Leveraging small scale quantum computers with unitarily downfolded Hamiltonians

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In this work, we propose a quantum unitary downfolding formalism based on the driven similarity renormalization group (QDSRG) that may be combined with quantum algorithms for both noisy and fault-tolerant hardware. The QDSRG is a classical polynomially-scaling downfolding method that avoids the evaluation of costly three- and higher-body reduced density matrices while retaining the accuracy of classical multireference many-body theories. We calibrate and test the QDSRG on several challenging chemical problems and propose a strategy for avoiding classical exponential-scaling steps in the QDSRG scheme. We report QDSRG computations of two chemical systems using the variational quantum eigensolver on IBM quantum devices: i) the dissociation curve of H2 using a quintuple-ζ basis and ii) the bicyclobutane isomerization reaction to trans-butadiene, demonstrating the reduction of problems that require several hundred qubits to a single qubit. Our work shows that the QDSRG is a viable approach to leverage near-term quantum devices for the accurate estimation of molecular properties.

I. INTRODUCTION

Molecule and materials that display strong electron correlation are hard to simulate with classical computers due to the exponential growth of the many-body Hilbert space [1]. Quantum computers [2, 3] are particularly well-suited to simulate many-body systems, as they can efficiently represent and perform operations on many-particle wave functions. These features make them a promising solution to the electron correlation problem [4, 5], which, in its most general form, still defies classical algorithms. However, the accurate modeling of realistic many-electron systems requires the use of large computational bases and, therefore, it is unlikely to be accessible to small-scale quantum computers with up to only a few hundred qubits. One of the most promising strategies to maximize the impact of near-term quantum devices is to pair a quantum algorithm with classical approaches that perform a reduction of the number of qubits required in a quantum computation [6].

Several strategies have been proposed to minimize quantum resources by combining quantum computations with traditional quantum chemistry approaches. Takeshita et al. [7] applied quantum algorithms in combination with the active-space approximation and orbital optimization. This idea was demonstrated experimentally for model molecules with up to ten orbitals using just two qubits [8]. Boynt et al. [9] obtained active-space 2-RDMs from quantum computations and post-processed them with two classical correlation methods, the anti-Hermitian contracted Schrödinger equation (ACSE) theory [10–12] and multiconfigurational pair-density functional theory (MC-PDFT) [13]. Fujii et al. combined the divide-and-conquer technique with quantum computations to solve the ground state of a 64-qubit two-dimensional Heisenberg model with 20-qubit simulations, [14] and later extended it to obtain excited states of periodic hydrogen chain [15]. Ryabinkin et al. [16] used low-order perturbative corrections to reduce the quantum resources required in their iQCC-VQE algorithm. Tammaro et al. [17] investigated the use of N-electron valence perturbation theory (NEVPT) [18, 19] in combination with the variational quantum eigensolver (VQE) [20–22] and quantum subspace expansion [23, 24] algorithms.

Huggins et al. recently proposed a hybrid algorithm that combines quantum shadow tomography with the auxiliary-field quantum Monte Carlo method, achieving the largest-to-date chemical simulation on hardware of a 16-qubit system [25]. Other works have focused on reducing the number of qubits and gates required by variational quantum algorithms using embedding techniques. For example, density-matrix embedding theory [26, 27] has been applied to simulate a H10 ring on an ion-trap quantum computer by decomposing this 20-qubit system into ten two-qubit problems [28]. Huang et al. have used quantum defect embedding theory to simulate spin defects on quantum computers [29]. Combing explicitly correlated methods with quantum algorithms is another strategy explored in several works [30–35] to achieve higher accuracy without increasing quantum resources. Motta et al. [30] used a canonical transcorrelated F12 (CT-F12) Hamiltonian [36] in conjunction with the variational quantum eigensolver method, whereas McArdle et al. [31] used Boys and Handy’s transcorrelated approach, which produces a non-Hermitian Hamiltonian containing up to three-body terms. A recent contribution also considers an a posteriori perturbative correction based on the explicitly correlated [2]r12 approach [32].

Quantum chemistry effective Hamiltonian theories [37–43] offer another way to downfold correlation effects into a small active-space quantum computation. In such ap-
proaches one partitions the orbital space into two sets, active and inactive, and a transformation is applied to the Hamiltonian to eliminate terms that couple these two spaces. The resulting Hamiltonian then accounts for electron correlation effects in the inactive orbitals via effective many-body interactions. In principle, it is straightforward to adapt this strategy to a quantum-classical hybrid setting whereby a highly entangled quantum state involving only the active orbitals is solved for on a quantum computer and the remaining weak correlation effects are recovered with a polynomially scaling classical algorithm. However, there are several major potential issues with effective Hamiltonian methods as formulated in a classical setting. A particularly severe limitation of some approaches is the need to measure three- and four-body reduced density matrices (RDMs), introducing a prohibitively large prefactor in quantum computations that scales as the sixth to the eight power of the number of active orbitals. A second important issue is the impact of noise in the measured RDMs on the energy (and other properties) and the numerical stability of methods that require the solution of nonlinear equations. Lastly, it is often necessary to go beyond low-order perturbative treatments to achieve accurate energetics. Several quantum downfolding methods have been proposed. The double unitary coupled-cluster (DUCM) approach [44–46] is a downfolding procedure based on a mean-field reference state. Le and Tran [47] have employed their one-body second-order Møller-Plesset perturbation theory (OBMP2) to create an effective Hamiltonian with modified one-body interactions for the VQE method.

In this work, we present a quantum downfolding approach based on the driven similarity renormalization group (DSRG) [48–51, 56] that addresses the challenges highlighted above. The DSRG is an integral reformulation of numerical flow-renormalization group methods [52–55]. Our quantum formulation of the DSRG (QDSRG) is compatible with any quantum algorithm capable of producing low-rank RDMs (up to partial or full second-order) and augments it with an accurate, numerically-robust, and nonperturbative treatment of weak (dynamical) correlation. We benchmark the performance of the QDSRG scheme in computing the dissociation curve of the nitrogen molecule and the adiabatic singlet-triplet splittings of the para-benzyne diradical. In addition to exact simulations, we demonstrate the usefulness of this strategy in the presence of realistic noise by combining the QDSRG with VQE experiments on IBM quantum computers. We compute the dissociation curve of the hydrogen molecule with a nearly-complete quintuple-ζ basis, as well as model the bicyclobutane isomerization pathways to trans-butadiene, which, to the best of our knowledge, is the first example of modeling an organic chemistry reaction on near-term quantum devices.

