

First-row hydrides: Dissociation and ground state energies using quantum Monte Carlo

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Accurate ground state energies comparable to or better than the best previous *ab initio* results can be obtained using the fixed-node quantum Monte Carlo (FN-DQMC) method. The residual energy, the nodal error due to the error in the nodal structure of a trial wave function, is examined in this study using nodal surfaces given by near HF-limit wave functions. The study is aimed at better understanding of the nodal error and the cancellation of nodal errors in calculating energy differences. Calculations have been carried out for the first-row hydrides LiH to FH and the corresponding atoms. The FN-DQMC ground state energies are among the lowest to date. The dissociation energies D_e have been calculated with accuracies of 0.5 kcal mol⁻¹ or better. For all hydrides, the dissociation energies are consistent with experimental values. The fixed-node quantum Monte Carlo method can therefore offer a very straight-forward way to calculate highly accurate dissociation energies. © 1996 American Institute of Physics. [S0021-9606(96)00641-1]

I. INTRODUCTION

The quantum Monte Carlo method has been successful in calculating accurately the ground state energy and other properties for many atoms and molecules.¹⁻³ For few-electron systems such as H₂, H₃, and LiH, quantum Monte Carlo methods provide exact solutions of the Schrödinger equation.¹ For larger systems, the fixed-node diffusion quantum Monte Carlo method (FN-DQMC) can provide highly accurate solutions.² The difference between the fixed-node energies and the exact nonrelativistic ground state energies, known as nodal error, is due to the error in the nodal surface of a trial wave function which is imposed on the solution of the Schrödinger equation. When calculating the chemically important energy differences, such as dissociation energies, ionization potentials, or electron affinities, standard analytic calculations can usually achieve a large cancellation of error in the total energy. Similarly, with nodal errors of the order of 10 kcal mol⁻¹ for ten-electron systems a significant cancellation is necessary if chemical accuracy of 1 kcal mol⁻¹ is to be achieved with the quantum Monte Carlo method.

In several QMC studies energy differences have been calculated using the fixed-node method, but only Subramaniam, Lee, Schmidt, and Moskowitz⁴ have calculated fixed-node energies and dissociation energies for a range of molecules. For the current study, we have calculated highly accurate fixed-node ground state energies of the first-row atoms and hydrides using well-defined nodal surfaces provided by near HF-limit wave functions. In a previous QMC study⁵ we were able to calculate the dissociation energy of FH in excellent agreement with experiment using this type of nodal surface. To determine how well the HF nodal surfaces can reproduce the experimental dissociation energies for a wider range of molecules we have calculated here the dissociation energies D_e and estimated the nodal errors for all remaining first-row hydrides. The results are compared with those of recent analytic calculations.

II. THE NODAL ERROR IN FIXED-NODE QUANTUM MONTE CARLO

The basis for the diffusion quantum Monte Carlo method (DQMC) is the time-dependent Schrödinger equation in imaginary time

$$\frac{\partial \Psi}{\partial \tau} = -H\Psi = \frac{1}{2}\nabla^2\Psi - V\Psi. \quad (2.1)$$

The stationary solution of this equation is the ground state wave function Ψ_0 . This equation is mathematically a diffusion equation and it can be simulated with a random walk of particles leading to a sample with a distribution corresponding to the stationary solution Ψ_0 .⁶

Importance sampling with an approximate or trial wave function Ψ_T is used to reduce the variance of the process. Transforming Eq. (2.1) into an equation for $f = \Psi_0\Psi_T$, interpreted as a probability density, is possible by multiplying Eq. (2.1) by Ψ_T and rearranging to obtain^{7,8}

$$\frac{\partial f}{\partial \tau} = \frac{1}{2}\nabla^2 f - \nabla[f\nabla \ln|\Psi_T|] - [E_{\text{loc}} - E_T]f \quad (2.2)$$

