Efficient protocol for quantum Monte Carlo calculations of hydrogen abstraction barriers: Application to methanol

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Abstract

Accurate calculation of hydrogen abstraction reaction barriers is a challenging problem, often requiring high level quantum chemistry methods that scale poorly with system size. Quantum Monte Carlo (QMC) methods provide an alternative approach that exhibit much better scaling, but these methods are still computationally expensive. We describe approaches that can significantly reduce the cost of QMC calculations of barrier heights, using the hydrogen abstraction of methanol by a hydrogen atom as an illustrative example. By analysing the combined influence of trial wavefunctions and pseudopotential quadrature settings on the barrier heights, variance, and time-step errors, we devise a simple protocol that minimises the cost of the QMC calculations while retaining accuracy comparable to large-basis coupled cluster theory. We demonstrate that this protocol is transferable to other hydrogen abstraction reactions.

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1 INTRODUCTION

Hydrogen abstraction reactions play important roles in many branches of organic chemistry, from the combustion of hydrocarbons¹ to damage in DNA as an indirect consequence of exposure to ionising radiation². Accurate calculations of reaction barrier heights are required to build kinetic models for these processes, however chemically reliable results often require a high-level treatment of electron correlation effects. This is illustrated by the H abstraction of methanol by an H atom, which has two main reaction channels,

with CH_2OH as the dominant product. These reactions are known to be important in the combustion of methanol under fuel-rich conditions³, and have been studied using a wide range of theoretical methods⁴⁻⁹. Despite the apparent simplicity of this system, studies have shown that accurate calculations of the barrier heights require methods that scale as a large power of the system size⁶, and that there are large discrepancies between methods. The performance of both MP2 theory and the popular B3LYP density functional¹⁰ are particularly poor for this system.

Real-space quantum Monte Carlo (QMC) methods offer a stochastic alternative to traditional high-level electronic structure methods, and have been shown to be highly accurate for energetic^{11,12} and structural properties¹³. The main advantages of QMC methods over more widely-used alternatives such as coupled cluster theory are their low scaling with system size (N^{3-4}), and their immense parallelisability¹⁴. Despite these advantages there have been relatively few QMC calculations of H abstraction barrier heights. The earliest example, of the reaction $\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2$ ^{15,16}, has very recently been revised to even higher accuracy¹⁷. Other examples include the reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$,¹⁸ and a study by Kollias *et al.* of the H abstraction of methanol by a Cl atom, which showed agreement with MP2 calculations¹⁹. More recent examples include the H abstraction by styrene of the H-terminated Si(001) surface²⁰, and calculations of the barrier heights of three H-transfer reactions involving small molecules²¹.

In order to achieve resolutions of chemical accuracy in the barrier heights, statistical uncertainties in the stochastic QMC energies need to be on the order of fractions of a kcal/mol. Even though QMC scales well, this need for small uncertainties makes the calculations computationally expensive. As with other electronic-structure theories, efficient use of QMC methods requires a number of methodological choices to be made, including the choice of trial wavefunction and treatment of non-local pseudopotentials. Wavefunction choice is often discussed in reports of QMC calculations, but the effects of the parameters governing the treatment of pseudopotentials, including quadrature grids and cutoffs, are rarely mentioned.

In this work we investigate the impact of these choices, and their mutual interactions, ~~by performing a detailed study of the barrier heights of H abstraction in methanol by an H atom.~~ We show that significant cost savings can be achieved, while still obtaining accurate barrier heights. In addition, we demonstrate that the approach is transferable, by evaluating the barrier heights of four unrelated H abstraction reactions. This enables a more black-box approach to be taken in similar QMC calculations.

