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ABSTRACT

Fixed-node diffusion quantum Monte Carlo (FN-DMC) is a widely trusted many-body method for solving the Schrödinger equation, known for its reliable predictions of material and molecular properties. Furthermore, its excellent scalability with system complexity and near-perfect utilization of computational power make FN-DMC ideally positioned to leverage new advances in computing to address increasingly complex scientific problems. Even though the method is widely used as a computational gold standard, reproducibility across the numerous FN-DMC code implementations has yet to be demonstrated. This difficulty stems from the diverse array of DMC algorithms and trial wave functions, compounded by the method's inherent stochastic nature. This study represents a community-wide effort to assess the reproducibility of the method, affirming that yes, FN-DMC is reproducible (when handled with care). Using the water–methane dimer as the canonical test case, we compare results from eleven different FN-DMC codes and show that the approximations to treat the non-locality of pseudopotentials are the primary source of the discrepancies between them. In particular, we demonstrate that, for the same choice of determinantal component in the trial wave function, reliable and reproducible predictions can be achieved by employing the T-move, the determinant locality approximation, or the determinant T-move schemes, while the older locality approximation leads to considerable variability in results. These findings demonstrate that, with appropriate choices of algorithmic details, fixed-node DMC is reproducible across diverse community codes—highlighting the maturity and robustness of the method as a tool for open and reliable computational science.

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I. INTRODUCTION

The credibility of a scientific result hinges on its reproducibility; independent and equivalent experiments should lead to the same conclusion. Achieving reproducibility is, however, not easy. There are several historical examples from both social and natural sciences[1–4] that have served to illustrate its challenges, and substantial ongoing effort is dedicated to addressing this so-called "reproducibility crisis."[5,6] The problem of reproducibility is particularly pertinent within computational experiments in the hard sciences, where different computational codes should ideally lead to the same prediction. Nonetheless, reproducibility can be compromised by small algorithmic differences, undocumented approximations, and undetected bugs in the simulation software or its dependencies (numerical libraries, compilers, etc.). Determining the source of discrepancies can be difficult, e.g., due to restricted source code availability.[7–9]

Here, we consider reproducibility in the context of the many-electron Schrödinger equation,[10] fundamental to the quantum mechanical description of matter, and its countless applications to physics, chemistry, biology, engineering, and materials science. In this context, the topic of reproducibility has been recently addressed[11,12] in two seminal papers for density functional theory (DFT)—the work-horse of materials science. However, despite its widespread success, DFT often falls short of providing the necessary quantitative and sometimes qualitative description of key complex systems. Fortunately, advances in hardware, algorithms, and fundamental theories are paving the way for the routine application of methods beyond the accuracy of DFT. The scope of these methods has recently broadened significantly beyond simple benchmarks toward an extensive description of molecules, surfaces, and condensed phases[13–18] that can include complex dynamics facilitated by machine learning potentials.[19–26]

Several quantum many-body approaches have been developed as alternatives to DFT for electronic structure calculations, particularly in systems where strong correlation or high accuracy is essential. Methods such as GW,[27,28] dynamical mean-field theory (DMFT),[29,30] coupled cluster theory,[31,32] and auxiliary-field quantum Monte Carlo (AFQMC)[33–36] have been successfully applied to both molecular and condensed-phase systems. More recently, full configuration interaction quantum Monte Carlo (FCIQMC)[37,38] and neural network-based quantum Monte Carlo[39–41] methods have also gained attention. However, among the quantum Monte Carlo methods, real-space fixed-node diffusion Monte Carlo (FN-DMC) remains the most widely used approach in materials science and quantum chemistry, offering a compelling balance between accuracy, scalability, and methodological maturity. Its use of explicitly correlated many-body wave functions and its favorable scaling with system size make it particularly attractive for benchmarking and systematic studies. For these reasons, this work focuses on FN-DMC and its reproducibility across a variety of independently developed community codes.

