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Quantitative estimation of localization errors of 3d transition metal pseudopotentials in diffusion Monte Carlo

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The necessarily approximate evaluation of non-local pseudopotentials in diffusion Monte Carlo (DMC) introduces localization errors. We estimate these errors for two families of non-local pseudopotentials for the first-row transition metal atoms Sc–Zn using an extrapolation scheme and multideterminant wavefunctions. Sensitivities of the error in the DMC energies to the Jastrow factor are used to estimate the quality of two sets of pseudopotentials with respect to locality error reduction. The locality approximation and T-moves scheme are also compared for accuracy of total energies. After estimating the removal of the locality and T-moves errors, we present the range of fixed-node energies between a single determinant description and a full valence multideterminant complete active space expansion. The results for these pseudopotentials agree with previous findings that the locality approximation is less sensitive to changes in the Jastrow than T-moves yielding more accurate total energies, however not necessarily more accurate energy differences. For both the locality approximation and T-moves, we find decreasing Jastrow sensitivity moving left to right across the series Sc–Zn. The recently generated pseudopotentials of Krogel *et al.* [Phys. Rev. B **93**, 075143 (2016)] reduce the magnitude of the locality error compared with the pseudopotentials of Burkatzki *et al.* [J. Chem. Phys. **129**, 164115 (2008)] by an average estimated 40% using the locality approximation. The estimated locality error is equivalent for both sets of pseudopotentials when T-moves is used. For the Sc–Zn atomic series with these pseudopotentials, and using up to three-body Jastrow factors, our results suggest that the fixed-node error is dominant over the locality error when a single determinant is used. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4991414>]

I. INTRODUCTION

Due to the advantageous scaling of the computational cost with respect to the number of electrons, diffusion Monte Carlo (DMC)^{1,2} is an *ab initio* many-body method that can be applied from molecules to solids where there may be large electron correlation effects.³ DMC in practice involves two main approximations: the fixed-node approximation^{2,4} and the pseudopotential approximation. Pseudopotentials, which are unavoidable for most solid systems, introduce two types of errors: (1) the pseudopotential itself might not be accurate enough and (2) the evaluation of the pseudopotential often involves localization errors. As the number of applications of DMC to solid systems increases,^{5–19} many studies have focused on understanding and reducing the fixed-node error.^{20–24} More accurate pseudopotentials for DMC have been developed,^{25–28} but localization errors have received less attention in comparison.^{29,30} The magnitude of all these errors is generally unknown, and they are difficult to disentangle. It is also relatively unexplored how these errors are reduced with multideterminant wavefunctions, which may be necessary to accurately describe properties of many transition metal species.

Most pseudopotentials used to model realistic systems have a non-local part to influence the different

angular-momentum components of the wavefunction, which is necessary to improve the pseudopotential transferability. Typically, pseudopotentials in open boundary molecular systems are combined with Gaussian basis sets for the orbitals. In systems with periodic boundary conditions, plane-wave basis sets are often used. Pseudopotentials from the studies of Burkatzki *et al.*²⁵ (denoted “BFD” in this work) and Krogel *et al.*²⁶ (denoted “OPT” in this work) have been generated for the 3d transition metal series specifically for use in QMC calculations. The BFD pseudopotentials are energy-consistent and have been parameterized to reproduce all-electron Hartree-Fock calculations with Gaussians, while the OPT pseudopotentials are norm-conserving and have been parameterized to reproduce all-electron local density approximation (LDA) calculations (while the cutoff and other parameters were chosen to better reproduce atomic and dimer properties). When a non-local operator is present in DMC, it is “localized” either fully as in the locality approximation (denoted “LA”)^{31,32} or partially as in the T-moves scheme (denoted “TM”).^{29,33} The magnitude of the errors incurred by these localization approximations is largely unknown, since they coexist with the fixed-node error and they are both dependent on the quality of the trial wavefunction.

The fixed-node approximation is used to control the fermion sign problem. This approximation enforces the nodes of the wavefunction projected in the DMC approach to remain the same as the nodes of the trial wavefunction (ψ_T). The fixed-node constraint can be represented formally by adding a

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potential term to the original Hamiltonian. We refer to the resulting operator as the “fixed-node Hamiltonian” [Eq. (1)], where the other nodal pocket is obtained from flipping the inequality,

$$H_{FN} = H + V_{FN}, \quad (1)$$

$$V_{FN}(R) = \begin{cases} 0 & \text{when } \psi_T > 0, \\ \infty & \text{otherwise.} \end{cases}$$

The fixed-node energy is variational with respect to the exact ground state energy and can be lowered by improving the nodes of the trial wavefunction. It has been generally assumed that the fixed-node approximation is the dominant contribution to the error in QMC calculations, although recent examples^{30,34,35} have shown a large error due to the localization approximation. Extrapolation schemes^{29,30} based on the Jastrow factor³⁶ disentangle the locality error from the fixed-node error, allowing for examination of their magnitudes separately.

