Electronic Excited States from a Variance-Based Contracted Quantum Eigensolver

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Electronic excited states of molecules are central to many physical and chemical processes, and yet they are typically more difficult to compute than ground states. In this paper we leverage the advantages of quantum computers to develop an algorithm for the highly accurate calculation of excited states. We solve a contracted Schrödinger equation (CSE)—a contraction (projection) of the Schrödinger equation onto the space of two electrons—whose solutions correspond identically to the ground and excited states of the Schrödinger equation. While recent quantum algorithms for solving the CSE, known as contracted quantum eigensolvers (CQE), have focused on ground states, we develop a CQE based on the variance that is designed to optimize rapidly to a ground or excited state. We apply the algorithm in a classical simulation without noise to computing the ground and excited states of H_4 and BH.

Introduction: Electronic excited states of molecules are critically important in any physical or chemical process that is not confined to the ground state such as photoabsorption and emission [1], non-adiabatic dynamics [2, 3], and electron scattering and transport [4, 5]. Despite their central importance excited states are more difficult to compute than ground states [6, 7]. Typical approaches compute the excited states as a response to the ground state [8–12], which has limitations whenever excited states differ substantially from the ground state, e.g. in double-or multi-excitation processes [13], charge-transfer states [14, 15], core excitations [16], Rydberg states [17], as well as conical intersections [18, 19].

One promising direction is to harness the potential advantages of quantum computers [20, 21]. In the absence of noise quantum computers can prepare and measure quantum states whose wave functions are challenging to represent and manipulate on classical devices, potentially realizing significant advantages relative to classical devices [22]. While recent molecular algorithms have primarily focused on computing ground states [21] or obtaining multiple excited states at once from response theory [23–28] or a Krylov expansion [23, 29–44], quantum computers may be particularly well suited to realizing more accurate and direct calculations of excited states. The possible advantages for ground states are in principle amplified for excited states.

In this paper we develop an algorithm for the highly accurate state-specific calculation of excited states on quantum devices. Consider the contraction of the Schrödinger equation onto the space of two electrons, known as the contracted Schrödinger equation (CSE) [45–49]. The CSE has two significant properties: (i) its solutions correspond identically to the ground-and excited-state solutions of the Schrödinger equation [45, 46] and (ii) its compact structure reveals an exact two-body exponential parameterization of both ground and excited states [50, 51]. Recent quantum-computing algorithms for solving the CSE or a part of the CSE, known as contracted quantum eigensolvers (CQEs) [52–57], have mainly focused on the ground state. We develop a CQE based on the energy variance that is designed to optimize rapidly to a ground or excited state. To demonstrate, we apply the algorithm in a classical simulation without noise to computing the ground and excited states of H_4 and BH.

Theory: For a many-electron system consider the Schrödinger equation

$$(\hat{H} - E_n)|\Psi_n\rangle = 0 \tag{1}$$

in which $\hat{H}$ is the Hamiltonian operator and $|\Psi_n\rangle$ is the N-electron wave function for the n^{th} state. Contraction over all electrons except two generates the CSE [45–49, 52]

$$\langle\Psi_n|\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k (\hat{H} - E_n)|\Psi_n\rangle = 0 \tag{2}$$

where $\hat{a}_i^\dagger$ and $\hat{a}_i$ are the creation and the annihilation operators for the i^{th} orbital. As proved by Nakatsuji [58] in first quantization and one of the authors [45] in second quantization, the CSE is satisfied by a wave function $|\Psi_n\rangle$ if and only if it satisfies the Schrödinger equation. The proofs show that the CSE implies the energy variance which implies the Schrödinger equation. Hence, the CSE determines a set of ground and excited states that is identical to that of the Schrödinger equation.

As shown previously, the CSE can be solved for the ground-state wave function by minimizing the following energy functional iteratively on a quantum computer [52–57]

$$\min_{{}^2F_m} E[\Psi_m[{}^2F_m]] \tag{3}$$

where

$$|\Psi_m\rangle = \mathrm{e}^{\hat{F}_m}|\Psi_{m-1}\rangle \tag{4}$$

in which

$$\hat{F}_m = \sum_{pqst} {}^2F_m^{pq;st} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_t \hat{a}_s \tag{5}$$

This wave function is the CSE ansatz with the special property that its iterative minimization with respect to each two-body operator $\hat{F}_m$ converges to an exact solution of the CSE and hence, an exact solution of the Schrödinger equation within a given finite basis set [50, 51]. The gradient of the energy with respect to the latest ${}^2F_m$ is the residual of the CSE. Hence, the gradient vanishes if and only if the CSE is satisfied. We can also implement subsets of the CSE ansatz on a quantum computer. For example, we have restricted the two-body operators $\hat{F}_m$ to be anti-Hermitian which generates strictly unitary transformations [52–56]. In this case the vanishing of the gradient causes the anti-Hermitian part of the CSE, known as the ACSE [48, 49, 59–62], to be satisfied.