FN-DMC is an accurate state-of-the-art computational approach for solving the Schrödinger equation for a variety of systems, including molecules, solids, and surfaces. This method obtains the electronic ground-state by performing an imaginary-time evolution from a starting trial wave function $\Psi_T(\mathbf{R})$. Within the Born–Oppenheimer approximation, $\mathbf{R}$ consists of the real space positions of all the electrons. Typically, $\Psi_T(\mathbf{R})$ is the product of an antisymmetric function (e.g., a Slater determinant or a sum of Slater determinants[42]) and a symmetric, positive function, called the Jastrow factor.[43] The Jastrow factor is explicitly dependent on electron–electron and electron–nucleus distances and is able to directly capture a significant fraction of the electronic correlation.

The FN-DMC projection is achieved with an ensemble of electron configurations, known as walkers, which evolve according to the imaginary-time Green function,[44] yielding a drift-diffusion process over discrete imaginary time steps, τ, to stochastically sample the ground-state wave function; the stochastic uncertainty is then inversely proportional to the square root of the number of samples. The main approximation in FN-DMC is that the fixed-node wave function is constrained to have the same nodal surface as $\Psi_T(\mathbf{R})$ in order to avoid the so-called *fermion sign problem*.[45] This introduces a variational error in the computed ground state energy. For

single-reference systems, this error is typically small even for simple single determinant trial wave functions built from DFT. FN-DMC exhibits almost perfect efficiency on modern supercomputers[46–48] and a cubic scaling per Monte Carlo step with system size,[49] making it often the only computationally affordable method beyond DFT for treating large condensed phase systems with more than 100 atoms. Over time, numerous algorithmic improvements have enhanced the accuracy, efficiency, and stability of FN-DMC. These advances have enabled the successful application of FN-DMC to a wide array of problems across the natural sciences, including the calculation of the energies of condensed phases and large molecules,[14,15,18,50–52] the binding of molecules on surfaces,[17,53–58] phase diagrams,[20,59–65] reaction barrier heights,[66–70] spin-polarized uniform electron gas,[71] two-dimensional electron liquid,[72] lithium systems,[73] electronic and optical properties of delafossites,[74] defect formation energies,[75,76] calculation of energy derivatives,[77–79] radical stabilization energies,[80] excited states,[81–90] training of quantum machine learning models,[91] electron–positron interactions,[92] polymorphism,[93–95] electronic bandgaps,[96] Landau-level mixing in quantum dots,[97] localization in quantum dots and quantum wires,[98–101] nearly exact density functional quantities,[102,103] and more. Recent progress in the use of neural networks as trial wave functions for FN-DMC[104–106] has served to boost its accuracy and potential future uptake even further.

There are numerous QMC codes currently used for research, many of which have been under development for over a decade. Each makes somewhat different algorithmic and implementation choices, such as the use of different Jastrow factors and methods for evaluating single-particle orbitals. In this study, we compare eleven such codes and provide details of the algorithmic and implementation choices in Sec. S8 of the supplementary material. This diversity raises open questions on the reproducibility of FN-DMC. If FN-DMC is to be widely accepted as a highly accurate reference method, it is important that consistent results can be obtained from these different FN-DMC codes. With this goal in mind, the present work represents a collaborative effort among the users and developers of eleven distinct FN-DMC codes to rigorously assess the reproducibility of FN-DMC.

