method is based on the projection of the ground state with the operator,

$$\Psi(\mathbf{r},\tau) = e^{-\tau H}\Psi(\mathbf{r},0), \quad \text{with} \quad H = -\tfrac{1}{2}\nabla^2 + V(\mathbf{r}). \quad (1)$$

$\Psi(\mathbf{r},\tau)$ provides a formal solution of the time-dependent Schrödinger equation in imaginary time ($\tau = it$),

$$\frac{\partial\Psi(\mathbf{r},\tau)}{\partial\tau} = \frac{1}{2}\nabla^2\Psi(\mathbf{r},\tau) - V(\mathbf{r})\Psi(\mathbf{r},\tau), \quad (2)$$

[a]Author to whom correspondence should be addressed. Electronic mail: luechow@uni-duesseldorf.de

which is a generalized diffusion equation. The propagation of $\Psi(\mathbf{r},\tau)$ in imaginary time is achieved with a stochastic process by simulating the diffusion. After long simulation time $\Psi(\mathbf{r},\tau)$ converges exponentially fast toward the exact ground state wave function which is seen when expanding $\Psi(\mathbf{r},\tau)$ in terms of the eigenfunctions Φ_i of H,

$$\Psi(\mathbf{r},\tau) = \sum_i a_i e^{-\tau E_i} \Phi_i. \qquad (3)$$

The efficiency of DQMC is improved substantially with importance sampling by introducing a *guide function* Ψ_G that "guides" the random walk toward regions where Ψ_G is large. The energy is calculated as

$$E_0 = \lim_{\tau \to \infty} \frac{\langle \Phi_G | H e^{-\tau H} \Phi_G \rangle}{\langle \Phi_G | e^{-\tau H} \Phi_G \rangle}, \qquad (4)$$

which is evaluated stochastically with the mixed estimator as a weighted average of local energy,[22]

$$E_{\text{loc}}(\mathbf{r}) = \frac{H\Phi_G(\mathbf{r})}{\Phi_G(\mathbf{r})}. \qquad (5)$$

Due to the required antisymmetry, the electronic ground state wave function has $3n-1$-dimensional nodal hypersurfaces for n electrons. An approximation to the true ground state is obtained when the nodes of Ψ_G are imposed on the random walk resulting in the fixed-node approximation (FN-DQMC).[9] Mathematically, the simulation now solves the Schrödinger equation with the nodes of Ψ_G as an additional boundary condition. It can be shown that the resulting fixed-node energy is variational: $E_0^{(\text{FN})} \geq E_0$.[23] The error

$$\Delta E_{\text{node}} = E_0^{(FN)} - E_0 \qquad (6)$$

is known as the *node location error*. If Ψ_G satisfies the Pauli principle so will the FN-DQMC solution Ψ_0.

Particularly efficient guide functions are of the form,

$$\Psi_G = e^U \Phi_{ab\ initio}, \qquad (7)$$

where $\Phi_{ab\ initio}$ is a single determinant (HF) or multideterminant [e.g., MCSCF or PNO-CI (Ref. 21)] wave function obtained from a preceding *ab initio* calculation and e^U a correlation function. Obviously, the node location error depends only on Φ. e^U is a "Jastrow" term depending explicitly on the electron–electron distances r_{ij},

$$U = U(\{r_{ij}\}), \qquad (8)$$

in order to satisfy the electron cusp condition. Although $E_0^{(\text{FN})}$ is independent of the choice for the correlation function the Jastrow term is indispensible because it removes the electron–electron singularities in the local energy E_{loc}. As in previous work, the correlation function e^U is of the Boys/Handy[24] type

$$U_{aij} = \sum_k^{N_a} c_{ka}(\bar{r}_{ai}^{\,l_{ka}}\bar{r}_{aj}^{\,m_{ka}} + \bar{r}_{aj}^{\,l_{ka}}\bar{r}_{ai}^{\,m_{ka}})\bar{r}_{ij}^{\,n_{ka}}, \qquad (9)$$

where a and i, j refer to the nuclei and the electrons, respectively, and where $\bar{r}$ is defined by $\bar{r} = r/(1+br)$. This func-

tion was introduced into QMC by Schmidt and Moskowitz.[25] The parameters of U are optimized by variance minimization with Monte Carlo methods.[26]