2 METHODS

The forward (F) and reverse (R) barrier heights of the reactions shown in Eqs. (1,2) are defined as the total energy differences

$$V_{1F} = E(\text{TS1}) - E(\text{CH}_3\text{OH}) - E(\text{H}) \tag{3}$$

$$V_{1R} = E(\text{TS1}) - E(\text{CH}_2\text{OH}) - E(\text{H}_2) \tag{4}$$

$$V_{2F} = E(\text{TS2}) - E(\text{CH}_3\text{OH}) - E(\text{H}) \tag{5}$$

$$V_{2R} = E(\text{TS2}) - E(\text{CH}_3\text{O}) - E(\text{H}_2) \tag{6}$$

where TS1 and TS2 are the transition-state structures for the reactions. ~~The molec-ular geometries for were obtained~~ from B3LYP calculations with the Roos augmented triple-zeta (ATZ) basis set²², using Gaussian09²³.

Practical QMC calculations require user-defined trial wavefunctions. The complexity of these wavefunctions strongly influence the computational cost of the calculations. Complicated wavefunctions are more expensive to optimise and evaluate at each Monte Carlo step, but more accurate wavefunctions lower the variance of the energy and therefore require fewer Monte Carlo steps to obtain a given statistical accuracy. In addition, the nodal surface of the wavefunction (the hypersurface on which it equals zero, and across which it changes sign) determines the systematic errors in fixed-node Diffusion Monte Carlo (DMC) calculations. The trial wavefunctions employed here have the Slater-Jastrow form,

$$\Psi_T = e^J D^\uparrow D^\downarrow \quad (7)$$

where the $D^{\uparrow,\downarrow}$ are Slater determinants constructed from single-particle orbitals, and J is a Jastrow factor containing explicit electron correlation terms.

The Jastrow factor we use is a sum of electron-electron (ee), electron-nucleus (eN), and electron-electron-nucleus (eeN) terms,

$$J = \sum_{i>j} \sum_A [J_{ee}(r_{ij}) + J_{eN}(r_{iA}) + J_{eeN}(r_{iA}, r_{jA}, r_{ij})] \quad (8)$$

where i, j label electrons, and A labels nuclei. These terms were constructed as compactly-supported natural polynomial expansions in the electron-electron and electron-nucleus distances,

$$J_{ee}(r_{ij}) = f(r_{ij}; L^{ee}) \sum_{l=0}^{N_{ee}} \alpha_l r_{ij}^l \quad (9)$$

$$J_{eN}(r_{iA}) = f(r_{iA}; L^{eN}) \sum_{l=0}^{N_{eN}} \beta_{l;A} r_{iA}^l \quad (10)$$

$$J_{eeN}(r_{iA}, r_{jA}, r_{ij}) = f(r_{iA}; L^{eeN}) f(r_{jA}; L^{eeN}) \sum_{l,m,n=0}^{N_{eeN}} \gamma_{lmn;A} r_{iA}^l r_{jA}^m r_{ij}^n \quad (11)$$

where L is the cutoff range, and $\{\alpha, \beta, \gamma\}$ are optimisable parameters. The cutoff function $f(r; L)$ is a C^2 -smooth Wendland function²⁴ which goes to zero at L ,

$$f(r; L) = \begin{cases} \left(1 - \frac{r}{L}\right)^4 \left(1 + 4\frac{r}{L}\right) & 0 \leq r \leq L \\ 0 & r > L \end{cases} \quad (12)$$

All the calculations presented here use fixed ranges of $L = 5$ Bohr. The relevant symmetries, electron-electron cusp condition, and the electron-nucleus no-cusp conditions were enforced by constraining the optimisable parameters in the Jastrow factor. We used the method described in the appendix of Ref.²⁵ for the more complicated eeN term. The free parameters in the Jastrow factor were optimised by minimising the total energy at the Variational Monte Carlo (VMC) level, using the linear method of Toulouse and Umrigar²⁶.