A key obstacle to the reproducibility of FN-DMC comes from the use of non-local pseudopotentials (NLPPs), which increase the efficiency of the method for systems with heavy atoms.[107–109] While all-electron FN-DMC calculations are possible for light atoms, the computational cost increases steeply with atomic number, scaling approximately as $O(Z^{\alpha})$ with α between 5.5 and 6.5, depending on the method details.[107,108,110] As a result, pseudopotentials are essential for practical FN-DMC applications involving heavier elements. NLPPs allow one to solve the Schrödinger equation solely for the valence electrons by substituting the full local nuclear potential with a smooth non-local potential near the nuclei. In general, NLPPs hinder reproducibility in electronic structure methods, as NLPPs constructed in different ways can lead to somewhat different predictions. NLPPs are a potential source of non-reproducibility in FN-DMC even when the same NLPPs are used, because non-local pseudopotential operators create an additional sign problem in the projector beyond the one that is always present for fermionic calculations. To avoid this sign problem, these operators must be "localized,"[111] or at least partially localized,[112] on a wave-function. A natural choice is to localize them on the trial wave-function $\Psi_T(\mathbf{R})$, introducing a dependence on both the determinantal and the Jastrow components of the wave function. Since the Jastrow factor is different in the different codes and its parameters are stochastically optimized, yielding possible noise and reproducibility issues, some authors choose to localize only on the determinantal component.[108,113–116] This removes the dependence on the Jastrow factor at the cost of losing the desirable property that the treatment of the pseudopotential is exact in the limit of exact Ψ_T. To summarize, there are currently four localization schemes: the locality approximation (LA),[111,117] the T-move (TM) approximation,[112,118,119] the determinant locality approximation (DLA),[108,113–116] and the determinant T-move (DTM) approximation.[116] These four schemes (LA, TM, DLA, and DTM) result in somewhat different projected wave-functions and, therefore, different total energies of physical systems.

As computational science matures, reproducibility and transparency are increasingly recognized as critical features of robust methodology. FN-DMC, while a powerful and widely used method, has historically lacked comprehensive cross-code validation. This work takes a step toward establishing that foundation by systematically comparing the four localization algorithms across eleven FN-DMC codes (named alphabetically): Amolqc, CASINO,[46] CHAMP-EU,[120] CHAMP-US,[121] CMQMC, PyQMC,[122] QMC=Chem,[123,124] QMCPACK,[48,125] QMeCha,[126] QWalk,[127] and TurboRVB.[47,128] Different forms of the Jastrow factor are necessarily tested as part of this evaluation.

We specifically consider the cases of the total energies of a methane molecule, a water molecule, and a methane–water dimer, and the corresponding interaction energy. We selected the water–methane dimer as a test case not only for its modest size—which allows tight statistical convergence—but also because it spans two different interaction regimes. It involves both weak intermolecular interactions (with a binding of only 27 meV) and intramolecular energetics, enabling a sensitive probe of algorithmic consistency across codes. In addition, it is a prototype of more complex systems, such as methane clathrates, important for gas storage and transportation. We show that consensus across all eleven codes can be made when utilizing the TM, DLA, and DTM approximations, particularly following careful control of the discretized time step.

II. RESULTS AND DISCUSSION

First, we compute the interaction energy of the methane–water dimer using the eleven codes for the four different localization schemes (where available). The interaction energy of the methane–water dimer,

$$E_{\text{int}} = E[\text{methane–water}] - E[\text{methane}] - E[\text{water}], \quad (1)$$

is defined as the difference between the energy of the complex, E[methane–water], minus the sum of the energies of the isolated water E[water] and methane E[methane] monomers (see Sec. III for details on the geometries and the DMC simulation setup). All the interaction energies are extrapolated to the zero time step limit according to the procedure described in the supplementary material and in Ref. 129.

We note that two results are reported for the TurboRVB code, namely, TurboRVB (DMC) and TurboRVB (LRDMC). TurboRVB (DMC) refers to the standard FN-DMC algorithm with time step

discretization and is available with the T-move scheme. However, production simulations of FN-projection in TurboRVB are typically performed with the lattice regularized DMC (LRDMC),[118,130] which is an alternative approach to DMC. In particular, LRDMC is based on a lattice regularization of the many-electron Hamiltonian over a spatial mesh, and the ground state is projected out via the Green function Monte Carlo method.[131–133] The zero mesh-size limit of the LRDMC prediction is equivalent to the zero time step limit of DMC and is, therefore, also included in this work. We also note that the T-move approximation itself comes in four different versions, as briefly discussed in the supplementary material, but when presenting the TM results, we will not distinguish between them because they differ only at finite time step, while we report here the extrapolated values at zero time steps, where they are equivalent.