To extend to excited states, we replace the iterative minimization of the energy by an iterative minimization of the energy variance

$$\min_{{}^2F_m} \mathrm{Var}[\Psi_m[{}^2F_m]] \tag{6}$$

where

$$\mathrm{Var}[\Psi_m[{}^2F_m]] = \langle \Psi_m | (\hat{H} - E_m)^2 | \Psi_m \rangle \tag{7}$$

in which

$$E_m = \langle \Psi_m | \hat{H} | \Psi_m \rangle \tag{8}$$

with the wave function given by the CSE ansatz in Eq. (4). Throughout we assume that the wave function $|\Psi_m\rangle$ has been renormalized to one if necessary. While the excited states are saddle points of the energy, they are minima of the variance. Moreover, any minimum is an exact stationary-state solution of the Schrödinger equation (and the CSE) if the variance vanishes. The variance has recently been applied for excited states in the context of the variational quantum eigensolver [63–67]; however, in these studies the variance is only used to guide the optimization. Here we use the CSE, which implies the variance [45, 58], to not only perform the optimization but also to determine the iterative structure of the wave function in Eq. (4). The CSE ansatz is formally exact with the important property that it remains exact even without reoptimization of the ${}^2F_{m-q}$ for $q > 0$ from previous iterations. The gradient of the variance with respect to ${}^2F_m$ can be computed as follows:

$$\frac{\partial \mathrm{Var}}{\partial \left({}^2F_m^{st;pq}\right)} = 2\langle \Psi_m | (\hat{\Gamma}^{pq}_{st} - {}^2D^{pq}_{st})(\hat{H} - E_m)^2 | \Psi_m \rangle, \tag{9}$$

in which $\hat{\Gamma}^{pq}_{st} = \hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_t \hat{a}_s$ and the elements of the 2-RDM are

$${}^2D^{pq}_{st} = \langle \Psi_m | \hat{\Gamma}^{pq}_{st} | \Psi_m \rangle. \tag{10}$$

Practically, we can approximate the minimization of the variance at the m^{th} iteration by selecting ${}^2F_m$ to be proportional to the direction of the gradient or a related search direction from any gradient-descent method with the proportionality constant (or step size) being determined by a line search. Other related generalizations of the variational principle in the CQE can also be considered. For example, we can: (1) solve the CSE or ACSE directly for the wave function, (2) minimize the least-squares norm of the CSE or ACSE, or (3) augment the variance functional with an additional functional such as a small amount of the energy functional.

Optimizing the energy variance is ideal for a quantum computer. While computing the variance requires not only the two-particle reduced density matrix (2-RDM) but also the four-particle RDM on a classical computer, we can readily compute it at the m^{th} iteration on a quantum computer by introducing an ancillary qubit to generate an extra wave function

$$|\tilde{\Psi}_m\rangle = \mathrm{e}^{i\delta\left(\hat{H} - E_m\right)} |\Psi_m\rangle \tag{11}$$

such that

$$\langle \Psi_m | (\hat{H} - E_m)^2 | \Psi_m \rangle \approx \frac{1 - \Re\langle \Psi_m | \tilde{\Psi}_m \rangle}{\delta^2/2} \tag{12}$$

where $\Re(z)$ returns the real part of z, the approximation is accurate to $O(\delta^2)$, and δ is a small parameter. This formula is an extension of the difference formulas employed in previous CQE algorithms [52] as well as in the context of open quantum systems [68]. As shown in previous work, the limit of δ approaching zero can be computed by using Richardson's extrapolation from a series of δ values [68, 69]. Recently we have shown how the residuals of both the CSE and ACSE can be efficiently calculated on a quantum computer from only a 2-RDM-like tomography [52, 57]. Similarly, the key term in the gradient of the variance with respect to ${}^2F$ in the CSE wave-function ansatz can be computed from a 2-RDM-like tomography

$$\langle \Psi_m | \hat{\Gamma}^{pq}_{st} (\hat{H} - E_m)^2 | \Psi_m \rangle \approx \frac{{}^2D^{pq}_{st} - \Re\langle \Psi_m | \hat{\Gamma}^{pq}_{st} | \tilde{\Psi}_m \rangle}{\delta^2/2} \tag{13}$$