The orbitals used in the Slater determinants were taken from B3LYP calculations. Although the orbitals themselves contain no description of electron correlation, it has been shown that using orbitals from a correlated method such as B3LYP results in better QMC energies than using Hartree-Fock orbitals²⁷. For all-electron calculations using the full electron-ion Coulomb potential, the orbitals were expanded in the Gaussian-type Roos ATZ basis set²², and cusp-corrected using a standard approach²⁸.

In addition to all-electron calculations, we also used non-local pseudopotentials to represent the ionic cores. The use of pseudopotentials can greatly reduce the cost of QMC calculations, as the removal of the chemically inert core electrons reduces the fluctuations in the local energy. Evaluation of the local energy requires the non-local potential to be projected onto the trial wavefunction. Following Mitas *et al.*²⁹, for each ion the contribution to this projection from an electron labelled i can be written as a sum over angular momenta l ,

$$\left(\frac{\hat{V}_{nl}\Psi_T}{\Psi_T} \right)_i = \sum_l \frac{(2l+1)}{4\pi} v_l(r_i) \int_{4\pi} P_l[\cos \theta_{i'}] \frac{\Psi_T(\dots, \mathbf{r}'_i, \dots)}{\Psi_T(\dots, \mathbf{r}_i, \dots)} d\Omega'_i \quad (13)$$

where v_l is the angular-momentum dependent radial potential, and the integral is over the surface of a sphere of radius r_i centred on the ion. In practice the integral is evaluated using a deterministic approach,

$$\int_{4\pi} f(\mathbf{r}'_i) d\Omega'_i \approx \sum_k^{N_Q} w_k f(\mathbf{r}_k) \quad (14)$$

where the N_Q weights w_k and points $\mathbf{r}_k$ are chosen according to a Gaussian quadrature rule, with values taken from Ref.²⁹. This projection must be evaluated for each electron within range of each ion, at each step of the DMC calculation, so the number of quadrature points and the range of the radial potentials can have a large impact on the cost of the

QMC calculation. We compared the effect of using two different pseudopotentials, both of which were explicitly constructed for use in QMC calculations, but using different methods. Both are Hartree-Fock pseudopotentials including scalar relativistic effects, but the Trail-Needs (TN)³⁰ potentials are shape-consistent, whereas the Burkatzki-Filippi-Dolg (BFD)³¹ potentials are energy-consistent. Our BFD calculations used the associated valence triple-zeta (VTZ) basis sets, and an improved H-atom potential³². Calculations with the TN potentials used the aug-cc-pVTZ-CDF basis set from Ref.³³.

Non-local pseudopotentials were treated beyond the locality approximation in DMC using the size-consistent T-moves approach³⁴. Imaginary time-step sizes of $\tau = (0.04, 0.02, 0.01, 0.005)$ a.u. were used for pseudopotential calculations. Smaller time-step sizes are required for all-electron calculations, and in this case values of $\tau = (0.02, 0.01, 0.005, 0.001)$ a.u. were used. All DMC energies were extrapolated to $\tau = 0$ using quadratic fits. Target population sizes of 8000 walkers were used in all DMC calculations. All the QMC calculations were performed using the CSIRO Quantum Monte Carlo code³⁵.

Forward and reverse barrier heights are not directly available from experiment. The highest level theoretical results available in the literature use coupled cluster methods, so to compare with these we also performed coupled cluster calculations using the CCSD(T) approach. These were performed using Molpro³⁶ with Dunning’s aug-cc-pVQZ basis set³⁷ and an unrestricted Hartree-Fock reference state.

Finally, we evaluated the accuracy of density functional theory using 12 different exchange-correlation functionals. The types of functionals chosen were the local density approximation (LDA³⁸), generalised gradient approximation (GGA) functionals (BLYP^{39,40}, PBE⁴¹, B97D3⁴²), meta-GGAs (TPSS⁴³, M06L⁴⁴), hybrid GGAs (B3LYP¹⁰, PBE0⁴⁵), hybrid meta-GGAs (B1B95⁴⁶, MPW1B95⁴⁷), and double hybrids (B2PLYP⁴⁸, mPW2PLYP⁴⁹).