II. THEORY

A. Unitary Hamiltonian downfolding via the DSRG

The DSRG method [48–51, 56] starts from a reference correlated state \( \Psi_0 \) and performs a unitary transformation of the Hamiltonian, \( \hat{H} \), that brings it to a block-diagonal form

\[
H \rightarrow \hat{H} = e^{-A}H e^{A},
\]

where the operator \( A \) is anti-Hermitian. The goal of this transformation is to remove the second-quantized components of \( \hat{H} \) that couple \( \Psi_0 \) to excited configurations, which we refer to as the nondiagonal components of \( \hat{H} \) (denoted as \( \hat{H}^N \)).

One of the challenges associated with eliminating these couplings (i.e., solving for \( \hat{H}^N = 0 \)) is the emergence of numerical instabilities, which are related to excitations with small energy denominators. To avoid this issue, the DSRG achieves only a partial block-diagonalization of \( \hat{H} \) by solving a set of regularized equations

\[
\hat{H}^N = R(s).
\]

In this equation, \( R(s) \) is an operator that depends on the flow parameter \( s \in [0, \infty) \), and its purpose is to suppress excited configurations associated with an energy denominator smaller than the energy cutoff \( \Lambda = 1/\sqrt{s} \). Hence, solving Eq. (2) imparts a dependence on \( s \) onto the \( A \) operator and the transformed Hamiltonian.

The DSRG operator \( A(s) \) is expressed in terms of a s-dependent coupled cluster particle-hole excitation operator [57–60] as \( A = T - T^\dagger \) with \( T = T_1 + T_2 + \ldots \) where each k-body component is

\[
T_k = \frac{1}{(k!)^2} \sum_{ij\ldots} \sum_{ab\ldots} t_{ij\ldots}^{ab\ldots}(s) \{ \hat{a}_{ij\ldots}, \}
\]

where we write the normal-ordered creation and annihilation operators in a compact form \( \{ \hat{a}_{ij\ldots} \} = \{ \hat{a}_{ij\ldots} \} = \{ \hat{a}_{ij\ldots}\cdots \hat{a}_{ij\ldots} \} [61, 62] \), and the cluster amplitudes \( t_{ij\ldots}^{ab\ldots}(s) \) are tensors antisymmetric with respect to the individual permutation of upper and lower indices. The hole space contains the occupied and partially occupied orbitals, while the particle space contains the partially occupied and unoccupied orbitals of the reference \( \Psi_0 \). One of the simplest nonperturbative truncation schemes is the linearized DSRG with one- and two-body operators [LDSRG(2)] [50] where: 1) \( T \) is truncated as \( T \approx T_1 + T_2 \), and 2) every commutator in the Baker–Campbell–Hausdorff expansion of \( \hat{H} \) contains only one- and two-body operators (indicated with subscript “1,2”)

\[
\hat{H} \approx H + \sum_{k=1}^{\infty} \frac{1}{k!} \left[ \cdots \left[ \left[ H, A_{1,2} \right]_{1,2} \right]_{1,2} \cdots \right]_{1,2}.
\]
The resulting DSRG transformed Hamiltonian contains up to two-body interactions. Once Eq. (2) is solved, the energy may computed as the expectation value of $H$

$$E = \langle \Psi_0 | H | \Psi_0 \rangle .$$

Alternatively, one may solve the eigenvalue problem

$$H | \tilde{\Psi}_0 \rangle = \tilde{E} | \tilde{\Psi}_0 \rangle ,$$

and obtain a relaxed reference state $\tilde{\Psi}_0$ and its corresponding energy $\tilde{E}$. It is often the case that multireference quantum chemistry methods, like for the example, the CASPT2 [63] or NEVPT2 [18, 19] methods, only evaluate the energy as an expectation value via equations analogous to Eq. (5). In this case one talks of a “diagonalize-then-perturb” approach and the resulting formalism only provides an energy correction rather than a properly downfolded Hamiltonian.

Solving the DSRG equations [Eq. (2)] requires the reduced density cumulants (RDCs) of the reference state (which we also simply refer to as “cumulants”) [64, 65]. A generic $k$-body reduced density cumulant $(\lambda_k)$ is the connected part of the corresponding $k$-body RDM $(\gamma_k)$, defined as $\gamma_{\lambda_{\mu_1}^{\mu_2} \ldots} = \langle \Psi_0 | a_p^{\dagger} a_q^{\dagger} \ldots a_s a_r | \Psi_0 \rangle$, where the product $a_p^{\dagger} a_q^{\dagger} \ldots a_s a_r$ contains $k$ creation and $k$ annihilation operators. The RDCs of the reference state encode all the information required to include correlation effects outside of the active orbitals. Therefore, any computational method capable of generating $\Psi_0$ and its RDMs can be interfaced with the DSRG downfolding procedure. It is convenient to express the DSRG equations in terms of cumulants as any truncated scheme preserves the size extensivity of the energy. Reduced density cumulants enter in the LDSRG(2) equations in the following way. Evaluation of the operator $A$ requires $\lambda_1$ and $\lambda_2$, while evaluation of the energy additionally requires $\lambda_3$ which is challenging to measure on near-term devices. In the next section, we analyze a modified DSRG approach amenable for a hybrid quantum-classical scheme.

### B. Hybrid quantum-classical DSRG downfolding

An outline of how the DSRG downfolding scheme may be adapted to a hybrid quantum-classical scheme is illustrated in Figure 1. We can break down the procedure into four steps:

1. **Orbital optimization.** The first step is an optimization of the molecular orbitals for a target electronic state. To ensure that this scheme is applicable to large active spaces, it is important that the cost of the orbital optimization scales as a low-order polynomial of the systems size. This step could employ a mean-field approximation (e.g. Hartree–Fock) or optimize the orbitals of a correlated state, as in the complete-active-space self-consistent-field (CASSCF) method. In the latter case, a quantum computation may be used to optimize the correlated state.