where the approximation is accurate to $O(\delta^2)$. While the left side formally depends upon the six-particle RDM, through a combination of state preparation and tomography, we can obtain the gradient of the variance with the CSE ansatz from only the measurement of the two-particle reduced transition matrix between the states $|\Psi_m\rangle$ and $|\tilde{\Psi}_m\rangle$. Formulas in Eqs. (12) and (13) assume that the Hamiltonian and wave function are real, but as in Refs. [52, 68], they can be readily generalized through additional measurements to treat complex Hamiltonians and wave functions as well as to realize higher-order approximations. The algorithm for the variance-based CQE for excited states is summarized in Table I.

Results: To demonstrate, we apply the variance-based CQE algorithm in a classical simulation without noise

TABLE I. Variance-based CQE algorithm.

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Algorithm: Variance-based CQE
 Given $m = 0$ and convergence tolerance $\epsilon$.
 Choose initial wave function $|\Psi_0\rangle$.
 Repeat until the energy variance is less than $\epsilon$.
    Step 1: Prepare $|\tilde{\Psi}_m\rangle = e^{i\delta(\hat{H}-E_m)}|\Psi_m\rangle$
    Step 2: Measure variance using Eq. (12)
    Step 3: Measure $\langle\Psi_m|\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_t\hat{a}_s|\tilde{\Psi}_m\rangle$ in Eq. (13)
    Step 4: Compute gradient from Eqs. (9) and (13)
    Step 5: Compute gradient-descent search direction $\hat{F}_{m+1}$
    Step 6: Prepare $|\Psi_{m+1}\rangle = e^{\hat{F}_{m+1}}|\Psi_m\rangle$
    Step 7: Optimize magnitude of $\hat{F}_{m+1}$ via Steps 1, 2, and 6
    Step 8: Set $m = m + 1$.
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to computing the excited states of the molecules H_4 and BH. The H_4 molecule is treated in its linear conformation with adjacent hydrogen atoms separated by 1 Å. We use a minimal Slater-type orbital (STO-6G) basis set [70] for both molecules as well as a frozen 1s core for the boron atom in BH. Molecular orbitals from the Hartree-Fock method and one-and two-electron integrals are obtained with the Quantum Chemistry Package in Maple [71]. In implementing the algorithm in Table I, we restrict the $\hat{F}$ operators to be anti-Hermitian, making the two-body exponential transformations unitary and perform exact line searches along directions from a limited-memory Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [72] with a single gradient stored. Initial guesses for the wave function are the Slater determinants from the Hartree-Fock orbitals; when $\langle\hat{S}_z\rangle = \pm 1$, we use a single high-spin Slater determinant, but when $\langle\hat{S}_z\rangle = 0$, unless noted otherwise, we use an equal linear combination of two determinants that are related by switching the α (spin up) and β (spin down) orbitals with the relative phases being +1 for a singlet and -1 for a triplet.

The ground state and the first 15 excited states of linear H_4 as computed from the variance-based CQE are shown in Table II. The algorithm is performed iteratively until the energy variance is less than 10^{-6} a.u. The number of iterations required for convergence varies from 7 for the second excited state to 39 for the fifteen excited state. At convergence the energy error is also less than 10^{-6} hartrees except for the fifth, thirteenth, and fifteenth excited states. Even though the energies of the excited states need not be upper bounds to the energies from exact diagonalization, we find that all excited-state energies are strictly above those from diagonalization. We also compute the least-squares error in the CSE—the sum of the squares of the errors in the CSE, which is approximately an order of magnitude less than the energy variance for each state. For the fifth excited state Fig. 1 shows the convergence of the energy error, variance, and least-squares CSE norm. We observe superlinear convergence towards zero in all three metrics for the error.

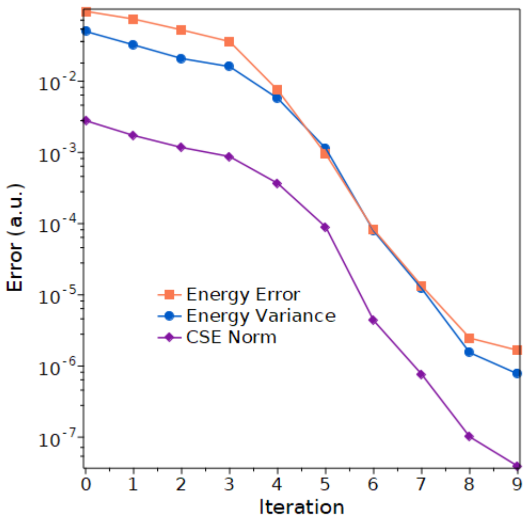

FIG. 1. Superlinear convergence of the energy error, variance, and least-squares CSE norm is shown for the fifth excited state of linear H_4.