3 RESULTS AND DISCUSSION

Barrier heights calculated using ~~density~~ functional, CCSD(T), and QMC methods are compared against results from the literature in Table 1.

Our CCSD(T) results, calculated at the B3LYP geometries, agree closely with previous

calculations. When compared against the results of Carvalho *et al.*⁸, who used CCSD(T)/cc-pVTZ geometries, the largest deviation we observe is only 0.3 kcal/mol. This demonstrates the accuracy of the B3LYP geometries, despite the inability of that level of theory to predict accurate barrier heights.

None of the exchange-correlation functionals we used are able to recover all the barrier heights to within chemical accuracy of the CCSD(T) reference values. The most accurate functionals are the double-hybrids, which perform well for the forward barriers. However, the reverse barrier V_{2R} deviates from the reference CCSD(T) value by over 5 kcal/mol. There is significant variation of barrier heights, even within the same class of functionals. For example, the forward barrier heights obtained using the meta-GGA functionals TPSS and M06L differ by around 7 kcal/mol. The extreme variability in the accuracy of the different density functionals emphasises the need for extensive benchmarking using higher level methods.

All-electron QMC calculations were performed using the complete Jastrow factor shown in Eq. 8, including the eeN terms. The barrier heights obtained using this method agree closely with the CCSD(T) results, for all but the V_{2F} barrier, where there is a difference of just over 1 kcal/mol. This disagreement is potentially due to the presence of non-dynamical correlation effects. The T_1 diagnostic⁵⁰ is a widely-used indicator of non-dynamical effects in coupled-cluster calculations. Typically, T_1 values of 0.02 or greater are taken as an indication that a single determinant reference state is insufficient, though some researchers suggest this value should be higher for open-shell systems⁵¹. Nearly all of the structures have small T_1 values, the exceptions being CH_3O (0.021) and TS2 (0.032).

Reference pseudopotential QMC results were obtained using both BFD and TN pseudopotentials, with the same sized Jastrow factor used in the all-electron calculations. The barrier heights are all within two standard deviations of the all-electron results. These pseudopotential calculations are actually more expensive per Monte Carlo step than the all-electron approach (1.54x, for the DMC calculation of CH_3OH), due to the need to repeatedly evaluate the integral in Eq. 13. The cost benefits of the pseudopotential approach come from the ability to use larger imaginary time-step sizes, and the reduced variance of the energy. As an example, for a fixed time-step size of $\tau = 0.005$ a.u., the BFD calculation of CH_3OH

is over 20% faster than the all-electron calculation, to obtain the same statistical accuracy. This reduction in cost will be significantly larger for systems containing heavier elements.

3.1 Approximations

To further reduce the computational cost of the QMC calculations, we investigated the effect of reducing both the complexity of the Jastrow factor and the treatment of the pseudopotentials. Dubecký *et al.*⁵² have shown that for noncovalent interactions a two-body Jastrow factor is sufficient, and we consider the same modification here, removing the most expensive eeN terms. For the pseudopotentials, we reduced the number of quadrature points in the evaluation of Eq. 13, and also reduced the range of both the local and non-local radial potentials. The notation used to define these settings is $x.y.z$. Here x denotes the size of the Jastrow factor, which is either 2J (indicating use of ee and eN terms) or 3J (indicating use of ee , eN , and eeN terms). The number of points used in the quadrature grid (N_Q in Eq. 14) is given by y . We used $y = 4$ tetrahedrally distributed points, and $y = 12$ icosahedrally distributed points, with the locations of the points on the unit sphere taken from Ref.²⁹. Finally, z is a parameter which determines the ranges of the radial parts of both the local and non-local pseudopotentials. The ranges r of the local potentials are chosen such that r is the point furthest from the nucleus which deviates by more than 10^{-z} from the bare Coulomb potential. Similarly, the range of the radial part of a non-local potential is defined as the point furthest from the nucleus which deviates by more than 10^{-z} from zero. The potentials are set to zero outside these ranges. This method of defining the ranges leads to different values for each element and for both types of pseudopotential used. For the elements considered here, the BFD potentials are shorter ranged than the TN potentials for each of our choices of $z = 8, 5, 3$. Using this notation, the settings used for the reference pseudopotential calculations in Table 1 are 3J.12.8.

