The Role of High-Order Electron Correlation Effects in a Model System for Non-valence Correlation-bound Anions

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The diffusion Monte Carlo (DMC), auxiliary field quantum Monte Carlo (AFQMC), and equation-of-motion coupled cluster (EOM-CC) methods are used to calculate the electron binding energy of the non-valence anion state of a model (H₂O)₄ cluster. Two geometries are considered, one at which the anion is unbound and the other at which it is bound in the Hartree-Fock approximation. It is demonstrated that DMC calculations can recover from the use of a Hartree-Fock trial wave function that has collapsed onto a discretized continuum solution, although larger electron binding energies are obtained when using a trial wave function of the anion that provides a more realistic description of the charge distribution, and, hence, of the nodal surface. For the geometry at which the cluster has a non-valence correlation-bound anion, both the AFQMC and DMC calculations with suitable trial wave functions give an EBE somewhat larger than the EOM-CCSD result. DMC calculations using multideterminant trial wave functions give electron binding energies in reasonable agreement with the EOM and other DMC results, but it proves to be very challenging to balance the errors in the energies of the neutral and anion in these calculations.

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I. INTRODUCTION

In recent years, there has been growing interest in a class of anions known as non-valence correlation-bound (NVCB) anions in which long-range correlation effects are crucial for the binding of the excess electron.\textsuperscript{1–14} By definition, NVCB anions are unbound in the Hartree-Fock (HF) approximation. Due to their highly spatially extended charge distributions, large, flexible basis sets are required for the theoretical characterization of NVCB anions. However, with such basis sets, the wave function from Hartree-Fock (HF) calculations on the excess electron system collapses onto the neutral plus an electron in an orbital that can be viewed as a discretized representation of a continuum solution.\textsuperscript{1} Methods that start from the HF wave function including second-order Møller-Plesset perturbation theory (MP2)\textsuperscript{15} or coupled-cluster singles and doubles with perturbative triples (CCSD(T))\textsuperscript{16} do not recover from this collapse onto the continuum, while methods such as orbital-optimized MP2 (OOMP2)\textsuperscript{17} or Bruckner coupled-cluster\textsuperscript{18} can overcome this problem.\textsuperscript{1} The majority of calculations of NVCB anions have employed the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) method.\textsuperscript{19} Among the NVCB anions studied computationally to date are $\text{C}_{60}$, $\text{C}_{6}\text{F}_{6}$, TCNE, $(\text{NaCl})_{2}$, $\text{Xe}_{n}$ clusters, large polyaromatic hydrocarbons, and certain $(\text{H}_{2}\text{O})_{n}$ clusters.\textsuperscript{1–3,8–14}

The EOM-CCSD method displays an $O(N^6)$ scaling with system size, and higher order EOM-CC methods are even more computationally demanding. As a result, most of the calculations of NVCB anions carried out to date have not been fully converged with respect to basis set or the level of excitations treated in the EOM procedure. We note, however, that by using domain-based local pair natural orbitals (DLPNO), electron affinity EOM-CCSD calculations have recently been carried out on systems described by up to 4,500 basis functions.\textsuperscript{20}

In the present work, we apply two quantum Monte Carlo (QMC) methods to the problem of calculating the electron binding energy (EBE) of the non-valence anion of a model $(\text{H}_{2}\text{O})_{4}$ cluster. The first approach considered is fixed-node diffusion Monte Carlo (DMC),\textsuperscript{21–24} using various single Slater determinant (SD) and multideterminant (MD) trial wave functions. DMC is a real-space method, with the major sources of error resulting from the use of finite time steps and the fixed-node approximation. The finite time step error can be largely eliminated by running calculations at different time steps and then extrapolating to the zero time step limit. The fixed-node error results from imposition of a nodal surface of the trial wave function, which is necessary to ensure Fermionic behavior, and can be addressed by a variety of means including expanding the number
of Slater determinants in the trial wave function or applying the backflow transformation.\textsuperscript{25} It is important to note that, by virtue of working in real space, fixed-node DMC energies are much less sensitive to the choice of the atomic basis set than methods that operate in a space of Slater determinants, such as EOM-CCSD. The second QMC approach considered is the auxiliary field QMC (AFQMC) method.\textsuperscript{26–32} AFQMC calculations sample an over-complete space of nonorthogonal Slater determinants, which formally preserve the antisymmetry of the electrons. The finite time step error can be mitigated as in DMC. The error that arises from constraining the phase of the wave function to zero can be systematically reduced by improving the trial wave function. Phase-less AFQMC is additionally subject to the limitations of the atomic basis set employed. DMC scales as $O(N^3)$ with system size, while AFQMC displays an $O(N^4)$ scaling in most implementations. One of the goals of these calculations is to determine whether DMC calculations can recover from the use of a trial wave function that has collapsed onto a discretized continuum orbital in the case of the excess electron. Additionally, we explore whether these two QMC methods are able to recover correlation effects that are missing in EOM-CCSD.

In our calculations, we employ a model (H$_2$O)$_4$ cluster that has been investigated in earlier studies by our group.\textsuperscript{1,2} In this model, depicted in Fig. 1, the monomers are arranged so that the net dipole moment is zero. If the distance $R$ is varied, with all other geometrical parameters held fixed, the system can be tuned from a regime (large $R$) that the excess electron weakly binds in the HF approximation to one (small $R$) at which it is not bound in the HF approximation. i.e., in which it is NVCh in nature.