The node location error is about $0.015\,E_{\text{h}}$ for the atoms C, N, O, F, and their hydrides when Φ is a HF wave function calculated with a sufficiently large STO basis set. It has been shown in a previous paper that the node location error cancels to a large extent when calculating energy differences such as dissociation energies or electron affinities.[10,11] For larger systems, it is desirable to employ standard Gaussian basis sets which would allow to use the wave functions from a standard *ab initio* calculation as $\Phi_{ab\ initio}$ in the guide function Φ_G. In all-electron DQMC-calculations Gauss-type orbitals lead to diverging local energies for electrons at the nucleus because the GTOs do not satisfy the electron–nucleus cusp condition. This problem does not arise when pseudopotentials replace the core electrons. This approach is used by Mitas, Grossman, and co-workers who have been able to carry out impressive calculations for large molecules with pseudopotential-DQMC.[12–15] In previous all-electron calculations on C_8, C_{10}, and C_{20} we used a combined STO-GTO basis set we denoted "S-31G**" where the contracted $1s$ function of the standard 6-31G** basis set is replaced by one STO for DQMC and a 10 GTO contraction fitted to the STO for the *ab initio* calculations.

While this approach is efficient, it is desirable to use standard basis sets in DQMC. This can be achieved by modifying the $1s$ function of the basis set only near the nucleus such that the electron–nucleus cusp condition is fulfilled. In our method, we interpolate from the contracted $1s$ basis function to a Slater-type function near the nucleus. This way the effect on the energy is considerably smaller than the replacement of the $1s$ function by an STO. The cusp correction is easily implemented because the radial parts of the basis functions are implemented with cubic splines.

In Fig. 1 the cusp correction is depicted for the $1s$ basis function of the carbon atom in the cc-pVTZ basis set. While it is seen that a cusp correction for radii smaller than 0.005 bohr is sufficient to remove the problem of diverging local energies for electrons near the nucleus we found that such a cusp correction does not reduce the variance of the process significantly. Thus, the efficiency of such a cusp-corrected basis is considerably inferior to the previously used mixed STO/GTO basis in DQMC calculations. The reason can be seen in Fig. 2 where the second derivative of the contracted $1s$ basis function and of the cusp-corrected function is shown. The fluctuations are significant in the range up to 0.1 bohr resulting in corresponding fluctuations of the local energy which in turn cause the steep increase of the variance compared to a STO basis. The contribution of the actual cusp correction is very small due the r^2 factor in the volume element.

The construction of the cusp-corrected function is as follows: The parameters of a Slater-type function $ae^{-\alpha r}+c$ are fitted to the contracted function with a least-squares minimization in the range $r < 0.2$ bohr, where c is at least an order of magnitude smaller than a. By allowing a nonzero c the fit is significantly improved. Due to the strong fluctuations of the second derivative of the contracted $1s$ function, special
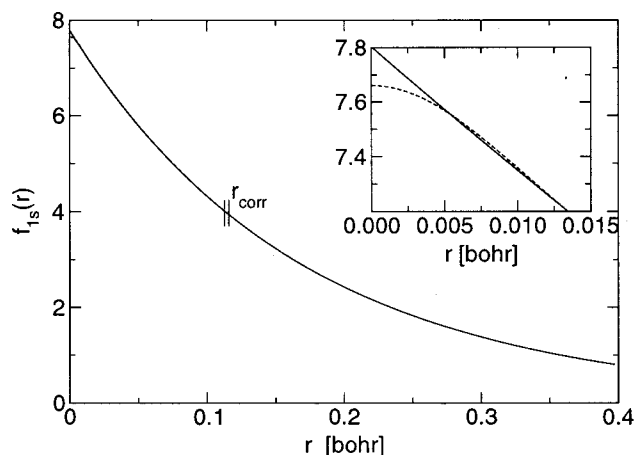
FIG. 1. Cusp correction (solid line) for the carbon $1s$ cc-pVTZ contracted basis function (dashed line) with a correction radius $r_{corr} = 0.115$ bohr.