In this work, we use the extrapolation variant from Krogel and Kent³⁰ to quantify the magnitude of localization errors for the locality approximation and T-moves. We then compare the quality of the two sets of pseudopotentials with respect to locality error reduction. For the BFD pseudopotentials, we additionally compare the magnitude of locality errors for single determinant and multideterminant wavefunctions. We compare the locality-error-corrected fixed-node energies to present a lower bound for the Hartree-Fock fixed-node error. We then compare the magnitude of the fixed-node errors to the magnitude of the locality errors for the 3d transition metal atomic series.

The rest of the paper is organized as follows: Sec. II describes localization errors and the extrapolation to the error-corrected limit, Sec. III outlines details of the calculations performed, Sec. IV presents our results and discussion, and Sec. V summarizes the major findings of this study.

II. LOCALIZATION ERRORS

Diffusion Monte Carlo (DMC) belongs to a class of projector methods in which the ground state is obtained by projecting the evolution operator in imaginary time. When applied to an arbitrary linear combination of eigenstates, the relative contribution of the lowest-eigenvalue eigenstate increases as follows:

$$\psi_0 = \lim_{t \rightarrow \infty} e^{-t(H-E_0)} \psi_T. \quad (2)$$

The DMC method takes advantage of the fact that the kinetic energy contribution of the Schrödinger equation turns into a diffusion propagator in imaginary time. Since the ground state of most many-body Hamiltonians is the bosonic solution, often a boundary condition is added to force the projected wavefunction to remain fermionic (antisymmetric with respect to the exchange of electronic coordinates). In the case of DMC, the projected wavefunction is constrained to share the same nodes^{2,4} (or phase)³⁷ of a trial wavefunction. The trial wavefunction is often written as a product of a symmetric function denoted as a Jastrow factor and a linear combination of determinants,

$$\psi_T(R) = e^{-J(R)} \sum_n C_n D_n^\dagger(R^\uparrow) D_n^\downarrow(R^\downarrow). \quad (3)$$

In practice, the expansion over determinants fixes the nodes and the phase of the trial wavefunction. For local potentials, the DMC ground state energy is entirely determined by the nodes (or phase) of the trial wavefunction. In this context, the Jastrow factor is often added to accelerate the convergence of the DMC algorithm, since the required statistics depend on how close the trial wavefunction is to the fixed-node ground state. The Jastrow factor and the coefficients of the multideterminant expansion are optimized variationally within the Monte Carlo approach (VMC) either by minimizing the variance of the energy, the energy itself, or a combination of the two. The fixed-node approximation in DMC results in a positive shift in the total energy above the true ground state.

When non-local pseudopotentials are used, an additional error is introduced during the pseudopotential evaluation. In the locality approximation (LA),^{32,33} the non-local pseudopotential contribution is estimated by its “localized” form, $\psi_T^{-1} V_{nl} \psi_T$, which is diagonal in position space. The error introduced in the total energy by the locality approximation can have any sign. Within the T-moves approximation (TM),^{29,33} the transition paths that change sign are localized using the trial wavefunction as before. The remaining paths are instead sampled with a nonlocal electron move. It has been shown that the partial localization employed in the T-moves approach restores the variational upper bound property in the energy and stabilizes the DMC run.^{29,33} More recent implementations also reformulate the original algorithm to make it size-consistent.³⁸

The ground state of the fixed-node Hamiltonian [Eq. (1)] can be expressed as a Jastrow factor times the fermionic part of the trial wavefunction.³⁹ In the limit where the trial wavefunction is the ground state of the fixed-node Hamiltonian, the results obtained within the locality and T-moves approximations are equivalent and are also identical to the trial wavefunction energy evaluated within VMC. Therefore, as the Jastrow factor is improved, we approach the triple equality,

$$E_{VMC}(\psi_{FN}) = E_{DMC}^{LA}(\psi_{FN}) = E_{DMC}^{TM}(\psi_{FN}). \quad (4)$$

Here, $E_{VMC}(\psi_{FN})$ is the fixed-node VMC energy, $E_{DMC}^{LA}(\psi_{FN})$ is the fixed-node DMC energy using the locality approximation (LA), and $E_{DMC}^{TM}(\psi_{FN})$ is the fixed-node DMC energy using T-moves (TM). For a complete discussion, the reader is referred to Ref. 30.