II. METHODOLOGY

A. EOM Coupled Cluster

The EOM methods considered in this study are EOM-MP2,\textsuperscript{34} EOM-CCSD,\textsuperscript{19} EOM-CCSD(T)(a),\textsuperscript{35} and EOM-CCSDT,\textsuperscript{36,37} listed in order of increasing sophistication in terms of treatment of correlation effects. In the EOM-MP2 and EOM-CCSD methods, the neutral molecule is treated at the MP2 and CCSD levels, respectively, and the amplitudes from these calculations are used to perform unitary transformation of the Hamiltonian. This "dressed" Hamiltonian is then used to carry out a 1-particle plus 2-particle-1-hole configuration interaction (CI) calculation on the anion. In the EOM-CCSDT method, the neutral species is first treated at the CCSDT level, and the
FIG. 1. The model \((H_2O)_4\) system considered in this study. \(R'\) held fixed at 3.46105 Å, and \(R\) is either 4 Å or 7 Å. Image generated using VMD.\textsuperscript{33}

transformed Hamiltonian is used to do CI calculation on the anion that includes up to 3-particle-2-hole configurations. The CCSD(T)(a)* method includes in an approximate manner both triple excitations in the ground state coupled cluster calculations and 3-particle-2-hole excitations in the treatment of the anion.\textsuperscript{35}

The main basis set used for the EOM calculations reported in this study is aug-cc-pVTZ+7s7p, formed by supplementing the aug-cc-pVTZ Gaussian-type orbital (GTO) basis set\textsuperscript{38,39} with a 7s7p set of diffuse functions centered at the middle of the cluster and similar to the set from Ref. 1. The exponents of the supplemental functions start at 0.023622, with each successive exponent being smaller by a factor of 3.2. However, as seen from Table I, the supplemental 7s7p set of diffuse functions can be truncated to 3s1p without significantly impacting the EBE as calculated at the EOM-CCSD level. Moreover, as shown in Table II, expanding the main basis set (i.e., the non-
TABLE I. Dependence of the total energies and the EBE of the model (H\textsubscript{2}O\textsubscript{4}) cluster at R = 4 Å on the supplemental diffuse basis functions. Results obtained using the EOM-CCSD method.

| basis set           | neutral (Ha) | anion (Ha) | EBE (meV) |
|---------------------|--------------|------------|-----------|
| aug-cc-pVTZ         | -305.327947  | -305.331344| 92.4      |
| aug-cc-pVTZ+1s      | -305.327953  | -305.332359| 119.9     |
| aug-cc-pVTZ+2s      | -305.327957  | -305.334226| 170.6     |
| aug-cc-pVTZ+3s      | -305.327958  | -305.334460| 176.9     |
| aug-cc-pVTZ+7s      | -305.327958  | -305.334462| 177.0     |
| aug-cc-pVTZ+7s1p    | -305.327979  | -305.334604| 180.3     |
| aug-cc-pVTZ+7s7p    | -305.327987  | -305.334622| 180.6     |
| aug-cc-pVTZ+3s1p    | -305.327979  | -305.334602| 180.2     |

supplemented portion) from aug-cc-pVTZ to aug-cc-pVQZ\textsuperscript{38,39} makes only a small impact on the EBE (4% at R = 4 Å). In contrast, reducing the main basis set to aug-cc-pVDZ\textsuperscript{38,39} leads to a 14% reduction in the EBE. (These results were obtained using the EOM-MP2 method, but as seen from comparison of the results in Tables I and II, using the aug-cc-pVTZ+3s1p basis set in both cases, the EBEs from the calculations with the EOM-CCSD and EOM-MP2 methods agree to within 0.5 meV.) The smaller aug-cc-pVDZ+3s1p basis will be used in the EOM-CCSDT calculations, which would have been computationally prohibitive with aug-cc-pVTZ+7s7p or aug-cc-pVTZ+3s1p basis set. The EOM calculation were carried out using the CFOUR program.\textsuperscript{40,41}

B. DMC

The DMC calculations were carried out using trial wave functions represented as products of one or more Slater determinants and a Jastrow factor with one-, two-, and three-body terms.\textsuperscript{42–44} The parameters in the Jastrow factors were optimized using variational Monte Carlo (VMC), and the resulting trial wave functions were then employed in subsequent DMC calculations. Three types of SD trial wave functions were employed. These used HF orbitals, Becke, 3-parameter, Lee–Yang–Parr (B3LYP) DFT orbitals,\textsuperscript{45–48} and natural orbitals (NOs) from small restricted single plus double excitation (SDCI) calculations designed to bind the excess electron even when it
TABLE II. Sensitivity of the EBE of the $(\text{H}_2\text{O})_4$ model at $R = 4$ Å to the “core” basis set. Results obtained using the EOM-MP2 method.

| Basis Set               | Neutral (Ha) | Anion (Ha)  | EBE (meV) |
|-------------------------|--------------|-------------|-----------|
| $R = 4.0$ Å             |              |             |           |
| aug-cc-pVDZ+3s1p        | -305.0371957 | -305.0428558| 154.0     |
| aug-cc-pVTZ+3s1p        | -305.3092869 | -305.3159306| 180.8     |
| aug-cc-pVQZ+3s1p        | -305.4008845 | -305.4078074| 188.4     |
| $R = 7.0$ Å             |              |             |           |
| aug-cc-pVDZ+3s1p        | -305.0383747 | -305.0432259| 132.0     |
| aug-cc-pVTZ+3s1p        | -305.3104923 | -305.3157472| 143.0     |
| aug-cc-pVQZ+3s1p        | -305.4021640 | -305.4075716| 147.1     |

is not bound in the HF approximation. In addition, DMC calculation were carried out using MD trial wave functions, with the determinants being determined either from the restricted SDCI procedure or from configuration interaction using a perturbative selection made iteratively (CIPSI) calculations. Details on these calculations are provided below.

To reduce the computational cost of the DMC calculations, the ccECP pseudopotentials were employed together with GTO basis sets that we designate as cc-pVDZ / ccECP, aug-cc-pVDZ / ccECP, aug-cc-pVDZ / ccECP+3s1p, and aug-cc-pVDZ / ccECP+7s7p. The "core" cc-pVDZ/ccECP basis set was designed for use with the ccECP pseudopotentials; the "aug" indicates that the diffuse aug functions from the aug-cc-pVDZ basis sets of Dunning and co-workers are included; and the 7s7p set of diffuse functions are those described above in the Section II A. The T-moves scheme was used to control the localization error for nonlocal pseudopotentials.

