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Diffusion quantum Monte Carlo calculations with a recent generation of effective core potentials for ionization potentials and electron affinities

Xiaojun Zhou, Hewang Zhao, Ting Wang, and Fan Wang[*]
Institute of Atomic and Molecular Physics, Key Laboratory of High Energy Density Physics and Technology, Ministry of Education, Sichuan University, Chengdu, People's Republic of China

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Pseudopotentials are an essential ingredient in diffusion quantum Monte Carlo (DMC) calculations to increase efficiency substantially. A new generation of effective core potentials (ccECP) has been recently developed for DMC calculations. In this paper, performance of DMC using ccECP potentials on total energies, ionization potentials (IPs) and electron affinities (EAs) of some second- and third-row atoms and molecules is investigated systematically with different types of trial wave functions. DMC results are compared with those of high-level coupled-cluster methods extrapolated to complete basis set limit (CC-CBS). Error of ccECP potentials on IPs and EAs is also evaluated through a comparison with those from all-electron calculations. Our results show that mean errors in DMC energies with the ccECP potentials are smaller than those with the pseudopotentials developed by Burkatzki, Filippi, and Dolg (BFD), when the same type of trial wave functions is adopted. Mean absolute deviations (MADs) on IPs of DMC compared with those of CC-CBS are about 1.6 kcal/mol with single-determinant-Jastrow trial wave functions, and 1 kcal/mol with multideterminant-Jastrow trial wave functions using either ccECP or BFD potentials. MADs on EAs with DMC using the ccECP potentials are about 1 kcal/mol and slightly larger than those with the BFD potentials. Our results show that ccECP potentials are able to provide reliable IPs and EAs in DMC calculations. Accuracy of IPs and EAs from DMC calculations using ccECP potentials is similar to that with the BFD potentials, although mean error in total DMC energies with ccECP potentials is smaller. Furthermore, error of ccECP potentials in DMC calculations on IPs and EAs is smaller than that of BFD potentials compared with all-electron results.

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I. INTRODUCTION

The diffusion Monte Carlo (DMC) method [1–3] is a stochastic scheme that can yield accurate energies for correlated quantum systems. In electronic structure calculations, DMC presents an attractive alternative to traditional high-accuracy quantum chemistry methods due to its cubic scaling with system size and high parallel efficiency [3]. The DMC method has been implemented on massively parallel computers with more than 100 000 cores and its computational speedup scales essentially linearly with the number of cores [4]. These properties of DMC hold considerable promise for providing accurate electronic energies of large or complex systems. In practice, DMC tends to have a large cost prefactor and it is still very expensive, especially in all-electron calculations, despite its appealing cubic scaling.

Computational cost of DMC calculations grows [5] as $Z^{5.5-6.5}$, where Z is the nuclear charge, and DMC calculations on heavy-atom systems are costly. This is because fluctuations in the local energy tend to be large in the core region, although core electrons typically have little effect on most properties of interest. Accurate pseudopotentials (PPs) are thus important in DMC calculations to replace core electrons and substantially improve efficiency of calculations. It is worth noting that most PPs developed in traditional quantum chemistry retains a coulomb singularity at the nucleus, which results in large fluctuations of the local energy or even infinite variance in DMC calculations [6]. Nonsingular PPs have been proposed in several groups particularly for DMC calculations [7–11]. Trial and Needs established nondivergent Dirac-Fock spin-orbit averaged relativistic pseudopotentials [7,8] (TNDF) and new energy-consistent correlated pseudopotentials [11] (eCEPP). Burkatzki, Filippi, and Dolg (BFD) developed nonsingular energy-consistent scalar-relativistic Hartree-Fock (HF) pseudopotentials [9,10]. Other PPs that can be employed in DMC calculation also exist, but corresponding basis sets are lacking [12,13]. Even for the TNDF potentials, basis sets are only available for H and B-Ne and the eCEPP potentials are only developed for H and Li-F as well as transition-metal (Sc-Fe, Cu) atoms. BFD potentials are one of the most commonly used PPs in DMC calculations. Reasonable results are achieved using BFD potentials on such as atomization energies [14], bond dissociation energies [15,16], excited energies [17–23], noncovalent interaction energies [24,25], barrier heights [26,27] and reaction energies [26], as well as ionization potentials and electron affinities [19]. More recently, Bennett and coworkers have proposed a new generation of effective core potentials [28–30] (ccECP) for H-Kr together with the corresponding correlation consistent basis sets. The error of these ccECP potentials has been tested at the coupled cluster single double (triple) CCSD(T) level

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[*] Corresponding author: wangf44@gmail.com

of theory [28–30], and results with ccECP potentials show smaller errors for atomic spectrum and binding curve than those of BFD, TNDF, and eCEPP potentials [28]. However, error of PPs depends on the employed electronic structure approaches and it could be larger in DMC calculations than that at the CCSD(T) level due to the localization error [31]. The error of ccECP potentials in DMC calculations is not evaluated, except for two recent works on atomization energies [14] and hydrogen bonds [32]. It is thus important to investigate performance of ccECP potentials in DMC calculations.

Use of the nonlocal pseudopotentials is straightforward within variational Monte Carlo (VMC) calculations, but it is more problematic in DMC. In DMC calculations, the matrix element for the evolution of the imaginary-time diffusion is not necessarily positive and a sign problem will still be encountered with the fixed-node approximation [33,34]. The locality approximation [35,36] (LA) is employed to circumvent this difficulty, which is formally equivalent to a replacement of the nonlocal operator in the Hamiltonian with a local expression. Error in the DMC energy introduced through this approximation is proportional to the square of the trial wave-function error [36]. Unlike the case in standard DMC calculations, the resulting fixed-node energy with LA is not an upper bound to the exact energy. The T-move approximation [33,34] (TM) provides an alternative to LA, which incorporates the negative matrix elements of the nonlocal potential as an additional displacement step in the random walk, whereas the positive matrix elements are directly added to the local potential. This approach recovers the upper-bound property of the DMC energy and increases stability of calculations, but is computationally slightly more expensive than LA and usually has a larger time-step bias [2,34]. In addition, DMC energy is found to be more sensitive to the choice of the Jastrow factor and its optimization technique with LA than that using TM [15,37]. Previous DMC studies on transition metals showed that LA introduced nonsystematic errors of up to several tens of kcal mol^{-1} in the energy of Cu and CuH when a poor Jastrow factor is employed [15].

A trial wave function is generally required in DMC calculations to improve statistical efficiency through importance sampling. The fixed-node (FN) approximation [38] is usually adopted in DMC calculations to avoid the fermion sign problem. The FN-DMC energy depends on the node surface of the trial wave function. In most practical FN-DMC calculations, a trial wave function with the form of a product between an antisymmetric wave function and a symmetric Jastrow correlation function is adopted. It should be noted that the antisymmetric wave function describes basic properties of the wave function and the Jastrow factor provides a compact description on the dynamically correlated electronic motion [3]. The simplest antisymmetric wave function is a single determinant (SD) where the single-particle orbitals are taken from a HF or DFT calculation [39]. Other more complicated antisymmetric wave functions such as the multideterminant wave function [40], valence bond wave function [41], Pfaffian wave function [42], antisymmetrized geminal power wave function [43] and backflow transformed wave function [44] have also been employed to improve accuracy of FN-DMC results.

