Title
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Permalink
https://escholarship.org/uc/item/0177d7rj

Journal
The Journal of chemical physics, 153(14)

ISSN
0021-9606

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Publication Date
2020-10-01

DOI
10.1063/5.0020310

Peer reviewed
A variational Monte Carlo approach for core excitations

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(Dated: July 3, 2020)

We present a systematically-improvable approach to core excitations in variational Monte Carlo. Building on recent work in excited-state-specific Monte Carlo, we show how a straightforward protocol, starting from a quantum chemistry guess, is able to capture core state’s strong orbital relaxations, maintain accuracy in the near-nuclear region during these relaxations, and explicitly balance accuracy between ground and core excited states. In water, ammonia, and methane, which serve as prototypical representatives for oxygen, nitrogen, and carbon core states, respectively, this approach delivers accuracies on par with the best available theoretical methods even when using relatively small wave function expansions.

I. INTRODUCTION

Quantum Monte Carlo (QMC) approaches\textsuperscript{1–4} have long been used to provide highly-accurate theoretical reference data from which other, less expensive methods can benefit. Since the pioneering work of Ceperley and Alder\textsuperscript{5} that led to the development of the local density approximation, there have been many cases where QMC methods have provided benchmarks for and insights into other theories. Examples include the phase stability of high-pressure hydrogen\textsuperscript{6}, the low-temperature properties of the Hubbard model\textsuperscript{7}, the stability of a covalently-bound O\textsubscript{2} molecule\textsuperscript{8} and the optical gap of ZnO\textsuperscript{9}. While the computational costs associated with taking large random samples can be intimidating, the various types of QMC methodology offer highly accurate and systematic predictions when paired with parallel computing.

In particular, QMC allows increasingly large expansions of Slater determinants to be coupled with correlation factors\textsuperscript{10–14} which allows both strong and weak correlation effects as well as basis set effects to be addressed simultaneously, especially in ground state contexts where projector Monte Carlo methods can be used to polish off the finer details.\textsuperscript{15} Crucially, the ability of the correlation factors (also called Jastrow factors) to deal with electron cusps and other weak-correlation effects means that accuracy is reached with far smaller determinant expansions than are necessary in quantum chemistry. In many cases, as in molecular O\textsubscript{2}, even relatively short expansions are sufficient to allow a clear balance to be established between the accuracy of different state\textsuperscript{15–18} or the same state at different molecular geometries.\textsuperscript{5} This balance enables by-design error cancellation and the delivery of high-accuracy energy differences, even in cases like O\textsubscript{2} where the wave functions at different geometries differ substantially in the character of their electron correlation.\textsuperscript{5}

One must bear in mind, however, that most success stories in QMC have been achieved by carefully removing any core electrons from the QMC simulation via pseudopotentials. Unlike quantum chemistry, where freezing core electrons or using pseudopotentials lowers the cost of correlation methods by a modest factor, the efficiency gain in QMC can be quite dramatic due to both the need to take smaller sampling steps when the kinetic energy scale is higher and the higher energy variance (and thus statistical uncertainty) that comes with the higher energy scale of core electrons. For example, the computational cost of all-electron diffusion Monte Carlo has been estimated to grow as roughly the sixth power of the nuclear charge.\textsuperscript{19,20} Given the recent advances in excited-state QMC methods\textsuperscript{21–36} and the electronic structure community’s continuing efforts\textsuperscript{24–35} to develop affordable theoretical methods for core excitations, it is interesting to ask whether the challenges that QMC faces for core electrons can be overcome so that for relatively light elements it can act as a reliable benchmark for more affordable theories, just as it has in other areas.

Interest in core excitations and X-Ray absorption spectroscopy (XAS) comes in large part from the chemical analysis then can offer through element, chemical environment, and spatial specificity.\textsuperscript{37–41} Recent improvements in X-Ray light sources’ temporal, spatial, and spectral resolutions\textsuperscript{42} have enhanced these advantages and opened the possibility for novel experiments in nuclear and electronic dynamics.\textsuperscript{43–44} With these increasing capabilities comes an increasing need for reliable theoretical methods that can unambiguously assigning experimental features of ever-more-exotic core spectra. Amidst the recent flurry of theoretical development in this area,\textsuperscript{21,22} we are eager to explore what QMC has to offer, beginning with its traditional role as a theoretical benchmark. In this study, we will address various challenges standing in the way of high-accuracy core-state QMC through a variational Monte Carlo (VMC) framework and provide proof-of-principle results in water, ammonia, and methane (representing the O, N, and C K-edges) demonstrating the promise of the approach.