The double-zeta rather than the larger triple-zeta basis set was used as the core basis set due to the relative insensitivity of DMC calculations to the choice of the atomic basis set. For most of the DMC calculations a fixed population of 16,000 walkers and time steps of 0.001, 0.003, and 0.005 a.u. were employed, with the reported results obtained by linear extrapolation to zero time step. However, this population is much larger and the time steps much smaller than what is actually required to achieve well converged energies with minimized finite time step and fixed population errors. Indeed, DMC calculations using Hartree-Fock trial wave functions, larger time steps (specifically 0.05, 0.1, and 0.2 a.u.) and a smaller population of only 1,000 walkers produce
an electron binding energy within error bars of that obtained using the smaller time steps and larger populations. Additionally, a DMC calculation with a B3LYP trial wave function with a time step of 0.05 is in agreement with the values obtained with the smaller time steps and larger populations suggesting that the parameters do not depend strongly on the choice of starting orbitals. In light of this, the 0.05 a.u. time step and smaller walker population were employed in the DMC calculations using CIPSI trial wave functions to mitigate the additional cost of the multideterminant space. The VMC and DMC calculations were carried out using the QMCPACK code.\textsuperscript{44,53} The orbitals for the SD-based trial wave functions and the restricted SDCl MD wave function were both generated using GAMESS,\textsuperscript{54–56} whereas the CIPSI wave functions were generated using the Quantum Package 2.0 code.\textsuperscript{57}

C. Restricted CI and CIPSI-generated Trial Wave Functions for DMC Calculations

The restricted SDCl procedure employed the HF wave function for the neutral molecule and a specially tailored SDCl wave function for the anion. Specifically for the anion, the calculations included all symmetry-allowed single and double excitations, with the latter restricted so that one of the electrons excited is from the orbital occupied by the excess electron in the HF wave function. This approach, when used with a flexible basis set such as aug-cc-pVTZ/ccECP+7s7p, gives a bound anion. NOs were generated from SDCl wave function of the anion and were used in a SD trial wave function for subsequent DMC calculations. In addition, the SDCl wave function itself (expanded in terms of HF orbitals) was used in MD DMC calculations on the anion for R = 4 Å. In this case, a threshold of 0.001 on the magnitude of coefficients in the CI expansion was used in choosing the retained determinants. This resulted in a wave function with 1,392 determinants for R = 4 Å.

By design, the restricted SDCl wave function does not allow for change of correlation of the valence electrons due to the presence of the excess electron. This possibility is allowed for in the CIPSI MD trial wave functions. The CIPSI calculations were carried out using B3LYP orbitals rather than Hartree-Fock orbitals because the former avoids the problem of collapse onto a discretized continuum solution at R = 4 Å.\textsuperscript{45–47} Since the CIPSI calculations have not approached the full configuration interaction limit as indicated by the second order perturbative correction to the energy, a judicious choice of starting orbitals is required to construct a physically meaningful trial wave function. In order to generate compact wave functions, NOs were iteratively refined
through successive CIPSI calculations, each using a reference space consisting of a single determinant of natural orbitals from the previous iteration. For each NO-generating CIPSI calculation, approximately 100,000 determinants were retained and used to generate natural orbitals for the next iteration, for a total of six natural orbital generation cycles. With the determinant of resulting NOs as a reference, a final CIPSI calculation was carried out stopping when at least 150,000 determinants were included in the variational space for the anion and at least 100,000 determinants for the neutral. From these final determinant spaces, two sets of DMC MD trial wave functions were generated, one using the full determinants space (MD/CIPSI NO) and one using only those determinants with coefficients greater than $1 \times 10^{-4}$ (MD/CIPSI NO truncated).

Both the restricted SDCI and the CIPSI calculations were carried out using the ccECP pseudopotentials. The aug-cc-pVDZ/ccECP+7s7p and aug-cc-pVDZ/ccECP+3s1p basis sets were used for the SDCI and CIPSI calculations, respectively.

D. AFQMC

AFQMC$^{26–32}$ utilizes the Hubbard-Stratonovich transformation$^{58}$ to represent the imaginary-time propagator as a multi-dimensional integral over auxiliary-fields. Ground-state properties are sampled from a random walk in the space of non-orthogonal Slater determinants subject to the phaseless constraint$^{29}$ introducing a bias which can be systematically reduced based on the quality of the nodal surface of the trial wave function employed. While sophisticated trial wave functions based on regularized orbital-optimized MP2 ($\kappa$-OOMP2)$^{59}$ or CASSCF$^{60–62}$ are required to obtain quantitative predictions for some biradicaloids and transition metals, high accuracy has been obtained, even for systems exhibiting non-trivial electron correlation such as dipole-bound anions,$^{63}$ with single-determinant trial wave functions consisting of HF or Kohn-Sham orbitals.$^{63,64}$

In this work we perform calculations with a GPU implementation of AFQMC,$^{65}$ utilizing single-precision floating-point arithmetic and two-electron integrals decomposed via a modified Cholesky decomposition ($10^{-5}$ cutoff).$^{66}$ We have verified that the use of double-precision does not significantly alter the results. The aug-cc-pVTZ+7s7p basis set was used for the AFQMC calculations with a small imaginary-time step of 0.005 a.u, and all electrons were correlated. For the neutral species, the Hartree-Fock SD is used as the trial wave function. For the anionic species, SD trial wave functions were selected to ensure an appropriate physical description of the bound electron. Namely, we used natural orbitals from the restricted SDCI calculation as detailed in
Section II C for \( R = 4 \text{ Å} \) and Hartree-Fock orbitals for \( R = 7 \text{ Å} \).

E. Radial orbital densities

To compare the description of the charge distribution of the excess electron as calculated using different theoretical methods, we generate radial electron density plots. This choice is motivated by the fact that the excess electron occupies an orbital belonging to the totally symmetric representation. The radial electron densities are generated by numerically integrating over the angular components of the singly occupied molecular or natural orbital. First, Molden files are created from the output data from the various generating programs using cclib when supported. With the Molden files as input, PySCF is used to generate the electron density on a uniform radial grid and 5810 point Lebedev-Laikov angular grid as tabulated in quadpy. Finally, a numerical integration is performed over the angular components. An example of this workflow is presented in detail in the Supplementary Information.

