Reproducibility of fixed-node diffusion Monte Carlo across diverse community codes: The case of water-methane dimer

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September 8, 2025

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 makes 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 (TM), the determinant locality approximation (DLA), or the determinant T-move (DTM) schemes, while the older locality approximation (LA) 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.

1 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 [2, 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, towards 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 $\Psi_{\mathrm{T}}(\mathbf{R})$. Within the Born-Oppenheimer approximation, $\mathbf{R}$ consists of the real space positions of all the electrons. Typically, $\Psi_{\mathrm{T}}(\mathbf{R})$ 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 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 $\Psi_{\mathrm{T}}(\mathbf{R})$, 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 band gaps [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 Section S8 of the Supplementary Information (SI). 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 $\Psi_{\mathrm{T}}(\mathbf{R})$, 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 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.

2 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,

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

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 the **Methods** section for details on the geometries and the DMC simulation set-up). All the interaction energies are extrapolated to the zero time-step limit according to the procedure described in the SI 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 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 SI 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 step, 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 the manuscript. 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 be highly accurate for weak intermolecular interactions [134] (details of the calculation are reported in Sec. S3 of the SI). Despite using only a single determinant in the trial wave functions and a DFT nodal surface for simplicity, broadly speaking,

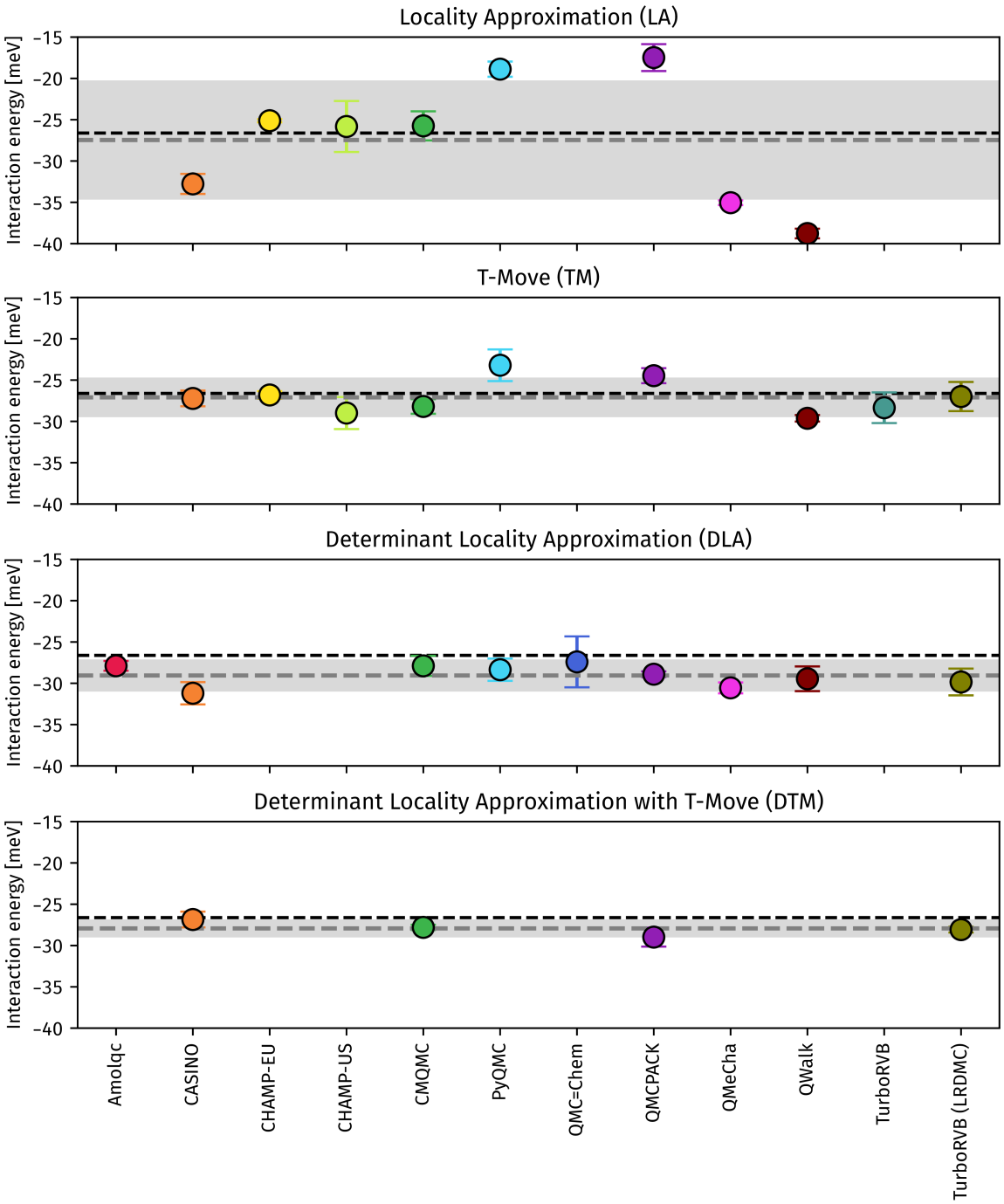

Figure 1: FN-DMC interaction energy of the methane-water dimer with four different methods. The black dashed horizontal line indicates the reference value of −27 meV computed with CCSDT(Q). The gray dashed line is the average among the interaction energies computed with different codes, and the shaded 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.

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 allows 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:

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

where N_α is the number of codes for which the localization method α is evaluated. The mean, μ_α, and the variance, σ^2_α, 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

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

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 (standard deviation of ca. 2 meV or less) centered on -27 meV, -29 meV and -28 meV respectively. The DTM scheme gives the narrowest distribution, centered on -28 meV, with a standard deviation of ca. 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 sufficiently small time step, 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

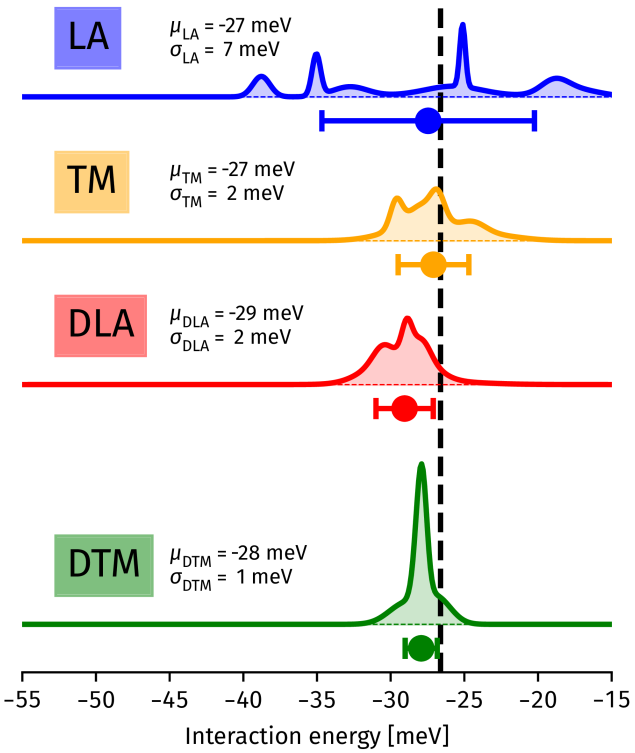

Figure 2: Probability distribution $P_\alpha(E)$ (Eq. 2) of the FN-DMC interaction energy of the methane-water dimer for four different schemes for treating NLPPs. The probability distribution for the LA method is spread across a large energy range of ca. 25 meV, showing the disagreement among different codes. The probability distribution is instead much narrower when the TM, DLA, and DTM algorithms are employed, implying the 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).