A useful quantity that we use to assess the quality of the pseudopotentials is the Jastrow sensitivity,³⁰

$$S_J = \Delta E_{DMC} / \Delta E_{VMC}, \quad (5)$$

which is defined as the slope extracted from a linear fit of DMC energies to VMC energies arising from different Jastrow factors. The set includes no Jastrow factor (J_0), a two-body Jastrow factor (J_2), and a three-body Jastrow factor (J_3). The Jastrow sensitivity is meaningful for results that do not deviate significantly from linear behavior. In the absence of locality error, $S_J = 0$, i.e., the energy for DMC is independent of the Jastrow factor. A pseudopotential that aims to reduce localization error should therefore aim to reduce the values of S_J . In Ref. 30, it has been argued that an extrapolation of the DMC energies as a function of the VMC energy can be used to estimate the fixed-node energy in the absence of localization errors by making use of Eq. (4). A similar

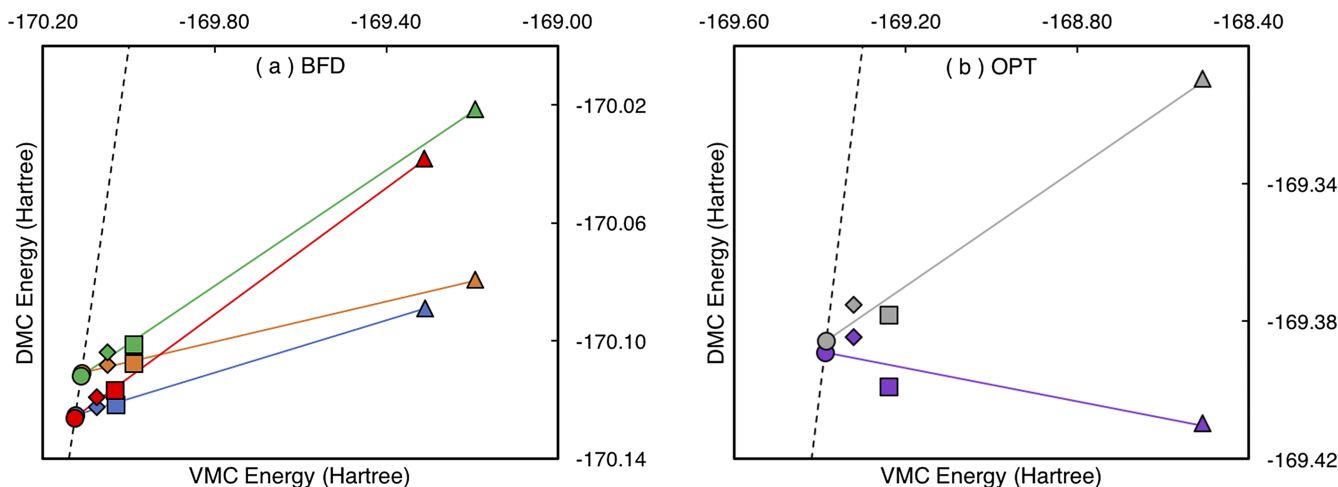


FIG. 1. Linear extrapolation of QMC energies toward the locality-error-corrected limit $E_{VMC}(\psi_{FN}) = E_{DMC}^{LA}(\psi_{FN}) = E_{DMC}^{TM}(\psi_{FN})$ for the Ni pseudo-atom using the (a) BFD pseudopotential and (b) OPT pseudopotential. The dashed lines show $E_{VMC} = E_{DMC}$ and solid lines are the linear least squares fits. Data shown are DMC and VMC energies using trial wavefunctions from either UHF, CAS, or PBE0, employing either the locality approximation or T-moves scheme in DMC. Shown here are energies using a UHF trial wavefunction with T-moves (green), UHF trial wavefunction with locality approximation (orange), CAS trial wavefunction with T-moves (red), CAS trial wavefunction with locality approximation (blue), PBE0 trial wavefunction with T-moves (gray), and PBE0 trial wavefunction with locality approximation (purple). Triangles are for J_0 , squares are for J_2 , diamonds are for J_3 , and circles are the extrapolated values.

extrapolation was used in the original studies introducing the T-moves approach.^{29,33} In this contribution, we make use of this extrapolation approach to compare two full sets of transition metal pseudopotentials.