The computed methane–water interaction energies are shown in Fig. 1. We plot the FN-DMC interaction energy computed with each code with a colored circle. In addition, the average among the interaction energies computed with different codes is reported with a gray dashed line, and its statistical error with a shaded gray region. The average value and its statistical error are computed as the mean value and the standard deviation of the probability distribution reported in Eq. (2), discussed later on in this paper. We compare the prediction of FN-DMC to the value computed by coupled cluster theory with single, double, triple, and perturbative quadruple excitations [CCSDT(Q)], which is expected to be highly accurate for weak intermolecular interactions[134] (details of the calculation are reported in Sec. S3 of the supplementary material). Despite using only a single determinant in the trial wave functions and a DFT nodal surface

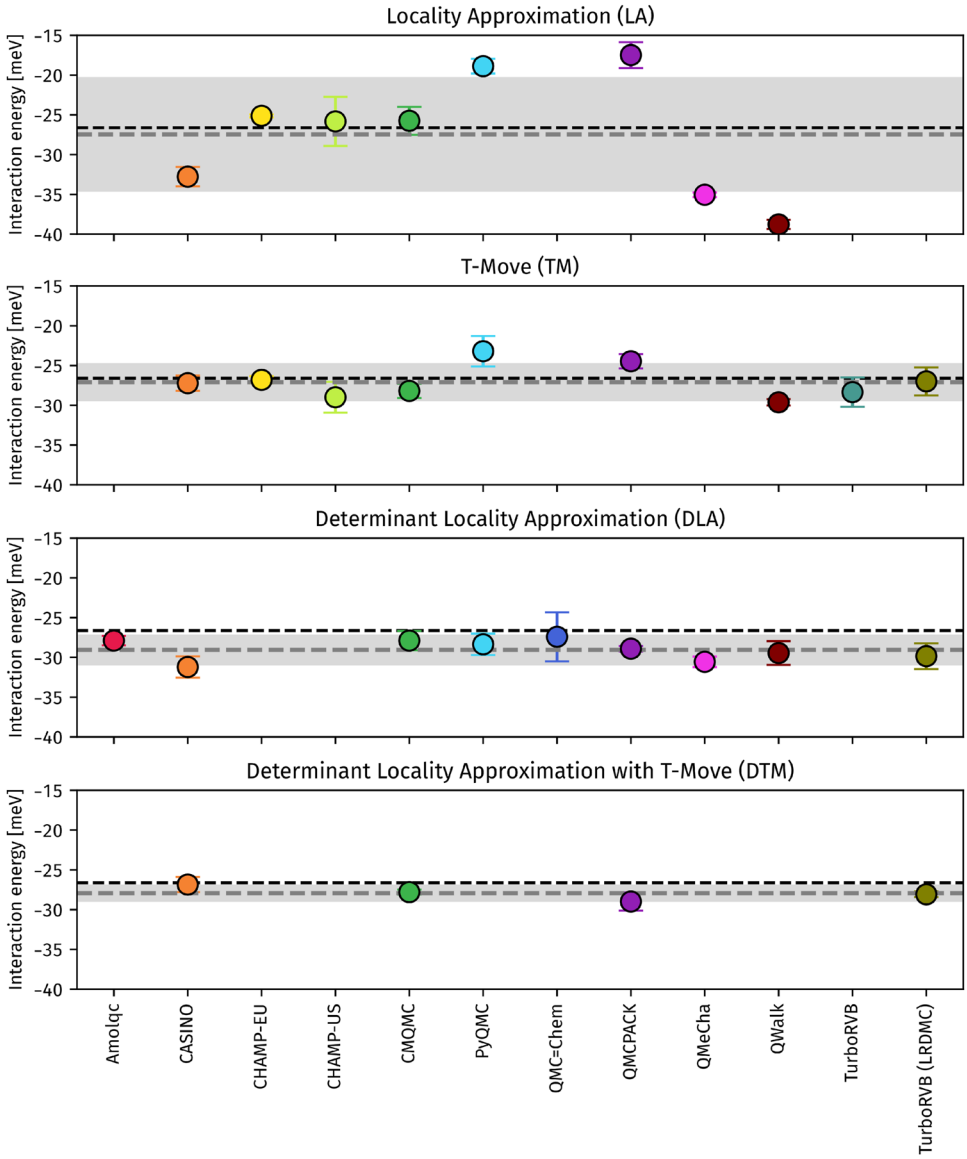

FIG. 1. FN-DMC interaction energy of the methane–water dimer with four different methods. The black dashed horizontal line indicates the reference value of −27 meV computed with CCSDT(Q). The gray dashed line is the average among the interaction energies computed with different codes, and the shaded area is its statistical error bar. The energy differences between the various codes are much larger when the LA scheme is employed, compared to the narrower energy range obtained with TM, DLA, and DTM. The computed averages always match the CCSDT(Q) value within the statistical error bar.

for simplicity, broadly speaking, the FN-DMC is in excellent agreement with CCSDT(Q) (black dashed line). However, a strikingly large spread of predictions across different codes is obtained when using the LA. In contrast, the TM, DLA, and DTM methods show a much narrower spread of the interaction energies.