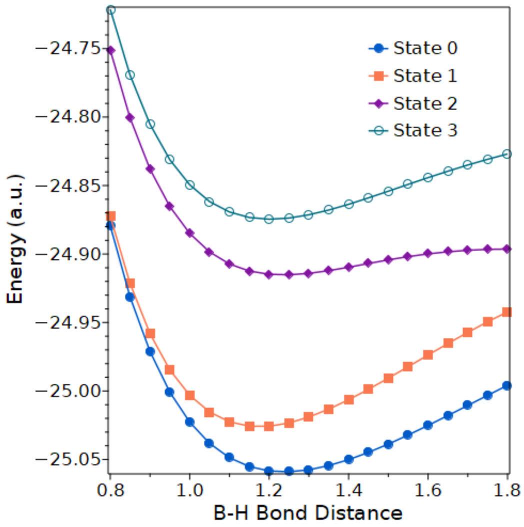

FIG. 2. Energies of the ground state and the first three excited states of BH are shown as functions of the bond distance. Symbols represent variance-based CQE energies while solid lines represent energies from exact diagonalization.

The energies of the ground state and the first three excited states of BH are shown as functions of the bond distance in Fig. 2. The solid lines denote the ground- and excited-state energies from exact diagonalization while the symbols denote the energies from the variance-based CQE. In each case the energy variance in the CQE is converged to less than 10^{-5} a.u. We observe that the CQE reproduces the potential energy curves with maximum energy errors of 0.00001, 0.00008, 0.00004, and 0.00024 hartrees for the ground and first three excited states, respectively.

TABLE II. The energy, energy error, variance, and least-squares CSE norm of the ground state and each of the first 15 excited states of linear H_4 from the variance-based CQE are shown. Energies are given in hartrees.

State	$2S+1$	$\langle \hat{S}_z \rangle$	Energy	Iterations	Energy Error	Variance	CSE Norm
0	1	0	-2.18096635	20	6.6×10^{-7}	8.0×10^{-7}	4.3×10^{-8}
1	3	-1	-1.95019128	8	4.0×10^{-7}	4.1×10^{-7}	3.4×10^{-8}
2	3	0	-1.95019128	7	3.9×10^{-7}	5.2×10^{-7}	2.3×10^{-8}
3	3	1	-1.95019128	8	4.0×10^{-7}	4.1×10^{-7}	3.4×10^{-8}
4	3	-1	-1.73654709	13	6.4×10^{-7}	3.7×10^{-7}	3.9×10^{-8}
5	3	0	-1.73654709	9	1.7×10^{-6}	7.8×10^{-7}	3.9×10^{-8}
6	3	1	-1.73654709	13	6.4×10^{-6}	3.7×10^{-7}	3.9×10^{-8}
7	1	0	-1.66711149	17	8.6×10^{-7}	9.8×10^{-7}	6.5×10^{-8}
8	1	0	-1.63892672	9	4.1×10^{-7}	3.3×10^{-7}	2.0×10^{-8}
9	3	-1	-1.45713456	17	7.9×10^{-7}	6.0×10^{-7}	7.1×10^{-8}
10	3	0	-1.45713456	21	7.7×10^{-8}	9.5×10^{-7}	7.6×10^{-8}
11	3	1	-1.45713456	17	7.9×10^{-7}	6.0×10^{-7}	7.1×10^{-8}
12	1	0	-1.34940191	37	9.1×10^{-7}	8.6×10^{-7}	5.4×10^{-8}
13	3	-1	-1.30398471	37	9.8×10^{-6}	7.3×10^{-7}	6.4×10^{-8}
14	3	0	-1.30398471	11	2.8×10^{-7}	3.7×10^{-7}	2.2×10^{-8}
15	3	1	-1.30398471	39	1.4×10^{-5}	9.6×10^{-7}	1.0×10^{-7}