III. RESULTS

The EBEs obtained from the EOM and AFQMC calculations are summarized in Table III, and the results from the various DMC calculations are summarized in Table IV. We consider first the results obtained for \( R = 4 \text{ Å} \), for which HF calculations do not bind the excess electron.

A. Results for \( R = 4 \text{ Å} \): the correlation bound region

From Table III, it is seen that the EOM-CCSD/aug-cc-pVTZ+7s7p calculations give a value of the EBE of 181 meV for the \((\text{H}_2\text{O})_4\) cluster model at \( R = 4 \text{ Å} \). This increases to 196 meV with the EOM-CCSD(T)(a)\(^*\) method. The AFQMC calculations using the same basis set and for the anion a single determinant of NOs from the restricted SDCI calculation for the trial wave function produce an EBE value of 194 ± 10 meV, comparable to that of EOM-CCSD(T)(a)\(^*\). While EOM-CCSDT calculations would be prohibitively expensive with the aug-cc-pVTZ+7s7p basis set, they were feasible with the aug-cc-pVDZ+3s1p basis set. The EOM-CCSD(T)(a)\(^*\) and EOM-CCSDT EBE values calculated with this basis set are nearly identical, and it is expected that this would also be the case with the aug-cc-pVTZ+7s7p basis set. The agreement between EOM-CCSD(T)(a)\(^*\) and
AFQMC suggests that the inclusion of triples are important to describing the NVCH anion of the model (H$_2$O)$_4$ system.

The restricted SDCI procedure, by itself, is not expected to give an accurate value of the EBE and is designed to generate appropriate trial wave functions for DMC or AFQMC calculations on the anion. In fact, the EBE resulting from the HF treatment of the neutral and the restricted SDCI treatment of the anion using the aug-cc-pVTZ+7s7p basis set is 345 meV, appreciably larger than the EOM and AFQMC values. This overbinding is likely due to an overestimation of the role of electrostatics since the restricted SDCI wave function like the HF wave function overestimates the magnitude of the dipole moment of the water molecules. We note also that the single determinant of NOs resulting from the restricted SDCI using the aug-cc-pVTZ+7s7p basis set on the anion is 160 meV above the neutral when the latter is treated in the HF approximation. This is not surprising since this calculation neglects correlation effects other than those incorporated in the determination of the orbitals. What is important is that the approaches based on the restricted SDCI procedure provide a realistic description of the orbital occupied by the excess electron and avoid the collapse onto the discretized continuum as was observed with the HOMO in the HF calculations.

In light of the close agreement between the EOM-CCSD(T)(a)* and AFQMC values of the EBE of the (H$_2$O)$_4$ model at R = 4 Å, it is highly relevant to determine whether DMC calculations with sufficiently flexible trial functions give an EBE close to the AFQMC and EOM value consistent with these results. DMC calculations using the aug-cc-pVDZ/ccECP+7s7p basis set and using a HF trial wave function give an EBE of 183 ± 10 meV, nearly identical to the EOM-CCSD result, somewhat smaller than the EOM-CCSD(T)(a)* and AFQMC results. Interestingly, essentially the same EBE is obtained from the DMC calculations using a Slater determinant of HF orbitals expanded in the aug-cc-pVDZ/ccECP basis set without the 7s7p supplemental set of diffuse functions. However, if the aug functions are also removed, the DMC calculations fail to bind the excess electron. We believe that this is a consequence of the fact that with the cc-pVDZ basis set there is a near zero probability of sampling regions of space at large distances from the molecule and which are important for describing the charge distribution of the excess electron.

A significantly larger value of the EBE is obtained from SD DMC calculations using B3LYP orbitals than obtained when using HF orbitals. The resulting EBE of 212 ± 11 meV, within statistical error, agrees with the EOM-CCSD(T)(a)* and AFQMC values. A similar value of the EBE is obtained from DMC calculations using a single determinant of HF orbitals for the neutral cluster.
TABLE III. EBEs of the (H\textsubscript{2}O\textsubscript{4}) model calculated using HF, EOM, and AFQMC methods and employing the aug-cc-pVTZ+7s7p basis set.

| Method | EBE (meV) |
|--------|-----------|
| **R = 4.0 Å** | |
| HF | -0.4 |
| EOM-CCSD | 180.6 |
| EOM-CCSD(T)(a)* | 195.8 |
| EOM-CCSDT\textsuperscript{a} | 197.5 |
| AFQMC SD/HF(N)//SD/NO SDCI(A) | 194 ± 10 |
| **R = 7.0 Å** | |
| HF | 41.3 |
| EOM-CCSD | 140.2 |
| EOM-CCSD(T)(a)* | 141.7 |
| EOM-CCSDT\textsuperscript{a} | 143.3 |
| AFQMC SD/HF | 181 ± 5 |

\textsuperscript{a} Estimated by adding the difference of EBEs calculated with the EOM-CCSD(T)(a)* and EOM-CCSDT methods and using the aug-cc-pVDZ+3s1p basis set to the EOM-CCSD(T)(a)* result calculated with the aug-cc-pVTZ+7s7p basis set.

and a single determinant of natural orbitals from the restricted SDCI procedure described in Section II C for the anion. DMC calculations using a SD of HF orbitals for trial wave function of the neutral and a trial wave function for the anion retaining 1,392 of the most important determinants from the restricted SDCI calculation gives an EBE of 202 ± 12 meV, close to the values obtained using the single determinants B3LYP orbitals or of NOs from the SDCI calculation (for the anion). The DMC value of the EBE resulting from the anionic trial wave function using a SD of NOs from the restricted SDCI MD calculation results is 205 ± 10 meV, similar to that from DMC calculations using as trial wave functions the MD restricted SDCI wave function for the anion and the HF wave function for the neutral.