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 SI. 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 $\sigma_{\mathrm{LA}} \sim 2.5\sigma_{\mathrm{DLA}}$, and in the methane monomer $\sigma_{\mathrm{LA}} \sim 10\sigma_{\mathrm{DTM}}$). 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 to the FN-DMC energy evaluations (between 10^{-4} and 10^{-5} Hartree, see SI), 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

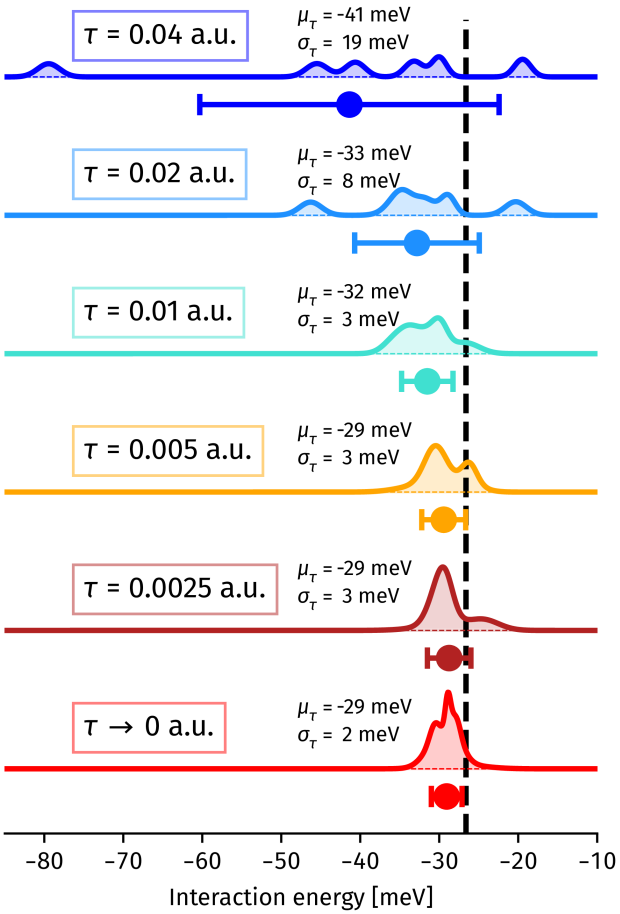

Figure 3: Convergence with respect to the simulation time step of the probability distribution, as defined in Eq. 2, for the DLA. The probability distribution is spread over a large energy range of over 20 meV at large time steps ($\tau > 0.01$ a.u.), while a narrow distribution is achieved only for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

(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.

3 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 SI) 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 potential (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 parametrization [138] of the local-density approximation. For the methane-water dimer,

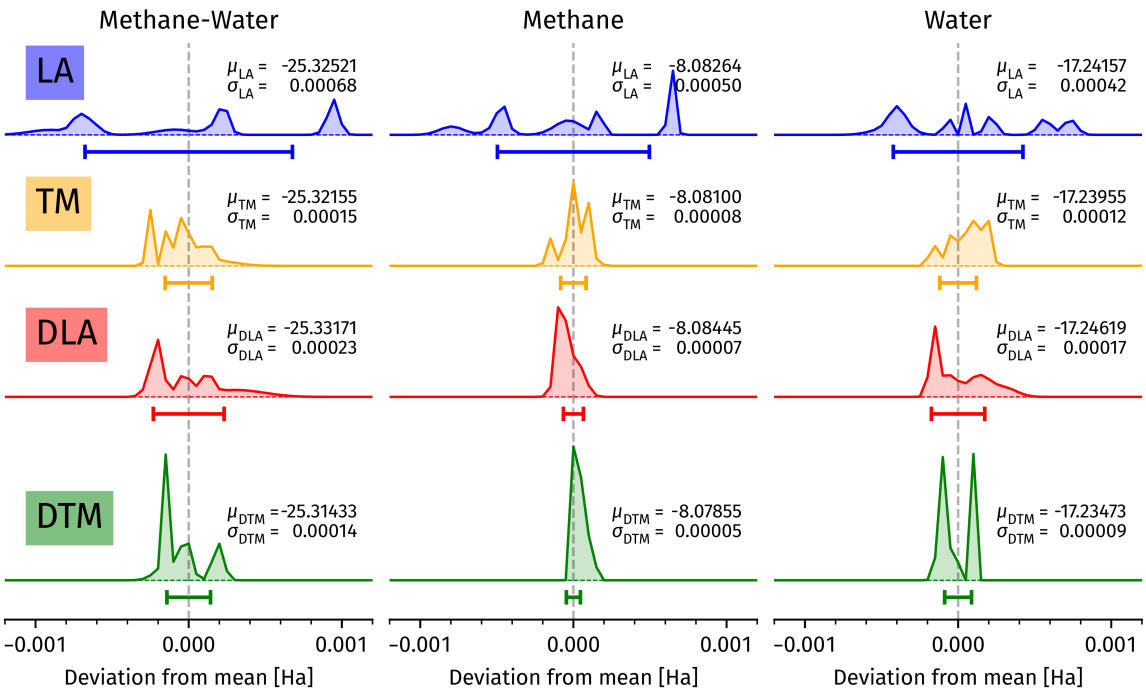

Figure 4: Probability distribution $P_\alpha(E)$ (Eq. 2) of the FN-DMC total energy (Hartree) of the methane-water dimer (left), methane (middle), and water (right), for four different schemes to treat NLPPs. The bars under the distributions indicate the standard deviation.

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 parametrization 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 0.001 to 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 SI. 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 SI.

4 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 which 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, 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.