in which E_T is a trial energy and $E_{\text{loc}} = H\Psi_T/\Psi_T$ is the local energy which is a function of position in configuration space. This equation can be simulated with a random walk incorporating a diffusion, a drift, and a branching or weighting step. The ground state energy E_0 can then be obtained as the expectation value of the local energy over the stationary distribution $p(\mathbf{R}) = \Psi_0\Psi_T/\int \Psi_0\Psi_T d\mathbf{R}$ where \mathbf{R} denotes a position vector in configuration space. Thus we have

$$E_0 = \int E_{\text{loc}}(\mathbf{R})p(\mathbf{R})d\mathbf{R} = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N E_{\text{loc}}(\mathbf{R}_i). \quad (2.3)$$

The random walk simulation of Eq. (2.2) requires a discretization of the imaginary time τ . The use of finite time steps introduces a *time step error* that can be eliminated by extrapolating to time step $\tau \rightarrow 0$. This form of the diffusion

quantum Monte Carlo method with importance sampling has been derived by Reynolds, Ceperley, Alder, and Lester.⁸

Because of the Pauli principle the ground state wave function for an electron system with more than two electrons has a nodal hypersurface and is thus not the lowest-energy solution of Eq. (2.1). The Pauli principle can be satisfied by imposing an appropriate nodal hypersurface on the stationary solution and solving Eq. (2.1) with the nodal hypersurface as an additional boundary condition.⁹ Since the nodal hypersurface is not fully determined by the Pauli principle the stationary solution will in general be only an approximation to the exact wavefunction, and it can be shown that the corresponding eigenvalue $E_0^{(\text{FN})}$ is an upper bound to the exact nonrelativistic eigenvalue E_0 .⁸ The difference

$$E_{\text{node}} = E_0^{(\text{FN})} - E_0 \quad (2.4)$$

is known as the *nodal error* and is dependent solely on the nodal hypersurface.

An approximate nodal hypersurface is most easily defined by the nodes of a trial wave function Ψ_T that satisfies the Pauli principle. The ground state wave function $\Psi_0^{(\text{FN})}$ within each nodal region of Ψ_T is then nodeless and thus the product of $\Psi_0^{(\text{FN})}$ with the trial function $f = \Psi_0^{(\text{FN})} \Psi_T$ is positive. The fixed-node energy can also be determined using the Green's function QMC method.^{4,10}

The general form for the trial wave function Ψ_T used in this work consists of the usual product of determinants for the α and β electrons multiplied by a positive correlation factor (Jastrow factor)

$$\Psi_T = \det \Phi^{(\alpha)} \det \Phi^{(\beta)} e^U, \quad U = \sum_{a,i < j} U_{aij}, \quad (2.5)$$

where Φ is an orbital product and U_{aij} is a correlation function symmetric with respect to all electron permutations. A more general form employs a multiconfiguration function

$$\Psi_T = \left[\sum_{i=1}^n c_i \det \Phi_i^{(\alpha)} \det \Phi_i^{(\beta)} \right] e^U, \quad (2.6)$$

where Φ_i denotes an orbital product of a configuration. In both cases, the fixed-node energy is dependent only on the orbital part of the trial wave function.

For this type of trial wave function, the nodal error is typically more than an order of magnitude smaller than the correlation energy but it is still significantly larger than chemical accuracy of 1 kcal mol⁻¹. The accurate determination of energy differences corresponding to dissociation energies, ionization potentials, and electron affinities with a fixed-node QMC method depends therefore on the efficient cancellation of the nodal error, making it important to control the nodal error. Like the standard basis sets and standard methods of the common analytic calculations "standard nodal surfaces" seem to be necessary for well-defined calculations of fixed-node energies.