II. THEORY

A. Overview

In pursuing a VMC-based, systematically improvable approach to core excitation energies and their corre-
sponding wave functions, there are a variety of issues that must be considered and addressed. First, as evidenced by the successes of theories that have it (e.g. NOCIS\textsuperscript{25} ∆SCF \textsuperscript{21} and ROKS\textsuperscript{35}) and the failures of theories that don’t (e.g. configuration interaction single\textsuperscript{25}), post-excitation orbital relaxations are essential when aiming for high accuracy in core excitation energies. Indeed, the accuracy of Hartree-Fock-based ∆-SCF predictions of core electron binding energies\textsuperscript{23} which give results within an eV of experiment despite neglecting 10 or more eV of correlation energy, strongly argue that one should, as in NOCIS\textsuperscript{25} not even worry about correlation effects until orbital relaxations have been sorted out. There are many ways one could address orbital relaxation in a VMC approach, such as incorporating them in the quantum chemistry starting point before even getting to VMC. However, to ensure we are providing a stringent test of VMC’s ability to treat core states, we will in the present study start from ground state Hartree-Fock orbitals and rely on recent advances in VMC orbital optimization\textsuperscript{22} to capture orbital relaxation effects.

A related challenge is how to optimize ground and core excited states within the same VMC framework. Some existing methods that work well for valence states, such as state-averaged VMC\textsuperscript{13} will not be appropriate for core excitations due to the strong orbital relaxations involved. Variance minimization\textsuperscript{15} is appropriate in principle, but relies on the initial guess being close to the desired state as all Hamiltonian eigenstates have a the same (zero) variance. In practice, the use of an approximate ansatz can make some states stronger attractors than others when minimizing the variance\textsuperscript{16} as the variance minima around different states will now have different depths. If the ansatz is too poor, some minima may disappear altogether. To guard against these issues, which we did see during some early and insufficiently-cautious attempts at core state optimization, we employ a variance minimization approach that is state-specific at every individual optimization step\textsuperscript{22} and enforce stronger safeguards on it than in previous work (see Section IIE).

A third and obvious challenge is that pseudopotentials are not appropriate for our purposes, at least not on the atom promoting a core electron. Although all-electron calculations are certainly not unheard of in ground state VMC (see e.g. work by Toulouse and Umrigar\textsuperscript{17}), we must take care here to treat the nuclear cusp and, more importantly\textsuperscript{18}, the wave function in its immediate vicinity carefully, as the local electric field and wave function changes significantly after the excitation. Unlike in ground state work, we should not expect errors in the treatment of this region to cancel when we take energy differences, and so treating this region accurately is a crucial. As discussed in Section IIB, we address this region through a combination of modifying the basis set and adding an extra short-range electron-nuclear Jastrow factor in addition to one with a more standard range.

Fourth and finally, QMC methods that are treating substantially different states must take care that their wave functions are of similar accuracy so that energy differences will not be biased. This issue is in some ways more severe than in basis-set-bound quantum chemistry, where the idea of a model chemistry has real value in that the basis set puts a hard limit on how much correlation energy can be recovered. So long as the unrecoverable correlation energy is similar in all states considered, cancellation of error is to some degree built in. In QMC, by contrast, sophisticated Jastrow factors and especially (although we do not employ it here) projector Monte Carlo methods make it possible, in principle, to reach 100% correlation recovery. This promise can be a double-edged sword, however, when states of very different character are being considered. If QMC is much better at correlation recovery in one case than the other, then energy differences can be biased to an extend that would be hard to manage within the guard rails of a finite basis set. As we are considering core excitations, in which substantial changes are being made among the electrons with the largest energy scales, caution in this regard is called for. This is especially true given that we are aiming for high accuracy, and thus using aggressive tools like three-body Jastrow factors and multi-Slater expansions to aid in correlation recovery. If our efforts are more effective in one state than the other, and let’s face it, most of these tools have been designed and used in ground states, then we may inadvertently introduce a bias in our quest for correlation recovery. As discussed in Section IIE, we will address these concerns by employing the energy variance as a measure of wave function accuracy to help ensure that our energy differences are balanced.