Acknowledgements

M.B. acknowledges the computational resources from the HPC facilities of the University of Luxembourg [140] (see hpc.uni.lu). M.D. acknowledges financial support from the European Union under the LERCO project number CZ.10.03.01/00/22_003/0000003, via the Operational Programme Just Transition, and computational resources from the IT4Innovations National Supercomputing Center (e-INFRA CZ, ID: 90140). M.C. acknowledges access to French computational resources at the CEA-TGCC center through the GENCI allocation number A0150906493. J.T.K., P.R.C.K., Y.L. and L.M. were supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, as part of the Computational Materials Sciences Program and Center for Predictive Simulation of Functional Materials. Part of the work of L.M. has been supported also by U.S. National Science Foundation grant DMR-2316007 and employed resources at NERSC at early stages for this project. M.C., E.S., R.S., and C.F. acknowledge partial support by the European Centre of Excellence

in Exascale Computing TREX — Targeting Real Chemical Accuracy at the Exascale. This project has received funding in part from the European Union's Horizon 2020 — Research and Innovation program — under grant agreement no. 952165. E.S., R.S., and C.F performed the calculations on the Dutch national supercomputer Snellius with the support of SURF Cooperative. K.N. acknowledges financial support from the JSPS Overseas Research Fellowships and from MEXT Leading Initiative for Excellent Young Researchers (Grant No. JPMXS0320220025) and computational resources from the Numerical Materials Simulator at National Institute for Materials Science (NIMS). L.K.W and W.W. were supported by U.S. National Science Foundation via Award No. 1931258. Y.S.A., A.Z. and D.A. acknowledge support from the European Union under the Next generation EU (projects 20222FXZ33 and P2022MC742) and from Leverhulme grant no. RPG-2020-038. A.M. and B.X.S. acknowledge support from the European Union under the "n-AQUA" European Research Council project (Grant No. 101071937). The portion of the work done by T.A.A. and C.J.U. received initial support under AFOSR (Grant No. FA9550-18-1-0095) and was completed under the Exascale Computing Project (17-SC-20-SC), a collaborative effort of the U.S. Department of Energy Office of Science and the National Nuclear Security Administration."

This research used resources of the Oak Ridge Leadership Computing Facility at the Oak Ridge National Laboratory, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC05-00OR22725. Calculations were also performed using the Cambridge Service for Data Driven Discovery (CSD3) operated by the University of Cambridge Research Computing Service (www.csd3.cam.ac.uk), provided by Dell EMC and Intel using Tier-2 funding from the Engineering and Physical Sciences Research Council (capital grant EP/T022159/1 and EP/P020259/1), and DiRAC funding from the Science and Technology Facilities Council (www.dirac.ac.uk). This work also used the ARCHER UK National Supercomputing Service (https://www.archer2.ac.uk), the United Kingdom Car Parrinello (UKCP) consortium (EP/ F036884/1). FDP, BXS, and AM acknowledge EuroHPC Joint Undertaking for awarding the project ID EHPC-REG-2024R02-130 access to Leonardo at CINECA, Italy.

References

[1] O. S. Collaboration, "Estimating the reproducibility of psychological science," Science, vol. 349, no. 6251, p. aac4716, 2015.

[2] G. Miller, "A Scientist's Nightmare: Software Problem Leads to Five Retractions," Science, vol. 314, no. 5807, pp. 1856–1857, 2006.

[3] C. F. Camerer, A. Dreber, E. Forsell, T.-H. Ho, J. Huber, M. Johannesson, M. Kirchler, J. Almenberg, A. Altmejd, T. Chan, E. Heikensten, F. Holzmeister, T. Imai, S. Isaksson, G. Nave, T. Pfeiffer, M. Razen, and H. Wu, "Evaluating replicability of laboratory experiments in economics," Science, vol. 351, no. 6280, pp. 1433–1436, 2016.

[4] C. F. Camerer, A. Dreber, F. Holzmeister, T.-H. Ho, J. Huber, M. Johannesson, M. Kirchler, G. Nave, B. A. Nosek, T. Pfeiffer, A. Altmejd, N. Buttrick, T. Chan, Y. Chen, E. Forsell, A. Gampa, E. Heikensten, L. Hummer, T. Imai, S. Isaksson, D. Manfredi, J. Rose, E.-J. Wagenmakers, and H. Wu, "Evaluating the replicability

of social science experiments in Nature and Science between 2010 and 2015," Nature Human Behaviour, vol. 2, no. 9, pp. 637–644, 2018.

[5] M. Baker, "1,500 scientists lift the lid on reproducibility," Nature, vol. 533, no. 7604, pp. 452–454, 2016.

[6] B. A. Nosek, G. Alter, G. C. Banks, D. Borsboom, S. D. Bowman, S. J. Breckler, S. Buck, C. D. Chambers, G. Chin, G. Christensen, M. Contestabile, A. Dafoe, E. Eich, J. Freese, R. Glennerster, D. Goroff, D. P. Green, B. Hesse, M. Humphreys, J. Ishiyama, D. Karlan, A. Kraut, A. Lupia, P. Mabry, T. Madon, N. Malhotra, E. Mayo-Wilson, M. McNutt, E. Miguel, E. L. Paluck, U. Simonsohn, C. Soderberg, B. A. Spellman, J. Turitto, G. VandenBos, S. Vazire, E. J. Wagenmakers, R. Wilson, and T. Yarkoni, "Promoting an open research culture," Science, vol. 348, no. 6242, pp. 1422–1425, 2015.

[7] M. Vihinen, "No more hidden solutions in bioinformatics," Nature, vol. 521, no. 7552, pp. 261–261, 2015.

[8] W. F. van Gunsteren, "The Seven Sins in Academic Behavior in the Natural Sciences," Angewandte Chemie International Edition, vol. 52, no. 1, pp. 118–122, 2013.

[9] D. C. Ince, L. Hatton, and J. Graham-Cumming, "The case for open computer programs," Nature, vol. 482, no. 7386, pp. 485–488, 2012.

[10] E. Schrödinger, "An undulatory theory of the mechanics of atoms and molecules," Phys. Rev., vol. 28, no. 6, p. 1049, 1926.

[11] K. Lejaeghere, G. Bihlmayer, T. Björkman, P. Blaha, S. Blügel, V. Blum, D. Caliste, I. E. Castelli, S. J. Clark, A. D. Corso, S. de Gironcoli, T. Deutsch, J. K. Dewhurst, I. D. Marco, C. Draxl, M. Dułak, O. Eriksson, J. A. Flores-Livas, K. F. Garrity, L. Genovese, P. Giannozzi, M. Giantomassi, S. Goedecker, X. Gonze, O. Grånäs, E. K. U. Gross, A. Gulans, F. Gygi, D. R. Hamann, P. J. Hasnip, N. A. W. Holzwarth, D. Iuşan, D. B. Jochym, F. Jollet, D. Jones, G. Kresse, K. Koepernik, E. Küçükbenli, Y. O. Kvashnin, I. L. M. Locht, S. Lubeck, M. Marsman, N. Marzari, U. Nitzsche, L. Nordström, T. Ozaki, L. Paulatto, C. J. Pickard, W. Poelmans, M. I. J. Probert, K. Refson, M. Richter, G.-M. Rignanese, S. Saha, M. Scheffler, M. Schlipf, K. Schwarz, S. Sharma, F. Tavazza, P. Thunström, A. Tkatchenko, M. Torrent, D. Vanderbilt, M. J. van Setten, V. V. Speybroeck, J. M. Wills, J. R. Yates, G.-X. Zhang, and S. Cottenier, "Reproducibility in density functional theory calculations of solids," Science, vol. 351, no. 6280, p. aad3000, 2016.