Figure 2 compares the radial charge distributions of the singly occupied orbital from the HF and B3LYP calculations on the excess electron system as well as of the NOs associated with the
TABLE IV. EBEs of the (H₂O)₄ model calculated using the DMC method and various trial wave functions. 

| wave function | basis set               | EBE (meV) |
|---------------|-------------------------|-----------|
|               |                         | R = 4.0 Å |
| SD/HF         | aug-cc-pVDZ+7s7p        | 183 ± 10  |
| SD/HF         | aug-cc-pVDZ             | 176 ± 12  |
| SD/HF         | cc-pVDZ                 | -528 ± 25 |
| SD/B3LYP      | aug-cc-pVDZ+7s7p        | 212 ± 11  |
| SD/HF(N)/SD/NO SDCI(A) | aug-cc-pVDZ+7s7p | 205 ± 10  |
| SD/HF(N)/MD/NO SDCI(A) | aug-cc-pVDZ+7s7p | 202 ± 12  |
| MD/CIPSI NO truncated | aug-cc-pVDZ+3s1p | 177 ± 11  |
| MD/CIPSI NO   | aug-cc-pVDZ+3s1p        | 190 ± 15  |
|               |                         | R = 7.0 Å |
| SD/HF         | aug-cc-pVDZ+7s7p        | 141 ± 14  |
| SD/B3LYP      | aug-cc-pVDZ+7s7p        | 164 ± 9   |
| SD/HF(N)/SD/NO SDCI(A) | aug-cc-pVDZ+7s7p | 160 ± 9   |
| MD/CIPSI NO truncated | aug-cc-pVDZ+3s1p | 168 ± 6   |
| MD/CIPSI NO   | aug-cc-pVDZ+3s1p        | 158 ± 17  |

a SD/X indicates that the trial wave function employed a single Slater determinant with X (either HF or B3LYP) orbitals. When different types of trial wave functions are used for the neutral (N) and anion (A) this is indicated by the double slash.

excess electron from EOM-CCSD, restricted SDCI and CIPSI calculations. The collapse of the singly occupied orbital from the HF calculations onto a discretized continuum orbital is readily apparent. In contrast, the NOs from the EOM-CCSD and restricted SDCI calculations and the singly occupied orbital from the B3LYP calculation on the anion are more localized and are qualitatively similar to one another. However, we note that the orbital from the B3LYP calculations has a spurious peak near 25 atomic units from the center of the cluster. This is a consequence of the self-interaction error in the B3LYP functional. The relevant NO extracted from the CIPSI calculations, which were carried using B3LYP orbitals, exhibits a similar shoulder. These results indicate the nodal surface for the anion is significantly improved when using a SD trial wave function that
FIG. 2. Radially integrated charge densities of the singly occupied orbitals from HF and B3LYP calculations and the singly occupied natural orbital from EOM-CCSD, SDCI, and CIPSI calculations of the model \((\text{H}_2\text{O})_4\) cluster anion at \(R = 4\) Å. All plots generated using Matplotlib.\textsuperscript{72}

has a physically reasonable charge distribution for the orbital occupied by the excess electron. Thus, although DMC calculations do recover from the collapse of the HF trial wave function onto a discretized continuum solution in the case of the anion, starting with such a trial function leads to a greater nodal surface error for the anion than for the neutral cluster.
Our final set of DMC calculations used multideterminantal trial wave functions determined from CIPSI calculations for the neutral and anionic clusters. The strategy used in performing the CIPSI calculations was presented in Section II C, where it was noted that these calculations, unlike those with the restricted SDCI wave functions, allow for the correlation between the valence electrons change due to the presence of the excess electron. The DMC calculations using the CIPSI trial wave function resulted $190 \pm 15$ meV for $R = 4 \text{ Å}$, slightly underbinding compared to the single determinant DMC value of the EBE obtained using B3LYP orbitals though in close agreement with the results of DMC calculations carried out with the restricted SDCI trial wave function and also with the results of EOM-CCSD(T)(a)* calculations. The truncated MD/CIPSI EBE is within statistical error of the MD/CIPSI value suggesting that given a large enough CIPSI space, pruning the determinants does not greatly impact the energy and allows for a reduction in computational demand of the QMC calculations.

B. Results for $R = 7 \text{ Å}$: the electrostatically bound region

We next consider the results obtained for the $(\text{H}_2\text{O})_4$ cluster model at $R = 7 \text{ Å}$, for which HF calculations with the aug-cc-pVTZ+7s7p basis set bind (by 41 meV) the excess electron. In this case, the EOM-CCSD and EOM-CCSD(T)(a)* calculations give EBEs of 140 meV and 142 meV, respectively, while the AFQMC calculations give a EBE of $181 \pm 5$ meV. The DMC calculations using SD HF trial wave functions give an EBE ($141 \pm 14$ meV) consistent with the EOM-CCSD and EOM-CCSD(T)(a)* results, while the DMC/B3LYP calculations give an EBE value that is slightly larger ($164 \pm 9$ meV). SD DMC calculations using for the anion the NOs from the restricted SDCI procedure give an EBE of $160 \pm 9$ meV, consistent with the SD DMC/HF result with statistical error. MD DMC calculations using the truncated CIPSI trial wave functions give a binding energy of $168 \pm 6$ meV, which is in agreement to the $158 \pm 17$ meV EBE obtained using untruncated CIPSI trial wave functions. This behavior is consistent with what was observed for the $R = 4 \text{ Å}$ cluster. Figure 3 shows the radial charge distribution of the excess electron at $R = 7 \text{ Å}$. Here, we see that the HF wave function does not collapse onto the continuum as it did in the $R = 4 \text{ Å}$ cluster. Another noticeable difference is the reduction of the long-range shoulder in the radial charge distribution of the HOMO from the B3LYP calculations on the anion and in the relevant NO from the CIPSI calculations on the anion carried out using B3LYP orbitals. It is not clear why issues caused by self-interaction error appear greater for $R = 4 \text{ Å}$ than for $R = 7 \text{ Å}$.
IV. CONCLUSION