2. **Reference preparation.** In the second step, we propose to employ an approximate reference state that might be obtained from a classical or a quantum computation. In this step, the spinorbital basis is partitioned into three subsets: core (doubly occupied), active (partially occupied), and virtual (empty). The quantum computation involves only the active orbitals and uses a modified one-electron operator that accounts for the interaction with the occupied core orbitals. With these restrictions, the quantum computation requires at most $2 N_A$ qubits, where $N_A$ is the number of active orbitals. As part of the quantum computation, the low-rank reduced density cumulants $(\lambda_k)$ and the approximate energy $(\langle \tilde{H} \rangle_{\lambda_k})$ of the reference state are evaluated.

3. **DSRG downfolding.** The third step consists of a classical DSRG computation using the approximate reduced density cumulants $(\lambda_k)$ from step 2. This step produces the anti-Hermitian operator $A$ and the DSRG transformed Hamiltonian. We also obtain the expectation value of $H$ with respect to the approximate RDCs, $(\langle \tilde{H} \rangle_{\lambda_k})$; however, this quantity is generally a poor approximation to the exact energy. This step has polynomial scaling in the number of active and total orbitals.

4. **Eigenvalue estimation.** In the last step of this procedure, the DSRG downfolded Hamiltonian is used in a quantum computation that estimates one of its eigenvalues $(\tilde{E})$.

For generality we separate steps 1 and 2 of the QDSRG scheme; however, if the orbital optimization step minimizes the energy of a correlated state generated via a quantum computation (e.g., like in CASSCF), then these steps can be combined into a single one.

The most crucial differences between the conventional DSRG formulation and the QDSRG scheme are the use of approximate density cumulants in the DSRG downfolding procedure and the eigenvalue estimation (step 4). Here we consider approximations of the cumulants that are consistent with the measurement of at most a quartic-scaling number of elements. The simplest approximation (1-QDSRG), retains only the diagonal elements of the one-body density cumulant, that is,

$$\tilde{\lambda}_u^v = \begin{cases} \lambda_u^v, & \text{if } u = v, \\ 0, & \text{otherwise}. \end{cases}$$

Since $\lambda_1 = \gamma_1$, this scheme requires only the diagonal parts of the one-body density matrix $\gamma_u^v = \langle \Psi_0 | a_p^{\dagger} a_q | \Psi_0 \rangle$. Therefore, if $\Psi_0$ is generated via a quantum computation, this would require performing $N_A + 1$ experiments to measure the energy $(\langle \tilde{H} \rangle)$ and the diagonal elements of $\gamma_1$. 

The next approximation (2-QDSRG) requires access to a quadratic number of elements of the RDCs, and consists in taking the full one-body density matrix ($\tilde{A}_1 = \lambda_1$) plus the diagonal components of the two-body reduced density cumulant

$$\tilde{\lambda}_{xy}^{uv} = \begin{cases} \lambda_{uv} & \text{if } u = x \text{ and } v = y, \\ \lambda_{uv}^{\dagger} & \text{if } u = y \text{ and } v = x, \\ 0, & \text{otherwise.} \end{cases}$$  

These cumulant approximations may be justified using a perturbative argument. At first order in perturbation theory (assuming a one-body diagonal zeroth-order operator, $H_0 = \sum_p \epsilon_p \{ \lambda_p \}$) one may show that the amplitudes corresponding to single and double excitations are given by [49]

$$t_i^{(1)} = \left[ f_i^k + \sum_{u \neq x} \Delta_{i}^{\dagger} \bar{\gamma}_{i}(1) \bar{\gamma}_{i} \right] \frac{1 - e^{-s(\Delta_{i})^2}}{\Delta_{i}^{\dagger}},$$  

$$t_{ab}^{ij}(1) = \langle ab \mid ij \rangle \frac{1 - e^{-s(\Delta_{ab}^{ij})^2}}{\Delta_{ab}^{ij}},$$

where the quantities $f_i^k$ and $\langle ab \mid ij \rangle$ are elements of an effective one-body operator and antisymmetrized two-electron integrals, respectively, while the denominators are defined as $\Delta_{i}^{\dagger} = \epsilon_i - \epsilon_a$ and $\Delta_{ab}^{ij} = \epsilon_j - \epsilon_a - \epsilon_b$, with $\epsilon_i = f_i^k$ [49]. These equations show that at first order, the double excitation component of $A$ is independent of the reference cumulants, and the single excitation component of $A$ depends only on the off-diagonal elements of the active-active block of $\bar{\gamma}_1$ [since when $x = u$ in Eq. (9) we have that $\gamma_i^{\dagger} \Delta_{i}^{\dagger} \bar{\gamma}_{i} = \gamma_i^{\dagger} (\epsilon_u - \epsilon_a) = 0$]. Therefore, the 2-QDSRG approximation is already consistent with a first-order approximation to the DSRG operator $A$, while 1-QDSRG neglects the off-diagonal terms of $\gamma_i^{\dagger}$ that enter into Eq. (9). The three-body cumulant $\lambda_3$ is neglected in both the 1-QDSRG and 2-QDSRG, and it may be shown to enter in the energy at second-order in perturbation theory. The impact of neglecting $\lambda_3$ in the DSRG was analyzed in previous studies [49, 66, 67].

To enable the pipeline of QDSRG computations, we implement functionalities that export integrals and read/write the reference density matrices from external files in Forte [68], an open-source plugin for the ab initio quantum chemistry package Psi4 [69]. We obtain the QDSRG effective Hamiltonian from Forte using a spin-free implementation [56].