[12] E. Bosoni, L. Beal, M. Bercx, P. Blaha, S. Blügel, J. Bröder, M. Callsen, S. Cottenier, A. Degomme, V. Dikan, K. Eimre, E. Flage-Larsen, M. Fornari, A. Garcia, L. Genovese, M. Giantomassi, S. P. Huber, H. Janssen, G. Kastlunger, M. Krack, G. Kresse, T. D. Kühne, K. Lejaeghere, G. K. H. Madsen, M. Marsman, N. Marzari, G. Michalicek, H. Mirhosseini, T. M. A. Müller, G. Petretto, C. J. Pickard, S. Poncé, G.-M. Rignanese, O. Rubel, T. Ruh, M. Sluydts, D. E. P. Vanpoucke, S. Vijay, M. Wolloch, D. Wortmann, A. V. Yakutovich, J. Yu, A. Zadoks, B. Zhu, and G. Pizzi, "How to verify the precision of density-functional-theory implementations via reproducible and universal workflows," Nature Reviews Physics, vol. 6, no. 1, pp. 45–58, 2024.

[13] M. Hellgren and L. Baguet, "Random phase approximation with exchange for an accurate description of crystalline polymorphism," Phys. Rev. Res., vol. 3, p. 033263, Sep 2021.

[14] F. Della Pia, A. Zen, D. Alfè, and A. Michaelides, "DMC-ICE13: Ambient and high pressure polymorphs of ice from diffusion Monte Carlo and density functional theory," The Journal of Chemical Physics, vol. 157, p. 134701, 10 2022.

[15] F. Della Pia, A. Zen, D. Alfè, and A. Michaelides, "How Accurate Are Simulations and Experiments for the Lattice Energies of Molecular Crystals?," Phys. Rev. Lett., vol. 133, p. 046401, Jul 2024.

[16] B. X. Shi, D. J. Wales, A. Michaelides, and C. W. Myung, "Going for Gold(-Standard): Attaining Coupled Cluster Accuracy in Oxide-Supported Nanoclusters," Journal of Chemical Theory and Computation, vol. 20, no. 12, pp. 5306–5316, 2024.

[17] B. X. Shi, A. Zen, V. Kapil, P. R. Nagy, A. Grüneis, and A. Michaelides, "Many-Body Methods for Surface Chemistry Come of Age: Achieving Consensus with Experiments," Journal of the American Chemical Society, vol. 145, no. 46, pp. 25372–25381, 2023.

[18] A. Zen, J. G. Brandenburg, J. Klimeš, A. Tkatchenko, D. Alfè, and A. Michaelides, "Fast and accurate quantum Monte Carlo for molecular crystals," Proceedings of the National Academy of Sciences, vol. 115, no. 8, pp. 1724–1729, 2018.

[19] N. O'Neill, B. X. Shi, K. Fong, A. Michaelides, and C. Schran, "To Pair or not to Pair? Machine-Learned Explicitly-Correlated Electronic Structure for NaCl in Water," The Journal of Physical Chemistry Letters, vol. 15, no. 23, pp. 6081–6091, 2024.

[20] A. Tirelli, G. Tenti, K. Nakano, and S. Sorella, "High-pressure hydrogen by machine learning and quantum Monte Carlo," Phys. Rev. B, vol. 106, p. L041105, Jul 2022.

[21] M. N. Tahir, H. Shang, J. Li, and X. Ren, "Efficient Structural Relaxation Based on the Random Phase Approximation: Applications to Water Clusters," The Journal of Physical Chemistry A, vol. 128, pp. 7939–7949, 09 2024.

[22] J. Daru, H. Forbert, J. Behler, and D. Marx, "Coupled Cluster Molecular Dynamics of Condensed Phase Systems Enabled by Machine Learning Potentials: Liquid Water Benchmark," Phys. Rev. Lett., vol. 129, p. 226001, Nov 2022.

[23] C. Schran, J. Behler, and D. Marx, "Automated Fitting of Neural Network Potentials at Coupled Cluster Accuracy: Protonated Water Clusters as Testing Ground," Journal of Chemical Theory and Computation, vol. 16, no. 1, pp. 88–99, 2020.

[24] D. M. Ceperley, S. Jensen, Y. Yang, H. Niu, C. Pierleoni, and M. Holzmann, "Training models using forces computed by stochastic electronic structure methods," Electron. Struct., vol. 6, p. 015011, mar 2024.

[25] G. Tenti, K. Nakano, A. Tirelli, S. Sorella, and M. Casula, "Principal deuterium Hugoniot via quantum Monte Carlo and Δ-learning," Phys. Rev. B, vol. 110, p. L041107, Jul 2024.

[26] K. Nakano, M. Casula, and G. Tenti, "Efficient calculation of unbiased atomic forces in ab initio variational Monte Carlo," Phys. Rev. B, vol. 109, p. 205151, May 2024.

[27] M. S. Hybertsen and S. G. Louie, "Electron correlation in semiconductors and insulators: Band gaps and quasiparticle energies," Phys. Rev. B, vol. 34, pp. 5390–5413, Oct 1986.

[28] G. Onida, L. Reining, and A. Rubio, "Electronic excitations: density-functional versus many-body green's-function approaches," Rev. Mod. Phys., vol. 74, pp. 601–659, Jun 2002.

[29] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, "Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions," Rev. Mod. Phys., vol. 68, pp. 13–125, Jan 1996.

[30] G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C. A. Marianetti, "Electronic structure calculations with dynamical mean-field theory," Rev. Mod. Phys., vol. 78, pp. 865–951, Aug 2006.

[31] J. McClain, Q. Sun, G. K.-L. Chan, and T. C. Berkelbach, "Gaussian-based coupled-cluster theory for the ground-state and band structure of solids," Journal of Chemical Theory and Computation, vol. 13, no. 3, pp. 1209–1218, 2017. PMID: 28218843.

[32] I. Y. Zhang and A. Grüneis, "Coupled Cluster Theory in Materials Science," Frontiers in Materials, vol. 6, jun 2019.

[33] G. Sugiyama and S. Koonin, "Auxiliary field monte-carlo for quantum many-body ground states," Annals of Physics, vol. 168, no. 1, pp. 1–26, 1986.

[34] S. Zhang, J. Carlson, and J. E. Gubernatis, "Constrained path monte carlo method for fermion ground states," Phys. Rev. B, vol. 55, pp. 7464–7477, Mar 1997.

[35] S. Zhang and H. Krakauer, "Quantum monte carlo method using phase-free random walks with slater determinants," Phys. Rev. Lett., vol. 90, p. 136401, Apr 2003.

[36] M. Motta and S. Zhang, "Ab initio computations of molecular systems by the auxiliary-field quantum monte carlo method," WIREs Computational Molecular Science, vol. 8, no. 5, p. e1364, 2018.

[37] G. H. Booth, A. J. W. Thom, and A. Alavi, "Fermion monte carlo without fixed nodes: A game of life, death, and annihilation in slater determinant space," The Journal of Chemical Physics, vol. 131, p. 054106, 08 2009.

[38] G. H. Booth, A. Grüneis, G. Kresse, and A. Alavi, "Towards an exact description of electronic wavefunctions in real solids," Nature, vol. 493, pp. 365–370, 2013.