To summarize, the approach to core states that we pursue here is designed to deal with large orbital relaxations, convergence to the correct state, excitation-induced changes in the near-nuclear region, and balancing accuracy. The resulting protocol, which we will describe in detail in the following sections, can be organized into four stages.

1. Choice of basis set and 1-body Jastrow
2. Guess preparation via quantum chemistry
3. State-specific variational Monte Carlo
4. Variance matching

B. Basis set and cusp considerations

As emphasized by Gill et al\textsuperscript{23} and more recently by Krylov et al\textsuperscript{33} uncontracting a standard basis set can be helpful when modeling core excitations. If anything, uncontraction can be even more helpful in the VMC context, as it allows one to eliminate variable redundancies and corresponding optimization difficulties in the near-nucleus region. As one-electron Jastrow factors can easily encode the analytically-known\textsuperscript{16} electron-nuclear cusp
at the nuclei as well as the shape of one-electron functions in its immediate vicinity, large Gaussian contraction schemes that work to shape this region ever closer in to the nuclei are not only unnecessary, but in fact problematic. To see why, consider Figure 1 where we show two relatively tight Gaussian primitives alongside a one-electron Jastrow factor build from cubic B-splines. Consider for now the ground state, where we can assume that a large contraction of Gaussian primitives will have the orbital shape more or less correct except for in the region extremely close to the nucleus. In this case, the Jastrow factor will need to switch from having nontrivial structure in the tiny region around the nucleus where the Gaussian-type orbital needs correcting to being essentially flat in the rest of space, where the orbital is already correct. The better the quality of the Gaussian-type orbital, the shorter the distance over which this switch must occur, and thus the tighter the spline grid will need to be near the core. Worse, to actually optimize the Jastrow in this tiny region, extremely large random samples will be required, as seeing an electron land in the region where the Jastrow matters will be a rare event.

These issues have been recognized before, and in cases like the ground state where the orbital shape is essentially correct outside the tiny cusp region, numerical methods have been developed to convert a Gaussian-type orbital into something more Slater like before many-electron QMC even gets started by slightly modifying the orbital shape at the very center. In our approach, however, the core excited state will not have optimal orbital shapes until late in the VMC optimization, and so this type of rigid before-QMC correction is less appropriate. Instead, we follow the uncontracted basis approach of Nakano et al and, as they recommend, remove the tightest Gaussian primitives (ζ ≥ 300) from the basis. To deal with near-nucleus orbital shaping that the basis can no longer deliver, we employ a short range electron-nuclear Jastrow that effects only the first 0.5 Bohr about the nucleus and contains 25 spline points (15 for hydrogen atoms). Note that this is a far less dense spacing than is required to make the switch discussed above in the case of a GTO with very tight primitives, and in practice we find it does not cause issues in our optimization. Of course, the appropriate range and spline-point density of this Jastrow will depend on how aggressive one is with the primitive-removal cutoff. Note that we also include 1-body electron-nuclear Jastrows, we as implemented in GAMESS. As shown in Figure 2, we partition the ground state restricted Hartree-Fock (RHF) orbitals into four categories. For our ground state wave function, we enforce double occupation of the core orbital and allow up to three excitations within the active orbitals. For the excited state, we require that one core electron be promoted into the active occupied to the active virtual excitations. For the non-core occupied orbitals, while the active vir-

![FIG. 1. A snippet of the short range cusped jastrow factor on the Nitrogen nucleus in Ammonia. The spacing of the spline control points is indicated on the Jastrow. Note this Jastrow is radially symmetric and only defined for $r_{e,N} > 0$, but we have plotted both positive and negative distances to show the cusped behavior more clearly. Also plotted are two Gaussians with $\zeta = 309.3$ and $\zeta = 9046$ which are the tightest function allowed and a function removed from the uncontracted basis, respectively. The Gaussians are not normalized and have been translated vertically.](image-url)
tuals consist of the remaining valence-shell orbitals plus the next 9 virtual orbitals, which in the systems studied here is a simple way to include the 3s, 3p, and 3d of the heavy atom. Note that, while the inactive virtual orbitals do not participate at the quantum chemistry stage, they are carried over into VMC so that they can participate in the orbital optimization. In future, it will likely be preferable to perform the excited state ORMAS CI calculation in a core-relaxed basis set, which could be generated via STEX, NOCIS, ROKS, or excited state mean field theory. That said, we start from RHF orbitals here in order to create a more stringent test of VMC’s ability to optimize core states.