3.2 Accuracy

As shown in Fig. 1, the different settings used for the Jastrow factor and pseudopotentials have very little effect on the predicted barrier heights. The majority of settings result in

no statistically significant change, and the largest changes are less than 1 kcal/mol. Overall the deviations from the reference values are statistically equivalent for both types of pseudopotential considered.

3.3 Cost

Despite the relatively insignificant changes in the barrier heights, the reduced settings can have a very strong effect on the computational cost of the QMC calculations. The timings for a complete DMC calculation of CH₃OH, relative to the reference settings using the BFD pseudopotentials, are shown in Fig. 2.

The largest time saving comes from eliminating the eeN terms in the Jastrow factor, which makes the DMC calculation of CH₃OH 3x faster per Monte Carlo step. This simplified Jastrow factor increases the variance of the local energy (see Sec. 3.4), but even when this effect is taken into account, we still obtain a speedup of around 2.5x for the time to achieve a fixed statistical accuracy in the total energy.

The next most important speedup comes from reducing the number of points in the quadrature grids. Evaluating the projection of the non-local operator onto the trial wavefunction requires multiple evaluations of the wavefunction ratio with the position of one electron moved. Even when using efficient methods for calculating this ratio, reducing the number of quadrature points from 12 to 4 results in a speedup of 1.7x when using the simpler 2J Jastrow factor. Reducing the ranges of the local and non-local parts of the pseudopotentials also reduces the cost of the calculations, but the improvement obtained is much smaller than when simplifying the Jastrow factor or reducing the number of quadrature points. When combined, all three measures provide a speedup greater than 5x, with no reduction in the quality of the barrier heights.

Our calculations using the TN pseudopotentials were always more expensive than when using the BFD potentials, as shown in Fig. 2. There are a number of reasons for this, the most important being simply the size of the one-electron basis set used to construct the B3LYP orbitals in the trial wavefunction. When expressed in spherical harmonic (as opposed to Cartesian) Gaussians, the CDF basis set used with the TN potentials has 35% more primitives than the BFD basis set. There is also some contribution from the fact that

the TN potentials contain a non-local term for H. The TN potentials contain s , p , and d channels for each element used in this work. The BFD potentials contain only s and p channels for C and O species, and only a local component for H. Finally, in the Gaussian representation of the pseudopotentials we used, the TN potentials contain many more terms than the BFD potentials. This has a very small effect on the cost, but it could be eliminated by representing both potentials on a radial grid.

3.4 Variance

Reducing the complexity of the trial wavefunction by removing the eeN terms from the Jastrow factor leads to an increase in the variance of the local energy, shown in Fig. 3. The results shown here are for energy-optimised trial wavefunctions. It should be possible to obtain lower variances by explicitly minimising the variance of the local energy rather than the total energy, though the gains are likely to be small.

Reducing the number of points in the quadrature grid has no effect on the variance when using the BFD pseudopotentials, but results in a 5% increase in the variance when using the TN potentials. This is likely due to the different angular momenta used in the construction of the different potentials. As mentioned above, the TN pseudopotentials use higher angular momentum terms than the BFD potentials, and so one would expect them to require a higher order quadrature rule. However, the effect is small, and does not translate in any statistically significant way to the quality of the energy barriers as shown in Fig. 1. Reducing the ranges of the local and non-local radial potentials has no noticeable effect on the variance for either type of pseudopotential.