III. CALCULATION DETAILS

Diffusion Monte Carlo calculations of Sc–Zn were performed for the neutral atoms in their ground states. Neon core semilocal pseudopotentials from the studies of Burkatzki *et al.*²⁵ (BFD) and Krogel *et al.*²⁶ (OPT) were compared. Using the OPT pseudopotentials, single particle orbitals were obtained from Quantum Espresso⁴⁰ with the PBE0⁴¹ functional in a 15 Å box. Planewaves were used with an energy cutoff of 400 Ry. The Kleinman-Bylander representation of the OPT pseudopotential was used in density functional theory (DFT), which contributes a secondary and small error to the fixed-node DMC results via the DFT orbitals. Using the BFD pseudopotentials, single particle orbitals were obtained from GAMESS⁴² with either unrestricted Hartree-Fock (UHF) or complete active space self-consistent field (CASSCF).⁴³ Gaussian basis sets that were constructed for the BFD pseudopotentials at the pVTZ level ($5s5p4d2f1g$) were used. The CASSCF wavefunctions were obtained by first optimizing the transition metal cation (stripped of all valence electrons) using RHF and then constructing $CAS(N,M)$ active spaces, where N is the number of valence electrons and $M = 9$ orbitals ($3d, 4s, 4p$). For the CASSCF wavefunctions, the determinants with coefficients $C_n \geq |0.01|$ were used in QMC (where $\sum C_n^2 = 1$). For Sc, Ti, V, and Fe, VMC energies with no Jastrow factor (J_0) are equivalent to the complete active space (CAS) energies to within VMC error bars of order 0.003 eV. For Cr, Mn, Ni, Cu, and Zn, VMC J_0 energies differ from the CAS energies within the range of 0.03–0.1 eV. The largest effect from dropping determinants with this coefficient threshold is observed for Co, with $\Delta E(\text{VMC } J_0 - \text{CAS})$ of 0.4 eV.

QMCPACK⁴⁴ was used for all DMC calculations. The two- and three-body Jastrow factors were optimized using VMC with the linear method⁴⁵ by variance minimization followed by energy minimization. DMC calculations were performed with 2000 walkers and a time step of 0.0025 Ha^{-1} . For the OPT pseudopotentials, p was used as the local channel to avoid ghost states in DFT; d was used as the local channel for the BFD pseudopotentials, consistent with their construction.²⁵ The nonlocal T-moves (TM) scheme^{29,33} was compared with the locality approximation (LA).^{32,33} Nexus⁴⁶ was used to facilitate the simulation workflow.

IV. RESULTS AND DISCUSSION

A representative example of this extrapolation to the locality-error-corrected limit $E_{VMC}(\psi_{FN}) = E_{DMC}^{LA}(\psi_{FN})$

TABLE I. Jastrow sensitivities $S_J = \Delta E_{DMC} / \Delta E_{VMC}$ for the BFD and OPT pseudopotentials with the locality approximation (LA) and T-moves (TM) using trial wavefunctions obtained from UHF, CAS, and PBE0. Mean sensitivities $\langle S_J \rangle$ and mean absolute sensitivities $\langle |S_J| \rangle$ across the series Sc–Zn are given; the localization error free case corresponds to $S_J = 0$.

	BFD		BFD		OPT	
	UHF LA	UHF TM	CAS LA	CAS TM	PBE0 LA	PBE0 TM
Sc	0.15	0.17	0.17	0.20	0.13	0.18
Ti	0.12	0.16	0.15	0.18	0.09	0.16
V	0.08	0.11	0.12	0.17	0.07	0.13
Cr	0.09	0.14	0.09	0.14	0.04	0.11
Mn	0.07	0.12	0.09	0.15	0.02	0.12
Fe	0.05	0.11	0.07	0.13	0.00	0.10
Co	0.04	0.10	0.06	0.13	−0.01	0.09
Ni	0.03	0.10	0.04	0.11	−0.02	0.09
Cu	0.02	0.09	0.03	0.10	−0.03	0.08
Zn	0.02	0.09	0.02	0.10	−0.04	0.09
$\langle S_J \rangle$	0.07	0.12	0.08	0.14	0.02	0.12
$\langle S_J \rangle$	0.07	0.12	0.08	0.14	0.05	0.12