One way to look at our ORMAS approach is as a particularly aggressive choice of core-valence separation (CVS) scheme that makes both the ground and excited state CI calculations variationally stable. Crucially, and this aspect carries over to VMC as the correlation factors are not so flexible as to refill the core, the lack of filled-core configurations within the excited state ansatz enables Auger coupling to the valence continuum. Less happily, the rigid core occupations in both states prevents the CI expansion from capturing core-core and non-Auger core-valence correlation effects. This would be more concerning if we were stopping at the quantum chemistry stage, but within VMC these effects will be at least partially captured by the two- and three-body Jastrow factors.

D. Variational Monte Carlo

With a multi-determinant expansion in hand, we add the Jastrow factors to complete the ansatz and proceed with our state-specific VMC optimization, all of which is handled by a development version of the QMCPACK software package. The full ansatz can be written as a product of the Jastrow factor and a truncation (see Section IV for truncation details) of the quantum chemistry determinant expansion.

$$\Psi = e^{-J(\vec{r})} \sum_I c_I |\Psi_I(\vec{r})\rangle$$

Here each $|\Psi_I(\vec{r})\rangle$ is a Slater determinant with associated CI coefficient $c_I$, and $e^{-J(\vec{r})}$ is the combined one-, two-, and three-body Jastrow correlation factor.

$$J(\vec{r}) = J_1(\vec{r}) + J_2(\vec{r}) + J_3(\vec{r})$$

$$J_1(\vec{r}) = \sum_{I,i,\sigma} U_I(|\vec{r}_{i,\sigma} - \vec{R}_I\rangle) + V_I(|\vec{r}_{i,\sigma} - \vec{R}_I\rangle)$$

$$J_2(\vec{r}) = \sum_{i,j,\sigma,\tau} W_{\sigma\tau}(|\vec{r}_{i,\sigma} - \vec{r}_{j,\tau}|)$$

Here $r_{i,\sigma}$ is the position of the $i$th spin-$\sigma$ electron, $R_I$ is the position of nuclei $I$, and the $U$, $V$, and $W$ functions are cardinal cubic B-splines with optimizable spline coefficients for the short- and long-range one-body Jastrow and the two-body Jastrow, respectively. Note that, for $W$, there are two sets of spline coefficients, one for like-spin electrons and one for opposite-spin electrons. Kato’s cusp conditions are enforced explicitly by the $U$ and $W$ functions. Finally, for $J_3$, we use the functional form of Needs et al.

We optimize our ansatz using a modified linear method implementation in a staged minimization of the objective function

$$\Omega = \frac{\langle \Psi | (\omega - H) | \Psi \rangle}{\langle \Psi | (\omega - H) | \Psi \rangle}$$

which, for an exact ansatz, targets the first Hamiltonian eigenstate with energy above the value $\omega$. If the approximate ansatz is accurate enough that each Hamiltonian eigenstate in the relevant region of variable space has its own separate variance minimum (as would be the case for an exact ansatz), and if the uncertainty in the Monte Carlo integration with which we estimate the objective function and its derivatives is low enough, then an optimization in which the initial guess starts within the basin of the desired variance minimum and in which $\omega$ is chosen and adjusted appropriately will converge to the variance minimum corresponding to the desired state. In practice, of course, some of these conditions may not be met, in which case the optimization is at risk of converging to a variance minimum that corresponds to a different Hamiltonian eigenstate than the one desired.