attention must be payed to its correction. In order to guarantee continuity in the second derivative it is possible to switch from the contracted function to the Slater function only at certain radii r_{corr} (see Fig. 2). We found it necessary to further smooth the connection of the two functions by inserting an interpolating polynomial in a very small interval of length 0.001 bohr at r_{corr} before the $1s$ function. In order to achieve differentiability in the second derivative we start with the construction of the interpolating polynomial of the second derivative. A cubic polynomial is chosen whose parameters are determined by requiring continuity and differentiability at the ends of the interval. The polynomials for the first derivative and the function itself are obtained by integration under the condition of continuity and differentiability again at both ends of the interval. This condition requires a slight modification for the Slater-type function which becomes by integration of the second derivative,

$$f_{Slater}(r) = ae^{-\alpha r} + b'r + c'. \tag{10}$$

For small intervals the b' and c' parameters deviate negligibly from 0 and c and guarantee differentiability for the cusp-corrected function. The final function and its two de-
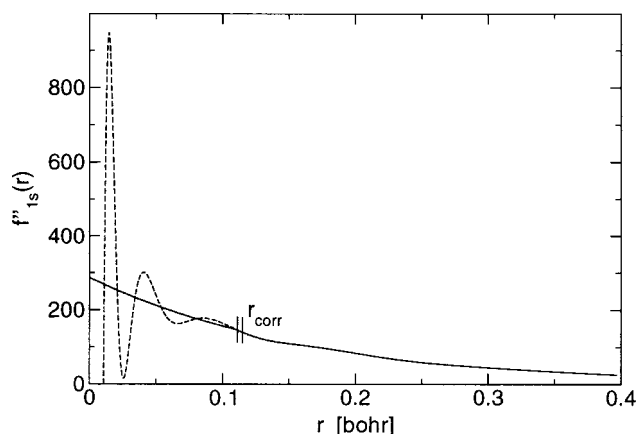
TABLE I. Variance reduction for different correction radii (in bohr). Carbon atom with cc-pVTZ basis set and nine-term Jastrow function.

r_{corr}	Var
0.000	50.0
0.035	1.9
0.080	0.94
0.115	0.78

rivatives are replaced by cubic splines and used in this form for the local energy evaluation. We use 4000 nonequally spaced spline points obtained from a mapping of the interval $[0, 1]$ onto $[0,\infty]$ with the function $x_i = \alpha ih/(1-ih)$, $i = 0,...,n-1$, where $h = 1/n$ and $\alpha = 0.1$.

Since the $2s$ function also lacks a correct electron-nucleus cusp, we constructed cusp-corrected $2s$ functions analogously. The radial part of the $2s$ function of the cc-pVTZ basis set is negative at $r = 0$. Therefore, the same form of the Slater-type function can be used with a negative value for α. The $2s$ correction is of minor importance, but it leads to a further reduction of the variance.

In Table I the reduction of the variance is demonstrated for the carbon atom. The guide function is the product of the HF/cc-pVTZ Slater determinant with different correction radii r_{corr} in the $1s$ and $2s$ function and the same nine-term Jastrow term of the Schmidt/Moskowitz type.[25] The actual values for the correction radii are due to the continuity requirement in the second derivative (see Fig. 2).

The reduction of the variance is not the only effect of the cusp correction. For actual FN-DQMC calculations it may be even more important that the time step error is greatly reduced by introducing the cusp correction in the form suggested here. The time step error for the C atom guide function with uncorrected $1s$ cc-pVTZ functions is so large that we have not been able to extrapolate savely to $\tau \to 0$. Instead, we employed the variational QMC (VQMC) method to calculate the energy difference ΔE between the uncorrected function and the corrected function with $r_{corr} = 0.115$ bohr. Using VQMC, we obtain $\Delta E = 0.1(3)$ mE_h, i.e., no devia-

FIG. 2. Cusp correction (solid line) for the second derivative of the carbon $1s$ cc-pVTZ contracted basis function (dashed line) with a correction radius $r_{corr} = 0.115$ bohr.
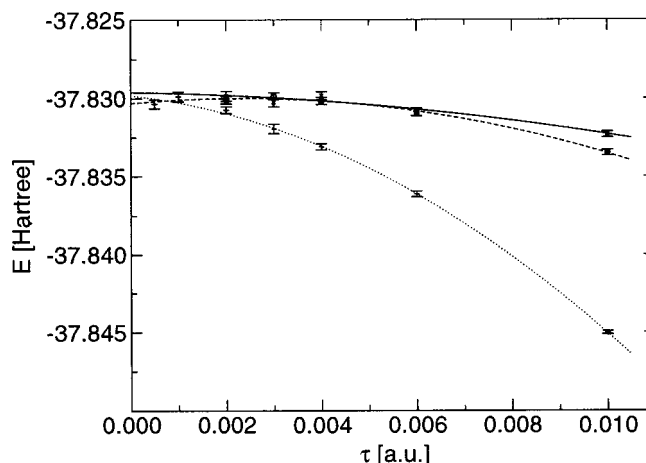