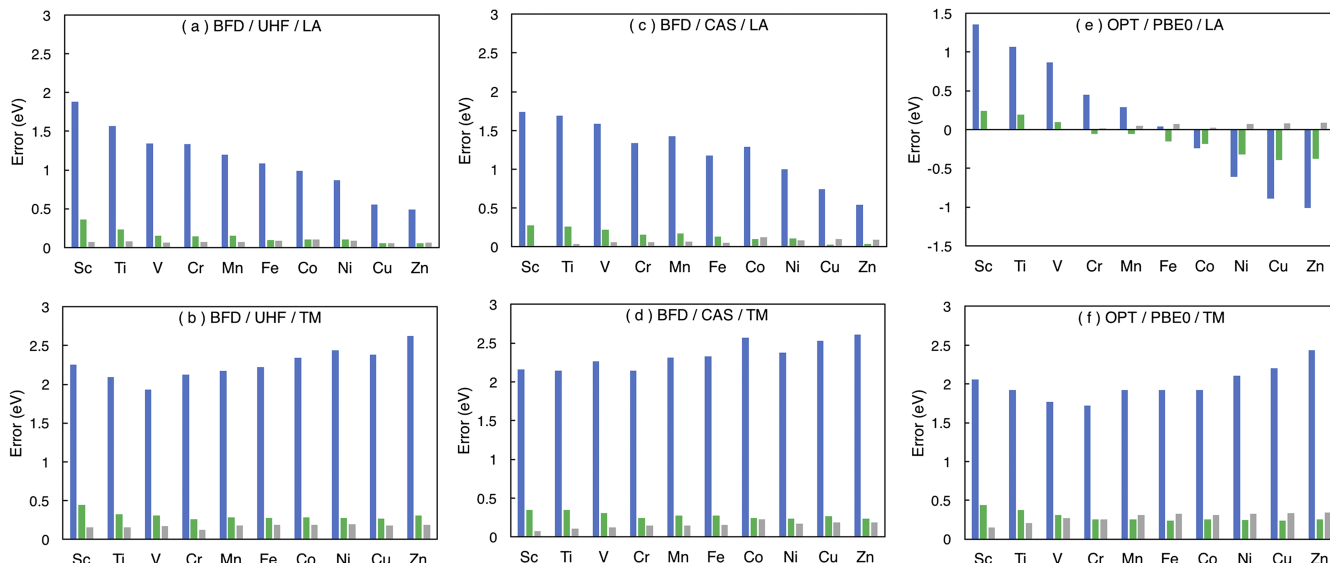


FIG. 2. Estimated DMC locality errors (eV) for the Jastrow set J_0 (blue), J_2 (green), and J_3 (gray) of the series Sc–Zn. The errors are quantified as $\Delta E_{J_x} = E_{J_x} - E_{FN}$, where J_x is either J_0 (no Jastrow), J_2 (two-body Jastrow), or J_3 (three-body Jastrow). The locality-error-corrected fixed-node energy E_{FN} is estimated as the mean of the extrapolation points $E_{VMC}(\psi_{FN}) = E_{DMC}^{LA}(\psi_{FN})$ and $E_{VMC}(\psi_{FN}) = E_{DMC}^{TM}(\psi_{FN})$. The locality approximation (left) and T-moves (right) are compared for the BFD pseudopotentials [(a)–(d)] and the OPT pseudopotentials [(e) and (f)]. UHF trial wavefunctions were used for [(a) and (b)], CAS trial wavefunctions were used for [(c) and (d)], and PBE0 trial wavefunctions were used for [(e) and (f)].

$= E_{DMC}^{TM}(\psi_{FN})$ is shown for the Ni pseudo-atom in Fig. 1. Each set of points with no Jastrow, a two-body Jastrow, and a three-body Jastrow is extrapolated to the locality error-corrected fixed-node energy. We obtain fixed-node energies $E_{VMC}(\psi_{FN}) = E_{DMC}^{LA}(\psi_{FN})$ for the locality approximation and $E_{VMC}(\psi_{FN}) = E_{DMC}^{TM}(\psi_{FN})$ for T-moves. We use the mean of these two fixed-node energies as our locality-error-corrected reference energies.