Ionization potentials (IPs) and electron affinities (EAs) for seven main-group atoms (C, N, O, Si, P, S, Cl) and seven related molecules (OH, O_2, PH, PH_2, SH, S_2, and Cl_2) are chosen as a benchmark set [45] by Truhlar *et al.* for testing exchange-correlation functions. To obtain reliable IPs and EAs, it is important to achieve total energies for the neutral and charged species with similar accuracy. IPs and EAs of some second- and third-row atoms have been calculated previously [46,47] using FN-DMC with either the single-determinant-Jastrow (SDJ) trial wave function or the multideterminant-Jastrow (MDJ) trial wave function. Those results show that FN-DMC calculations using an appropriate trial wave functions is able to provide reliable IPs and EAs for these atoms and results are even approaching chemical accuracy. In this paper, FN-DMC calculations using the newly developed ccECP potentials are carried out for ground state energies of these systems. Accuracy of ccECP potentials and BFD potentials in DMC calculations will be evaluated by comparing with all-electron results. Performance of FN-DMC with ccECP potentials using the TM and LA approach for the above neutral and ionic systems with UHF, ROHF, UB3LYP [48], ROB3LYP [48], CASCI [49] and CASSCF [49,50] wave function as the antisymmetrized part of trial wave functions will be evaluated by comparing with high level coupled-cluster results at the complete basis set limit and experimental values.

This article is organized as follows: theoretical methods and computational details are given in Sec. II. FN-DMC results using ccECP potentials and different types of trial wave functions are presented in Sec. III. We discuss effects of these trial wave functions using ccECP potentials on DMC energies, IPs and EAs, and compare ccECP results with those from BFD potentials using the TM and LA strategies as well as all-electron results. Conclusions are drawn in Sec. IV.

II. METHODS AND COMPUTATIONAL DETAILS

The Slater-Jastrow trial wave function employed in this work takes the following form:

$$\Psi_T^{\mathrm{SJ}}(\mathbf{R}) = \Phi_S(\mathbf{R}) e^{J(\mathbf{R})}, \tag{1}$$

where $J(\mathbf{R})$ is the Jastrow factor, Φ_{S} is a single determinant wave function or a multideterminant wave function. In SDJ trial wave functions, the orbitals are generated with the GAUSSIAN 09 program [51] via a UHF, ROHF, UB3LYP or ROB3YP calculation. For the MDJ trial wave functions, the orbitals and determinant coefficients in the multideterminant wave function are obtained using the PySCF program [52] via a CASCI or CASSCF calculation. All the determinants with an absolute weight coefficient larger than 0.002 are included in the trial wave function. Note that spin restricted open-shell B3LYP obitals are employed in CASCI calculations.

The Jastrow factor serves to introduce many-particle dynamic correlation effects and to enforce the electron-electron cusp condition. The electron-electron terms, the electron-nucleus terms, and the electron-electron-nucleus terms are included in the Jastrow factor adopted in this work and the detailed form for this correlation factor is reported in Ref. [39]. The Jastrow factor is important for improving computational efficiency and stability as well as time-step bias of FN-DMC calculations [3]. The FN-DMC energy is not influenced by the Jastrow factor in all-electron calculations, but this is not the case when PPs are employed because of an approximate treatment on the nonlocal part of PPs in FN-DMC [36]. Therefore, one needs to optimize the Jastrow factor more carefully to achieve reliable FN-DMC results when PPs are used.

The ccECP and BFD potentials are adopted for these elements, except for hydrogen in the present work. Previous work demonstrated that FN-DMC results are not very sensitive to the employed basis set [53] and the aug-cc-*pVTZ* basis set [9,10,28–30] developed for the ccECP and BFD potentials are chosen. It should be noted that diffuse basis functions with BFD potentials are taken from those in the all-electron aug-cc-*pVTZ* basis set [54]. The TM scheme is adopted to reestablish the variational principle and ensure computational stability in FN-DMC calculations with all types of trial wave functions. The LA scheme is also employed in FM-DMC calculations using UHF, UB3LYP, and CASSCF wave functions and their results are compared with those with the TM scheme. To obtain a quantitative estimate on errors of the ccECP potentials in DMC calculations, all-electron DMC calculations using the aug-cc-*pVTZ* basis set [54] are also carried out using the UB3LYP wave function. It should be noted that scalar relativistic effects are considered in ccECP and BFD potentials, but it is not included in all-electron calculations.

All the QMC calculations were carried out using the CASINO program [2]. The parameters in the Jastrow factor are optimized with an unweighted variance minimization [55] followed by an energy minimization [56]. Linear coefficients in MDJ are also optimized at the VMC level to achieve lower DMC energies. In the variance and energy minimizations, 20 000 configurations are used in each of eight optimization cycles. The best trial wave functions are subsequently adopted in FN-DMC calculations. To minimize time-step bias, we performed FN-DMC calculations at time steps of 0.02, 0.06, and 0.10 a.u. with PPs and 0.002, 0.006, and 0.010 a.u. in all-electron calculations. An additional time-step of 0.0002 a.u. is adopted for the third-row element systems in all-electron calculations to ensure a reliable extrapolation. Total energies were extrapolated to the zero time step by a quadratic fitting. In this work, the algorithm of Zen *et al.* is also employed in DMC calculations to reduce time-step error and restore size consistency [57].

Coupled-cluster theory [58] (CC) is a high-level quantum chemical approach for electronic energies. However, CC calculations become expensive if high level excitations are included in the cluster operator. It is also costly to perform high level CC calculations with sufficiently large basis sets. To obtain highly accurate energies, the basis-set extrapolation scheme described in Ref. [59] has been adopted to achieve high level CC energies at the complete basis set limit (CC-CBS) in this work. The following total energy expression is employed in the present work:

$$E = E_{\mathrm{HF}}^{\infty} + \Delta E_{\mathrm{CCSD(T)}}^{\infty} + \Delta E_{\mathrm{CCSDT}}^{\infty} + \Delta E_{\mathrm{CCSDT(Q)}}^{\infty} + \Delta E_{\mathrm{CCSDTQ}}^{D} + \Delta E_{\mathrm{core}}. \tag{2}$$

E_{HF}^{∞} in Eq. (2) is the estimate of the HF energy at the complete basis set limit, approximated by extrapolating HF energies E_{HF}^{X} computed using the aug-cc-*pVXZ* ($X = T, Q, 5$) basis sets with the following formula:

$$E_{\mathrm{HF}}^{\infty} = E_{\mathrm{HF}}^{X} + \mathrm{a}\exp(-bX). \tag{3}$$

$\Delta E_{\mathrm{CCSD(T)}}^{\infty}$ in Eq. (2) is an estimate of correlation energy at the CCSD(T) level [60] at the complete basis set limit. It is obtained by extrapolating correlation energy at this level with the aug-cc-*pVXZ* ($X = 5$, Q) basis sets using the following equation:

$$\Delta E_{\mathrm{CC}}^{\infty} = \Delta E_{\mathrm{CC}}^{X} - c/X^{3}. \tag{4}$$

Similarly, $\Delta E_{\mathrm{CCSDT}}^{\infty}$ is the difference between correlation energies with CCSDT [61] and CCSD(T) at the basis sets limit obtained with $X = T, Q$ and $\Delta E_{\mathrm{CCSDT(Q)}}^{\infty}$ is that between CCSDT(Q) [62,63] and CCSDT with $X = D, T$. $\Delta E_{\mathrm{CCSDTQ}}^{D}$ is an estimate of the correlation energies between CCSDTQ [64,65] and CCSDT(Q) using the aug-cc-*pVDZ* basis set. ΔE_{core} is the core-electron correlation energies obtained at the CCSD(T) level in all-electron calculations with the aug-cc-p*CVQZ* [54] basis set and the corresponding frozen-core calculations with aug-cc-*pVQZ*:

$$\Delta E_{\mathrm{core}} = E_{ae}(\mathrm{CCSD(T)}) - E_{fc}(\mathrm{CCSD(T)}, \tag{5}$$

The above CC calculations are carried out using the MRCC program package [66] interfaced through the CFOUR program package [67]. All calculations in this paper are performed on the National Supercomputing Center of Shengzhen.