FIG. 3. Time step error for the carbon atom with different cusp correction radii $r = 0.035$ (dotted line), $r = 0.080$ (dashed line), and $r = 0.115$ bohr (solid line).

TABLE II. Total energies in E_h calculated with DQMC/HF/cc-pVTZ compared to CCSD(T)/cc-p-VXZ, X=D,T.

		CCSD(T)[a]	
	FN-DQMC	cc-pVTZ	cc-pVDZ
H_2	−1.1739(1)	−1.1723	−1.1634
CH_2	−39.1165(3)	−39.0614	−39.0220
CH_4	−40.5005(3)	−40.4381	−40.3868
NH_3	−56.5485(4)	−56.4732	−56.4020
H_2O	−76.4207(2)	−76.3322	−76.2410
C_2H_2	−77.3110(4)	−77.1876	−77.1092
C_2H_4	−78.5644(3)	−78.4388	−78.3544
HNC	−93.3737(3)	−93.2513	−93.1632
HCN	−93.3987(4)	−93.2751	−93.1884
HF	−100.4466(3)	−100.3379	−100.2275
N_2	−109.5046(3)	−109.3739	−109.2753
N_2H_2	−110.6054(5)	−110.4780	−110.3670
CO	−113.2877(4)	−113.1555	−113.0544
H_2CO	−114.4739(4)	−114.3338	−114.2183
HNO	−130.4371(4)	−130.2984	−130.1710
H_2O_2	−151.5213(3)	−151.3586	−151.1937
HOF	−175.5120(4)	−175.3343	−175.1519
CO_2	−188.5429(4)	−188.3271	−188.1475
F_2	−199.4841(4)	−199.2961	−199.0975
O_3	−225.3410(4)	−225.1326	−224.9091

[a]CCSD(T) results from Klopper *et al.* (Ref. 19).

tion of statistical significance is found. The increase of the time step error is possibly caused by the fluctuation of the drift near the nucleus due to the contraction (Fig. 3).

III. RESULTS AND CONCLUSION

With the new cusp correction procedure, we are now able to employ directly *ab initio* wave functions obtained with standard methods and standard basis sets in FN-DQMC calculations. Assuming sufficiently small time steps the remaining node location error depends only on the nodes of

this wave function. In this paper, we assess the accuracy of the DQMC/HF/cc-pVTZ method where the nodes are taken from a HF wave function calculated with the cc-pVTZ basis set. We use a test set of 20 molecules and 17 reactions that has been used previously by Klopper *et al.* for a similar purpose.[19] Klopper *et al.* use this test set to investigate their highly accurate CCSD(T)-R12 method. We compare our results with the reference reaction enthalpies compiled in this paper and the CCSD(T) results obtained with the cc-pVDZ and cc-pVTZ basis sets.

Since geometry optimizations with DQMC are at this time not competitive with standard methods the procedure used here is the combination of geometry optimization on the MP2/cc-pVTZ level and a subsequent DQMC/HF/cc-pVTZ single point calculation. For molecules too large for the MP2/cc-pVTZ optimization this method would be replaced by a DFT optimization using a hybrid gradient corrected functional such as B3LYP.

In Table II the total energies calculated with the DQMC/HF/cc-pVTZ method are listed for the 20 molecules of the reaction test set suggested by Klopper *et al.*[19] The time step used in these calculations is $\tau = 0.005$ a.u. leading to time step error of about 3 mE_h, e.g., for the water molecule. We found that the time step error cancels when calculating energy differences. A few reactions have been repeated with a time step of $\tau = 0.002$ a.u. and only statistically insignificant changes were found. The CCSD(T) energies in Table II are taken from Klopper *et al.*[19] These energies are obtained at geometries optimized with the CCSD(T)/cc-pCVQZ method and all electrons correlated. In FN-DQMC all electrons are naturally correlated while in the CCSD(T) results in Table II only the valence electrons are correlated which explains in part the considerably lower total DQMC energies for all molecules considered here.