3.5 Time-step error

The changes to the Jastrow factor and treatment of pseudopotentials also have an effect on the time-step error in DMC, as shown in Fig. 4. We used a non-symmetric branching factor in our DMC calculations with T-moves, which results in large time-step (τ) errors, but with a predominantly linear behaviour that is easily extrapolated to $\tau = 0$. Using a symmetric branching factor does result in a smaller error for a given value of τ , but in practice we

have frequently observed that the increased curvature means that reliable extrapolation to $\tau = 0$ still requires relatively small values of τ . Using symmetric branching with T-moves is slightly more expensive than non-symmetric branching, as it requires a second evaluation of the local energy at each DMC step if a T-move is accepted. Our current approach is to use non-symmetric branching if performing a full extrapolation to $\tau = 0$, and to use symmetric branching if a single small value of τ is used.

As with the variance, the largest effect on the time-step error is the quality of the trial wavefunction. Using the larger 3J Jastrow factor results in smaller time-step errors than when using the 2J form. The quality of the Jastrow factor also has a small effect on the final $\tau = 0$ DMC energy, which comes from the projection of the non-local pseudopotential onto the trial wavefunction (Eq. 13).

The majority of the quadrature grid and cutoff settings result in time-step errors that are mutually indistinguishable. Using the simpler 2J Jastrow factor, the use of a short range in the pseudopotentials has a larger effect than the number of quadrature points. Using the shortest range (corresponding to $z = 3$) produces noticeably higher energies, regardless of the number of quadrature points used. As the difference in cost between using ranges corresponding to $z = 3$ and $z = 5$ is so small, it is safer to use the larger value, which has no visible effect on the time-step error.

3.6 Transferability

The results so far indicate that BFD.2J.4.5 is a reliable low-cost DMC protocol for calculating the barrier heights of the reactions (1) and (2). To assess its transferability to other systems, we compared it to the more expensive BFD.3J.12.8 protocol for four additional H abstraction reactions. These reactions were taken from the HTBH38/04 database⁵³ and include two reactions with the heavier elements S and Cl.

The results of these calculations are shown in Table 2, which lists the barrier heights relative to reference values obtained from a combination of theoretical and experimental results⁵⁴. Both DMC protocols obtain barrier heights within chemical accuracy (within statistical uncertainties) of the reference values. They also agree with each other to within a fraction of a kcal/mol, showing that the reduced BFD.2J.4.5 protocol is transferable to

other reaction barriers. The largest difference is in the forward barrier height for the reaction $\text{OH} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$, though at 0.54 kcal/mol, this is still less than 2 statistical error bars.

4 CONCLUSIONS

We have used real-space QMC methods to calculate the reaction barrier heights of the two main channels for H abstraction of methanol by an H atom, a problem that requires a high-level treatment of electron correlation effects. The combination of B3LYP geometries and QMC energies predicts barrier heights that agree with CCSD(T) values to within chemical accuracy.

The cost of the QMC calculations can be minimised by simplifying the trial wavefunction and the treatment of non-local pseudopotentials. The largest cost saving can be achieved by using a simple Jastrow factor that includes only two-body correlation effects. By combining this simplified trial wavefunction with a sparse quadrature grid in the projection of the non-local pseudopotential, and applying cutoffs to the ranges of these potentials, we were able to reduce the cost of DMC calculations by a factor of 5x over our reference calculations, with no loss in accuracy.

In the notation defined in Sec. 3, our recommended protocol is 2J.4.5, using the BFD pseudopotentials. ~~We have shown that this approach is transferable to similar problems, including reactions involving the heavier elements S and Cl. However, a caveat is that one should be careful with the choice of integration grids for systems containing much heavier elements.~~ These cases are likely to be more sensitive to the number of quadrature points due to the importance of larger angular momenta in the pseudopotentials.