[39] G. Carleo and M. Troyer, "Solving the quantum many-body problem with artificial neural networks," Science, vol. 355, no. 6325, pp. 602–606, 2017.

[40] D. Pfau, J. S. Spencer, A. G. D. G. Matthews, and W. M. C. Foulkes, "Ab initio solution of the many-electron schrödinger equation with deep neural networks," Phys. Rev. Res., vol. 2, p. 033429, Sep 2020.

[41] J. Hermann, Z. Schätzle, and F. Noé, "Deep neural network solution of the electronic schrödinger equation," Nature Chemistry, vol. 12, no. 10, pp. 891–897, 2020.

[42] J. C. Slater, "The Theory of Complex Spectra," Phys. Rev., vol. 34, pp. 1293–1322, Nov 1929.

[43] R. Jastrow, "Many-Body Problem with Strong Forces," Phys. Rev., vol. 98, pp. 1479–1484, Jun 1955.

[44] R. Grimm and R. Storer, "Monte-Carlo solution of Schrödinger's equation," J. Comput. Phys., vol. 7, no. 1, pp. 134–156, 1971.

[45] M. Troyer and U.-J. Wiese, "Computational Complexity and Fundamental Limitations to Fermionic Quantum Monte Carlo Simulations," Phys. Rev. Lett., vol. 94, p. 170201, May 2005.

[46] R. J. Needs, M. D. Towler, N. D. Drummond, P. López Ríos, and J. R. Trail, "Variational and diffusion quantum Monte Carlo calculations with the CASINO code," The Journal of Chemical Physics, vol. 152, p. 154106, 04 2020.

[47] K. Nakano, C. Attaccalite, M. Barborini, L. Capriotti, M. Casula, E. Coccia, M. Dagrada, C. Genovese, Y. Luo, G. Mazzola, A. Zen, and S. Sorella, "TurboRVB: A many-body toolkit for ab initio electronic simulations by quantum Monte Carlo," The Journal of Chemical Physics, vol. 152, p. 204121, 05 2020.

[48] J. Kim, A. D. Baczewski, T. D. Beaudet, A. Benali, M. C. Bennett, M. A. Berrill, N. S. Blunt, E. J. L. Borda, M. Casula, D. M. Ceperley, S. Chiesa, B. K. Clark, R. C. Clay, K. T. Delaney, M. Dewing, K. P. Esler, H. Hao, O. Heinonen, P. R. C. Kent, J. T. Krogel, I. Kylänpää, Y. W. Li, M. G. Lopez, Y. Luo, F. D. Malone, R. M. Martin, A. Mathuriya, J. McMinis, C. A. Melton, L. Mitas, M. A. Morales, E. Neuscamman, W. D. Parker, S. D. P. Flores, N. A. Romero, B. M. Rubenstein, J. A. R. Shea, H. Shin, L. Shulenburger, A. F. Tillack, J. P. Townsend, N. M. Tubman, B. V. D. Goetz, J. E. Vincent, D. C. Yang, Y. Yang, S. Zhang, and L. Zhao, "QMCPACK: an open source ab initio quantum Monte Carlo package for the electronic structure of atoms, molecules and solids," Journal of Physics: Condensed Matter, vol. 30, p. 195901, apr 2018.

[49] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, "Quantum Monte Carlo simulations of solids," Rev. Mod. Phys., vol. 73, pp. 33–83, Jan 2001.

[50] Y. S. Al-Hamdani, P. R. Nagy, A. Zen, D. Barton, M. Kállay, J. G. Brandenburg, and A. Tkatchenko, "Interactions between large molecules pose a puzzle for reference quantum mechanical methods," Nature Communications, vol. 12, no. 1, p. 3927, 2021.

[51] Y. Luo, A. Benali, L. Shulenburger, J. T. Krogel, O. Heinonen, and P. R. C. Kent, "Phase stability of TiO2 polymorphs from diffusion Quantum Monte Carlo," New Journal of Physics, vol. 18, p. 113049, Nov. 2016.

[52] J. A. Santana, J. T. Krogel, P. R. C. Kent, and F. A. Reboredo, "Cohesive energy and structural parameters of binary oxides of groups IIA and IIIB from diffusion quantum Monte Carlo," The Journal of Chemical Physics, vol. 144, p. 174707, May 2016.

[53] Y. S. Al-Hamdani, A. Zen, and D. Alfè, "Unraveling H2 chemisorption and physisorption on metal decorated graphene using quantum Monte Carlo," The Journal of Chemical Physics, vol. 159, p. 204708, 11 2023.

[54] H. Shin, Y. Luo, A. Benali, and Y. Kwon, "Diffusion Monte Carlo study of O_2 adsorption on single layer graphene," Phys. Rev. B, vol. 100, p. 075430, Aug 2019.

[55] G. Lee, I. Hong, J. Ahn, H. Shin, A. Benali, and Y. Kwon, "Hydrogen separation with a graphenylene monolayer: Diffusion Monte Carlo study," The Journal of Chemical Physics, vol. 157, p. 144703, 10 2022.

[56] J. W. Lawson, C. W. Bauschlicher, J. Toulouse, C. Filippi, and C. Umrigar, "Quantum Monte Carlo study of the cooperative binding of NO2 to fragment models of carbon nanotubes," Chemical Physics Letters, vol. 466, no. 4, pp. 170–175, 2008.

[57] Y. S. Al-Hamdani, M. Ma, D. Alfè, O. A. von Lilienfeld, and A. Michaelides, "Communication: Water on hexagonal boron nitride from diffusion Monte Carlo," The Journal of Chemical Physics, vol. 142, p. 181101, 05 2015.

[58] Y. S. Al-Hamdani, D. Alfè, and A. Michaelides, "How strongly do hydrogen and water molecules stick to carbon nanomaterials?," The Journal of Chemical Physics, vol. 146, p. 094701, 03 2017.

[59] J. Chen, X. Ren, X.-Z. Li, D. Alfè, and E. Wang, "On the room-temperature phase diagram of high pressure hydrogen: An ab initio molecular dynamics perspective and a diffusion Monte Carlo study," The Journal of Chemical Physics, vol. 141, p. 024501, 07 2014.

[60] N. D. Drummond, B. Monserrat, J. H. Lloyd-Williams, P. L. Ríos, C. J. Pickard, and R. J. Needs, "Quantum Monte Carlo study of the phase diagram of solid molecular hydrogen at extreme pressures," Nature Communications, vol. 6, no. 1, p. 7794, 2015.

[61] L. Monacelli, M. Casula, K. Nakano, S. Sorella, and F. Mauri, "Quantum phase diagram of high-pressure hydrogen," Nature Physics, vol. 19, no. 6, pp. 845–850, 2023.

[62] B. Monserrat, N. D. Drummond, P. Dalladay-Simpson, R. T. Howie, P. López Ríos, E. Gregoryanz, C. J. Pickard, and R. J. Needs, "Structure and Metallicity of Phase V of Hydrogen," Phys. Rev. Lett., vol. 120, p. 255701, Jun 2018.