### III. CALIBRATION

#### A. Noiseless simulations

To investigate the accuracy of the QDSRG procedure for quantum computing, we examine a numerical example. We consider the H$_2$ molecule at four geometries using a triple-$\zeta$ basis. As the H$_2$ molecule is stretched, the $1\sigma_g$ and $1\sigma_u$ orbitals become near-degenerate, and the reference state must be taken of the form $|\Psi_0\rangle = c_g |1\sigma_g|^2 + c_u |1\sigma_u|^2$ to guarantee a continuous and qualitatively correct solution for all bond lengths. Table I reports the energy error with respect to a full configuration interaction (FCI) computation for the LDSRG(2) and the QLDSRG(2) methods. We report both the average energy $\langle H \rangle$ and the eigenvalue of $H$ using active spaces of various size and different orbitals choices. In analyzing these results we focus on the largest error and use the labels A–H to refer to a specific row of Table I.

The importance of optimizing the orbitals is reflected in the significant difference in the accuracy of the LDSRG(2) $\langle H \rangle$ when the orbitals $1\sigma_g$ and $1\sigma_u$ come from a restricted Hartree–Fock (RHF) or CASSCF orbitals (using only the $1\sigma_g$ and $1\sigma_u$ MOs), whereby the latter optimize both the orbitals and coefficients of the determinant that define $\Psi_0$. The LDSRG(2) error with RHF orbitals
TABLE I. Energy error for the hydrogen molecule (in mEh) computed with the LDSRG(2) and QLDSRG(2) methods. All computations use a cc-pVTZ basis [70] and the flow parameter value \( s = 0.5 \text{E}_\text{h}^{-2} \). Energy errors are computed with respect to full configuration interaction (FCI) energies reported in the last row of the table. For the LDSRG(2), the expectation value of the energy is designated with \( \langle H \rangle \), whereas \( \tilde{H} \) for the QD-SRG methods we report two sets of data. The ones labeled \( \gamma_3 = 0 \) use an approximate three-body cumulant reconstructed from \( \lambda_1 \) and \( \lambda_2 \). Results for line M employ CCSD natural orbitals and the one-body relaxed CCSD reduced density matrix as input to the QD-SRG procedure.

| Case | Method | Orbital Type | Active orbitals | 0.75 | 1.00 | 2.25 | 3.00 |
|------|--------|--------------|----------------|------|------|------|------|
| A    | LDSRG(2) (\( (H) \)) | RHF | \( \{1\sigma_g, 1\sigma_u\} \) | 0.306 | 7.337 | 15.454 | 17.428 |
| B    | LDSRG(2) (\( (H) \)) | CASSCF(2,2) | \( \{1\sigma_g, 1\sigma_u\} \) | 0.791 | 1.007 | 0.307 | 0.041 |
| C    | LDSRG(2) (\( (H) \)) | CASSCF(2,2) | \( \{1\sigma_g, 2\sigma_g, 2\sigma_u\} \) | 0.064 | 0.280 | 0.080 | 0.012 |
| D    | LDSRG(2) (\( \text{eig.} \hat{H} \)) | CASSCF(2,2) | \( \{1\sigma_g, 1\sigma_u\} \) | 0.331 | 0.070 | 0.242 | 0.041 |
| E    | 2-QLDSRG(2) (\( \gamma_3 = 0 \)) | CASSCF(2,2) | \( \{1\sigma_g, 1\sigma_u\} \) | 0.327 | 0.055 | 0.235 | 0.039 |
| F    | 1-QLDSRG(2) (\( \gamma_3 = 0 \)) | CASSCF(2,2) | \( \{1\sigma_g, 1\sigma_u\} \) | 2.455 | 6.422 | 4.591 | 1.203 |
| G    | 1-QLDSRG(2) (\( \gamma_3 = 0 \)) | CASSCF(2,2) | \( \{1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u\} \) | 0.601 | 2.193 | 1.383 | 0.564 |
| H    | 1-QLDSRG(2) (\( \gamma_3 = 0 \)) | CASSCF(2,2) | \( \{1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, 3\sigma_g, 3\sigma_u\} \) | 0.324 | 0.511 | 0.071 | -0.051 |
| I    | 2-QLDSRG(2) | CASSCF(2,2) | \( \{1\sigma_g, 1\sigma_u\} \) | 1.065 | 2.981 | 2.152 | 0.354 |
| J    | 1-QLDSRG(2) | CASSCF(2,2) | \( \{1\sigma_g, 1\sigma_u\} \) | 1.061 | 2.732 | 1.890 | 0.327 |
| K    | 1-QLDSRG(2) | CASSCF(2,2) | \( \{1\sigma_g, 2\sigma_g, 2\sigma_u\} \) | 0.016 | 1.392 | 0.935 | 0.070 |
| L    | 1-QLDSRG(2) | CASSCF(2,2) | \( \{1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, 3\sigma_g, 3\sigma_u\} \) | -0.104 | 0.293 | 0.130 | 0.008 |
| M    | 1-QLDSRG(2) | CCSD NOs | \( \{1\sigma_g, 1\sigma_u\} \) | 1.059 | 2.927 | 2.095 | 0.351 |

For the QD-SRG methods, we report two sets of results. We first examine the ones denoted with \( \gamma_3 = 0 \), which use a three-body cumulant reconstructed from \( \lambda_1 \) and \( \lambda_2 \) [64, 65, 71, 72] and, therefore, differ slightly from the approximations defined in the previous section. However, this definition is consistent with the fact that a reference containing two electrons always yields a zero three-body RDM. We note that the 2-QD-SRG approach (E) leads to small errors (max 0.4 mEh) that are similar to those of case D, whereas \( \gamma_3 \approx 1 \) (C) if the reference state is augmented with determinants formed out of a larger active space that includes the \( 2\sigma_g \) and \( 2\sigma_u \) orbitals. Diagonalization of \( \hat{H} \) in an active space containing the \( 1\sigma_g \) and \( 1\sigma_u \) MOs (D) yields a maximum error similar to the one of case (C).