The data reported in Fig. 1 allow us to estimate a probability distribution of the interaction energy for each analyzed method. In particular, we write the DMC energy estimated with the code i and the method α (α = LA, TM, DLA, DTM) as $E_{\alpha,i}$, and its statistical error bar as $\sigma_{\alpha,i}$. Following the central limit theorem, we expect each DMC estimate to be distributed according to a normal distribution, with mean $\bar{E}_{\alpha,i}$ and standard deviation $\bar{\sigma}_{\alpha,i}$. Since we do not know $\bar{E}_{\alpha,i}$ and $\bar{\sigma}_{\alpha,i}$, we use here the current estimates $E_{\alpha,i}$ and $\sigma_{\alpha,i}$ and define the probability distribution of the energy E for the method α as follows:

$$P_\alpha(E) = \frac{1}{N_\alpha} \sum_{i \in \text{codes}} \frac{1}{\sqrt{2\pi\sigma_{\alpha,i}^2}} e^{-\frac{(E-E_{\alpha,i})^2}{2\sigma_{\alpha,i}^2}}, \tag{2}$$

where N_α is the number of codes for which the localization method α is evaluated. The mean, μ_α, and the variance, σ_α^2, of the energy for the distribution $P_\alpha(E)$ are, respectively,

$$\mu_\alpha = \int E P_\alpha(E)\, dE = \frac{1}{N_\alpha} \sum_{i \in \text{codes}} E_{\alpha,i} \tag{3}$$

and

$$\sigma_\alpha^2 = \int (E-\mu_\alpha)^2 P_\alpha(E)\, dE = \frac{1}{N_\alpha} \sum_{i \in \text{codes}} \sigma_{\alpha,i}^2 + \frac{1}{N_\alpha} \sum_{i \in \text{codes}} (E_{\alpha,i}-\mu_\alpha)^2. \tag{4}$$

In particular, the variance takes into account both the statistical error bar of each FN-DMC evaluation ($\sigma_{\alpha,i}$) and its deviation from the mean value ($E_{\alpha,i} - \mu_\alpha$).

The probability distributions are plotted in Fig. 2. When the LA is employed, the probability distribution is spread across a large energy range of 25 meV, with a standard deviation of 7 meV. The agreement across different codes significantly improves with the TM, DLA, and DTM schemes, with the probability distributions showing a quite localized peak (a standard deviation of ~2 meV or less) centered on −27, −29, and −28 meV, respectively. The DTM scheme gives the narrowest distribution, centered on −28 meV, with a standard deviation of ~1 meV, but since only four out of the eleven codes implemented DTM, this is of limited significance. Overall, the analysis of the probability distributions showcases that algorithms more sophisticated than LA need to be employed to guarantee reproducibility among different FN-DMC codes.