Together with these cost-reducing measures, the accuracy, favourable scaling, and low memory requirements of QMC methods indicate this is a practical route to tackle H abstraction in much larger systems.

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Figure 1: Deviations of DMC barrier heights from the 3J.12.8 reference values, using ~~BFD and TN pseudopotentials for~~ different Jastrow factor and pseudopotential settings. The settings use the notation $x.y.z$, where x denotes the size of the Jastrow factor, y is the number of points used in the quadrature grid for evaluating non-local pseudopotentials, and z is a measure of the cutoff applied to the radial parts of the pseudopotentials. For more details see Sec. 3.

Figure 2: DMC Timings for CH_3OH relative to BFD.3J.12.8 settings. Solid points indicate relative times for a fixed number of Monte Carlo steps. Open points indicate relative times to achieve a fixed statistical uncertainty.

Figure 3: VMC variance of the local energy for CH_3OH using different settings for the Jastrow factor and pseudopotentials.

Figure 4: DMC energies as a function of imaginary time-step for the TS2 geometry, using the BFD pseudopotentials.

Figure 1
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Figure 2
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Method	V_{1F}	V_{1R}	V_{2F}	V_{2R}
LDA	-3.5	-0.1	1.8	-7.7
BLYP	1.1	12.0	3.3	6.5
PBE	2.0	8.3	5.7	3.2
B97D3	0.8	12.5	3.9	7.3
TPSS	-0.9	11.4	1.1	7.3
M06L	7.0	10.1	7.8	8.2
B3LYP	3.6	13.3	6.9	9.2
B3LYP/6-31+G(d,p) [6]	3.2	12.9	-	-
PBE0	5.5	11.0	10.4	8.0
B1B95	6.8	13.5	11.3	10.5
B1B95/MG3S [6]	7.0	13.5	-	-
mPW1B95	6.9	12.8	11.5	10.0
mPW1B95/MG3S [6]	7.1	12.9	-	-
B2PLYP	10.0	17.6	14.0	17.2
mPW2PLYP	9.8	17.0	13.9	16.7
MP2/6-31+G(d,p) [6]	16.8	18.0	-	-
CCSD(T)/aug-cc-pVQZ [6]	9.6	15.6	-	-
CCSD(T)/cc-pVQZ [8]	9.8	15.8	15.1	12.0
CCSD(T)/aug-cc-pVQZ	9.5	15.5	15.1	11.7
DMC (All-electron)	9.9(1)	15.5(1)	16.3(1)	12.1(1)
DMC (BFD)	9.8(2)	15.0(2)	15.9(2)	12.1(2)
DMC (TN)	9.9(2)	15.6(2)	15.7(2)	12.2(2)

Table 1: Reaction barrier heights for the H abstraction of methanol by an H atom (in kcal/mol) using different methods. Statistical uncertainties in the last digit of the DMC results are shown in parentheses. All DFT calculations used the Roos-ATZ basis, unless stated otherwise.

Reaction	BFD.3J.12.8		BFD.2J.4.5	
	ΔV_F	ΔV_R	ΔV_F	ΔV_R
$\text{H} + \text{HCl} \longrightarrow \text{H}_2 + \text{Cl}$	0.052(94)	-0.633(92)	0.02(12)	-0.89(12)
$\text{OH} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	0.59(17)	0.48(18)	1.14(22)	0.75(22)
$\text{H} + \text{H}_2\text{S} \longrightarrow \text{H}_2 + \text{HS}$	0.67(11)	0.77(11)	0.28(12)	0.42(12)
$\text{NH}_2 + \text{CH}_3 \longrightarrow \text{CH}_4 + \text{NH}$	0.63(13)	0.53(13)	0.48(17)	0.14(18)

Table 2: Deviation of forward (ΔV_F) and reverse (ΔV_R) reaction barrier heights (in kcal/mol) from reference values, using different DMC protocols. Statistical uncertainties in the last digit of the DMC results are shown in parentheses.