In this study, we have applied EOM-CC and two different quantum Monte Carlo methods to calculate the EBE of a model (H$_2$O)$_4$ cluster at two geometries, one at which the anion is bound in the HF approximation and the other at which it is not. Diffusion Monte Carlo calculations using single determinant trial functions based on Hartree-Fock orbitals are shown to bind the ex-
cess electron even when the initial wave function for the anion has collapsed onto the neutral plus discretized continuum orbital. However, such calculations significantly underestimate the EBE, whereas SD DMC calculations using trial wave functions for the anion with a more realistic charge distribution for the excess electron give larger EBE values consistent with the results from the EOM-CCSD(T)(a)* and AFQMC calculations. For the model system, the restricted SDCI represents a physically-correct, economical way to create trial wave functions for QMC calculations on anions that are not bound in the Hartree-Fock approximation. However, the (H$_2$O)$_4$ cluster is not a strongly correlated system, and it remains to be seen if this strategy is effective for systems in which the neutral species is strongly correlated or whether such systems will require multideterminant trial wave functions.

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AIP PUBLISHING DATA SHARING POLICY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

1V. K. Voora, A. Kairalapova, T. Sommerfeld, and K. D. Jordan, “Theoretical approaches for treating non-valence correlation-bound anions,” J. Chem. Phys. 147, 214114 (2017).
2. A. Kairalapova, K. D. Jordan, D. N. Maienshein, M. C. Fair, and M. F. Falcetta, “Prediction of a Nonvalence Temporary Anion Shape Resonance for a Model (H2O)4 System,” J. Phys. Chem. A 123, 2719–2726 (2019).

3. A. Kairalapova, K. D. Jordan, M. F. Falcetta, D. K. Steiner, B. L. Sutter, and J. S. Gowen, “Prediction of a Non-Valence Temporary Anion State of (NaCl)2,” J. Phys. Chem. B 123, 9198–9205 (2019).

4. J. P. Rogers, C. S. Anstöter, and J. R. R. Verlet, “Ultrafast dynamics of low-energy electron attachment via a non-valence correlation-bound state,” Nat. Chem. 10, 341–346 (2018).

5. J. P. Rogers, C. S. Anstöter, and J. R. R. Verlet, “Evidence of Electron Capture of an Outgoing Photoelectron Wave by a Nonvalence State in (C6F6)n−,” J. Phys. Chem. Lett. 9, 2504–2509 (2018).

6. J. N. Bull, C. S. Anstöter, and J. R. R. Verlet, “Ultrafast valence to non-valence excited state dynamics in a common anionic chromophore,” Nat. Commun. 10, 5820 (2019).

7. J. R. R. Verlet, C. S. Anstöter, J. N. Bull, and J. P. Rogers, “Role of Nonvalence States in the Ultrafast Dynamics of Isolated Anions,” J. Phys. Chem. A 124, 3507–3519 (2020).

8. V. K. Voora, L. S. Cederbaum, and K. D. Jordan, “Existence of a Correlation Bound s-Type Anion State of C60,” J. Phys. Chem. Lett. 4, 849–853 (2013).

9. V. K. Voora and K. D. Jordan, “Nonvalence Correlation-Bound Anion States of Spherical Fullerenes,” Nano Lett. 14, 4602–4606 (2014).

10. V. K. Voora and K. D. Jordan, “Nonvalence Correlation-Bound Anion State of C6F6: Doorway to Low-Energy Electron Capture,” J. Phys. Chem. A 118, 7201–7205 (2014).

11. T. H. Choi and K. D. Jordan, “Model potential study of non-valence correlation-bound anions of (C60)n clusters: the role of electric field-induced charge transfer,” Faraday Discuss. 217, 547–560 (2019).

12. V. K. Voora and K. D. Jordan, “Nonvalence Correlation-Bound Anion States of Polycyclic Aromatic Hydrocarbons,” J. Phys. Chem. Lett. 6, 3994–3997 (2015).

13. T. Sommerfeld, B. Bhattarai, V. P. Vysotskiy, and L. S. Cederbaum, “Correlation-bound anions of NaCl clusters,” J. Chem. Phys. 133, 114301 (2010).

14. V. G. Bezchastnov, V. P. Vysotskiy, and L. S. Cederbaum, “Anions of Xenon Clusters Bound by Long-Range Electron Correlations,” Phys. Rev. Lett. 107, 133401 (2011).

15. C. Moller and M. S. Plesset, “Note on an Approximation Treatment for Many-Electron Systems,” Phys. Rev. 46, 618–622 (1934).
K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, “A fifth-order perturbation comparison of electron correlation theories,” Chem. Phys. Lett. 157, 479–483 (1989).

R. C. Lochan and M. Head-Gordon, “Orbital-optimized opposite-spin scaled second-order correlation: An economical method to improve the description of open-shell molecules,” J. Chem. Phys. 126, 164101 (2007).

J. Čížek, J. Paldus, and L. Šroubková, “Cluster expansion analysis for delocalized systems,” Int. J. Quantum Chem. 3, 149–167 (1969).

D. C. Comeau and R. J. Bartlett, “The equation-of-motion coupled-cluster method. Applications to open- and closed-shell reference states,” Chem. Phys. Lett. 207, 414–423 (1993).

A. K. Dutta, M. Saitow, B. Demoulin, F. Neese, and R. Izsák, “A domain-based local pair natural orbital implementation of the equation of motion coupled cluster method for electron attached states,” J. Chem. Phys. 150, 164123 (2019).

R. C. Grimm and R. G. Storer, “Monte-Carlo solution of Schrödinger’s equation,” J. Comput. Phys. 7, 134 – 156.

J. B. Anderson, “A random-walk simulation of the Schrödinger equation: H_3^+,” J. Chem. Phys. 63, 1499–1503 (1975).

J. B. Anderson, “Quantum chemistry by random walk. H^2P, H_3^+ d_3h^1A_1^′, H_2^3Σ_u^+, H_4^1Σ_g^+, Be^1S,” J. Chem. Phys. 65, 4121–4127 (1976).