There is a slight difference in the variability of the extrapolated locality-error-corrected fixed-node energies for the OPT pseudopotentials compared with the BFD pseudopotentials, i.e., the difference between $E_{VMC}(\psi_{FN}) = E_{DMC}^{LA}(\psi_{FN})$ and $E_{VMC}(\psi_{FN}) = E_{DMC}^{TM}(\psi_{FN})$. The difference between these two fixed-node energies across the transition metal series ranges from 0.01 to 0.09 eV for the BFD pseudopotentials and ranges from 0.02 to 0.16 eV for the OPT pseudopotentials.

What we refer to as the Jastrow sensitivity $S_J = \Delta E_{DMC} / \Delta E_{VMC}$ is the slope of the linear fit to the energies obtained with each Jastrow set shown in Fig. 1. A smaller absolute value of S_J indicates that currently available Jastrow factors and optimization techniques are more likely to reduce locality errors below an acceptable level. It also indicates the range where the energies of different systems involving the same pseudopotentials can be compared with confidence. Jastrow sensitivities are given in Table I for all 3d pseudo-atoms.

Figure 1(a) illustrates the difference between a single determinant UHF trial wavefunction and a multideterminant CAS trial wavefunction for the Ni BFD pseudopotential. For both trial wavefunctions, we see that LA and TM approach the error-corrected energy limit from above, with TM having a larger Jastrow sensitivity compared with LA. This is true for all BFD pseudo-atoms of the first-row transition metal series.

We see a shift lowering the energy going from DMC-UHF to DMC-CAS, which is expected given that the fixed-node energy is variational. This energy shift is seen for all BFD pseudo-atoms, with the exception of the Cu pseudo-atom. What is surprising, however, is that the DMC-CAS Jastrow sensitivity is always equal to or larger than the DMC-UHF Jastrow sensitivity (as shown in Table I). One might intuitively expect the DMC-CAS locality error to be smaller than the DMC-UHF locality error; however, these results suggest that although the fixed-node energy is lowered, the locality error is not decreased for DMC-CAS compared to DMC-UHF.

For the OPT pseudopotentials shown in Fig. 1(b), the TM scheme still approaches the error-corrected limit from above, but the LA may approach the error-corrected limit either from above or from below. The LA approaches the limit from below for all the later-row transition metals, as reflected by the change in sign of the Jastrow sensitivity from Fe through Zn shown in Table I. This has implications with respect to accuracy of energy differences (rather than accuracy of total energies), which is discussed in more detail below.

As shown in Table I, we observe decreasing Jastrow sensitivities moving left to right from Sc to Zn for both sets of pseudopotentials, for both LA and TM, using either single determinants (OPT and BFD) or multideterminant expansions (BFD only). Mean (and mean absolute) Jastrow sensitivities are given at the bottom of Table I to compare against the ideal case without localization error ($S_J = 0$). DMC-UHF TM and DMC-PBE0 TM perform very similarly. It is interesting that DMC-CAS has higher sensitivities than DMC-UHF. This is due to the larger error in J_0 for DMC-CAS compared with DMC-UHF, noting that DMC-CAS has lower errors for J_2 and J_3 compared with DMC-UHF (see Fig. 2, Table II, and discussion below).

TABLE II. Mean localization errors $\langle \Delta E_{J_x} \rangle$ and mean absolute localization errors $\langle |\Delta E_{J_x}| \rangle$ (eV) for each Jastrow factor across the series Sc–Zn for the BFD and OPT pseudopotentials using trial wavefunctions obtained from UHF, CAS, and PBE0.

	BFD		BFD		OPT	
	UHF LA	UHF TM	CAS LA	CAS TM	PBE0 LA	PBE0 TM
$\langle \Delta E_{J_0} \rangle$	1.13	2.26	1.25	2.34	0.13	2.00
$\langle \Delta E_{J_2} \rangle$	0.15	0.30	0.15	0.28	-0.10	0.28
$\langle \Delta E_{J_3} \rangle$	0.08	0.17	0.07	0.15	0.04	0.28
$\langle \Delta E_{J_0} \rangle$	1.13	2.26	1.25	2.34	0.68	2.00
$\langle \Delta E_{J_2} \rangle$	0.15	0.30	0.15	0.28	0.21	0.28
$\langle \Delta E_{J_3} \rangle$	0.08	0.17	0.07	0.15	0.04	0.28

Estimated locality errors are shown in Fig. 2. The errors are quantified as $\Delta E_{J_x} = E_{J_x} - E_{FN}$, where J_x is either J_0 (no Jastrow), J_2 (two-body Jastrow), or J_3 (three-body Jastrow). The locality-error-corrected fixed-node energy E_{FN} is estimated as the mean of the extrapolation points $E_{VMC}(\psi_{FN}) = E_{DMC}^{LA}(\psi_{FN})$ and $E_{VMC}(\psi_{FN}) = E_{DMC}^{TM}(\psi_{FN})$.