[63] D. Alfè, M. Alfredsson, J. Brodholt, M. J. Gillan, M. D. Towler, and R. J. Needs, "Quantum Monte Carlo calculations of the structural properties and the B1-B2 phase transition of MgO," Phys. Rev. B, vol. 72, p. 014114, Jul 2005.

[64] E. Sola and D. Alfè, "Melting of Iron under Earth's Core Conditions from Diffusion Monte Carlo Free Energy Calculations," Phys. Rev. Lett., vol. 103, p. 078501, Aug 2009.

[65] M. Barborini, M. Calandra, F. Mauri, L. Wirtz, and P. Cudazzo, "Excitonic-insulator instability and Peierls distortion in one-dimensional semimetals," Phys. Rev. B, vol. 105, p. 075122, Feb 2022.

[66] X. Zhou, Z. Huang, and X. He, "Diffusion Monte Carlo method for barrier heights of multiple proton exchanges and complexation energies in small water, ammonia, and hydrogen fluoride clusters," The Journal of Chemical Physics, vol. 160, p. 054103, 02 2024.

[67] S. Manten and A. Lüchow, "On the accuracy of the fixed-node diffusion quantum Monte Carlo method," The Journal of Chemical Physics, vol. 115, pp. 5362–5366, 09 2001.

[68] K. Krongchon, B. Busemeyer, and L. K. Wagner, "Accurate barrier heights using diffusion Monte Carlo," The Journal of Chemical Physics, vol. 146, p. 124129, 03 2017.

[69] M. Barborini and L. Guidoni, "Reaction pathways by quantum Monte Carlo: Insight on the torsion barrier of 1,3-butadiene, and the conrotatory ring opening of cyclobutene," J. Chem. Phys., vol. 137, p. 224309, 12 2012.

[70] E. T. Swann, M. L. Coote, A. S. Barnard, and M. C. Per, "Efficient protocol for quantum monte carlo calculations of hydrogen abstraction barriers: Application to methanol," International Journal of Quantum Chemistry, vol. 117, no. 9, p. e25361, 2017.

[71] M. Ruggeri, P. L. Ríos, and A. Alavi, "Correlation energies of the high-density spin-polarized electron gas to meV accuracy," Phys. Rev. B, vol. 98, p. 161105, Oct 2018.

[72] S. Azadi, N. D. Drummond, and S. M. Vinko, "Quantum monte carlo study of the phase diagram of the two-dimensional uniform electron liquid," 2024.

[73] K. M. Rasch and L. Mitas, "Fixed-node diffusion Monte Carlo method for lithium systems," Phys. Rev. B, vol. 92, p. 045122, Jul 2015.

[74] H. Shin, P. Ganesh, P. R. C. Kent, A. Benali, A. Bhattacharya, H. N. Lee, O. Heinonen, and J. T. Krogel, "DFT+U and quantum Monte Carlo study of electronic and optical properties of AgNiO2 and AgNi1-xCoxO2 delafossite," Phys. Chem. Chem. Phys., vol. 26, pp. 6967–6976, 2024.

[75] J. Yu, L. K. Wagner, and E. Ertekin, "Fixed-node diffusion Monte Carlo description of nitrogen defects in zinc oxide," Phys. Rev. B, vol. 95, p. 075209, Feb 2017.

[76] T. Ichibha, K. Saritas, J. T. Krogel, Y. Luo, P. R. C. Kent, and F. A. Reboredo, "Existence of La-site antisite defects in 3 (M = Mn, Fe, and Co) predicted with many-body diffusion quantum Monte Carlo," Scientific Reports, vol. 13, no. 1, p. 6703, 2023.

[77] S. Moroni, S. Saccani, and C. Filippi, "Practical Schemes for Accurate Forces in Quantum Monte Carlo," Journal of Chemical Theory and Computation, vol. 10, no. 11, pp. 4823–4829, 2014.

[78] J. van Rhijn, C. Filippi, S. De Palo, and S. Moroni, "Energy Derivatives in Real-Space Diffusion Monte Carlo," Journal of Chemical Theory and Computation, vol. 18, no. 1, pp. 118–123, 2022.

[79] E. Slootman, I. Poltavsky, R. Shinde, J. Cocomello, S. Moroni, A. Tkatchenko, and C. Filippi, "Accurate Quantum Monte Carlo Forces for Machine-Learned Force Fields: Ethanol as a Benchmark," Journal of Chemical Theory and Computation, vol. 20, no. 14, pp. 6020–6027, 2024.

[80] M. C. Per, E. K. Fletcher, E. T. Swann, and D. M. Cleland, "Reliable radical stabilization energies from diffusion Monte Carlo calculations," Journal of Computational Chemistry, vol. 41, no. 27, pp. 2378–2382, 2020.

[81] P. M. Zimmerman, J. Toulouse, Z. Zhang, C. B. Musgrave, and C. J. Umrigar, "Excited states of methylene from quantum Monte Carlo," J. Chem. Phys., vol. 131, p. 124103, Sep 28 2009.

[82] M. Barborini, S. Sorella, and L. Guidoni, "Structural Optimization by Quantum Monte Carlo: Investigating the Low-Lying Excited States of Ethylene," J. Chem. Theory Comput., vol. 8, no. 4, pp. 1260–1269, 2012.

[83] M. Barborini and E. Coccia, "Investigating Disjoint Non-Kekulé Diradicals with Quantum Monte Carlo: The Tetramethyleneethane Molecule through the Jastrow Antisymmetrized Geminal Power Wave Function," J. Chem. Theory Comput., vol. 11, no. 12, pp. 5696–5704, 2015.

[84] A. Scemama, A. Benali, D. Jacquemin, M. Caffarel, and P.-F. Loos, "Excitation energies from diffusion Monte Carlo using selected configuration interaction nodes," J. Chem. Phys., vol. 149, July 2018.

[85] A. Scemama, M. Caffarel, A. Benali, D. Jacquemin, and P.-F. Loos, "Influence of pseudopotentials on excitation energies from selected configuration interaction and diffusion Monte Carlo," Results Chem., vol. 1, p. 100002, Jan. 2019.

[86] M. Dash, J. Feldt, S. Moroni, A. Scemama, and C. Filippi, "Excited States with Selected Configuration Interaction-Quantum Monte Carlo: Chemically Accurate Excitation Energies and Geometries," J. Chem. Theory Comput., vol. 15, pp. 4896–4906, Sept. 2019.

[87] A. Cuzzocrea, S. Moroni, A. Scemama, and C. Filippi, "Reference Excitation Energies of Increasingly Large Molecules: A QMC Study of Cyanine Dyes," J. Chem. Theory Comput., vol. 18, pp. 1089–1095, Feb. 2022.

[88] N. S. Blunt and E. Neuscamman, "Excited-State Diffusion Monte Carlo Calculations: A Simple and Efficient Two-Determinant Ansatz," Journal of Chemical Theory and Computation, vol. 15, no. 1, pp. 178–189, 2019.