Both forms for the trial wave function offer the possibility of using orbitals from standard *ab initio* calculations combined with a correlation factor that may be optimized with a Monte Carlo method. The fixed-node energy $E_0^{(\text{FN})}$ is then

well defined in terms of the basis set and the method (HF or MCSCF) of a short analytical calculation. QMC methods have been used to optimize the MO's or the CI coefficients of a multiconfiguration wave function with respect to the variance, but a reduction of the variance does not necessarily cause a reduction of the nodal error.¹¹ Additionally, the variance minimization is a nonlinear problem with many parameters if the MO's are to be optimized. Typically, there will be many shallow local minima and the nodal error will be dependent on the optimization procedure and the random samples.

In this work, we used orbitals of near HF-limit quality to determine the nodal surfaces and calculated the corresponding fixed-node energies for the first-row atoms and hydrides. The nodal errors are calculated using new estimates of the nonrelativistic ground state energies for both the atoms and hydrides. The dissociation energies are obtained from the fixed-node energies. For Be and BeH we also calculated the fixed-node energies for small MCSCF wave functions used as trial functions defining the nodes.

III. CALCULATIONS

The VQMC calculations were carried out using the generalized Metropolis algorithm with the proposed moves determined by the drift-diffusion algorithm, and the DQMC calculations were carried out using a modified form of the standard drift-diffusion algorithm.⁸ The walkers were assigned a weight and were split or joined when the weight became larger or smaller than given thresholds as suggested by Umrigar, Nightingale, and Runge.¹² We also used a cutoff term for the drift term as suggested by DePasquale, Rothstein, and Vrbik.¹³

For the correlation factor e^U , we employed a form of U_{aij} given by Schmidt and Moskowitz¹⁴ and based on that developed by Boys and Handy for transcorrelated wave functions¹⁵

$$U_{aij} = \sum_k^{N_a} c_{ka} (\bar{r}_{ai}^{-l_{ka}} \bar{r}_{aj}^{-m_{ka}} + \bar{r}_{aj}^{-l_{ka}} \bar{r}_{ai}^{-m_{ka}}) \bar{r}_{ij}^{-n_{ka}}, \quad (3.1)$$

where a and i, j refer to the nuclei and the electrons, respectively, and where \bar{r} is defined by $\bar{r} = br / (1 + br)$. Different values of b were chosen for \bar{r}_{ij} and \bar{r}_{ai} .

The orbitals ϕ_i for the atoms were taken from the Hartree-Fock STO wave functions of Clementi and Roetti.¹⁶ For the molecules we modified the STO basis set from Cade and Huo¹⁷ by using the same orbital exponents for σ and π -type orbitals and by dispensing with the f -type atomic orbitals. After expanding the STO's into 10 (for 1s) to 6 (for 3d) GTO's we obtained the MO coefficients for the STO basis with GAMESS.¹⁸ Experimental bond lengths were used. The resulting RHF/ROHF energies are within 2 kcal mol⁻¹ of the HF-SCF limit for each molecule and the corresponding Slater determinants are believed to yield nodal errors indistinguishable at the present accuracy from the nodal error for the exact HF-SCF wave functions.

The correlation function for the atoms was the 9-term function with four electron-electron, three electron-nucleus,

TABLE I. Ground state and correlation energies for first-row atoms: exact nonrelativistic (E_{nr}), RHF/ROHF-limit (E_{SCF}), VQMC (E_{VQMC}), DQMC (E_{DQMC}) energies, and total correlation energies CE_{total} with the percentage of CE obtained with DQMC.

	E_{nr}^a (hartrees)	E_{SCF}^a (hartrees)	E_{VQMC}^b (hartrees)	E_{DQMC} (hartrees)	CE_{total} (mhartrees)	CE_{DQMC} (%)
Li(2S)	-7.478 06	-7.432 73	-7.4731(6)	-7.478 03(5)	45.33	99.9(1)
Be(1S)	-14.667 36	-14.573 02	-14.6332(8)	-14.657 6(4)	94.34	89.7(4)
		-14.616 64 ^c	-14.6588(8) ^d	-14.667 2(2) ^d		99.8(2)
B(2P)	-24.653 93	-24.529 06	-24.6113(8)	-24.640 8(4)	124.8	89.5(3)
C(3P)	-37.845 0	-37.688 62	-37.7956(7)	-37.829 3(5)	156.4	90.0(3)
N(4S)	-54.589 3	-54.400 93	-54.5390(6)	-54.575 8(5)	188.4	92.8(3)
O(3P)	-75.067	-74.809 40	-75.0109(4)	-75.051 8(4)	258	94
F(2P)	-99.734	-99.409 35	-99.6685(5)	-99.717 6(3)	325	95

^aDavidson *et al.* (Ref. 20).