In the present study, where the excited state ansatz starts with unrelaxed orbitals and with Jastrow factors that have no structure aside from the explicitly-enforced cusp conditions, it is hard to argue that the initial guess and statistical precision are good enough to avoid trouble. Indeed, if we immediately start optimizing all orbital, CI, and Jastrow parameters simultaneously with a
As has long been practiced for the ground state linear method, our implementation uses an independent sample to evaluate whether the objective function is actually lowered by any of the three different proposed update steps (one for each setting of the stabilizing shifts) and rejects any update that raises the objective function. To help avoid large fluctuations in the variance and objective function, we employ a clipping scheme, which serves much the same purpose as a more statistically rigorous modified guiding function while being far easier to implement. Note that ω is treated as a constant during a given linear method iteration — it is only ever updated in between linear method evaluations — and so the objective function that is making the decision to accept or reject a parameter update is state-specific, which is a key difference compared to straightforward variance minimization. Even with our carefully staged optimization, we find that, if we do not employ this rigorous check-and-reject step, some of our optimizations can wander off to other states, adding additional support to the concerns raised by Filippi and coworker and highlighting the value of developing more robust state-specific approaches. We note that adapting a hybrid optimization scheme to work with excited state objective functions has proven effective in this regard but that work is ongoing and is not the focus of the present study.

Rather than assuming that our ground and excited state wave functions are of equal quality and thus likely to produce excitation energies that benefit from error cancellation, we employ variance matching to help ensure balance and accurate energy differences. The variance

\[ \sigma^2 = \langle (\hat{H} - E)^2 \rangle \]  

is non-negative for any wave function and is only zero for an exact Hamiltonian eigenstate, making it a strong measure of an approximate wave function’s quality. Of course, lower variances are better, but when taking energy differences, it seems equally important that the states in question be balanced, and so there is an argument for intentionally limiting one state’s flexibility so as to prevent it from being much better treated than the other and thus biasing energy differences. It is worth noting, though, that in using variance matching to encourage error cancellation, one is tacitly assuming that the states’ energy errors have the same sign. Although there is no rigorous guarantee of this, a qualitatively-correct ansatz for a low-lying state will tend to be in error by containing many small contributions from high-energy eigenstates, and so typically errors relative to a chemically relevant state’s true energy will be positive. In approaches that selectively take the most important low-lying determinants to construct their ansatz, this happy situation is even more likely to be true, as the ansatz is by design missing contributions from only higher-lying determinants.

Now, core states are not low-lying in the energy spectrum, but the same basic logic should apply to them. The only determinants that are lower in energy than those used in our excited state determinant expansion are those that have a filled core, and although there is some Auger-like correlation energy associated with them, it is typically less than 0.1 eV. This is much smaller than the correlation energy we are missing due to an incomplete capture of correlation effects associated with higher-lying determinants. Furthermore, these Auger correlations are at least partially captured through our two- and three-body Jastrow factors. Thus, although there are some correlation terms that may work to push our core state towards erroring low, these are expected to be vastly outweighed by correlation terms that push us towards erroring high. Indeed, Figure clearly shows that our excited state energy decreases as we improve the ansatz and decreases its variance.

In practice, we take the following approach to achieve energy differences between variance-matched wave functions. First, in the ground state, we discard all determinants whose ORMAS CI coefficients have absolute values below 0.02 when constructing our VMC ansatz, which leads to ground state wave functions with fewer than ten determinants in each of the three molecules considered here. After the ground state VMC optimization
FIG. 3. A demonstration of our variance matching approach in the case of methane’s lowest core excited state. Each point gives the energy (relative to the ground state) and variance of the ansatz at one of the last 24 iterations of a wave function optimization, i.e. at the end of the final stage in which all variational parameters are optimized together. The three groups of points represent three different ansatzes, in which we retained 104, 184, and 308 determinants from the ORMAS wave function so as to straddle the ground state variance and allow for interpolation. A simple linear regression on all 72 points permits a straightforward interpolation of what the excited state’s energy would be if the excited state exactly matched the ground state variance, as shown by the arrow.

We prefer the approach of Figure 3 both for its simplicity and because it removes the somewhat arbitrary choice of nonlinear fitting function. So long as one is interpolating over a small distance, a linear approximation is both straightforward and reasonable. In Section III B below, we explicitly test how sensitive this approach is to increasing the interpolation distance and find that in practice the sensitivity is quite low.