The error obtained using the locality approximation (Fig. 2, left) decreases moving left to right across the Sc–Zn series; the error obtained using T-moves remains roughly consistent across the Sc–Zn series (Fig. 2, right). With the locality approximation, we see the largest locality error for the Sc atom, consistent with previous studies showing that the Sc atom yields the largest errors in DMC total energies.^{29,47}

The change in sign of the Jastrow sensitivity is evident in Fig. 2(e) for the late-row pseudo-atoms where the locality approximation approaches the limit from below. This has important implications when assessing the accuracy of energy differences rather than the accuracy of total energies (which is the focus of the current study). Although we see in Fig. 2 and Table II that the LA consistently has smaller locality errors than TM for total energies, the results of this study cannot allow us to determine whether LA or TM has better error cancellation for energy differences. When examining energy difference properties, e.g., ionization potentials, it has been recently shown that TM has better error cancellation for the 4th ionization potential of the Ce pseudo-atom.³⁰

For the BFD pseudopotentials, we observe comparable locality errors for single-determinants [Figs. 2(a) and 2(b)] and multi-determinants [Figs. 2(c) and 2(d)]. The locality errors are larger for DMC-CAS wavefunctions with no Jastrow (J_0), which is also reflected in the slightly larger Jastrow sensitivity for DMC-CAS compared with DMC-UHF. The mean deviation for DMC based on CAS and UHF trial wavefunctions is comparable at the J_2 and J_3 levels, with the localization error for DMC-CAS calculations slightly smaller than DMC-UHF.

It is interesting to note that J_3 has larger errors than J_2 for the heavier elements using the OPT pseudopotentials with TM [Fig. 2(f)]. For the corresponding OPT/PBE0 VMC energies $\Delta E = E_{VMC} - E_{FN}$, improvements in the Jastrow factor (J_0, J_2, J_3) consistently lead to lower energies. This suggests that Jastrow optimization via VMC energy minimization is not always ideal for TM and an alternative—and as yet unknown—optimization target might be preferential. It may also suggest

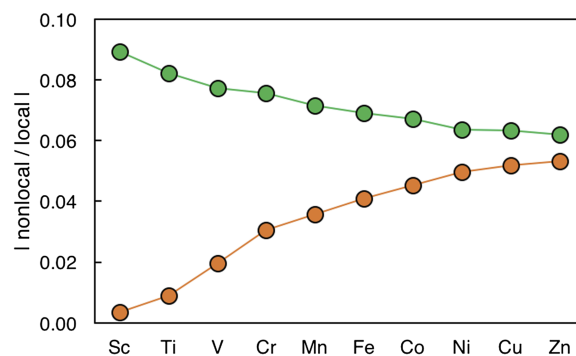


FIG. 3. Absolute value of the ratio of the nonlocal energy to the local energy for the BFD pseudopotentials (green) and the OPT pseudopotentials (orange).

that there is something missing in our numerical parameterization of the Jastrow factor for the heavier elements which is more pronounced for TM than for LA.

In all cases, the magnitude of the DMC localization errors using the locality approximation is smaller than the errors using T-moves, although we again reiterate that this is only for *total* energies. We observe the smallest errors with LA for the OPT pseudopotentials using PBE0. A possible explanation for the small error is that the ratio of nonlocal/local energy is smaller for the OPT pseudopotentials compared with the BFD pseudopotentials (Fig. 3). The trends going from Sc to Zn in Fig. 3 are rationalized since the local channel is p for the OPT pseudopotentials and d for the BFD pseudopotentials.

As illustrated in Fig. 1(a), once the locality error has been removed via extrapolation, we can compare the DMC fixed-node energies between a single determinant (UHF) description and a multi-determinant description (CAS). Given the small size of the CAS space employed here, these values serve as a lower bound for the fixed-node error of DMC-UHF. Table III lists the differences in energies $\Delta(E_{FN}^{UHF} - E_{FN}^{CAS})$ after extrapolation. Since we imposed the constraint that only CI coefficients larger than 0.01 were included in the QMC simulations, the number of Slater determinants (SDs) is quite small.