As mentioned earlier, a practical realization of the QD-SRG scheme requires either two quantum computations (one to generate the orbitals and approximate cumulants plus a final diagonalization step) or it may use orbitals and cumulants from a polynomially-scaling classical method as a starting point. Here we demonstrate how this second option may be realized in practice using natural orbitals from coupled cluster theory [73]. In the results labeled “M”, we use coupled cluster theory with singles and doubles (CCSD) to compute an approximate density matrix \( \gamma_{1,2}^{\text{CCSD}} \) that spans the entire orbital space. The orbitals are then rotated to the natural basis (defined as the basis in which \( \gamma_{1,2}^{\text{CCSD}} \) is diagonal). The active space occupation numbers are then scaled so that their sum equals to the number of electrons in the active orbitals (2) and these are used to reconstruct an approximate diagonal \( \lambda_1 \). A comparison of the 1-QD-SRG data using CCSD NOs (M) and CASSCF(2,2) orbitals (J), shows that these two procedures give energies that are within 0.2 mEh. We reexamine the use of CCSD NOs as a way to reduce the cost of QDSRG computations in Sec. IV.

In Appendix B, we provide a comparison of the QD-SRG scheme with the DUCC downfolding approach for the H\(_2\) molecule and the beryllium atom using data from Ref. [44]. Both methods employ an exponential unitary transformation of the Hamiltonian, but differ in several ways. For example, whereas, DUCC is formulated in a single-reference setting, the QD-SRG method derives the A operator from a correlated state. This and other differences, have important consequences on the accuracy of these two methods, with our comparison showing that the QD-SRG leads to smaller errors (up to an order of magnitude smaller), especially in computations with fewer active orbitals.

B. Sensitivity to noise

We conclude our initial assessment of the QD-SRG approach by analyzing the sensitivity to stochastic errors introduced by quantum devices. As shown in Figure 1, step 2 of the QD-SRG procedure allows for the approx-
FIG. 2. Energy error for the hydrogen molecule (in mEh) computed with the QLDSRG(2) with various amounts of stochastic noise (σ) added to the RDMs. For a given value of σ, semi-opaque circles aligned vertically show the distribution of errors from 50 computations, while horizontal bars represent the average error. All computations use a cc-pVTZ basis [70] and the flow parameter value s = 0.5E−2. Energy errors are computed with respect to noiseless values. Data obtained imposing γ3 = 0 in the reconstruction of the approximate three-body cumulant.

In this case, there will be a compounding of errors due to the fact that the measured densities (later converted into cumulants) will be subject to finite measurement errors and gate and measurement noise. To study the effect of noise on the measured RDMs, we performed QDSRG computations on the H2 molecule at bond distances of 0.75 and 1.5 Å. Following Ref. [74], we model noise by augmenting the cumulants with stochastic error sampled from a Gaussian distribution with standard deviation σ and zero mean [N(0,σ²)].

\[ γ_{x'y'...}^{\text{measured}} = γ_{x'y'...} + N(0,σ²). \]  

This is a simple noise model that can mimic finite measurement errors, but cannot account for correlated noise among qubits and decoherence. Noise is added to the unique elements of the RDMs to avoid breaking antisymmetry with respect to permutation of the upper/lower indices (e.g., γ_{xy} = −γ_{yx} = −γ_{yz} = γ_{zy}). However, we do not enforce fermionic N-representability conditions [75–78] onto the resulting RDMs, which likely leads to overestimating the resulting energy errors. Several works discuss how to utilize the N-representability constraints to accelerate and improve hybrid quantum algorithms mainly via reducing the measurement scaling [79, 80], which might be combined with the QDSRG approach to improve its accuracy.

Figure 2 shows the energy error computed with respect to noiseless results for the 1- and 2-QLDSRG(2) schemes (enforcing γ3 = 0). At both geometries we observe that the 1-QLDSRG(2) is less sensitive to noise, and that the average energy error increases linearly with σ. Interestingly, the average error is slightly higher at the shorter bond distance (0.75 Å) than at the elongated one (1.5 Å). In both cases, a value of σ = 0.01 seems sufficient to recover the energy with an error less than 1 kcal/mol (≈ 1.6 mEh). These results can then inform an analysis of the quantum resources necessary to measure the RDMs with an accuracy sufficient for a hybrid quantum-classical procedure based on the QDSRG.

In summary, the preliminary results reported in Sec. IIIA and IIIB show that even a very drastic approximation of the cumulants that enter the DSRG combined with diagonalization of the resulting transformed Hamiltonian can yield energies with small absolute energy errors, even under the presence of noise. We expand this analysis to molecules with more complex electronic structures and larger basis sets in Sec. IV. There, we also report the results of experiments on NISQ devices that show the potential usefulness of QDSRG in leveraging near-term quantum computers.

IV. RESULTS AND DISCUSSION

In this section, we report two types of QDSRG results: the noiseless exact computations in Secs. IV A and IV B, and device computations (Sec. IV C) where we combine the QDSRG with variational quantum computations performed on IBM hardware.

A. Dissociation curve of the nitrogen molecule

As the first benchmark of the QDSRG scheme we compute the potential energy curve for the ground singlet state of N2 using an active orbital containing six orbitals (build from combinations of the six 2p N orbitals). Figure 3a shows the potential energy curve for the LD-SRG(2), the two approximate variants of the QDSRG, CCSD [81], and CCSD(T) [82]. In the DSRG computations, we employ CASSCF(6,6) orbitals and use the corresponding state as a reference, while the CCSD and CCSD(T) results employ restricted Hartree–Fock references. The DSRG methods produce curves that are nearly indistinguishable, except in the recoupling region (1.6–2.0 Å) where the QDSRG energy is slightly higher.
In our next example, we apply the QDSRG scheme to a medium-sized molecule. We compute the adiabatic singlet-triplet splitting \( \Delta E_{ST} = E_T - E_S \) of \( \text{para}-\text{benzyne} \). The singlet ground state of this molecule exhibits pronounced diradical character and is dominated by two closed-shell determinants. \( \text{para}-\text{benzyne} \) and its isomers, have been studied extensively both in experiments [84] and in theory [83, 85–92].

Here we compute the singlet-triplet splitting using CASSCF(2,2) orbitals for the singlet state and ROHF orbitals for the triplet state. The experimental splitting is taken from the ultraviolet photoelectron spectroscopy results of Ref. [84]. We utilize the singlet and triplet geometries from Ref. [83], which were optimized at the Mk-MRCCSD/cc-pVTZ level of theory. All computations use the cc-pVDZ basis set [70], and the value of the DSRG flow parameter is set to 1.0 \( E_h^{-1} \), based on previous studies [66, 93, 94]. We freeze the six 1s-like orbitals on carbon atoms in the DSRG correlation treatment.