[89] S. Shepard, R. L. Panadés-Barrueta, S. Moroni, A. Scemama, and C. Filippi, "Double Excitation Energies from Quantum Monte Carlo Using State-Specific Energy Optimization," Journal of Chemical Theory and Computation, vol. 18, no. 11, pp. 6722–6731, 2022.

[90] F. A. Reboredo, P. R. C. Kent, and J. T. Krogel, "Evaluation of the excitation spectra with diffusion Monte Carlo on an auxiliary bosonic ground state," The Journal of Chemical Physics, vol. 159, p. 114118, 09 2023.

[91] B. Huang, O. A. von Lilienfeld, J. T. Krogel, and A. Benali, "Toward DMC Accuracy Across Chemical Space with Scalable Δ-QML," Journal of Chemical Theory and Computation, vol. 19, no. 6, pp. 1711–1721, 2023.

[92] J. A. Charry Martinez, M. Barborini, and A. Tkatchenko, "Correlated Wave Functions for Electron–Positron Interactions in Atoms and Molecules," Journal of Chemical Theory and Computation, vol. 18, no. 4, pp. 2267–2280, 2022.

[93] W. A. Al-Saidi and C. J. Umrigar, "Fixed-node diffusion Monte Carlo study of the structures of m-benzyne," The Journal of Chemical Physics, vol. 128, p. 154324, 04 2008.

[94] G. Ferlat, M. Hellgren, F.-X. Coudert, H. Hay, F. Mauri, and M. Casula, "van der Waals forces stabilize low-energy polymorphism in B2O3: Implications for the crystallization anomaly," Physical Review Materials, vol. 3, no. 6, p. 063603, 2019.

[95] Y. Nikaido, T. Ichibha, K. Hongo, F. A. Reboredo, K. C. H. Kumar, P. Mahadevan, R. Maezono, and K. Nakano, "Diffusion Monte Carlo Study on Relative Stabilities of Boron Nitride Polymorphs," The Journal of Physical Chemistry C, vol. 126, no. 13, pp. 6000–6007, 2022.

[96] M. Dubecký, S. Minárik, and F. Karlický, "Benchmarking fundamental gap of Sc2C(OH)2 MXene by many-body methods," The Journal of Chemical Physics, vol. 158, p. 054703, 02 2023.

[97] G. S. Jeon, A. D. Güclu, C. J. Umrigar, and J. K. Jain, "Composite-fermion antiparticle description of the hole excitation in a maximum-density droplet with a small number of electrons," Phys. Rev. B, vol. 72, p. 245312, Dec 2005.

[98] A. Ghosal, A. D. Güclu, C. J. Umrigar, D. Ullmo, and H. U. Baranger, "Correlation-induced inhomogeneity in circular quantumdots," NATURE PHYSICS, vol. 2, pp. 336–340, May 2006.

[99] A. Ghosal, A. D. Güclu, C. J. Umrigar, D. Ullmo, and H. U. Baranger, "Incipient Wigner localization in circular quantum dots," Phys. Rev. B, vol. 76, p. 085341, Aug 2007.

[100] A. D. Güclu, A. Ghosal, C. J. Umrigar, and H. U. Baranger, "Interaction-induced strong localization in quantum dots," Phys. Rev. B, vol. 77, p. 041301, Jan 2008.

[101] A. D. Güclu, C. J. Umrigar, H. Jiang, and H. U. Baranger, "Localization in an inhomogeneous quantum wire," Phys. Rev. B, vol. 80, p. 201302, Nov 2009.

[102] C. Filippi, X. Gonze, and C. J. Umrigar, "Generalized gradient approximations to density functional theory: Comparion with exact results," in Recent Developments and Applications of Density Functional Theory (Elsevier, ed.), 1996.

[103] A. Savin, C. J. Umrigar, and X. Gonze, "Relationship of kohn-sham eigenvalues to excitation energies," CHEMICAL PHYSICS Lett., vol. 288, pp. 391–395, May 22 1998.

[104] G. Cassella, H. Sutterud, S. Azadi, N. D. Drummond, D. Pfau, J. S. Spencer, and W. M. C. Foulkes, "Discovering Quantum Phase Transitions with Fermionic Neural Networks," Phys. Rev. Lett., vol. 130, p. 036401, Jan 2023.

[105] J. Hermann, J. Spencer, K. Choo, A. Mezzacapo, W. M. C. Foulkes, D. Pfau, G. Carleo, and F. Noé, "Ab initio quantum chemistry with neural-network wavefunctions," Nature Reviews Chemistry, vol. 7, no. 10, pp. 692–709, 2023.

[106] W. Ren, W. Fu, X. Wu, and J. Chen, "Towards the ground state of molecules via diffusion Monte Carlo on neural networks," Nature Communications, vol. 14, no. 1, p. 1860, 2023.

[107] D. Ceperley, "The statistical error of green's function Monte Carlo," Journal of Statistical Physics, vol. 43, no. 5, pp. 815–826, 1986.

[108] B. Hammond, P. Reynolds, and W. Lester, "Valence quantum Monte Carlo with ab initio effective core potentials," The Journal of Chemical Physics, vol. 87, no. 2, pp. 1130–1136, 1987.

[109] B. L. Hammond, P. J. Reynolds, and W. A. Lester, "Damped-Core Quantum Monte Carlo Method: Effective Treatment for Large-Z Systems," Phys. Rev. Lett., vol. 61, pp. 2312–2315, Nov 1988.

[110] A. Ma, N. D. Drummond, M. D. Towler, and R. J. Needs, "All-electron quantum monte carlo calculations for the noble gas atoms he to xe," Phys. Rev. E, vol. 71, p. 066704, Jun 2005.

[111] L. Mitáš, E. L. Shirley, and D. M. Ceperley, "Nonlocal pseudopotentials and diffusion Monte Carlo," The Journal of Chemical Physics, vol. 95, pp. 3467–3475, 09 1991.

[112] M. Casula, "Beyond the Locality Approximation in the Standard Diffusion Monte Carlo Method," Phys. Rev. B, vol. 74, p. 161102, Oct. 2006.

[113] M. M. Hurley and P. A. Christiansen, "Relativistic effective potentials in quantum Monte-Carlo calculations," J. Chem. Phys., vol. 86, p. 1069, 1987.

[114] H. Flad, A. Savin, and H. Preuss, "Reduction of the computational effort in quantum Monte Carlo calculations with pseudopotentials through a change of the projection operators," The Journal of Chemical Physics, vol. 97, pp. 459–463, 07 1992.

[115] M. Caffarel, T. Applencourt, E. Giner, and A. Scemama, Using CIPSI Nodes in Diffusion Monte Carlo, ch. 2, pp. 15–46. American Chemical Society, 2016.

[116] A. Zen, J. G. Brandenburg, A. Michaelides, and D. Alfè, "A New Scheme for Fixed Node Diffusion Quantum Monte Carlo with Pseudopotentials: Improving Reproducibility and Reducing the Trial-Wave-Function Bias," J. Chem. Phys., vol. 151, p. 134105, 10 2019.