III. RESULTS AND DISCUSSION

A. Effects of trial wave functions

DMC energies with ccECP potentials for these systems using different trial wave functions are compared with CC-CBS energies. It should be noted that the TM approach is employed in these DMC calculations and DMC energies satisfy the variational principle. DMC energies using different trial wave functions as well as CC-CBS energies with ccECP potentials for all the systems are listed in Table S1 of the Supplementary Material [68]. Errors in DMC energies for each system together with mean errors with different trial wave functions are presented in Table I. According to results in this table, DMC energies are always higher than those of CC-CBS when PPs are used. We note that DMC energy can be even lower than that of CC-CBS in all-electron calculations, which may be because core-electron correlation is not described with sufficient accuracy in CC-CBS calculations. It can be seen from Table I that mean error of DMC/CASSCF energies is the smallest and that of DMC/CASCI energies is slightly higher. Mean DMC energies with MDJ trial wave functions are lower than those with SDJ trial wave function. On the other hand, B3LYP orbitals afford lower DMC energies on average than HF orbitals. DMC/UB3LYP energies are marginally lower than DMC/ROB3LYP energies, while ROHF orbitals give rise to lower DMC energies than UHF orbitals. This is possibly due to a more significant spin contamination in UHF determinants than in UB3LYP determinants. Mean errors in DMC energies for systems containing atoms of different rows are also listed at the bottom of Table I. It can be seen that mean errors in DMC energies of third-row systems are about

TABLE I. Errors in DMC energies with ccECP potentials using different types of trial wave functions with respect to CC-CBS energies. The statistical uncertainty in the last digit is shown in parentheses (unit: kcal/mol).

	Energy errors							
System	UHF	ROHF	ROB3LYP	UB3LYP	CASCI	CASSCF	S^2_{UHF}	S^2_{UB3LYP}
C^+	10.4(1)	10.3(1)	10.4(1)	10.4(1)	3.5(1)	2.5(1)	0.76	0.75
C	7.7(1)	7.6(1)	7.3(1)	7.3(1)	5.5(1)	4.3(1)	2.01	2.00
C^-	6.0(1)	6.1(1)	6.3(1)	5.8(1)	6.4(1)	6.4(1)	3.76	3.76
N^+	9.7(1)	9.6(1)	9.6(1)	9.6(1)	5.8(1)	4.8(1)	2.01	2.00
N	6.4(1)	7.2(1)	7.6(1)	6.6(1)	7.4(1)	7.1(1)	3.76	3.75
O^+	6.9(1)	7.8(1)	8.1(1)	7.2(1)	7.9(1)	7.8(1)	3.76	3.75
O	8.7(1)	9.3(1)	9.4(1)	8.8(1)	9.3(1)	9.4(1)	2.01	2.00
O^-	10.0(1)	9.9(1)	10.2(1)	10.1(1)	10.1(1)	10.2(1)	0.77	0.76
OH^+	8.9(1)	9.6(1)	9.7(1)	8.9(1)	8.9(1)	8.0(1)	2.02	2.01
OH	9.7(1)	9.9(1)	9.5(1)	9.5(1)	9.4(1)	8.6(1)	0.76	0.75
OH^-	9.8(1)	9.9(1)	9.5(1)	9.4(1)	9.3(1)	9.2(1)	0	0
O_2^+	30.3(2)	29.6(2)	27.4(2)	27.2(2)	21.1(2)	18.0(2)	0.76	0.75
O_2	24.7(2)	23.1(2)	22.2(2)	21.5(2)	21.3(2)	19.6(2)	2.05	2.01
O_2^-	27.6(2)	25.3(2)	23.3(2)	23.2(2)	23.8(2)	21.4(2)	0.79	0.76
Si^+	1.3(1)	1.36(4)	1.3(1)	1.2(1)	1.07(4)	1.07(4)	0.77	0.76
Si	1.9(1)	1.40(4)	1.5(1)	1.3(1)	1.2(1)	1.3(1)	2.02	2.01
Si^-	1.2(1)	1.2(1)	1.0(1)	1.1(1)	0.9(1)	1.1(1)	3.75	3.75
P^+	1.9(1)	1.2(1)	1.3(1)	1.4(1)	1.2(1)	1.14(4)	2.01	2.00
P	1.5(1)	1.8(1)	1.7(1)	1.5(1)	1.5(1)	1.62(4)	3.75	3.75
P^-	2.2(1)	2.3(1)	2.5(1)	1.8(1)	2.0(1)	2.3(1)	2.03	2.01
PH^+	3.9(1)	4.3(1)	3.6(1)	3.5(1)	2.9(1)	2.9(1)	0.77	0.76
PH	3.5(1)	3.5(1)	3.1(1)	3.0(1)	3.2(1)	3.2(1)	2.03	2.01
PH^-	3.3(1)	3.3(1)	2.9(1)	2.6(1)	2.7(1)	2.7(1)	0.77	0.76
PH_2^+	5.2(1)	5.2(1)	4.7(1)	4.6(1)	3.5(1)	3.4(1)	0	0
PH_2	4.9(1)	4.5(1)	4.2(1)	3.9(1)	4.0(1)	3.9(1)	0.77	0.76
PH_2^-	3.5(1)	3.4(1)	2.7(1)	2.6(1)	2.9(1)	3.0(1)	0	0
S^+	1.56(4)	1.8(1)	1.7(1)	1.5(1)	1.7(1)	1.8(1)	3.75	3.75
S	3.8(1)	3.8(1)	3.4(1)	3.3(1)	3.5(1)	3.8(1)	2.01	2.01
S^-	3.5(1)	3.0(1)	2.9(1)	2.7(1)	2.7(1)	3.2(1)	0.76	0.76
SH^+	4.4(1)	4.5(1)	4.0(1)	3.8(1)	3.9(1)	3.8(1)	2.02	2.01
SH	5.7(1)	5.2(1)	4.9(1)	5.0(1)	4.8(1)	4.8(1)	0.77	0.76
SH^-	4.1(1)	4.3(1)	3.6(1)	3.5(1)	3.6(1)	3.9(1)	0	0
S_2^+	16.4(2)	16.7(2)	14.2(1)	14.1(2)	12.4(1)	12.9(1)	0.78	0.76
S_2	14.6(2)	13.2(1)	11.9(1)	12.0(1)	12.3(1)	12.7(1)	2.06	2.01
S_2^-	13.9(2)	13.3(2)	11.9(2)	11.1(1)	11.6(1)	12.1(2)	0.78	0.76
Cl^+	4.4(1)	4.3(1)	3.8(1)	3.8(1)	3.9(1)	4.1(1)	2.01	2.00
Cl	6.2(1)	5.7(2)	5.3(1)	5.4(1)	5.2(1)	5.6(1)	0.76	0.75
Cl^-	3.8(1)	3.9(1)	3.6(1)	3.6(1)	3.5(1)	3.8(1)	0	0
$Cl_2{}^+$	18.9(2)	17.8(2)	15.9(2)	15.7(2)	15.4(2)	16.0(1)	0.78	0.75
Cl_2	17.0(2)	16.9(2)	14.7(2)	14.1(2)	13.4(2)	15.2(2)	0	0
$Cl_2{}^-$	12.9(2)	12.1(2)	10.8(2)	10.5(2)	11.3(2)	12.0(2)	0.77	0.75
Mean(all)	8.3	8.2	7.6	7.4	7.0	6.8		
Mean (2nd-row)	12.6	12.5	12.2	11.8	10.7	9.8		
Mean (3rd-row)	6.1	5.9	5.3	5.1	5.0	5.3		

4–6 kcal/mol smaller than those of second-row systems. This may be because electron correlation in second-row systems is stronger than that in third-row systems.