Table II reports the singlet-triplet splitting obtained by the LDRG(2) and QLDSRG(2) methods. All splittings are shifted by 0.30 kcal mol\(^{-1}\) to account for zero-point vibrational energy (ZPVE) corrections [83]. Labels for methods are consistent with those in Table I. For the active space consisting of two \( \sigma \) orbitals, compared to the LDRG(2) average energy \( \langle \bar{H} \rangle \) (2.72 kcal mol\(^{-1}\)) and the singlet-triplet splitting \( \Delta \bar{H} \) (3.42 kcal mol\(^{-1}\)) improves the singlet-triplet gap by 0.7 kcal mol\(^{-1}\). For the QDSRG methods, interestingly, the more drastic approximation 1-QLDSRG(2) (3.30 kcal mol\(^{-1}\)) gives better prediction than the 2-QLDSRG(2) (2.69 kcal mol\(^{-1}\)), which might be attributed to error cancellation. Imposing \( \gamma_3 = 0 \) seems to have different effects on two approximations: the error worsens for the 1-QLDSRG(2) by 0.15 kcal mol\(^{-1}\) while improves for the 2-QLDSRG(2) by 0.46 kcal mol\(^{-1}\). Unlike the \( \text{H}_2 \) cases reported in Table I, for this problem, we do not see consistent improvements of results when enlarging the active space by adding six \( \pi \) orbitals from the set of CASSCF(2,2) orbitals.

**B. Singlet-triplet gaps of \( \text{para}-\text{benzyne} \)**

In our next example, we apply the QDSRG scheme to a medium-sized molecule. We compute the adiabatic singlet-triplet splitting \( \Delta E_{ST} = E_T - E_S \) of \( \text{para}-\text{benzyne} \). The singlet ground state of this molecule exhibits pronounced diradical character and is dominated by two closed-shell determinants. \( \text{para}-\text{benzyne} \) and its isomers, have been studied extensively both in experiments [84] and in theory [83, 85–92].

Here we compute the singlet-triplet splitting using CASSCF(2,2) orbitals for the singlet state and ROHF orbitals for the triplet state. The experimental splitting is taken from the ultraviolet photoelectron spectroscopy results of Ref. [84]. We utilize the singlet and triplet geometries from Ref. [83], which were optimized at the Mk-MRCCSD/cc-pVTZ level of theory. All computations use the cc-pVDZ basis set [70], and the value of the DSRG flow parameter is set to 1.0 \( E_h^{-1} \), based on previous studies [66, 93, 94]. We freeze the six 1s-like orbitals on carbon atoms in the DSRG correlation treatment.

Table II reports the singlet-triplet splitting obtained by the LDRG(2) and QLDSRG(2) methods. All splittings are shifted by 0.30 kcal mol\(^{-1}\) to account for zero-point vibrational energy (ZPVE) corrections [83]. Labels for methods are consistent with those in Table I. For the active space consisting of two \( \sigma \) orbitals, compared to the LDRG(2) average energy \( \langle \bar{H} \rangle \) (2.72 kcal mol\(^{-1}\)) and the singlet-triplet splitting \( \Delta \bar{H} \) (3.42 kcal mol\(^{-1}\)) improves the singlet-triplet gap by 0.7 kcal mol\(^{-1}\). For the QDSRG methods, interestingly, the more drastic approximation 1-QLDSRG(2) (3.30 kcal mol\(^{-1}\)) gives better prediction than the 2-QLDSRG(2) (2.69 kcal mol\(^{-1}\)), which might be attributed to error cancellation. Imposing \( \gamma_3 = 0 \) seems to have different effects on two approximations: the error worsens for the 1-QLDSRG(2) by 0.15 kcal mol\(^{-1}\) while improves for the 2-QLDSRG(2) by 0.46 kcal mol\(^{-1}\). Unlike the \( \text{H}_2 \) cases reported in Table I, for this problem, we do not see consistent improvements of results when enlarging the active space by adding six \( \pi \) orbitals from the set of CASSCF(2,2) orbitals.

**C. Hardware implementation**

In this section, we combine the 2-QLDSRG(2) method with the VQE [20–22] on the IBM quantum computers to demonstrate the ability of this hybrid scheme to compute the total energies under realistic noise from near-term quantum devices. We use the Qiskit [95] package to construct circuits and execute them on hardware.

Ideally we would measure both density matrices and the QDSRG energy (steps 2 and 4 in Figure 1) from a quantum computation. Due to the high level of noise from near-term devices and the fact that density matrices are more sensitive to noise than the energy, we employ a quantum computer only to estimate the eigenvalue of the 2-QLDSRG(2) effective Hamiltonian \( \bar{H} \). We use the VQE...
algorithm to optimize a trial wave function and measure its energy. To reduce the quantum resources (the number of qubits, the circuit depth, etc) and minimize errors, we explore a symmetry-preserving one-qubit ansatz (see Appendix A for details).

For each experiment on the device, we carry out the maximum number of measurements allowed, which differs by device. To ameliorate measurement errors, we utilize readout-error-mitigation tools in the Qiskit-Ignis module to construct a calibration matrix and apply its inverse to the raw measurement counts of each experiment.