Using these data, the electronic contribution to the reac-

TABLE III. Electronic contribution to the reaction enthalpies ΔH_e (in kJ mol^{-1}) from experiments and from DQMC/HF/cc-pVTZ and CCSD(T)/cc-pVXZ, X=D,T calculations with differences $\Delta\Delta H_e$ to the experimental results.

		DQMC		cc-pVTZ		cc-pVDZ	
Reaction	Expt ΔH_e	ΔH_e	$\Delta\Delta H_e$	ΔH_e	$\Delta\Delta H_e$	ΔH_e	$\Delta\Delta H_e$
$CH_2^a + H_2 \rightarrow CH_4$	−544(2)	−552(2)	−8	−537	7	−529	15
$C_2H_2 + H_2 \rightarrow C_2H_4$	−203(2)	−209(2)	−6	−207	−4	−215	−12
$C_2H_2 + 3H_2 \rightarrow 2CH_4$	−446(2)	−442(2)	4	−451	−5	−457	−11
$N_2H_2 \rightarrow N_2 + H_2$	−174[b]	−192(2)	−18	−179	−5	−188	−14
$CO + H_2 \rightarrow H_2CO$	−21(1)	−32(2)	−11	−16	5	−1	20
$N_2 + 3H_2 \rightarrow 2NH_3$	−164(1)	−186(2)	−22	−146	18	−101	63
$F_2 + H_2 \rightarrow 2HF$	−563(1)	−618(2)	−55	−545	18	−510	53
$O_3 + 3H_2 \rightarrow 3H_2O$	−933(2)	−1050(2)	−117	−912	21	−850	83
$H_2CO + 2H_2 \rightarrow CH_4 + H_2O$	−251(1)	−262(2)	−11	−241	10	−217	34
$H_2O_2 + H_2 \rightarrow 2H_2O$	−365(2)	−384(2)	−19	−351	14	−328	37
$CO + 3H_2 \rightarrow CH_4 + H_2O$	−272(1)	−294(2)	−22	−257	15	−218	54
$HCN + 3H_2 \rightarrow CH_4 + NH_3$	−320(3)	−338(2)	−18	−313	7	−289	31
$HNO + 2H_2 \rightarrow H_2O + NH_3$	−444(1)	−485(2)	−41	−427	17	−381	63
$HNC \rightarrow HCN$	−64[b]	−66(2)	−2	−63	1	−66	−2
$H_2O + F_2 \rightarrow HOF + HF$	−129(4)	−141(2)	−12	−115	14	−107	22
$CO_2 + 4H_2 \rightarrow 2H_2O + CH_4$	−244(1)	−272(2)	−28	−226	18	−178	66
$2CH_2^a \rightarrow C_2H_4$	−844(3)	−871(2)	−27	−830	14	−815	29

[a]Singlet $\tilde{a}\ {}^1A_1$ state of methylene.
[b]CCSD(T)-R12 energies used instead of experimental energies (Ref. 19).

tion enthalpies can be calculated for the whole test set. In Table III the DQMC results are compared with the non relativistic reference data obtained from experimental 0 K enthalpies corrected for vibrational and relativistic contributions[27,19,28] and with the CCSD(T) enthalpies calculated from the molecular energies. Both the calculated reaction enthalpies and their differences to the respective reference energies are listed in Table III. By inspection it is seen that the DQMC/HF/cc-pVTZ energies deviate less from the reference data than the CCSD(T)/cc-pVDZ energies but more than the CCSD(T)/cc-pVTZ values. All three methods have the largest deviations for the reaction with ozone, and FN-DQMC fails here completely. This failure was anticipated because ozone is the only molecule in the set with significant contribution of nondynamical correlation to the energy. Both methods, CCSD(T) and DQMC/HF are single reference methods that should be used only with great care for molecules with nondynamical correlation contribution. In the case of DQMC, the remedy is easy; the HF Slater determinant should be replaced by a MCSCF wave function that catches the nondynamical correlation part while DQMC evaluates the dynamical part. DQMC/MCSCF has been used previously for a variety of atoms and molecules.[22,29,30]

Since all reactions have been written as exothermic reaction it is obvious from Table III that the deviations from the reference data are not statistical. While CCSD(T)/cc-pVTZ almost in all cases underestimates the exothermicity DQMC/HF/cc-pVTZ overestimates the exothermicity by about the same amount.