III. RESULTS

A. Transition Energies

As a preliminary test of this VMC approach to core excitations, we have applied it to the heavily studied ten electron series of methane, ammonia, and water. As seen in Table I, the approach consistently predicts ground-to-excited transition energies that are 0.2 to 0.3 eV above experiment once relativistic effects are accounted for. We suspect that this tendency to error slightly high may be due to the fact that our ORMAS excited state calculations are being done in an unrelaxed orbital basis and so likely do a worse job than the corresponding ground state calculations at predicting which determinants will be most important in the final VMC orbital basis. Although unrelaxed orbitals were used intentionally in order to provide a strenuous test of our VMC optimization, it will clearly be worthwhile in future to test the efficacy of performing ORMAS CI for excited states in a relaxed orbital basis. Although VMC does bias slightly high, the consistency with which it does so is interesting in light of the fact that the VMC optimization gets harder as the nuclei get heavier, as one would expect. For example, the per-electron variance at the end of our H$_2$O optimizations is roughly twice the per-electron variance achieved in CH$_4$, suggesting that in H$_2$O our wave functions are less accurate. Variance matching appears to do its job and make up for this, as the accuracies of the predicted ground-to-excited and excited-to-excited transition energies in all three molecules are very similar.

Comparing with other recent theoretical approaches to core excitations, we find the accuracy of VMC to be highly competitive. For ground-to-excited transition energies, VMC substantially outperforms equation of motion coupled cluster and NOCIS. When using the SCAN functional, ROKS is if anything even more accurate than VMC for these ground-to-excited transitions, although
TABLE I. Transition energies (eV) for core excited states in methane, ammonia, and water. Experimental transition energies have been adjusted to remove relativistic effects. Theoretical results (for both ground-to-excited and excited-to-excited transition energies) are reported as errors relative to the adjusted experimental numbers. For the VMC calculations, molecular geometries were taken from CCCDB.nist.gov. Values for fc-CVS-EOM-CCSD are taken from the corresponding supporting information. VMC statistical uncertainties are less than 0.01 eV.

| State | Experiment | VMC | ROKS/SCAN | fc-CVS-EOM-CCSD | CVS-LR-CCSD | NOCIS |
|-------|------------|-----|-----------|----------------|-------------|-------|
| **transition energies from the ground state:** | | | | | | |
| CH₄ 1s → 3a₁/3s | 286.60b,c | 0.31 | -0.2 | - | - | - |
| 1s → 2t₁/3p | 287.90c | 0.21 | 0.0 | - | - | -0.63 |
| NH₃ 1s → 4a₁/3s | 400.45d | 0.30 | -0.13 | 0.73 | 1.68 | 0.63 |
| 1s → 2e/3p | 402.12d | e | -0.04 | 0.72 | 1.66 | 0.47 |
| 1s → 5a₁/3p | 402.65d | 0.19 | 0.23 | 0.85 | - | 1.00 |
| OH₂ 1s → 4a₁/3s | 533.62c | 0.21 | 0.0 | 0.78 | 2.06 | 0.53 |
| 1s → 2b₁/3p | 535.51c | 0.31 | -0.1 | 0.70 | 1.96 | - |
| **transition energies from the lowest core excited state:** | | | | | | |
| CH₄ 3a₁/3s → 2t₂/3p | 1.30 | -0.10 | 0.2 | - | - | - |
| NH₃ 4a₁/3s → 2e/3p | 1.67 | -0.07 | 0.09 | -0.01 | -0.02 | -0.16 |
| 4a₁/3s → 5a₁/3p | 2.20 | -0.11 | 0.36 | 0.12 | - | 0.37 |
| OH₂ 4a₁/3s → 2b₁/3p | 1.89 | 0.10 | -0.1 | -0.08 | -0.10 | - |

a Adjustments for relativistic effects of 0.10, 0.21, and 0.38 eV were applied for C, N, and O, respectively.
b Adjusted for one ν₄ vibrational quanta.
c Taken from Table 3 of Schirmer et al. 63

d Taken from Table 6 of Schirmer et al. 63

e Taken from Figure 1 of Schirmer et al. 63

its error is less systematic. Other density functionals have been reported to be less accurate than SCAN for core excitations, although how much varies significantly across functionals of different types. For excited-to-excited transition energies, which when looking at spectra are what determine peak separations, VMC’s accuracy is similar to equation of motion coupled cluster and NOCIS. Thus, in these molecules, we find that VMC appears quite capable of fulfilling its traditional role as a theoretical benchmark, being competitive with both the best available method for ground-to-excited transitions and the best available methods for excited-to-excited transitions. When thinking about a method’s possible future value as a benchmark method in systems without clear experimental data, it is important to consider how systematically improvable a method is in addition to how accurate it is. Unlike the other methods in Table 1, this type of VMC approach is quite straightforward to improve systematically by simply enlarging the determinant expansion. 15