Conclusions: Here we present a variance-based CQE for computing highly accurate molecular excited states on quantum computers. The CQE is a family of algorithms in which a contraction of the Schrödinger equation to the space of two particles (CSE) is solved for stationary-state energies and their 2-RDMs. The structure of the CSE implies an exact ansatz for any ground- or excited-state wave function in which a two-body exponential transformation is iteratively applied and optimized to update a trial wave function. Importantly, unlike iterative variational quantum eigensolvers, the CQE does not need to reoptimize previous transformations to satisfy the CSE and thereby solve the Schrödinger equation. While recent work with CQE has focused on the ground state, here we present a CQE algorithm for excited states in which we iteratively minimize the energy variance with respect to the CSE (or ACSE) ansatz. We show that the variance-based CQE yields highly accurate ground-and excited-state energies for the example cases of H_4 and BH in the absence of noise. Future work will examine the application of the variance-based CQE on noisy intermediate-scale quantum (NISQ) computers. The present approach represents an important step towards the accurate modeling of molecular excited states on NISQ and fault-tolerant quantum computers.

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[1] V. W.-W. Yam, Using synthesis to steer excited states and their properties and functions, Nature Synthesis **2**, 94 (2023).

[2] T. R. Nelson, S. Fernandez-Alberti, and S. Tretiak, Modeling excited-state molecular dynamics beyond the Born–Oppenheimer regime, Nature Computational Science **2**, 689 (2022).

[3] Y. Wang, Y. Guan, H. Guo, and D. R. Yarkony, Enabling complete multichannel nonadiabatic dynamics: A global representation of the two-channel coupled, 1,21A and 13A states of NH3 using neural networks, The Journal of Chemical Physics **154**, 094121 (2021).

[4] J. E. Greenwald, J. Cameron, N. J. Findlay, T. Fu, S. Gunasekaran, P. J. Skabara, and L. Venkataraman, Highly nonlinear transport across single-molecule junctions via destructive quantum interference, Nature Nanotechnology **16**, 313 (2021).

[5] L.-Y. Hsu, B.-Y. Jin, C.-h. Chen, and S.-M. Peng, Reaction: New Insights into Molecular Electronics, Chem **3**, 378 (2017).

[6] L. González and R. Lindh, eds., *Quantum Chemistry and Dynamics of Excited States* (Wiley, New York, 2021).

[7] C. L. Benavides-Riveros, L. Chen, C. Schilling, S. Mantilla, and S. Pittalis, Excitations of Quantum Many-Body Systems via Purified Ensembles: A Unitary-Coupled-Cluster-Based Approach, Physical Review Letters **129**, 066401 (2022), 2201.10974.

[8] H. J. Monkhorst, Calculation of properties with the coupled-cluster method, International Journal of Quantum Chemistry **12**, 421 (1977).

[9] E. Runge and E. K. U. Gross, Density-Functional Theory for Time-Dependent Systems, Physical Review Letters **52**, 997 (1984).

[10] J. F. Stanton and R. J. Bartlett, The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties, The Journal of Chemical Physics **98**, 7029 (1993).

[11] D. A. Mazziotti, Extraction of electronic excited states from the ground-state two-particle reduced density matrix, Physical Review A **68**, 052501 (2003).

[12] M. Casida and M. Huix-Rotllant, Progress in Time-Dependent Density-Functional Theory, Annual Review of Physical Chemistry **63**, 287 (2012), 1108.0611.

[13] N. T. Maitra, F. Zhang, R. J. Cave, and K. Burke, Double excitations within time-dependent density functional theory linear response, The Journal of Chemical Physics **120**, 5932 (2004).

[14] A. Dreuw and M. Head-Gordon, Failure of Time-Dependent Density Functional Theory for Long-Range Charge-Transfer Excited States: The Zincbacteriochlorin-Bacteriochlorin and Bacteriochlorophyll-Spheroidene Complexes, Journal of the American Chemical Society **126**, 4007 (2004).

[15] D. Mester and M. Kállay, Charge-Transfer Excitations within Density Functional Theory: How Accurate Are the Most Recommended Approaches?, Journal of Chemical Theory and Computation **18**, 1646 (2022).

[16] T. Moitra, L. Konecny, M. Kadek, A. Rubio, and M. Repisky, Accurate Relativistic Real-Time Time-Dependent Density Functional Theory for Valence and Core Attosecond Transient Absorption Spectroscopy., The journal of physical chemistry letters **14**, 1714 (2023), 2211.16383.

[17] J. Li, Y. Jin, N. Q. Su, and W. Yang, Combining localized orbital scaling correction and Bethe-Salpeter equation for accurate excitation energies., The Journal of chemical physics **156**, 154101 (2022), 2207.00508.