Our first example is a computation of the dissociation curve of H$_2$, which is a representative benchmark system for quantum computing. Figure 1 shows the dissociation curve and the energy error for the H$_2$ molecule in the cc-pV5Z basis [70] (110 orbitals) obtained by the one-qubit 2-QLDSRG(2) computations on the ibmq_lagos quantum computer. A direct second-quantized quantum computation would require 220 qubits (ignoring qubit tapering or other symmetry adaptation techniques). We also report the 2-QLDSRG(2) energy errors and the standard deviations of the device results in Table III. The effectiveness of the QDSRG downfolding method can be seen from the small errors of the 2-QLDSRG(2) energies, which differ from noiseless simulations at most by 0.5 mE$_h$ for all geometries. The 2-QLDSRG(2) energies from the device have unsigned average errors lower than 1 mE$_h$ for over half of the geometries, with a maximum error of 2.0 mE$_h$. Empirically, it is important to collect the measurement statistics of $10^6$ shots to obtain a reliable estimate of the average energy from the device. From this example, we see that errors from hardware (finite measurements, decoherence, etc.) are more significant than errors from the QDSRG downfolding.

| Method       | $\Delta E_{ST}$ / kcal mol$^{-1}$ | $E_T$ / E$_h$ | $E_S$ / E$_h$ |
|--------------|----------------------------------|--------------|--------------|
| CASSCF(2,2)  | 0.27                             | -229.416126  | -229.416074  |
| LDSRG(2) ($\langle \hat{H} \rangle$) | 2.72                             | -230.194973  | -230.198828  |
| LDSRG(2) (eig. $\hat{H}$) | 3.42                             | -230.194973  | -230.199444  |
| 2-QLDSRG(2) ($\gamma_3 = 0$) | 3.15                             | -230.194762  | -230.199308  |
| 1-QLDSRG(2) ($\gamma_3 = 0$) | 3.15                             | -230.194762  | -230.196354  |
| 2-QLDSRG(2) | 2.69                             | -230.194762  | -230.19567   |
| 1-QLDSRG(2) | 3.30                             | -230.194411  | -230.19917   |
| Active orbitals: $\{\sigma_g,\sigma_u, 6 \times \pi\}$
| LDSRG(2) (eig. $\hat{H}$) | 2.61                             | -230.196267  | -230.19943   |
| 2-QLDSRG(2) | 2.85                             | -230.196262  | -230.200325  |
| 1-QLDSRG(2) | 4.16                             | -230.196225  | -230.202375  |

TABLE III. The errors of 2-QLDSRG(2) energies in mE$_h$ (with respect to FCI energies) along the H$_2$ dissociation curve (Figure 4). For results from the ibm_lagos device, we show the unsigned average energy errors and standard deviations (in mE$_h$). Unsigned energy errors blow 1 mE$_h$ are highlighted in bold font.

For our second set of hardware experiments, we consider a larger and more chemically-relevant problem, the pericyclic rearrangement reaction of bicyclo[1.1.0]butane (bicyclobutane) to trans-buta-1,3-diene (trans-butadiene). This isomerization process goes through a concerted conrotatory movement of the methylene groups with an activation barrier (enthalpy) of 40.6 ± 2.5 kcal mol$^{-1}$ [99], suggested by early experimental studies [99, 101–104]. This mechanism has been investigated in many computational studies using high-level electronic structure methods, including MRMBPT [96, 105, 106], MRCI [106], variants of single-reference coupled-cluster methods including CR-CC(2,3) [96, 107] and CC(t;3) [98], the diffusion quantum Monte Carlo [97] and the ACSE method [105, 108].

These theoretical studies also investigate the unfavor
concerted disrotatory pathway [96, 97, 105–107], characterized by a transition state that is estimated to be 15–25 kcal mol\(^{-1}\) higher in energy than the conrotatory one. Both transition states display significant biradical character [96] and their ground state wave functions have large contributions from multiple determinants, requiring a multireference treatment. This makes the system suitable to treat with the QDSRG method. Previous studies also confirmed that for both concerted pathways, the reaction will continue to reach an intermediate gauche-butadiene and then proceeds through a low-energy rotational barrier to get to the trans-butadiene product.

We compute the reaction enthalpies along the full concerted conrotatory and disrotatory pathways from bicyclobutane to trans-butadiene. Cartesian coordinates of the structures of all six stationary points optimized at the CASSCF(10,10)/cc-pVDZ level of theory are taken from Ref. [96]. Zero-point vibrational energies (ZPVE) corrections taken from Ref. [96]. OMR3-DMC and CC(t;3) results are also in the cc-pVTZ basis.

**TABLE IV. LDSRG(2) and QLDSRG(2) (exact and device) computations of the relative enthalpies (in kcal mol\(^{-1}\)) with respect to the bicyclobutane reactant of the conrotatory transition state and the disrotatory transition state, the gauche-butadiene intermediate, the transition state connecting gauche-butadiene and trans-butadiene, and the trans-butadiene product.**

|                | conrotatory TS | disrotatory TS | gauche-butadiene | gauche-trans TS | trans-butadiene |
|----------------|---------------|----------------|------------------|-----------------|-----------------|
| LDSRG(2) (\(H\)) | 41.3          | 58.5           | -24.5            | -21.5           | -27.7           |
| LDSRG(2) (eig. \(H\)) | 39.6         | 58.6           | -24.5            | -21.4           | -27.8           |
| Exact           | 41.5          | 58.9           | -24.3            | -21.3           | -27.5           |
| ibmq_manila\(^a\) | 42.6          | 57.8           | -23.8            | -22.2           | -27.4           |
| ibmq_lagos\(^b\) | 42.7          | 59.6           | -23.3            | -20.7           | -26.4           |
| ibmq_jakarta\(^c\) | 40.5          | 57.5           | -25.6            | -22.4           | -28.4           |
| Exact           | 39.8          | 58.8           | -24.5            | -21.4           | -27.7           |
| ibmq_manila\(^a\) | 39.6          | 58.6           | -24.5            | -21.5           | -28.1           |
| ibmq_lagos\(^b\) | 39.0          | 57.7           | -25.2            | -22.2           | -28.6           |
| ibmq_jakarta\(^c\) | 39.1          | 58.4           | -25.2            | -21.7           | -28.0           |
| OMR3-DMC\(^d\)  | 40.4(5)       | 58.6(5)        | -25.2(5)         | -22.2(5)        | -27.9(5)        |
| CC(t;3)\(^e\)   | 40.2          | 60.1           | -25.3            | -22.6           | -28.3           |
| Experiment      | 40.6 ± 2.5\(^f\) |              |                  | -25.9 ± 0.4\(^g\) | |

\(^a\)The average is over 8 experiments (20000 shots per experiment).
\(^b\)The average is over 10 experiments (32000 shots per experiment).
\(^c\)The average is over 10 experiments (20000 shots per experiment).
\(^d\)From Ref. [97].
\(^e\)From Ref. [98].
\(^f\)From Ref. [99].
\(^g\)The reaction enthalpy at 298 K is based on enthalpies of the formation of bicyclo[1.1.0]butane and buta-1,3-diene reported in Ref. [100].