^bSchmidt/Moskowitz (Ref. 14).

^cMCSCF energy (see the text).

^dUsing MCSCF trial wave function.

and two electron–electron–nucleus terms from Schmidt and Moskowitz.¹⁴ The corresponding correlation functions for the hydrides consisted of 14 terms and were optimized with respect to the variance using iterative fixed samples.¹⁴ Both the linear coefficients c_{ka} and the nonlinear parameters b were optimized. For the optimization we used the Levenberg–Marquardt method¹⁹ that requires only the gradient of the parameters but converges like a Newton–Raphson-based method. Only one or two iteration steps were required for the variance to be sufficiently converged.

The correlation factor of Schmidt and Moskowitz performs as well for the hydrides as it does for the atoms and recovers from 63% of the correlation energy for BeH to 78% for FH (see Tables I and II) in VQMC calculations.

For Be and BeH we also employed a short multiconfiguration expansion multiplied by a correlation factor as trial wave function Ψ_T . For Be a four-CSF expansion resulting from an active space of ($2s, 2p$) was determined with GAMESS in an MCSCF calculation. The corresponding orbital space for BeH is ($2\sigma, 3\sigma, 1\pi$) resulting in six CSF's or six

pairs of determinants for the orbital part of Ψ_T . The MCSCF energies (see Tables I and II) correspond to 54% and 15% recovery of the correlation energies of Be and BeH, respectively. The high percentage for Be is due to the well-known near degeneracy of the $1s^2 2s^2$ and $1s^2 2p^2$ configurations.

The FN-DQMC calculations were carried out on the IBM SP2 machines of the Center for Academic Computing at the Pennsylvania State University and the Maui High Performance Computer Center. The VQMC calculations and the wave function optimization were done on an IBM RS/6000 workstation.

IV. RESULTS AND DISCUSSION

For the first-row atoms and hydrides we carried out VQMC and DQMC calculations using the trial wave functions described above. In order to obtain the fixed-node energy for the HF nodes we carried out DQMC calculations for several time steps τ and extrapolated with a quadratic polynomial to $\tau=0$. The time steps were chosen such that the

TABLE II. Ground state and correlation energies for first-row hydrides: exact nonrelativistic (E_{nr}), RHF/ROHF (E_{SCF}), VQMC (E_{VQMC}), DQMC (E_{DQMC}) energies, and total correlation energies CE_{total} with the percentage of CE obtained with DQMC. Experimental bond lengths have been used.^g

	E_{nr} (hartrees)	E_{SCF} (hartrees)	E_{VQMC} (hartrees)	E_{DQMC} (hartrees)	CE_{total} (mhartrees)	CE_{DQMC} (%)
LiH ($^1\Sigma^+$)	-8.070 21(5) ^a	-7.987 35 ^b	-8.0459(3)	-8.0701(2)	82.8	99.9(2)
BeH ($^2\Sigma^+$)	-15.246 8	-15.153 18 ^c	-15.212(1)	-15.2406(2)	93.6	93.5(2)
		-15.167 36 ^d	-15.2231(8) ^f	-15.2457(2) ^f		98.9(2)
BH ($^1\Sigma^+$)	-25.287 9	-25.131 95 ^e	-25.212(2)	-25.2759(5)	156.0	92.3(3)
CH ($^2\Pi$)	-38.478 7	-38.280 26 ^e	-38.425(2)	-38.4630(5)	198.4	92.1(3)
NH ($^3\Sigma^-$)	-55.220	-54.979 18 ^e	-55.162(2)	-55.2055(8)	241	93.9(3)
OH ($^2\Pi$)	-75.736 ₉	-75.422 19 ^e	-75.648(2)	-75.7213(8)	315	95.0(2)
FH ($^1\Sigma^+$)	-100.459 ₅	-100.071 85 ^e	-100.375(2)	-100.4429(6)	388	95.6(2)

^aChen/Anderson (Ref. 22).