A key factor in DMC is the convergence with respect to the simulation time step. The projection is only accurate for

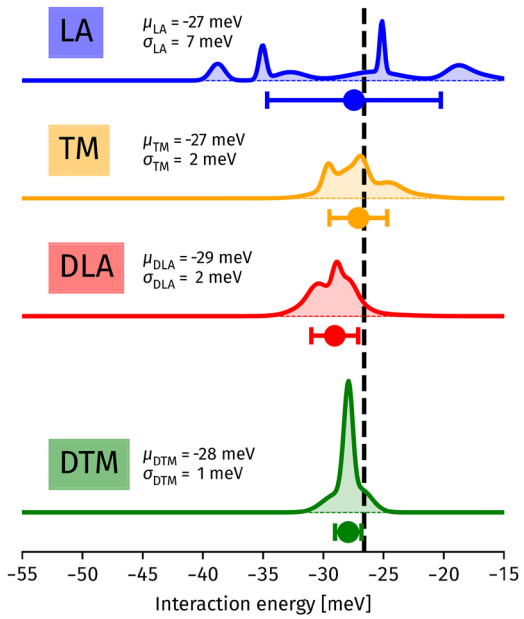

FIG. 2. Probability distribution $P_\alpha(E)$ [Eq. (2)] of the FN-DMC interaction energy of the methane–water dimer for four different schemes for treating NLPPs. The probability distribution for the LA method is spread across a large energy range of ~25 meV, showing the disagreement among different codes. The probability distribution is instead much narrower when the TM, DLA, and DTM algorithms are employed, implying agreement on the final estimate of the interaction energy among different codes. The black vertical dashed line indicates the reference value computed with CCSDT(Q).

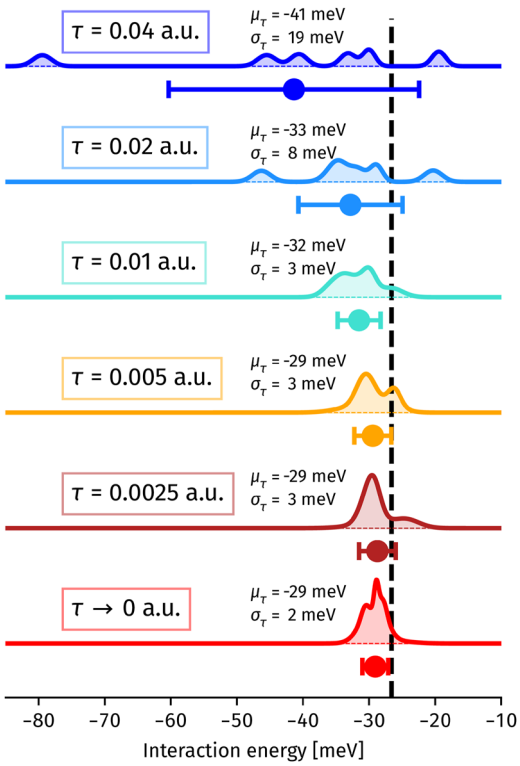

FIG. 3. Convergence with respect to the simulation time step of the probability distribution, as defined in Eq. (2), for the DLA. The probability distribution is spread over a large energy range of over 20 meV at large time steps ($\tau > 0.01$ a.u.), while a narrow distribution is achieved only for the smallest time step ($\tau = 0.0025$ a.u..). The black vertical dashed line indicates the reference value computed with CCSDT(Q).