W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, “Quantum Monte Carlo simulations of solids,” Rev. Mod. Phys. 73, 1–51 (2001).

P. López Ríos, A. Ma, N. D. Drummond, M. D. Towler, and R. J. Needs, “Inhomogeneous backflow transformations in quantum Monte Carlo calculations,” Phys. Rev. E 74, 066701 (2006).

R. Blankenbecler, D. J. Scalapino, and R. L. Sugar, “Monte Carlo calculations of coupled boson-fermion systems. I,” Phys. Rev. D 24, 2278–2286 (1981).

G. Sugiyama and S. Koonin, “Auxiliary field Monte-Carlo for quantum many-body ground states,” Annals of Physics 168, 1 – 26 (1986).

D. J. Scalapino and R. L. Sugar, “Monte Carlo calculations of coupled boson-fermion systems. II,” Phys. Rev. B 24, 4295–4308 (1981).

S. Zhang and H. Krakauer, “Quantum Monte Carlo Method using Phase-Free Random Walks with Slater Determinants,” Phys. Rev. Lett. 90, 136401 (2003).

S. Zhang, J. Carlson, and J. E. Gubernatis, “Constrained path Monte Carlo method for fermion ground states,” Phys. Rev. B 55, 7464–7477 (1997).
31 M. Motta and S. Zhang, “Ab initio computations of molecular systems by the auxiliary-field quantum Monte Carlo method,” Wiley Interdiscip. Rev.: Comput. Mol. Sci. 8, e1364 (2018).

32 S. Zhang, “Ab Initio Electronic Structure Calculations by Auxiliary-Field Quantum Monte Carlo,” in Handbook of Materials Modeling: Methods: Theory and Modeling, edited by W. Andreoni and S. Yip (Springer International Publishing, 2018) pp. 1–27.

33 W. Humphrey, A. Dalke, and K. Schulten, “VMD: Visual molecular dynamics,” J. Mol. Graphics 14, 33–38 (1996).

34 J. F. Stanton and J. Gauss, “Perturbative treatment of the similarity transformed Hamiltonian in equation-of-motion coupled-cluster approximations,” J. Chem. Phys. 103, 1064–1076 (1995).

35 D. A. Matthews and J. F. Stanton, “A new approach to approximate equation-of-motion coupled cluster with triple excitations,” J. Chem. Phys. 145, 124102 (2016).

36 S. A. Kucharski, M. Włoch, M. Musiał, and R. J. Bartlett, “Coupled-cluster theory for excited electronic states: The full equation-of-motion coupled-cluster single, double, and triple excitation method,” J. Chem. Phys. 115, 8263–8266 (2001).

37 K. Kowalski and P. Piecuch, “The active-space equation-of-motion coupled-cluster methods for excited electronic states: Full EOMCCSDt,” J. Chem. Phys. 115, 643–651 (2001).

38 T. H. Dunning, “Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen,” J. Chem. Phys. 90 (1989), 10.1063/1.456153.

39 R. A. Kendall, T. H. Dunning, and R. J. Harrison, “Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions,” J. Chem. Phys. 96 (1992), 10.1063/1.462569.

40 J. F. Stanton, J. Gauss, L. Cheng, M. E. Harding, D. A. Matthews, and P. G. Szalay, “CFOUR, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package,” With contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, O. Christiansen, F. Engel, R. Faber, M. Heckert, O. Heun, M. Hilgenberg, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, T. Kirsch, K. Klein, W.J. Lauderdale, F. Lipparini, T. Metzroth, L.A. Mück, D.P. O’Neill, D.R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jorgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.

41 D. A. Matthews, L. Cheng, M. E. Harding, F. Lipparini, S. Stopkowicz, T.-C. Jagau, P. G. Szalay, J. Gauss, and J. F. Stanton, “Coupled-cluster techniques for computational chemistry:
The CFOUR program package,” J. Chem. Phys. 152, 214108 (2020).

42 R. Jastrow, “Many-Body Problem with Strong Forces,” Phys. Rev. 98, 1479–1484 (1955).

43 N. D. Drummond, M. D. Towler, and R. J. Needs, “Jastrow correlation factor for atoms, molecules, and solids,” Phys. Rev. B 70, 235119 (2004).

44 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. Tumbman, 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,” J. Phys.: Condens. Matter 30, 195901 (2018).

45 A. D. Becke, “Density-functional exchange-energy approximation with correct asymptotic behavior,” Phys. Rev. A 38, 3098–3100 (1988).

46 C. Lee, W. Yang, and R. G. Parr, “Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density,” Phys. Rev. B 37, 785–789 (1988).

47 S. H. Vosko, L. Wilk, and M. Nusair, “Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis,” Can. J. Phys. 58, 1200–1211 (1980).

48 P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, “Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields,” J. Phys. Chem. 98, 11623–11627 (1994).

49 B. Huron, J. P. Malrieu, and P. Rancurel, “Iterative perturbation calculations of ground and excited state energies from multiconfigurational zeroth-order wavefunctions,” J. Chem. Phys. 58, 5745–5759 (1973).

50 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,” J. Chem. Phys. 149, 134108 (2018).

51 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,” J. Chem. Phys. 147, 224106 (2017).
M. Casula, “Beyond the locality approximation in the standard diffusion Monte Carlo method,” Physical Review B 74, 161102 (2006).

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,” J. Chem. Phys. 152, 174105 (2020).

M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, “General atomic and molecular electronic structure system,” J. Comput. Chem. 14, 1347–1363 (1993).

M. S. Gordon and M. W. Schmidt, “Chapter 41 - Advances in electronic structure theory: GAMESS a decade later,” in Theory and Applications of Computational Chemistry, edited by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria (Elsevier, 2005) pp. 1167–1189.