To further evaluate performance of these trial wave functions on DMC energies of different types of systems, mean errors in DMC energies for cations, anions and neutral species with different trial wave functions are illustrated in Fig. 1. It can be seen from this figure that DMC/CASSCF energies are the lowest on average only for cations and neutral species, whereas mean error of DMC/UB3LYP energies is the smallest for anions. Among these three types of species, mean error of DMC energies is the smallest for anions and the largest for cations when SDJ trial wave functions are employed, while it is the smallest for cations and the largest for neutral species with MDJ trial wave functions. DMC energies with MDJ trial wave functions are reduced sizably for cations compared with those using SDJ trial wave functions, while they are similar for neutral species and anions. One would thus expect that multideterminant trial wave function has a more pronounced effect on IPs than that on EAs. Furthermore, DMC energies

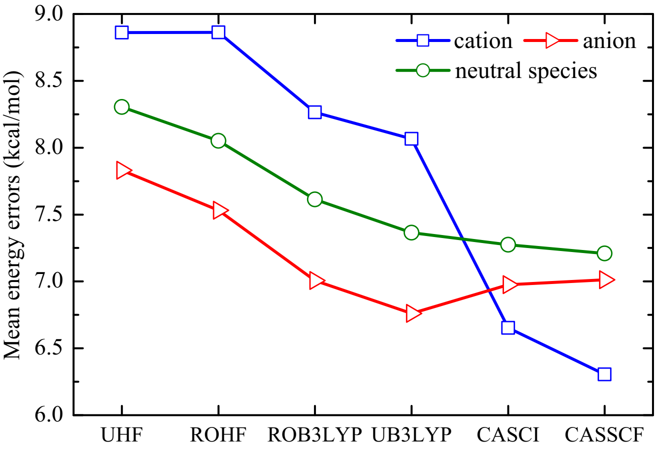

FIG. 1. Mean errors in DMC total energies for cations, anions as well as neutral species with different types of trial wave functions.

using CASSCF wave function are somewhat lower than those using CASCI wave function for cations. This indicates that orbital optimization in CASSCF wave function has certain effects on these positively charged species.

Percentage of the correlation energy obtained with DMC using UB3LYP, CASCI, and CASSCF wave functions with respect to the CC-CBS correlation energy for each system is plotted in Fig. 2 to illustrate relative error in DMC energies. Among SDJ trial wave functions, the UB3LYP wave function provides the lowest mean DMC energies and only DMC/UB3LYP results are presented in this figure. It can be seen that percentage of correlation energy in DMC calculations using MDJ trial wave functions always exceeds 90%. Nevertheless, DMC/UB3LYP can only recover 80%, 88% and 86% of the correlation energy for C^+, C, and N^+, respectively, which is due to the well-known $2s - 2p$ near degeneracy effect. This near degeneracy effect is less pronounced for C^- than C^+ and C. It should be noted CASCI or CASSCF wave function only contains 2–3 determinants for these atoms. The percentage of correlation energies with DMC/CASCI or DMC/CASSCF for C^+, C, and N^+ is larger than 91% and the corresponding DMC energies are about 2–8 kcal/mol lower than those of DMC/UB3LYP. This indicates that at least a few determinants are required to describe static correlation in these systems and achieve reliable DMC energies.

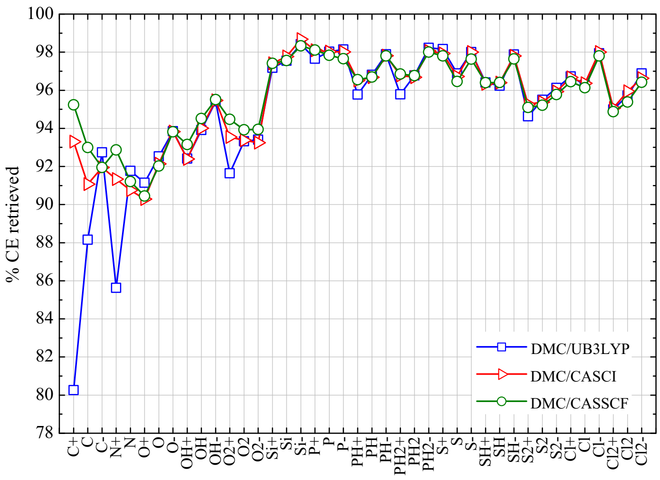

FIG. 2. Percentage of the correlation energy (%CE) retrieved for each system with DMC using different types of trial wave functions.

One can also see from Fig. 2 that the percentages of DMC correlation energy for third-row systems are larger than second-row systems in most cases. In fact, absolute errors in DMC correlation energies for third-row systems are also smaller than those in second-row systems except for S_2, Cl_2 and their corresponding charged species. According to Table I, DMC/CASSCF energies are lower than those of DMC/UB3LYP by more than 1 kcal/mol for O_2^+, O_2, O_2^-, PH_2^+ and S_2^+. In fact, improvement in DMC energies for O_2^+ even reaches 9 kcal/mol with CASSCF wave function containing 87 determinants. However, it can be seen from Fig. 2 that percentage of correlation energy with DMC/CASSCF is only slightly larger than those with DMC/UB3LYP for these systems. This may be due to their relatively large correlation energy. One can also see from Fig. 2 that percentages of correlation energies with DMC/CASSCF are slightly larger than those with DMC/CASCI for second-row systems. This is consistent with the fact that mean error in DMC/CASSCF energies is smaller than that of DMC/CASCI energies for second-row systems.