^bHandy *et al.* (Ref. 23).

^cMontgomery/Ochterski/Petersson (Ref. 24).

^dMCSCF energy (see the text).

^ePeterson/Kendall/Dunning (Ref. 25).

^fUsing MCSCF trial wave function.

^gHuber/Herzberg (Ref. 26).

energy for smallest time step and the extrapolated value yielded overlapping error bars. We used eight time steps from 0.001 to 0.02 hartree⁻¹ for FH and time steps ranging from 0.001 to 0.1 hartree⁻¹ for Li. For all molecules except BH the coefficient for the linear term in the extrapolating polynomial was zero within the statistical uncertainty.

The results for both the VQMC and the DQMC calculations are given in Tables I and II. The uncertainties indicated correspond to one standard deviation in the last digit given. To determine the nodal error the exact nonrelativistic ground state energies are required. The most reliable determination of the nonrelativistic energies for the atoms is probably that by Davidson *et al.*²⁰ We list their values in Table I. A reliable theoretical determination of the nonrelativistic clamped-nucleus ground state energies of the hydrides to mhartree accuracy is considerably more difficult to obtain. For each of these we subtract the experimental dissociation energy D_e from the combined nonrelativistic ground state energies of the atoms. Assuming accurate values for the atoms, possible error may be due to finite mass, spin-orbit, or other relativistic contributions to the experimental dissociation energy D_e . The spin-orbit effects have been calculated and only in the case of FH has a significant contribution (0.38 kcal mol⁻¹) been found.²⁵ In Table IV we list the corrected, “nonrelativistic,” value for the dissociation energy of FH used to determine the nonrelativistic ground state energy of -100.460 hartree in Table II. The experimental dissociation energies of BH and NH have, to our knowledge, not yet been measured with the accuracy achieved for the other hydrides. The difficulty for BH is a barrier in the A ¹Π state. A new evaluation of the barrier height yields for BH $D_e=84.1$ kcal mol⁻¹²⁸ whereas Bauschlicher *et al.*³¹ obtain an estimate of 84.8 ± 0.5 kcal mol⁻¹ using a theoretical determination of the barrier height. The first value is used here to calculate the nonrelativistic energy for BH listed in Table II. Since the experimental dissociation energy of NH is known only to be in the range 80.5–84.7 cm⁻¹²⁹ we use the theoretical estimate of 82.3 ± 0.7 kcal mol⁻¹ by Bauschlicher and Langhoff³² to obtain the estimate $E_{nr}=-55.220$ hartree for the ground state energy of NH.

In Tables I and II we list, in addition to the ground state energy, the correlation energy and the percentage of the correlation energy recovered by the FN-DQMC calculation. The fixed-node energies are for all systems among the lowest variational total energies found in the literature. The lowest percentage of the correlation energy is obtained for the Be and B atoms. In both cases the well-known near-degeneracy of the $2s^2-2p^2$ configurations result in unusual large correlation energies and considerably smaller contributions of the HF configuration to the exact wave function. The nodal errors for atoms and hydrides are shown in Table III and Fig. 1. The error bars given for the larger systems are due to uncertainties in the nonrelativistic energies.

The results for the Li and Be atom are special because their fixed-node energies are independent of the orbitals. It is remarkable that the nodal error for Li is less than 0.1 mhartree whereas the nodal error for Be is about 10 mhartree. Including the $2p^2$ configuration for the Be atom reduces the

TABLE III. DQMC nodal errors E_{node} for SCF wave functions for first-row atoms (A) and hydrides (AH), and their difference ΔE_{node} .