G. M. J. Barca, C. Bertoni, L. Carrington, D. Datta, N. De Silva, J. E. Deustua, D. G. Fedorov, J. R. Gour, A. O. Gunina, E. Guidetz, T. Harville, S. Irle, J. Ivanic, K. Kowalski, S. S. Leang, H. Li, W. Li, J. J. Lutz, I. Magoulas, J. Mato, V. Mironov, H. Nakata, B. Q. Pham, P. Piecuch, D. Poole, S. R. Pruitt, A. P. Rendell, L. B. Roskop, K. Ruedenberg, T. Sattasathuchana, M. W. Schmidt, J. Shen, L. Slipchenko, M. Sosonkina, V. Sundriyal, A. Tiwari, J. L. Galvez Vallejo, B. Westheimer, M. Wloch, P. Xu, F. Zahariev, and M. S. Gordon, “Recent developments in the general atomic and molecular electronic structure system,” J. Chem. Phys. 152, 154102 (2020).

Y. Garniron, T. Applencourt, K. Gasperich, A. Benali, A. Ferté, J. Paquier, B. Pradines, R. Assaraf, P. Reinkingardt, J. Toulouse, P. Barbaresco, N. Renon, G. David, J. P. Malrieu, M. Vérité, M. Caffarel, P. F. Loos, E. Giner, and A. Scemama, “Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs,” J. Chem. Theory Comput. 15, 3591–3609 (2019).

J. Hubbard, “Calculation of partition functions,” Phys. Rev. Lett. 3, 77 (1959).

J. Lee, F. D. Malone, and M. A. Morales, “Utilizing essential symmetry breaking in auxiliary-field quantum Monte Carlo: Application to the spin gaps of the C_{36} fullerene and an iron porphyrin model complex,” J. Chem. Theory Comput. 16, 3019–3027 (2020).

B. Rudshteyn, D. Coskun, J. L. Weber, E. J. Arthur, S. Zhang, D. R. Reichman, R. A. Friesner, and J. Shee, “Predicting Ligand-Dissociation Energies of 3d Coordination Complexes with Auxiliary-Field Quantum Monte Carlo,” J. Chem. Theory Comput. 16, 3041–3054 (2020).
61 J. Shee, B. Rudshteyn, E. J. Arthur, S. Zhang, D. R. Reichman, and R. A. Friesner, “On Achieving High Accuracy in Quantum Chemical Calculations of 3d Transition Metal-Containing Systems: A Comparison of Auxiliary-Field Quantum Monte Carlo with Coupled Cluster, Density Functional Theory, and Experiment for Diatomic Molecules,” J. Chem. Theory Comput. 15, 2346–2358 (2019).

62 M. Kumar, J. Shee, B. Rudshteyn, D. R. Reichman, R. A. Friesner, C. E. Miller, and J. S. Francisco, “Multiple Stable Isoprene-Ozone Complexes Reveal Complex Entrance Channel Dynamics in the Isoprene+ Ozone Reaction,” J. Am. Chem. Soc. (2020), 10.1021/jacs.0c02360.

63 H. Hao, J. Shee, S. Upadhyay, C. Ataca, K. D. Jordan, and B. M. Rubenstein, “Accurate predictions of electron binding energies of dipole-bound anions via quantum Monte Carlo methods,” J. Phys. Chem. Lett. 9, 6185–6190 (2018).

64 J. Shee, E. J. Arthur, S. Zhang, D. R. Reichman, and R. A. Friesner, “Singlet–Triplet Energy Gaps of Organic Biradicals and Polyacenes with Auxiliary-Field Quantum Monte Carlo,” J. Chem. Theory Comput. 15, 4924–4932 (2019).

65 J. Shee, E. J. Arthur, S. Zhang, D. R. Reichman, and R. A. Friesner, “Phaseless auxiliary-field quantum Monte Carlo on graphical processing units,” J. Chem. Theory Comput. 14, 4109–4121 (2018).

66 W. Purwanto, H. Krakauer, Y. Virgus, and S. Zhang, “Assessing weak hydrogen binding on Ca⁺ centers: An accurate many-body study with large basis sets,” J. Chem. Phys. 135, 164105 (2011).

67 N. M. O’boyle, A. L. Tenderholt, and K. M. Langner, “cclib: A library for package-independent computational chemistry algorithms,” J. Comput. Chem. 29, 839–845 (2008).

68 Q. Sun, T. C. Berkelbach, N. S. Blunt, G. H. Booth, S. Guo, Z. Li, J. Liu, J. D. McClain, E. R. Sayfutyarova, S. Sharma, S. Wouters, and G. K.-L. Chan, “PySCF: the Python-based simulations of chemistry framework,” Wiley Interdiscip. Rev.: Comput. Mol. Sci. 8, e1340 (2018).

69 Q. Sun, X. Zhang, S. Banerjee, P. Bao, M. Barbry, N. S. Blunt, N. A. Bogdanov, G. H. Booth, J. Chen, Z.-H. Cui, J. J. Erkisen, Y. Gao, S. Guo, J. Hermann, M. R. Hermes, K. Koh, P. Koval, S. Lehtola, Z. Li, J. Liu, N. Mardirossian, J. D. McClain, M. Motta, B. Mussard, H. Q. Pham, A. Pulkin, W. Purwanto, P. J. Robinson, E. Ronca, E. R. Sayfutyarova, M. Scheurer, H. F. Schurkus, J. E. T. Smith, C. Sun, S.-N. Sun, S. Upadhyay, L. K. Wagner, X. Wang, A. White, J. D. Whitfield, M. J. Williamson, S. Wouters, J. Yang, J. M. Yu, T. Zhu, T. C. Berkelbach, S. Sharma, A. Y. Sokolov, and G. K.-L. Chan, “Recent developments in the PySCF program
V. I. Lebedev and D. Laikov, “A quadrature formula for the sphere of the 131st algebraic order of accuracy,” in *Doklady Mathematics*, Vol. 59 (Pleiades Publishing, Ltd., 1999) pp. 477–481.

N. Schlömer, N. R. Papior, D. Arnold, M. Ancellin, and R. Zetter, “nschloe/quadpy v0.15.2,” (2020).

J. D. Hunter, “Matplotlib: A 2D graphics environment,” *Computing in Science & Engineering* 9, 90–95 (2007).