B. T-move and locality approximation

The difference between DMC energies using the LA scheme and those using the TM scheme with different trial wave functions is discussed in this section. To investigate dependence of this difference on quality of the trial wave function, DMC calculations using UHF, UB3LYP, and CASSCF wave functions with the LA scheme are carried out and their DMC energies are listed in Table S2 of the Supplemental Material [68]. UHF and UB3LYP determinants are the poorest and the best antisymmetrized part in SDJ, respectively, while MDJ with CASSCF wave function is the best trial wave function in this work. The Jastrow factor employed in DMC calculations with the TM scheme is the same as that with the LA scheme. Our results show that DMC energies with LA are always lower than that with TM if the same trial wave function is employed, but they are still higher than CC-CBS energies even though variational principle is not retained with LA. This indicates error in total energy due to node surface is always larger than that in the approximate treatment of PPs for these systems. These results imply DMC using LA renders smaller errors in correlation energy than that with TM. Mean DMC/UHF energies with the LA approach is around 0.7 kcal/mol smaller than that with TM, while this difference is reduced to 0.6 kcal/mol with UB3LYP or CASSCF wave functions. These results demonstrate that better trial wave function affords slightly smaller difference between total DMC energies with the two strategies in treating PPs. A detailed comparison in errors of DMC/CASSCF correlation energies for each system using the LA and TM schemes is shown in Fig. 3. It can be seen from this figure that the difference between correlation energies of these two schemes becomes more pronounced for systems with a relatively large error in correlation energy. Similar results are obtained with DMC/UB3LYP correlation energies. We note

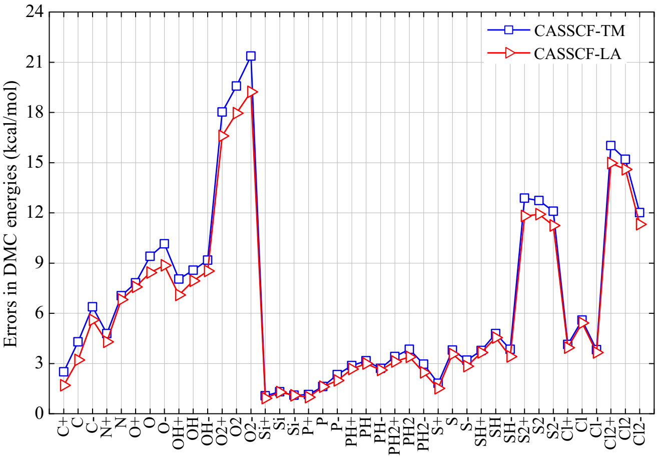

FIG. 3. Errors in DMC/CASSCF energies using the T-move scheme and locality approximation.

that DMC/CASSCF correlation energy with LA is lower than that with TM for C, O^-, O_2^+, O_2, O_2^-, S_2^+, and $Cl_2{}^+$ by more than 1 kcal/mol.

DMC energies of O_2^+ with different types of trial wave functions at time steps of 0.02, 0.06, and 0.10 a.u. using the TM and LA schemes to treat PPs are plotted in Fig. 4. According to this figure, DMC energies with LA are actually higher than that with TM at larger time steps when the same trial wave function is adopted. One can see that the TM scheme has a larger time-step bias than the LA scheme since the slope in the DMC energies vs time steps curve is larger with the TM scheme. This is consistent with previous findings [37]. DMC energies with LA thus become lower than those with TM in the limit of $\tau \rightarrow 0$. In addition, time-step bias of DMC/UHF energy with LA is similar to that of DMC/UB3LYP or DMC/CASSCF energy. This indicates that the time-step bias with the LA scheme is insensitive to the employed trial wave function. In addition, DMC/UHF energy with LA is about 1.7 kcal/mol lower than that with TM, while it is about 1.4 kcal/mol using DMC/CASSCF. This demonstrates that difference between DMC energy with LA and that with TM at the zero time-step limit does not change much with the antisymmetrized part of the trial wave function. The DMC energy with LA is shown to be more sensitive to the Jastrow factor than that with TM [15,37]. The Jastrow factors are optimized carefully in this work. These results imply that the Jastrows factor may have a more pronounced effect on the difference between the DMC energy with LA and that using TM than the antisymmetrized part in the trial wave function It is worth mentioning that the stability problem rises up in DMC calculations with LA when calculating C^+ and C^- at certain time steps and other time steps are adopted for these systems. Furthermore, computational cost with the LA approach is slightly less expensive than that with TM according to our calculations. The LA approach may be preferred with a carefully optimized Jastrow factor if stability problem does not show up.

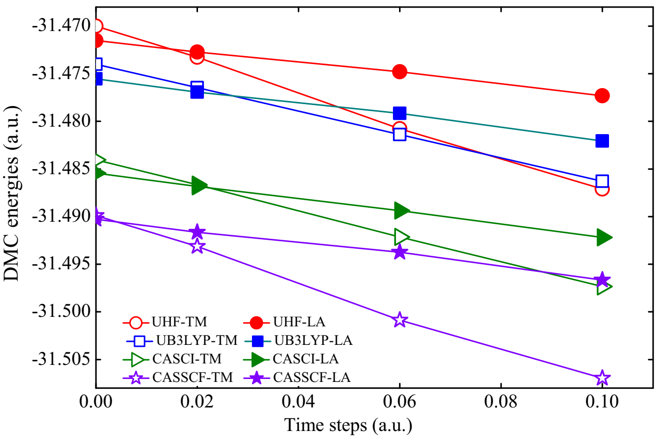

FIG. 4. DMC energies of O_2^+ with different types of trial wave functions using T-move and locality approximation schemes at different time steps.

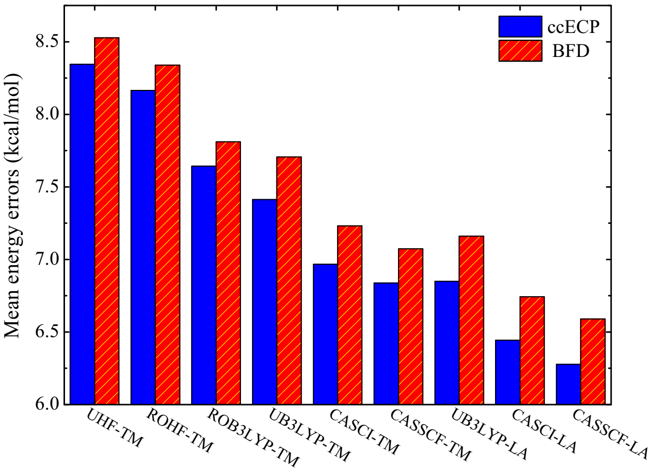

FIG. 5. Mean errors in DMC energies using ccECP and BFD potentials with different trial wave functions and nonlocal-treating strategies.

C. ccECP and BFD potentials

DMC energies with these trial wave functions as well as CC-CBS energies using BFD potentials for all the systems are listed in Table S3 of the Supplemental Material [68]. Mean errors in DMC energies with respect to CC-CBS results using ccECP and BFD potentials are illustrated in Fig. 5. It can be seen from this figure that trends in mean errors of DMC energies with different types of trial wave functions using ccECP potentials are the same as those with BFD potentials. In addition, mean errors of DMC energies with ccECP potentials are always smaller than those of BFD potentials for all the systems when the same type of trial wave function is employed. In fact, mean errors in DMC energies with ccECP potentials for cations and neutral species are similar to those with BFD potentials when the same type of trial wave function is used, while they are somewhat smaller for anions. Diffuse basis functions are important for anions and this may be due to that diffuse basis functions employed in our calculations are not optimal for BFD potentials. The difference between mean errors of DMC energies with ccECP potentials and those with BFD potentials tends to be slightly larger with

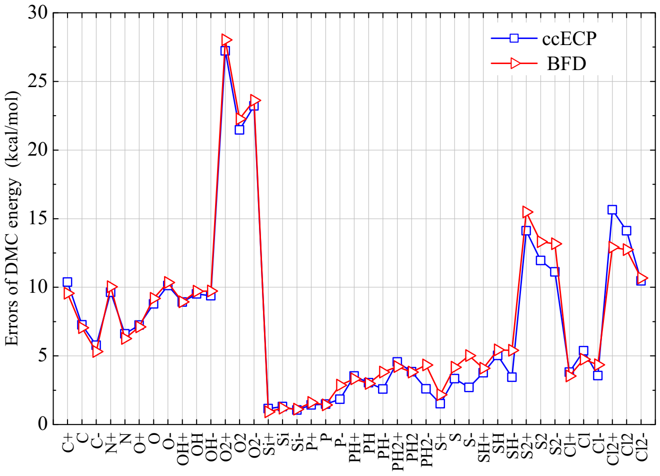

FIG. 6. Errors in DMC/UB3LYP energies using ccECP and BFD potentials with the T-move scheme.