We can compare our valence CAS DMC energies for the Ti atom with those reported in the work of Burkatzki *et al.*²⁵ The CAS optimized VMC energy reported in Ref. 25 is $-58.1650(8)$ Hartree, compared with $-58.16857(9)$ Hartree computed in this work. The corresponding DMC energy with the locality approximation from Ref. 25 is $-58.1975(7)$ Hartree, compared with $-58.1991(4)$ Hartree computed in this work. The CAS (N, M) space for Ti in Ref. 25 was CAS(4,6), where $M = 6$ is composed of $3d$ and $4s$ orbitals. The CAS (N, M) space used in this work was comparable with CAS(4,9), where here we also include the $4p$ orbitals.

Even with the constraint on the number of Slater determinants via the 0.01 coefficient threshold, we observe energy differences between DMC-CAS and DMC-UHF of up to 3.76 eV, which is larger in magnitude than any estimated locality error. At the three-body Jastrow level with the locality approximation, locality errors are smaller in magnitude than the DMC-UHF fixed-node errors (Table III).

TABLE III. Three-body Jastrow locality errors $\Delta(E_{J_3} - E_{FN})$ for DMC-UHF with the BFD pseudopotentials using the locality approximation (LA) or T-moves (TM). The locality-error-corrected fixed-node energy E_{FN} is estimated as the mean of the extrapolation points $E_{VMC}(\psi_{FN}) = E_{DMC}^{LA}(\psi_{FN})$ and $E_{VMC}(\psi_{FN}) = E_{DMC}^{TM}(\psi_{FN})$. Estimated lower bounds to the DMC-UHF fixed-node errors $\Delta(E_{FN}^{UHF} - E_{FN}^{CAS})$ are also given. All energies are in eV. The final column gives the number of Slater determinants used from the CAS expansion.

	$\Delta(E_{J_3}^{UHF} - E_{FN})$	$\Delta(E_{J_3}^{UHF} - E_{FN})$	$\Delta(E_{FN}^{UHF} - E_{FN}^{CAS})$	# CAS SDs
	LA	TM		
Sc	0.07	0.16	0.15	20
Ti	0.08	0.16	3.76	21
V	0.06	0.17	2.89	16
Cr	0.07	0.12	0.00	4
Mn	0.07	0.18	2.59	12
Fe	0.09	0.19	1.50	15
Co	0.10	0.19	2.18	15
Ni	0.09	0.20	0.39	12
Cu	0.05	0.18	-1.39	18
Zn	0.07	0.19	0.23	14

V. SUMMARY

In this contribution, we have evaluated the Jastrow sensitivities for two families of non-local pseudopotentials in DMC due to localization errors. For the first-row transition metal atoms (Sc–Zn), we used an extrapolation scheme to estimate the localization errors and to estimate the fixed-node errors by comparing to multideterminant wavefunctions. We argue that Jastrow sensitivities are a parameter that should be considered to assess the quality of pseudopotentials. To our knowledge, this has not been a consideration or constraint applied in any pseudopotential construction thus far. In particular, when total energies of different solids are compared, both localization errors and fixed-node errors can be expected to change since the optimal Jastrow factors and the Slater part of the trial wavefunction change (thus pseudopotentials with small sensitivities are key). Methods such as Auxiliary-Field Quantum Monte Carlo (AFQMC)⁴⁸ do not suffer from locality errors; however, we find here that the locality errors are not the dominant source of error in DMC as compared to fixed-node errors. For the atoms tested in this set, we also compared the locality approximation and T-moves scheme for accuracy of total energies. The results presented here corroborate previous findings that the locality approximation is less sensitive to changes in the Jastrow than T-moves yielding more accurate total energies, however not always more accurate energy differences. For both the locality approximation and T-moves, we find decreasing Jastrow sensitivity moving left to right across the series Sc–Zn. The recently generated pseudopotentials of Krogel *et al.*²⁶ reduce the magnitude of the locality error by an estimated 40% with the locality approximation compared with the pseudopotentials of Burkatzki *et al.*²⁵ Errors using T-moves are the same for both sets of pseudopotentials. Assuming that locality and T-moves errors can be removed by an extrapolation scheme, we present lower bounds for DMC-UHF fixed-node errors as the difference from DMC with full valence multideterminant CAS expansions. For the Sc–Zn atomic series with these pseudopotentials, and using up to three-body Jastrow, our results

suggest that the fixed-node error is dominant over the locality error.

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