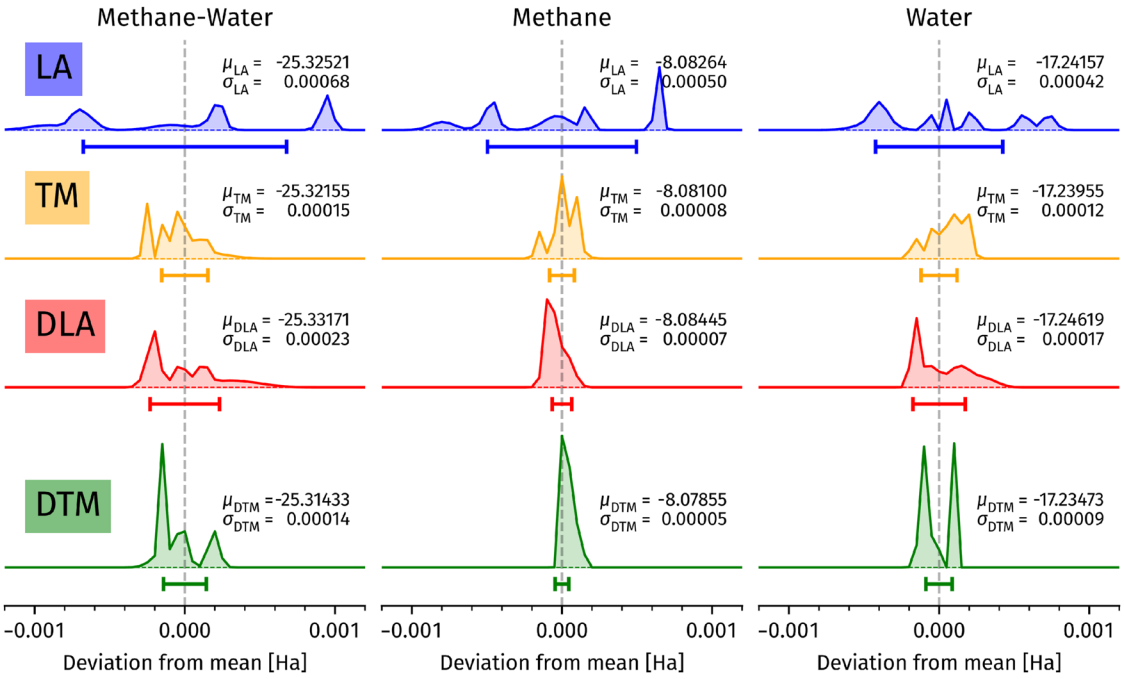

FIG. 4. Probability distribution $P_\alpha(E)$ [Eq. (2)] of the FN-DMC total energy (Hartree) of the methane–water dimer (left), methane (middle), and water (right), for four different schemes to treat NLPPs. The bars under the distributions indicate the standard deviation.

sufficiently small time steps, requiring calculations at various time steps τ to be performed and extrapolated to the limit $\tau \to 0$. The required time step depends on both the system being studied and the accuracy of the trial wave function. For this reason, we also analyze the dependence of the probability distribution $P_\alpha(E)$ on the simulation time step and report it in Fig. 3. In particular, we consider the case of the DLA, for which we have computed the interaction energy with several codes at multiple time steps ($\tau = 0.04, 0.02, 0.01, 0.005, 0.0025$ a.u.). We notice that, for a large time step $\tau = 0.04$ a.u., the DLA energy predictions are spread across a large energy range of over 60 meV. Decreasing the time step leads to a significant reduction in the distribution's variance. At the time step of $\tau = 0.0025$ a.u., the probability distribution becomes very narrow, indicating agreement among different codes. We highlight here that the converged time step is system-dependent, and the time step behavior is highly sensitive to different codes and approximations, as shown in the supplementary material. Therefore, an analysis of the convergence with respect to the simulation's time step is important to achieve a converged and reproducible FN-DMC energy and a fair comparison across different packages.

Finally, we focus on the FN-DMC total energies of the methane-water dimer and its constituent monomers, which are the fundamental quantities entering the computation of the interaction energy. In Fig. 4, we report the probability distribution $P_\alpha(E)$ of the total energies extrapolated to zero time step. As in the case of the interaction energy, we find that the total energies computed in the TM, DLA, and DTM approximations differ much less among the codes than when the LA is employed. Their distributions are significantly narrower, displaying standard deviations in a range from 2.5 to 10 times smaller than the LA case (e.g., in the water molecule $\sigma_{LA} \sim 2.5\sigma_{DLA}$, and in the methane monomer $\sigma_{LA} \sim 10\sigma_{DTM}$). Moreover, the standard deviations σ_αs of the TM, DLA, and DTM total energy distributions are close to the theoretical minimum allowed by the precision of the performed FN-DMC simulations, as σ_αs are mostly determined by the stochastic error associated with the FN-DMC energy evaluations (between 10^{-4} and 10^{-5} hartree; see the supplementary material), so the first term on the right hand side of Eq. (4). This behavior is expected for the DLA and DTM schemes that depend only on the determinant part of the wave functions (identical in all calculations). Remarkably, despite using different Jastrow factors, all codes yield very similar extrapolated total energies even with the TM scheme, which has the desirable property of treating the pseudopotential exactly in the limit of an exact Ψ_T.