In conclusion, we find the DQMC/HF/cc-pVTZ method capable of predicting the reaction energies in a series of reactions of small molecules with an accuracy almost as good as the CCSD(T)/cc-VTZ method and better than the CCSD(T)/cc-pVDZ method. While the scaling of these methods with the system size is like n^7, the DQMC method scales only like n^3 to n^4.

ACKNOWLEDGMENTS

[1] A. Lüchow and J. B. Anderson, Annu. Rev. Phys. Chem. **51**, 501 (2000).
[2] J. B. Anderson, Rev. Comput. Chem. **13**, 133 (1999).
[3] D. M. Ceperley and L. Mitas, Adv. Chem. Phys. **93**, 1 (1996).
[4] J. B. Anderson, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, edited by S. R. Langhoff (Kluwer, Dordrecht, 1995).
[5] J. B. Anderson, Int. J. Radiat. Phys. Chem. **14**, 85 (1995).
[6] D. M. Ceperley and B. J. Alder, J. Chem. Phys. **81**, 5833 (1984).
[7] B. Chen and J. B. Anderson, J. Chem. Phys. **102**, 4491 (1995).
[8] A. Lüchow and J. B. Anderson, J. Chem. Phys. **105**, 4636 (1996).
[9] J. B. Anderson, J. Chem. Phys. **65**, 4121 (1976).
[10] A. Lüchow and J. B. Anderson, J. Chem. Phys. **105**, 7573 (1996).
[11] G. Morosi, M. Mella, and D. Bressanini, J. Chem. Phys. **111**, 6755 (1999).
[12] J. C. Grossman, L. Mitas, and K. Raghavachari, Phys. Rev. Lett. **75**, 3870 (1995).
[13] T. Torelli and L. Mitas, Phys. Rev. Lett. **85**, 1702 (2000).
[14] J. Grossman and L. Mitas, Phys. Rev. B **52**, 16735 (1995).
[15] J. C. Grossman and L. Mitas, Phys. Rev. Lett. **79**, 4353 (1997).
[16] Y. Shlyakhter, S. Sokolova, A. Lüchow, and J. B. Anderson, J. Chem. Phys. **110**, 10725 (1999).
[17] S. Sokolova, A. Lüchow, and J. B. Anderson, Chem. Phys. Lett. **323**, 229 (2000).
[18] J. T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[19] W. Klopper, K. L. Bak, P. Jørgensen, J. Olsen, and T. Helgaker, J. Phys. B **32**, R103 (1999).
[20] J. B. Anderson, J. Chem. Phys. **63**, 1499 (1975).
[21] A. Lüchow and R. F. Fink, J. Chem. Phys. **113**, 8457 (2000).
[22] C. J. Umrigar, M. P. Nightingale, and K. J. Runge, J. Chem. Phys. **99**, 2865 (1993).
[23] B. L. Hammond, J. W. A. Lester, and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).
[24] S. F. Boys and N. C. Handy, Proc. R. Soc. London, Ser. A **310**, 43 (1969).
[25] K. E. Schmidt and J. W. Moskowitz, J. Chem. Phys. **93**, 4172 (1990).
[26] H. Conroy, J. Chem. Phys. **41**, 1331 (1964).
[27] J. M. W. Chase, *NIST-JANAF Thermochemical Tables*, 4th ed. (AIP, Woodbury, NY, 1998).
[28] K. L. Bak, P. Jørgensen, J. Olsen, T. Helgaker, and W. Klopper, J. Chem. Phys. **112**, 9229 (2000).
[29] H.-J. Flad, M. Caffarel, and A. Savin, in *Recent Advances in Quantum Monte Carlo Methods*, edited by J. W. A. Lester (World Scientific, Singapore, 1997).
[30] S. Sokolova and A. Lüchow, Chem. Phys. Lett. **320**, 421 (2000).