[18] J. W. Snyder and D. A. Mazziotti, Photoexcited conversion of gauche-1,3-butadiene to bicyclobutane via a conical intersection: Energies and reduced density matrices from the anti-Hermitian contracted Schrödinger equation, The Journal of Chemical Physics **135**, 024107 (2011).

[19] Y. Wang and D. R. Yarkony, Conical intersection seams in spin–orbit coupled systems with an even number of electrons: A numerical study based on neural network fit surfaces, The Journal of Chemical Physics **155**, 174115 (2021).

[20] K. Head-Marsden, J. Flick, C. J. Ciccarino, and P. Narang, Quantum Information and Algorithms for Correlated Quantum Matter, Chemical Reviews **121**, 3061 (2021).

[21] K. Bharti, A. Cervera-Lierta, T. H. Kyaw, T. Haug, S. Alperin-Lea, A. Anand, M. Degroote, H. Heimonen, J. S. Kottmann, T. Menke, W.-K. Mok, S. Sim, L.-C. Kwek, and A. Aspuru-Guzik, Noisy intermediate-scale quantum algorithms, Reviews of Modern Physics **94**, 015004 (2022).

[22] S. Lloyd, A potentially realizable quantum computer., Science (New York, N.Y.) **261**, 1569 (1993).

[23] Q. Gao, G. O. Jones, M. Motta, M. Sugawara, H. C. Watanabe, T. Kobayashi, E. Watanabe, Y.-y. Ohnishi, H. Nakamura, and N. Yamamoto, Applications of quantum computing for investigations of electronic transitions in phenylsulfonyl-carbazole TADF emitters, npj Computational Materials **7**, 70 (2021), 2007.15795.

[24] A. Asthana, A. Kumar, V. Abraham, H. Grimsley, Y. Zhang, L. Cincio, S. Tretiak, P. A. Dub, S. E. Economou, E. Barnes, and N. J. Mayhall, Equation-of-motion variational quantum eigensolver method for computing molecular excitation energies, ionization potentials, and electron affinities, arXiv 10.48550/arxiv.2206.10502 (2022), 2206.10502.

[25] A. Kumar, A. Asthana, C. Masteran, E. F. Valeev, Y. Zhang, L. Cincio, S. Tretiak, and P. A. Dub, Quantum Simulation of Molecular Electronic States with a Transcorrelated Hamiltonian: Higher Accuracy with Fewer Qubits, Journal of Chemical Theory and Computation **18**, 5312 (2022).

[26] M. Q. Hlatshwayo, Y. Zhang, H. Wibowo, R. LaRose, D. Lacroix, and E. Litvinova, Simulating excited states of the Lipkin model on a quantum computer, Physical Review C **106**, 024319 (2022), 2203.01478.

[27] A. Asthana, A. Kumar, V. Abraham, H. Grimsley, Y. Zhang, L. Cincio, S. Tretiak, P. A. Dub, S. E. Economou, E. Barnes, and N. J. Mayhall, Quantum self-consistent equation-of-motion method for computing molecular excitation energies, ionization potentials, and electron affinities on a quantum computer, Chemical Science **14**, 2405 (2023).

[28] Y. Kim and A. Krylov, Two algorithms for excited-states quantum solvers: Theory and application to EOM-UCCSD, ChemRxiv 10.26434/chemrxiv-2023-fml2k (2023).

[29] J. R. McClean, M. E. Kimchi-Schwartz, J. Carter, and W. A. d. Jong, Hybrid quantum-classical hierarchy for mitigation of decoherence and determination of excited states, Physical Review A **95**, 042308 (2017), 1603.05681.

[30] J. I. Colless, V. V. Ramasesh, D. Dahlen, M. S. Blok, M. E. Kimchi-Schwartz, J. R. McClean, J. Carter, W. A. d. Jong, and I. Siddiqi, Computation of Molecular Spectra on a Quantum Processor with an Error-Resilient Algorithm, Physical Review X **8**, 011021 (2018), 1707.06408.

[31] K. M. Nakanishi, K. Mitarai, and K. Fujii, Subspace-search variational quantum eigensolver for excited states, Physical Review Research **1**, 033062 (2019), 1810.09434.

[32] T. Bian, D. Murphy, R. Xia, A. Daskin, and S. Kais, Quantum computing methods for electronic states of the water molecule, Molecular Physics **117**, 2069 (2019).