A	E_{node} (A) (mhartrees)	E_{node} (AH) (mhartrees)	ΔE_{node} (mhartrees)
Li	0.03(5)	0.1(2)	0.1(2)
Be	9.8(4)	6.2(5)	-3.6(6)
	0.2(2) ^a	1.1(2) ^a	0.8(3) ^a
B	13.1(4)	12.0(5)	1.1(6)
C	15.7(5)	15.7(5)	0.0(7)
N	13.5(5)	[14.5]	...
O	15.2	15.6	0.4(9)
F	16.4	16.6	0.2(7)

^aUsing MCSCF functions.

nodal error to 0.2 ± 0.2 mhartree and the fixed-node energy to -14.6672(2) hartree. This result is consistent with a more accurate calculation by Umrigar, Nightingale, and Runge¹² who obtained -14.66719(3) hartree for the Be ground state energy. For BeH, we obtained with the multiconfiguration trial wave function $E_0^{(\text{FN})}=-15.2458(3)$ hartree which is, to our knowledge, the lowest calculated variational energy for this molecule to date. Our total energies are consistent with the fixed-node results of Subramaniam *et al.*⁴ but have error bars that are more than an order of magnitude smaller.

The values in Table I–III show that while the correlation energy increases strongly with the number of electrons and the nuclear charge the nodal error increases only slowly such that the fixed-node energies of FH, OH, and F recover 95% of the correlation energy.

In Table IV, the experimental dissociation energies D_e are compared with the dissociation energies obtained from FN-DQMC, from VQMC, and from other *ab initio* calculations. The VQMC dissociation energies show inconsistent deviations from the exact values and are less accurate than the 20-year-old calculations of Meyer and Rosmus²¹ in spite the fact that the VQMC total energies are comparable to the most accurate *ab initio* results. For NH, we obtain with VQMC $E_0=-55.162(2)$ hartree compared to E_0

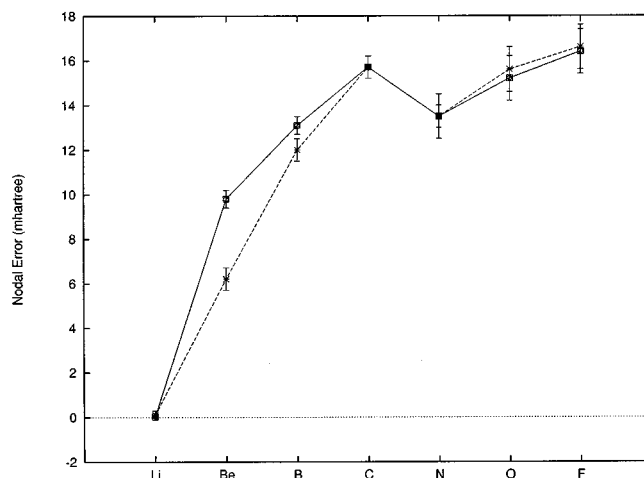


FIG. 1. DQMC nodal errors E_{node} for SCF wave functions for first-row atoms (solid line) and hydrides (dashed line).

TABLE IV. Dissociation energies D_e in kcal mol⁻¹ calculated with QMC compared with experimental and selected other theoretical results.