UB3LYP, CASCI, and CASSCF wave functions. In addition, their difference with the LA scheme is similar to that with the TM scheme. It is worth mentioning that DMC energies with these three types of trial wave functions are lower than those with the other types of trial wave functions.

The difference between mean errors of DMC/UB3LYP energies with the two PPs is the largest and errors of DMC/UB3LYP energies for each system using ccECP and BFD potentials are plotted in Fig. 6. It can be seen from this figure that errors in DMC/UB3LYP energies with ccECP potentials are close to or smaller than those with BFD potentials for most of the systems except for Cl_2 and Cl_2^+, where they are about 1–3 kcal/mol larger. In addition, differences between DMC energy errors with ccECP and those with BFD potentials are less than 0.4 kcal/mol for most of the second-row systems. On the other hand, errors in DMC energies with ccECP potentials are usually about 1.0–2.3 kcal/mol smaller than those with BFD potentials for anions of third-row systems.

D. IPs and EAs

In practical calculations, one is always interested in energy differences. We present DMC results on IPs and EAs in this part. Accuracy of ccECP potentials in DMC/UB3LYP calculations is evaluated by comparing IPs and EAs with those from all-electron DMC/UB3LYP calculations. The accuracy of BFD potentials is also studied. Furthermore, performance of the DMC method using ccECP and BFD potentials with different types of trial wave functions on IPs and EAs are also investigated.

The difference between IPs or EAs using ccECP potentials and those in all-electron calculations at the DMC/UB3LYP and CC-CBS levels for these systems are listed in Table II. Results with BFD potentials are also listed in this table. It can be seen from this table that this difference is less than 1 kcal/mol with the ccECP potentials, except for IPs of S and Cl as well as EAs of P and S_2 at the DMC/UB3LYP level. Error of the ccECP potentials at the DMC/UB3LYP level on IPs is the largest for S, i.e., 2 kcal/mol, and this error on EA is the largest for P, i.e., 1.6 kcal/mol among all the systems. On the other hand, the difference between results with BFD potentials and those from all-electron calculations at the DMC/UB3LYP level reaches 3 kcal/mol for IP of C and 2.2 kcal/mol for EAs of S_2 and Cl_2. The mean absolute difference (MAD) between IPs using ccECP potentials and those in all-electron calculations at the DMC/UB3LYP level is 0.7 kcal/mol, while it is 1.2 kcal/mol with BFD potentials for these systems. They are 0.6 kcal/mol with ccECP potentials and 0.8 kcal/mol with BFD potentials for EAs at the DMC/UB3LYP level. These results indicate that the error of the ccECP potentials is smaller than that of BFD potentials on IPs of these systems, while errors of the two potentials are similar for EAs with DMC/UB3LYP. MADs on IPs using ccECP and BFD potentials at the CC-CBS level are 0.4 and

TABLE II. Deviations of ionization potentials and electron affinities using the ccECP and BFD potentials at DMC/UB3LYP and CC-CBS levels with respect to all-electron results. In parentheses it is shown the statistical uncertainty in the last digit (unit: kcal/mol).

	DMC/UB3LYP				CC-CBS			
	IP-ccECP	IP-BFD	EA-ccECP	EA-BFD	IP-ccECP	IP-BFD	EA-ccECP	EA-BFD
C	−0.7(2)	−3.0(2)	0.2(2)	−0.3(2)	0.7	−1.1	0.3	−0.5
N	−0.2(2)	−1.7(2)	–	–	1.2	−1.0	–	–
O	−0.9(2)	−2.3(2)	−0.7(3)	−0.5(3)	0.2	−0.7	−0.2	−0.2
OH	−0.5(3)	−1.2(3)	0.3(3)	0.2(3)	0.2	−0.5	−0.2	−0.1
O_2	−0.04(46)	−0.3(4)	−0.8(5)	−0.6(5)	−0.4	−0.6	−0.3	−0.4
Si	0.2(3)	0.3(2)	0.1(3)	0.02(27)	0	0.2	−0.2	−0.1
P	0.7(2)	0.2(2)	−1.6(3)	−2.1(3)	1.0	0.3	−1.4	−0.8
PH	−0.2(3)	−0.5(3)	0.2(3)	−0.2(3)	0.5	0.4	−1.5	−0.7
PH_2	0.5(3)	0.1(3)	−0.4(3)	−0.8(3)	0.5	0.4	−3.9	−2.6
S	−2.0(3)	−2.6(3)	−0.5(3)	−1.0(3)	−0.5	−1.0	−1.9	−0.8
SH	−1.0(3)	−1.2(3)	0.9(3)	0.1(3)	−0.5	−0.6	−1.3	−0.6
S_2	−0.8(5)	−1.4(5)	−1.1(5)	−2.2(5)	0.2	−0.4	−0.8	−1.2
Cl	−0.9(3)	−1.5(3)	0.9(3)	0.3(3)	0.2	−0.7	−1.4	−0.6
Cl_2	1.2(5)	−1.1(5)	−0.3(5)	−2.2(5)	0.1	−0.9	0.1	−0.2
MAD	0.7	1.2	0.6	0.8	0.4	0.6	1.0	0.7

TABLE III. Deviations of ionization potentials between DMC results with different trial wave functions and CC-CBS results as well as experimental values. In parentheses it is shown the statistical uncertainty in the last digit (unit: kcal/mol).