B. Robustness of Variance Matching

While the accuracies seen in the previous section suggest our variance matching procedure is working well, we nonetheless feel it is important to test its sensitivity to the degree of interpolation employed. It is difficult to predict a priori what excited state expansion lengths will nicely straddle the ground state variance, and so unless a large number of excited state optimizations are done, how tightly the excited states straddle the ground state will not be controlled systematically. To test how sensitive variance matching is to the degree of interpolation, we have therefore performed an additional methane optimization with a much larger determinant expansion and compared interpolations with and without it in order to see the effect of interpolating over a wider variance range.

As seen in Figure 4, the excitation energy prediction changes by less than 0.05 eV when including this extra excited state calculation in the linear regression. Notably, the variance range is now large enough that a clear non-linearity can be seen in the relationship between energy and variance. Nonetheless, a simple linear regression still gives almost the same answer as before. If one wanted to improve the suitability of using a linear regression, the least accurate excited state wave function could be omitted, which would lead to a linear fit over a somewhat smaller variance range. As the energy vs variance should be a smooth function, linear fits should be increasingly appropriate as the variance range is reduced. This approach leads to an excitation energy prediction that is even closer (now within 0.02 eV) to the original interpolation (i.e. the one without the 2600-determinant expansion). Thus, different interpolations make little difference here, although we do see that predictions are slightly more consistent when the linear regression is done over shorter ranges.
FIG. 4. A comparison of difference variance matching linear regressions for the $2\alpha/3\beta$ excitation in methane. The original fit is as reported in Table I, while the larger fit includes an additional set of points from a significantly larger determinant expansion. Even with two different fits, the excitation energy prediction changes by less than 0.05 eV. A third fit (not shown) that includes only the three larger wave functions gives a prediction within 0.02 eV of the original.

IV. CONCLUSION

We have presented a systematically-improvable approach to core excitation energies that accounts for correlation and orbital relaxation while explicitly balancing the accuracies of the ground and excited state wave functions. The approach involves a careful choice of basis set and electron-nuclear correlation factor, a straightforward restricted active space approach for generating an initial determinant expansion, variational Monte Carlo, and the use of the variance matching technique for enhancing error cancellation. As the computational bottleneck is clearly the Monte Carlo optimization, this is by no means a low-cost approach, but the very high accuracies it displays in our preliminary tests on water, ammonia, and methane suggest that it should be useful for benchmarking other theoretical methods in systems where experimental data is absent or less reliable. Notably, other recently-developed theoretical methods (ROKS, fc-CVS-CoM-CCSD, and CVS-LR-CCSD) that offer comparable accuracies for ground-to-excited and/or excited-to-excited transition energies are much harder to improve systematically.

Looking forward, many extensions to this approach present themselves. For starters, it seems obvious that in future, an orbital relaxed basis should be used for the excited state restricted active space calculations, as this will almost certainly improve their ability to predict which determinants will ultimately be important for correlation recovery. Another straightforward step would be to use our approach to prepare nodal surfaces for diffusion Monte Carlo, although some caution is in order here as this could in principle at least spoil the error cancellation that variance matching provides. Of course, extending variance matching itself to projector Monte Carlo methods may help. In terms of potentially useful benchmarking applications, the area of doublet radical core states has received increasing theoretical attention lately\footnote{25,31,36,70,71}, and is an area where experimental data is less commonly available. Another promising application area is in pump-probe experiments aimed at photochemical processes (e.g. in DNA bases\footnote{72}), where a molecule with an existing valence excitation is subjected to an additional core excitation. The resulting doubly excited states are especially challenging for modern quantum chemistry, but do not present any formal problems for the Monte Carlo approach developed here. In cases like this where the cost of Monte Carlo is not prohibitive, it would be interesting to employ it to help benchmark more affordable theories in this challenging area.

Acknowledgements — This work was supported by the Office of Science, Office of Basic Energy Sciences, the U.S. Department of Energy, Contract No. DE-AC02-05CH11231. Calculations used the LBNL Lawrencium computing cluster.

Data Availability Statement — The data that supports the findings of this study are available within the article.
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