[117] P. A. Christiansen, "Relativistic effective potentials in transition metal quantum Monte Carlo simulations," J. Chem. Phys., vol. 95, p. 361, 1991.

[118] M. Casula, S. Moroni, S. Sorella, and C. Filippi, "Size-consistent variational approaches to nonlocal pseudopotentials: Standard and lattice regularized diffusion Monte Carlo methods revisited," The Journal of Chemical Physics, vol. 132, p. 154113, 04 2010.

[119] T. A. Anderson and C. J. Umrigar, "Nonlocal pseudopotentials and time-step errors in diffusion monte carlo," J. Chem. Phys., vol. 154, p. 214110, 2021.

[120] Shinde, R.; Landinez Borda, E. J.; Shepard, S.; Slootman, E.; Cuzzocrea, A.; Azizi, V.; Lopez-Tarifa, P.; Renaud, N.; Umrigar, C. J.; Moroni, S.; Filippi, C. *Cornell-Holland Ab-Initio Materials Package (CHAMP-EU)*, 2024; https://github.com/filippi-claudia/champ (accessed 2024-7-31).

[121] Anderson, T. A.; Filippi, C.; Petruziello, F. R.; Güclu A. D.; Toulouse J.; Umrigar, C. J. *Cornell-Holland Ab-Initio Materials Package (CHAMP-US)*, 2024; https://github.com/QMC-Cornell/CHAMP (accessed 2024-10-22).

[122] W. A. Wheeler, S. Pathak, K. G. Kleiner, S. Yuan, J. N. B. Rodrigues, C. Lorsung, K. Krongchon, Y. Chang, Y. Zhou, B. Busemeyer, K. T. Williams, A. Muñoz, C. Y. Chow, and L. K. Wagner, "PyQMC: An all-Python real-space quantum Monte Carlo module in PySCF," The Journal of Chemical Physics, vol. 158, p. 114801, 03 2023.

[123] A. Scemama, M. Caffarel, E. Oseret, and W. Jalby, "QMC=Chem: A Quantum Monte Carlo Program for Large-Scale Simulations in Chemistry at the Petascale Level and beyond," in High Performance Computing for Computational Science - VECPAR 2012 (M. Daydé, O. Marques, and K. Nakajima, eds.), (Berlin, Heidelberg), pp. 118–127, Springer Berlin Heidelberg, 2013.

[124] A. Scemama, M. Caffarel, E. Oseret, and W. Jalby, "Quantum Monte Carlo for large chemical systems: Implementing efficient strategies for petascale platforms and beyond," J. Comput. Chem., vol. 34, pp. 938–951, Apr. 2013.

[125] P. R. C. Kent, A. Annaberdiyev, A. Benali, M. C. Bennett, E. J. Landinez Borda, P. Doak, H. Hao, K. D. Jordan, J. T. Krogel, I. Kylänpää, J. Lee, Y. Luo, F. D. Malone, C. A. Melton, L. Mitas, M. A. Morales, E. Neuscamman, F. A. Reboredo, B. Rubenstein, K. Saritas, S. Upadhyay, G. Wang, S. Zhang, and L. Zhao, "QMCPACK: Advances in the development, efficiency, and application of auxiliary field and real-space variational and diffusion quantum Monte Carlo," The Journal of Chemical Physics, vol. 152, p. 174105, 05 2020.

[126] M. Barborini, "Quantum Mecha (QMeCha) package β.1.3 (private repository)," 2023.

[127] L. K. Wagner, M. Bajdich, and L. Mitas, "QWalk: A quantum Monte Carlo program for electronic structure," Journal of Computational Physics, vol. 228, no. 9, pp. 3390–3404, 2009.

[128] K. Nakano, O. Kohulák, A. Raghav, M. Casula, and S. Sorella, "TurboGenius: Python suite for high-throughput calculations of ab initio quantum Monte Carlo methods," The Journal of Chemical Physics, vol. 159, p. 224801, 12 2023.

[129] Comparable values of the interaction energy (within a statistical uncertainty of the order of the meV) are obtained for the smallest time step $\tau = 0.0025$a.u. for the codes and localization schemes where such a time step is used.

[130] M. Casula, C. Filippi, and S. Sorella, "Diffusion Monte Carlo Method with Lattice Regularization," Phys. Rev. Lett., vol. 95, p. 100201, Sep 2005.

[131] D. F. B. ten Haaf, H. J. M. van Bemmel, J. M. J. van Leeuwen, W. van Saarloos, and D. M. Ceperley, "Proof for an upper bound in fixed-node Monte Carlo for lattice fermions," Phys. Rev. B, vol. 51, pp. 13039–13045, May 1995.

[132] M. Calandra Buonaura and S. Sorella, "Numerical study of the two-dimensional Heisenberg model using a Green function Monte Carlo technique with a fixed number of walkers," Phys. Rev. B, vol. 57, pp. 11446–11456, May 1998.

[133] S. Sorella and L. Capriotti, "Green function Monte Carlo with stochastic reconfiguration: An effective remedy for the sign problem," Phys. Rev. B, vol. 61, pp. 2599–2612, Jan 2000.

[134] J. Rezac, M. Dubecky, P. Jurecka, and P. Hobza, "Extensions and applications of the A24 data set of accurate interaction energies," Phys. Chem. Chem. Phys., vol. 17, pp. 19268–19277, 2015.

[135] A. Zen, S. Sorella, M. J. Gillan, A. Michaelides, and D. Alfè, "Boosting the accuracy and speed of quantum Monte Carlo: Size consistency and time step," Phys. Rev. B, vol. 93, p. 241118, Jun 2016.

[136] M. C. Bennett, C. A. Melton, A. Annaberdiyev, G. Wang, L. Shulenburger, and L. Mitas, "A new generation of effective core potentials for correlated calculations," The Journal of Chemical Physics, vol. 147, p. 224106, 12 2017.

[137] A. Annaberdiyev, G. Wang, C. A. Melton, M. C. Bennett, L. Shulenburger, and L. Mitas, "A new generation of effective core potentials from correlated calculations: 3d transition metal series," The Journal of Chemical Physics, vol. 149, p. 134108, 10 2018.

[138] J. P. Perdew and A. Zunger, "Self-interaction correction to density-functional approximations for many-electron systems," Phys. Rev. B, vol. 23, pp. 5048–5079, May 1981.

[139] E. Posenitskiy, V. G. Chilkuri, A. Ammar, M. Hapka, K. Pernal, R. Shinde, E. J. Landinez Borda, C. Filippi, K. Nakano, O. Kohulák, S. Sorella, P. de Oliveira Castro, W. Jalby, P. L. Ríos, A. Alavi, and A. Scemama, "TREXIO: A file format and library for quantum chemistry," The Journal of Chemical Physics, vol. 158, p. 174801, 05 2023.

[140] S. Varrette, P. Bouvry, H. Cartiaux, and F. Georgatos, "Management of an Academic HPC Cluster: The UL Experience," in Proc. of the 2014 Intl. Conf. on High Performance Computing & Simulation (HPCS 2014), (Bologna, Italy), pp. 959–967, IEEE, July 2014.