[33] M. Motta, C. Sun, A. T. K. Tan, M. J. O'Rourke, E. Ye, A. J. Minnich, F. G. S. L. Brandão, and G. K.-L. Chan, Determining eigenstates and thermal states on a quantum computer using quantum imaginary time evolution, Nature Physics **16**, 205 (2020), 1901.07653.

[34] J. R. McClean, Z. Jiang, N. C. Rubin, R. Babbush, and H. Neven, Decoding quantum errors with subspace expansions, Nature Communications **11**, 636 (2020), 1903.05786.

[35] T. Takeshita, N. C. Rubin, Z. Jiang, E. Lee, R. Babbush, and J. R. McClean, Increasing the Representation Accuracy of Quantum Simulations of Chemistry without Extra Quantum Resources, Physical Review X **10**, 011004 (2020), 1902.10679.

[36] A. Francis, A. A. Agrawal, J. H. Howard, E. Kökcü, and A. F. Kemper, Subspace Diagonalization on Quantum Computers using Eigenvector Continuation, arXiv 10.48550/arxiv.2209.10571 (2022), 2209.10571.

[37] B. Huang, M. Govoni, and G. Galli, Simulating the Electronic Structure of Spin Defects on Quantum Computers, PRX Quantum **3**, 010339 (2022), 2112.04435.

[38] N. V. Tkachenko, Y. Zhang, L. Cincio, A. I. Boldyrev, S. Tretiak, and P. A. Dub, Quantum Davidson Algorithm for Excited States, arXiv 10.48550/arxiv.2204.10741 (2022), 2204.10741.

[39] C. L. Cortes and S. K. Gray, Quantum Krylov subspace algorithms for ground- and excited-state energy estima-

tion, Physical Review A **105**, 022417 (2022), 2109.06868.

[40] Y. Shen, K. Klymko, J. Sud, D. B. Williams-Young, W. A. d. Jong, and N. M. Tubman, Real-Time Krylov Theory for Quantum Computing Algorithms, arXiv 10.48550/arxiv.2208.01063 (2022), 2208.01063.

[41] N. Yoshioka, H. Hakoshima, Y. Matsuzaki, Y. Tokunaga, Y. Suzuki, and S. Endo, Generalized Quantum Subspace Expansion, Physical Review Letters **129**, 020502 (2022), 2107.02611.

[42] M. Motta, G. O. Jones, J. E. Rice, T. P. Gujarati, R. Sakuma, I. Liepuoniute, J. M. Garcia, and Y.-y. Ohnishi, Quantum chemistry simulation of ground- and excited-state properties of the sulfonium cation on a superconducting quantum processor, Chemical Science **14**, 2915 (2023), 2208.02414.

[43] K. Kanno, M. Kohda, R. Imai, S. Koh, K. Mitarai, W. Mizukami, and Y. O. Nakagawa, Quantum-Selected Configuration Interaction: classical diagonalization of Hamiltonians in subspaces selected by quantum computers, arXiv 10.48550/arxiv.2302.11320 (2023), 2302.11320.

[44] S. Choi and A. F. Izmaylov, Measurement optimization techniques for excited electronic states in near-term quantum computing algorithms, arXiv 10.48550/arxiv.2302.11421 (2023), 2302.11421.

[45] D. A. Mazziotti, Contracted Schrödinger equation: Determining quantum energies and two-particle density matrices without wave functions, Physical Review A **57**, 4219 (1998).

[46] H. Nakatsuji and K. Yasuda, Direct Determination of the Quantum-Mechanical Density Matrix Using the Density Equation, Physical Review Letters **76**, 1039 (1996).

[47] F. Colmenero and C. Valdemoro, Approximating q-order reduced density matrices in terms of the lower-order ones. II. Applications, Physical Review A **47**, 979 (1993).

[48] D. A. Mazziotti, Anti-Hermitian Contracted Schrödinger Equation: Direct Determination of the Two-Electron Reduced Density Matrices of Many-Electron Molecules, Physical Review Letters **97**, 143002 (2006).

[49] J.-N. Boyn and D. A. Mazziotti, Accurate singlet–triplet gaps in biradicals via the spin averaged anti-Hermitian contracted Schrödinger equation, The Journal of Chemical Physics **154**, 134103 (2021), 2104.00626.

[50] D. A. Mazziotti, Exactness of wave functions from two-body exponential transformations in many-body quantum theory, Physical Review A **69**, 012507 (2004).

[51] D. A. Mazziotti, Exact two-body expansion of the many-particle wave function, Physical Review A **102**, 030802 (2020), 2010.02191.