	UHF		ROHF		UB3LYP		ROB3LYP		CASCI		CASSCF		CASSCF- LA		UB3LYP
	ccECP	BFD	ccECP	BFD	ccECP	BFD	ccECP	BFD	ccECP	BFD	ccECP	BFD	ccECP	BFD	AE
C	2.7(1)	2.2(1)	2.8(1)	2.3(1)	3.1(1)	2.5(1)	3.1(1)	2.1(1)	−2.0(1)	−2.2(1)	−1.8(1)	−1.8(1)	−1.5(2)	−1.9(1)	4.4(2)
N	3.3(1)	3.9(1)	2.5(1)	3.1(1)	3.0(1)	3.3(1)	2.1(1)	3.3(1)	−1.6(1)	−0.5(1)	−2.3(1)	−0.9(1)	−2.5(1)	−1.8(1)	4.5(2)
O	−1.9(1)	−2.2(1)	−1.5(1)	−1.8(1)	−1.6(1)	−2.1(1)	−1.3(1)	−1.5(1)	−1.3(1)	−1.4(1)	−1.6(1)	−1.7(1)	−0.9(2)	−1.7(1)	−0.5(2)
OH	−0.8(2)	−1.4(1)	−0.3(2)	−0.2(1)	−0.6(1)	−0.8(2)	0.2(2)	0.2(1)	−0.4(2)	−0.7(1)	−0.5(1)	−1.0(1)	−0.8(2)	−0.7(1)	−0.03(2)
O_2	5.6(3)	5.8(3)	6.6(3)	6.4(3)	5.8(3)	5.8(3)	5.2(3)	4.9(3)	−0.3(2)	−1.5(2)	−1.5(2)	−1.7(2)	−1.4(3)	−2.0(2)	5.4(4)
Si	−0.6(1)	−0.7(1)	−0.03(6)	−0.3(1)	−0.1(1)	−0.3(1)	−0.2(1)	−0.6(1)	−0.1(1)	−0.3(1)	−0.2(1)	−0.5(1)	−0.4(1)	−0.4(1)	−0.4(2)
P	0.5(1)	0.8(1)	−0.6(1)	0.1(1)	−0.1(1)	0.2(1)	−0.4(1)	0.2(1)	−0.3(1)	−0.2(1)	−0.5(1)	−0.1(1)	−0.6(1)	−0.2(1)	0.3(2)
PH	0.4(1)	0.7(1)	0.7(1)	0.5(1)	0.5(1)	0.4(1)	0.5(1)	0.3(1)	−0.3(1)	−0.4(1)	−0.3(1)	−0.3(1)	−0.3(1)	−0.5(1)	1.2(3)
PH_2	0.3(1)	0.2(1)	0.8(1)	0.4(1)	0.7(1)	0.4(1)	0.6(1)	0.5(1)	−0.5(1)	−0.8(1)	−0.5(1)	−0.3(1)	−0.3(1)	−0.4(1)	0.8(3)
S	−2.3(1)	−2.5(1)	−2.0(1)	−2.1(1)	−1.8(1)	−2.0(1)	−1.7(1)	−1.9(1)	−1.8(1)	−2.0(1)	−2.0(1)	−2.1(1)	−2.1(1)	−2.0(1)	−0.4(3)
SH	−1.2(1)	−1.6(1)	−0.6(1)	−1.3(1)	−1.3(1)	−1.3(1)	−1.0(1)	−1.2(1)	−1.0(1)	−1.4(1)	−1.0(1)	−1.4(1)	−0.9(1)	−1.1(1)	−0.8(3)
S_2	1.8(2)	2.2(2)	3.6(2)	3.4(2)	2.2(2)	2.2(2)	2.3(2)	1.8(2)	0.2(2)	0.5(2)	0.2(2)	−0.3(2)	−0.1(2)	−0.6(2)	3.1(4)
Cl	−1.8(1)	−1.5(1)	−1.4(1)	−0.9(1)	−1.5(1)	−1.2(1)	−1.5(1)	−0.9(1)	−1.4(1)	−1.1(1)	−1.5(1)	−0.9(1)	−1.5(1)	−1.1(1)	−0.4(3)
Cl_2	1.9(3)	1.8(2)	0.9(2)	1.0(2)	1.5(2)	0.2(2)	1.3(3)	0.1(2)	2.1(2)	1.1(2)	0.8(2)	0.5(2)	0.4(2)	0.2(2)	0.4(4)
MAD	1.8	1.9	1.7	1.7	1.7	1.6	1.5	1.4	0.9	1.0	1.0	1.0	1.0	1.0	1.3
MAD(exp)	2.1	1.9	2.1	1.8	2.1	1.7	1.9	1.6	1.2	1.5	1.3	1.5	1.1	1.6	1.8

0.6 kcal/mol, respectively, compared with the all-electron results, while it is 1 kcal/mol on EAs for ccECP potentials and 0.7 kcal/mol for BFD potentials. This demonstrates that the error of the ccECP potentials on IPs at the CC-CBS level is similar to that of the BFD potentials, while it is slightly larger for EAs of these systems.

The errors of IPs and EAs for each system from DMC calculations with different types of Slater-Jastrow trial wave function using ccECP and BFD potentials as well as in all-electron calculations with respect to the corresponding CC-CBS results are listed in Tables III and IV, respectively. MADs with respect to the corresponding CC-CBS results as well as experimental results are also listed in these two tables. IPs and EAs obtained with CC-CBS using ccECP and BFD potentials as well as in all-electron calculations for all the systems are listed in Table S4 of the Supplemental Material [68] together with experimental values [45,69,70]. The contribution of zero-point energy has been excluded in the experimental values.

According to results in Table III, MADs on IPs using DMC with ccECP potentials for these systems are rather close to those with BFD potentials. In fact difference in errors of IPs with these two potentials is less than 0.5 kcal/mol in most cases. In addition, DMC with SDJ trial wave functions using either ccECP or BFD potentials gives rise to IPs with MAD of around 1.6 kcal/mol compared with CC-CBS results for these systems, whereas it is around 1 kcal/mol with MDJ trial wave functions. MAD of IPs with DMC/UB3LYP in all-electron calculations is smaller than that with PPs, but it is still somewhat larger than those using MDJ trial wave

TABLE IV. Deviations of electron affinities between DMC results with different trial wave functions and CC-CBS results as well as experimental values. In parentheses it is shown the statistical uncertainty in the last digit (unit: kcal/mol).

	UHF		ROHF		UB3LYP		ROB3LYP		CASCI		CASSCF		CASSCF- LA		UB3LYP
	ccECP	BFD	ccECP	BFD	ccECP	BFD	ccECP	BFD	ccECP	BFD	ccECP	BFD	ccECP	BFD	AE
C	1.7(1)	1.7(1)	1.4(1)	1.0(1)	1.5(1)	1.8(1)	1.0(1)	1.4(1)	−0.9(1)	−0.4(1)	−2.1(1)	−1.7(1)	−2.4(2)	−1.8(1)	1.6(2)
O	−1.32)	−1.4(1)	−0.6(2)	−0.9(1)	−1.3(1)	−1.2(1)	−0.8(2)	−0.7(1)	−0.9(2)	−0.7(1)	−0.8(1)	−1.4(1)	−0.4(2)	−0.9(1)	−0.9(2)
OH	−0.1(2)	−0.02(17)	0.02(2)	−0.03(1)	0.1(2)	−0.01(2)	−0.02(2)	−0.1(2)	0.1(2)	−0.1(2)	−0.6(2)	−0.8(2)	−0.6(2)	−0.6(2)	−0.3(2)
O_2	−2.9(3)	−2.5(3)	−2.3(3)	−2.4(3)	−1.7(3)	−1.4(3)	−1.1(3)	−0.9(2)	−2.5(3)	−1.9(3)	−1.8(2)	−1.5(2)	−1.3(3)	−1.2(3)	−1.2(4)
Si	0.7(1)	0.3(1)	0.2(1)	−0.04(1)	0.3(1)	0.1(1)	0.5(1)	0.3(1)	0.3(1)	−0.2(1)	0.2(1)	−0.1(1)	0.2(1)	−0.1(1)	−0.02(3)
P	−0.8(1)	−1.6(1)	−0.6(1)	−1.4(1)	−0.4(1)	−1.5(1)	−0.8(1)	−2.0(1)	−0.5(1)	−1.5(1)	−0.7(1)	−1.4(1)	−0.4(1)	−1.6(1)	−0.2(3)
PH	0.2(1)	−1.3(1)	0.2(1)	−0.9(1)	0.5(1)	−0.8(1)	0.1(1)	−0.8(1)	0.5(1)	−0.9(1)	0.5(1)	−1.1(1)	0.4(1)	−0.9(1)	−1.3(3)
PH_2	1.4(2)	−0.6(2)	1.0(1)	−0.5(1)	1.3(1)	−0.5(1)	1.5(1)	−0.2(1)	1.1(1)	−0.4(1)	0.9(1)	−0.6(1)	0.9(2)	−0.3(1)	−2.3(3)
S	0.4(1)	−0.8(1)	0.8(1)	−0.9(1)	0.7(1)	−0.9(1)	0.6(1)	−1.0(1)	0.8(1)	−0.7(1)	0.6(1)	−0.9(1)	0.7(1)	−0.91(1)	−0.7(3)
SH	1.5(1)	0.1(1)	0.9(1)	−0.2(1)	1.6(1)	0.02(1)	1.4(1)	0.2(1)	1.2(1)	−0.1(1)	0.9(1)	−0.04(1)	1.1(1)	−0.4(1)	−0.7(3)
S_2	0.7(2)	−0.5(2)	−0.1(2)	−0.9(2)	0.8(2)	0.2(2)	−0.04(2)	−0.1(2)	0.7(2)	0.2(2)	0.6(2)	−0.4(2)	0.7(2)	−0.1(2)	1.1(5)
Cl	2.3(1)	0.6(1)	1.8(1)	0.3(1)	1.8(1)	0.4(1)	1.7(1)	0.1(1)	1.8(1)	0.3(1)	1.8(1)	0.3(1)	1.8(1)	0.4(1)	−0.5(3)
Cl_2	4.1(2)	2.9(2)	4.8(2)	3.1(2)	3.6(2)	2.1(2)	3.9(2)	2.5(2)	2.1(2)	1.9(2)	3.2(2)	2.5(2)	3.3(2)	1.9(2)	4.0(5)
MAD	1.4	1.1	1.1	1.0	1.2	0.8	1.0	0.8	1.0	0.7	1.1	1.0	1.1	0.8	1.1
MAD(exp)	1.7	1.6	1.5	1.4	1.4	1.3	1.4	1.3	1.2	1.2	1.4	1.5	1.3	1.4	1.0