III. METHODS

The interaction energy of the methane–water dimer is computed by subtracting the isolated molecule energies from the methane–water complex, as defined in Eq. (1). The geometry of the dimer (shown in the supplementary material) was obtained from Ref. 135. The geometries of the monomers are the same as in the dimer. In this study, in order to try to achieve consistent results, all eleven codes were required to use the same correlation consistent effective core potentials (ccECPs)[136,137] and the corresponding triple-zeta basis set (ccECP-ccpVTZ), as well as a Slater–Jastrow wave function with a single Slater determinant, whose orbitals are obtained from DFT calculations

using the Perdew–Zunger parameterization[138] of the local-density approximation. For the methane–water dimer, this was sufficient to obtain accurate results. Some of the codes exchanged wave function data via the TREXIO library.[139] This choice ensures that any observed variation is due to implementation-level or algorithmic factors rather than differences in the choice of geometry, pseudopotential, basis set, or single-particle orbitals. Every code implements a slightly different parameterization of the Jastrow factor, but all codes include in the Jastrow factor an electron–electron (e–e), an electron–nucleus (e–n), and an electron–electron–nucleus (e–e–n) term. The variational parameters of the Jastrow factor have been optimized by minimizing either the variational energy or the variance, according to the recommended scheme within each code. The time steps employed in each simulation are in the range of 0.001–0.1 a.u. The final estimates reported in Fig. 1 were extrapolated to the $\tau \to 0$ limit using the procedure described in the supplementary material. Further details specific to each code, the schemes used to deal with the localization error, the time step extrapolation, and the tests on the size consistency error are reported in the supplementary material.

IV. SUMMARY AND CONCLUSIONS

In this work, we investigated the reproducibility of FN-DMC calculations across 11 popular QMC codes, which differ in the details of the algorithms used. This study represents a significant collaborative effort, involving more than 300 FN-DMC calculations, spanning 11 codes, multiple DMC time steps, and different pseudopotential localization schemes. Our results establish FN-DMC as a robust reference method by demonstrating its reproducibility.

In particular, we conducted a thorough analysis of two key obstacles to FN-DMC reproducibility, namely, the use of NLPPs and finite time step bias. We systematically compared four localization schemes, LA, TM, DLA, and DTM, for the interaction energy of the methane–water dimer and the total energies of the methane and water molecules and of the dimer. We found that agreement in the interaction energy across all eleven codes is achieved in the limit of zero time step when employing the TM, DLA, and DTM approximations. Notably, we achieve agreement within a standard deviation of 3 meV on the interaction energy of the methane–water complex, approximately two hundred thousand times smaller than the total energy of the dimer. Larger discrepancies are observed with the LA scheme. Agreement in total energies across codes is also achieved, at sub-millihartree precision. In particular, the total energies with the TM, DLA, and DTM schemes have a standard deviation among the codes that is smaller than 6 meV. This agreement further reinforces the reproducibility of FN-DMC.

Looking ahead, extending this cross-code effort to periodic solids would be a natural next step. However, such systems introduce additional layers of complexity—including basis set periodization, Brillouin zone sampling, and finite-size corrections—that go beyond the scope of this initial benchmark. Moreover, as only a subset of the participating codes currently support periodic boundary conditions, we deliberately focused here on molecular systems in open boundary conditions to establish a controlled but challenging comparison for FN-DMC reproducibility.

SUPPLEMENTARY MATERIAL

See the supplementary material for comprehensive details on the computational setup used in this study, including the geometry of the systems, descriptions of the trial wave functions, and specific parameters for each of the 11 FN-DMC codes. Additional data are provided on time step convergence studies, localization error analysis, and interaction and total energy comparisons. The file also includes technical implementation notes from each code, information on Jastrow factor optimization, and complete tables of all raw FN-DMC energies and statistical uncertainties used to generate the figures in the main text.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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