	Experiment	DQMC	VQMC	Other theory
LiH	58.00 ^a	57.8(1)	45.7(4)	57.2 ^f
BeH	49.8(3) ^b	52.1(3)	49.4(8)	49.6, ^f 49.8 ^g
		49.3(2)	40.3(7)	
BH	84.1 ^c	84.8(4)	63(1)	80.5, ^f 84.35, ^b 84.4 ⁱ
CH	83.9 ^a	83.9(4)	81(1)	80.0, ^f 82.9, ⁱ 83.3, ^j 81.3 ^k
NH	80.5–84.7 ^d	81.4(5)	77(1)	77.9, ^f 81.4, ⁱ 81.8, ^j
OH	106.6 ^a	106.4(5)	86(1)	100.1, ^f 105.0, ⁱ 105.6 ^j
FH	141.5 ^e	141.3(4)	130(1)	134.4, ^f 138.8, ⁱ 141.3, ^j 141.8 ^m

^aHuber/Herzberg (Ref. 26).^bColin/Dreze/Steinhauer (Ref. 27).^cPersico (Ref. 28).^dHofzumahaus/Stuhl (Ref. 29).^eZemke (Ref. 30), corrected for spin-orbit effect.^fMeyer/Rosmus (Ref. 21).^gMontgomery *et al.* (Ref. 24).^hBauschlicher/Langhoff/Taylor (Ref. 31).ⁱPeterson/Kendall/Dunning (Ref. 25).^jBauschlicher/Langhoff (Ref. 32).^kBauschlicher/Langhoff (Ref. 33).^lPeterson/Dunning (Ref. 34).^mBartlett (Ref. 35).

= -55.154 08 as the estimated complete basis set limit for a CAS+1+2 calculation from Peterson, Kendall, and Dunning (PKD).²⁵ The VQMC dissociation energy $D_e = 77(1)$ kcal mol⁻¹ on the other hand is 5 kcal mol⁻¹ below the estimated value of 82.3 ± 0.7 kcal mol⁻¹ whereas PKD obtain very good agreement with the FN-DQMC result and the estimate. The inconsistency of the VQMC results is probably due to the inadequacy of the optimization process because the trial wave functions are for practical reasons optimized with respect to small variance instead of low energy. Due to the statistical nature of the optimization process the variance was not well enough converged to ensure convergence of the variational energies to better than 1 mhartree. Larger samples in the optimization process will be necessary for better convergence.

The FN-DQMC results in Table IV have error bars of less than 0.5 kcal mol⁻¹ and are, with one exception, in perfect agreement with the experimental data. For the exception, BeH, agreement can be obtained after inclusion of the configurations resulting from the $1s^2 2p^2$ configuration on Be. A comparison with recent *ab initio* calculations shows that the accuracy of the FN-DQMC results can be matched only by the most sophisticated methods. Compared with most calculations our approach is very straightforward. The FN-DQMC dissociation energy for FH has already been discussed⁵ and is in perfect agreement with experiment and recent calculations. For OH, the error bar of our value $D_e = 106.4(5)$ kcal mol⁻¹ again includes the experimental value of 106.6 kcal mol⁻¹, while in recent MRCI calculations with very large basis sets PKD obtained 105.0 kcal mol⁻¹ and Bauschlicher and Langhoff³² calculated 105.6 kcal mol⁻¹. Adding the Davidson correction, PKD obtain 106.3 kcal mol⁻¹. For NH our result is slightly above the estimate 82.3 ± 0.7 kcal mol⁻¹ of Bauschlicher and Langhoff,³² but in excellent agreement with the calculated dissociation energies of PDK

and Bauschlicher and Langhoff. For CH our agreement with experiment is perfect. BL and PKD calculate D_e values slightly above ours. For BH our calculated dissociation value 84.8(3) kcal mol⁻¹ is slightly below the corrected experimental value 84.1 kcal mol⁻¹ determined by Persico,²⁸ but matches the recommended value 84.8(5) kcal mol⁻¹ by Bauschlicher, Langhoff, and Taylor.³¹ For BeH our dissociation energy is 2 kcal mol⁻¹ off the experimental value using the SCF nodes, but in excellent agreement when using MC-SCF nodes.

In conclusion, we have been able to obtain the dissociation energies D_e for the first-row hydrides in a very straightforward way with accuracies of about 0.5 kcal mol⁻¹ or better using the FN-DQMC method and nodal surfaces given by near HF-limit wave functions.

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