functions. Compared with experimental results, MADs of IPs are about 2 kcal/mol and 1.3 kcal/mol in DMC calculations with ccECP potentials using SDJ and MDJ trial wave functions, respectively. On the other hand, error in IPs with BFD potentials is smaller than that with ccECP potentials in DMC calculations using SDJ trial wave functions, while it is slightly larger with MDJ trial wave functions. In addition, all-electron DMC/UB3LYP provides MAD on IPs similar to that with PPs when experimental values are employed as reference. We note that MADs of IPs with CC-CBS are 0.8 kcal/mol using ccECP potentials, 1 kcal/mol with BFD potentials and 0.6 kcal/mol in all-electron calculations.

One can also see from Table III that absolute errors in IPs with ccECP potentials using MDJ are similar to those with SDJ except for O_2 and S_2. In fact, errors in IPs for these two molecules using ccECP potentials are rather close to those in all-electron calculations at the DMC/UB3LYP level. IPs of O_2 and S_2 are improved by about 4 kcal/mol and 2 kcal/mol, respectively, when MDJ trial wave functions are employed. IPs with DMC using MDJ trial wave functions are underestimated for all the systems except for Cl_2. This is because MDJ trial wave functions result in a more significant reduction in energies for cations than that of the corresponding neutral species. Furthermore, IPs of DMC/CASSCF with the LA approach is close to that with the TM approach, and their differences are less than 0.3 kcal/mol in most cases, even though DMC with the LA approach always provides lower energies.

According to the results in Table IV, EAs are not improved in DMC calculations with MDJ trial wave functions compared with those using SDJ trial wave function. This is consistent with the fact that mean DMC energies of the anions and neutral species with MDJ trial wave function are similar to those with SDJ trial wave function. One can see from this table that errors of EAs from DMC calculations with ccECP potentials are close to those with BFD potentials for second-row systems, while they are 1–2 kcal/mol larger for most of the third-row systems. EAs for third-row systems are generally overestimated with ccECP potentials and error in DMC energy with ccECP potentials for third-row anions is smaller than that with BFD potentials. The BFD potential thus provides EAs with a smaller error than ccECP potentials. MADs of EAs using ccECP potentials or in all-electrons calculations for these systems are around 1.1 kcal/mol compared with the CC-CBS results, while it is about 0.7–1.0 kcal/mol with BFD potentials. Similar to the case of IPs, MAD on EAs with the LA scheme is close to that with the TM scheme. Compared with experimental values, error of EAs with DMC is about 1.6 kcal/mol using the UHF or ROHF determinant in the trial wave function, while it is reduced to 1.2–1.4 kcal/mol with DFT determinant or MDJ trial wave functions. Nevertheless, MAD of EAs from all-electron DMC/UB3LYP calculations is slightly smaller than that with the ccECP potentials. In fact, the MAD of EAs with CC-CBS and ccECP potentials is already 1 kcal/mol compared with experimental results, and it is about 0.7 kcal/mol with BFD potentials and 0.6 kcal/mol in all-electron calculations. Errors in EAs with DMC are only slightly larger than that with CC-CBS. Compared with previous works on IPs and EAs with DMC, the accuracy of the present DMC calculations is similar to that in Ref. [46], while IPs with chemical accuracy is obtained in Ref. [47]. This is probably because a larger number of determinants are employed in their trial wave functions.

IV. CONCLUSION

In this paper, a systematic investigation on performance of ccECP potentials in DMC calculations by studying total energies, IPs and EAs of some second- and third-row atoms and molecules with different trial wave functions is carried out. Errors in total energies and energy differences in DMC calculations using the ccECP potentials are evaluated by comparing with high-level CC results extrapolated to the complete basis set limit. Moreover, error of ccECP potentials is also studied by comparing IPs and EAs with those from all-electron calculations. Dependence of energy difference between TM and LA strategies on quality of the trial wave functions is also examined in our work. Furthermore, the accuracy of DMC results using ccECP potentials is also compared with those of BFD potentials.

Our results show MDJ trail wave functions have a more pronounced effect on energies of cations than neutral systems and anions. In addition, mean errors in DMC energies with ccECP potentials for second-row systems are 4–6 kcal/mol larger than those of third-row species. DMC energies with the LA scheme are always lower than those with the TM scheme, while they are still higher than CC-CBS energies. Results on O_2^+ indicate that the difference between DMC energies with the LA scheme and those with the TM scheme does not change much with the employed trial wave functions if the Jastrow factor is optimized carefully. Compared with results using BFD potentials, the mean error in DMC energies with ccECP potentials is smaller with the same type of trial wave function. In fact, error in DMC energies with the ccECP potentials is smaller than that with the BFD potentials mainly for third-row anions when the same types of trial wave functions are adopted.

The MADs of IPs from DMC calculations with respect to CC-CBS results for these systems are about 1.6 kcal/mol with SDJ trial wave functions and they are reduced to around 1 kcal/mol using the MDJ trial wave functions with either ccECP or BFD potentials. On the other hand, MADs of EAs in DMC with the ccECP potentials are about 1 kcal/mol and slightly larger than those with the BFD potentials. Compared with experimental results, MADs of IPs or EAs with CC-CBS is about 0.6–1.0 kcal/mol, and those from DMC calculations are somewhat larger. These results show that ccECP potentials are able to provide reliable IPs and EAs in DMC calculations. The accuracy of IPs and EAs from DMC calculations using ccECP potentials is similar to that with the BFD potentials, although mean error in total DMC energies with ccECP potentials is smaller. Furthermore, the error of ccECP potentials in DMC/UB3LYP calculations on IPs and EAs is smaller than that of BFD potentials compared with all-electron results.

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