[52] S. E. Smart and D. A. Mazziotti, Quantum Solver of Contracted Eigenvalue Equations for Scalable Molecular Simulations on Quantum Computing Devices, Physical Review Letters **126**, 070504 (2021), 2004.11416.

[53] J.-N. Boyn, A. O. Lykhin, S. E. Smart, L. Gagliardi, and D. A. Mazziotti, Quantum-classical hybrid algorithm for the simulation of all-electron correlation, The Journal of Chemical Physics **155**, 244106 (2021), 2106.11972.

[54] S. E. Smart and D. A. Mazziotti, Accelerated Convergence of Contracted Quantum Eigensolvers through a Quasi-Second-Order, Locally Parameterized Optimization, Journal of Chemical Theory and Computation **18**, 5286 (2022).

[55] S. E. Smart, J.-N. Boyn, and D. A. Mazziotti, Resolving correlated states of benzyne with an error-mitigated contracted quantum eigensolver, Physical Review A **105**, 022405 (2022), 2103.06876.

[56] S. E. Smart and D. A. Mazziotti, Many-fermion simulation from the contracted quantum eigensolver without fermionic encoding of the wave function, Physical Review A **105**, 062424 (2022), 2205.01725.

[57] S. E. Smart and D. A. Mazziotti, Verifiably Exact Solution of the Electronic Schrodinger Equation on Quantum Devices, arXiv 10.48550/arxiv.2303.00758 (2023), 2303.00758.

[58] H. Nakatsuji, Equation for the direct determination of the density matrix, Physical Review A **14**, 41 (1976).

[59] D. A. Mazziotti, Multireference many-electron correlation energies from two-electron reduced density matrices computed by solving the anti-Hermitian contracted Schrödinger equation, Physical Review A **76**, 052502 (2007).

[60] D. A. Mazziotti, Anti-Hermitian part of the contracted Schrödinger equation for the direct calculation of two-electron reduced density matrices, Physical Review A **75**, 022505 (2007).

[61] G. Gidofalvi and D. A. Mazziotti, Direct calculation of excited-state electronic energies and two-electron reduced density matrices from the anti-Hermitian contracted Schrödinger equation, Physical Review A **80**, 022507 (2009).

[62] J. W. Snyder, A. E. Rothman, J. J. Foley, and D. A. Mazziotti, Conical intersections in triplet excited states of methylene from the anti-Hermitian contracted Schrödinger equation, The Journal of Chemical Physics **132**, 154109 (2010).

[63] F. Zhang, N. Gomes, Y. Yao, P. P. Orth, and T. Iadecola, Adaptive variational quantum eigensolvers for highly excited states, Physical Review B **104**, 075159 (2021), 2104.12636.

[64] D.-B. Zhang, B.-L. Chen, Z.-H. Yuan, and T. Yin, Variational quantum eigensolvers by variance minimization, Chinese Physics B **31**, 120301 (2022).

[65] I. Hobday, P. Stevenson, and J. Benstead, Variance minimisation on a quantum computer for nuclear structure, arXiv 10.48550/arxiv.2209.07820 (2022), 2209.07820.

[66] G. Boyd and B. Koczor, Training Variational Quantum Circuits with CoVaR: Covariance Root Finding with Classical Shadows, Physical Review X **12**, 041022 (2022), 2204.08494.

[67] S. Liu, S.-X. Zhang, C.-Y. Hsieh, S. Zhang, and H. Yao, Probing many-body localization by excited-state variational quantum eigensolver, Physical Review B **107**, 024204 (2023), 2111.13719.

[68] A. W. Schlimgen, K. Head-Marsden, L. M. Sager, P. Narang, and D. A. Mazziotti, Quantum Simulation of Open Quantum Systems Using a Unitary Decomposition of Operators, Physical Review Letters **127**, 270503 (2021), 2106.12588.

[69] K. Seki and S. Yunoki, Quantum Power Method by a Superposition of Time-Evolved States, PRX Quantum **2**, 10.1103/prxquantum.2.010333 (2021), 2008.03661.

[70] W. J. Hehre, R. F. Stewart, and J. A. Pople, Self-Consistent Molecular-Orbital Methods. I. Use of Gaussian Expansions of Slater-Type Atomic Orbitals, The Journal of Chemical Physics **51**, 2657 (1969).

[71] RDMChem, Quantum Chemistry Toolbox in Maple (2023).

[72] D. C. Liu and J. Nocedal, On the limited memory BFGS method for large scale optimization, Mathematical Pro-

gramming **45**, 503 (1989).