Compared to the experimental value [99], both LDSRG(2) and the 2-QLDSRG(2) methods give relative enthalpies of the conrotatory transition state that are in good agreement, while the relative enthalpies of trans-butadiene predicted by the two methods are slightly underestimated [100]. For the other three stationary points, experimental data are not available; therefore, we compare our results with data from two high-level approaches, the optimized multireference diffusion quantum Monte Carlo (OMR3-DMC) [97] and an active-space coupled-cluster method with corrected triple excitations termed CC(t;3) [98] using the same cc-pVTZ basis. The relative enthalpy of the disrotatory transition state predicted by the LDSRG(2) and 2-QLDSRG(2) methods agrees with the OMR3-DMC result (58.6 kcal mol\(^{-1}\)) [97] and are slightly lower than the CC(t;3) value (60.1 kcal mol\(^{-1}\)) [98]. For both gauche-butadiene and the transition state connecting gauche-butadiene and trans-butadiene, the LDSRG(2) and the 2-QLDSRG(2) results are about 1 kcal mol\(^{-1}\) lower than the OMR3-DMC and CC(t;3) values. The 2-QLDSRG(2) results from three devices are in good agreement with the result from noiseless simulations, with most devices yielding values within 1 kcal mol\(^{-1}\) from the exact result. The best device results
FIG. 4. Dissociation curve (a) and energy error (b) for the hydrogen molecule computed with the 2-QLDSRG(2) using one qubit on the ibm_lagos device. Energy errors are with respect to FCI energies. For each geometry, semi-opaque blue circles aligned vertically show the distribution of energies (energy errors) from 9 experiments, with each experiment consisting of 32000 measurements, while horizontal bars in blue denote average energies or average energy errors. All computations use the cc-pV5Z basis [70] (110 basis functions), CASSCF(2,2) orbitals, and the flow parameter value $s = 0.5$ $E_h^{-2}$. The grey-shaded area indicates unsigned energy errors below 1 m$E_h$. The unsigned energy errors and the standard deviations are reported in Table III.

(data in bold font in Table IV) give unsigned errors less than 0.5 kcal mol$^{-1}$ for all six stationary points.

The results for the bicyclobutane $\rightarrow$ trans-butadiene reaction demonstrate that the QDSRG method can effectively downfold the dynamical correlation for a large basis with 204 orbitals, reducing the number of qubits from several hundreds to just one.

V. CONCLUSION

In this work, we introduced a practical unitary downfolding method that enables accurate molecular computations on near-term quantum computers. The QDSRG is agnostic to the type of quantum algorithm (e.g., variational, phase estimation) and can be used with both noisy near-term computers and future fault-tolerant hardware.

Therefore, we expect that the QDSRG will be a useful method to leverage small quantum computers in applications to large molecules and large basis sets.

The QDSRG is based on the driven similarity renormalization group (DSRG) [48], a classical numerically-robust and polynomial-scaling approach to block-diagonalize many-body Hamiltonians. In this work, we propose a “diagonalize-then-dress-then-diagonalize” strategy that combines truncation of the reduced density cumulants provided to the DSRG with diagonalization of the resulting similarity-transformed Hamiltonian. This downfolding procedure may be justified by a perturbative analysis of the DSRG equations and leads to two practical computational schemes: in the 1-QDSRG we retain only the diagonal part of the one-body RDM, whereas in the 2-QDSRG we retain the full one-body RDM and the diagonal part of the two-body cumulants. These two schemes require the estimation of a number of reduced density matrix elements that is at most linear or quadratic in the number of active orbitals ($N_A$), substantially reducing the demands of conventional multireference theories, which require $N_A^7$ to $N_A^8$ RDM elements.

Our calibration of the QDSRG shows that the use of orbitals optimized for a reference correlated state is crucial to compute accurate energies. The QDSRG results show that the 2- approximation is able to accurately predict energies along the bond-breaking coordinate in a minimal active space. The 1- approximation leads to larger errors, but these can be suppressed by increasing the active space size. To simulate the effect of noise, we examined QDSRG computations starting with inaccurate RDMs and found that milliHartree accuracy can be retained when the standard deviation of the RDMs errors is as large as $10^{-3}$–$10^{-2}$.

In our computations on the more challenging $N_2$ and $p$-benzyne molecules, we were also able to accurately predict potential energy curves and singlet-triplet gaps using the QDSRG. In the case of $N_2$, we demonstrate how the first two steps of the QDSRG procedure (orbital optimization and reference preparation) could be approximated with the classical polynomial-scaling CCSD method, using the corresponding one-body reduced density matrix. Finally, we demonstrate the QDSRG procedure in combination with the VQE algorithm on the IBM quantum devices. We extend computations of the $H_2$ dissociation curve with a nearly-complete quintuple-$\zeta$ basis, corresponding to a full computation with 220 qubits. In this example, we find that hardware errors still remain the most significant source of error in comparison to the QDSRG downfolding error. We also apply the QDSRG method to model the reaction pathways of the bicyclobutane $\rightarrow$ trans-butadiene isomerization process using a basis of 204 orbitals. We are able to obtain high-quality device results that reach sub-kcal mol$^{-1}$ accuracy with respect to the exact QDSRG and two high-level classical electronic structure approaches.

The extension of the QDSRG with explicit correlation methods and to electronically excited states are two inter-


FIG. 5. Conrotatory and disrotatory pathways describing the isomerization of bicyclo[1.1.0]butane (bicyclobutane) to trans-buta-1,3-diene (trans-butadiene). Enthalpies in kcal mol$^{-1}$ are relative to the reactant for relevant stationary points computed with the 2-QLDSRG(2) method using one qubit on the device ibmq_manila. Black horizontal bars represent the 2-QLDSRG(2) results obtained with noiseless simulations. The device results are shown in the parentheses. Semi-opaque blue circles aligned vertically show the distribution of the relative enthalpies from 8 experiments (20000 measurements per experiment), while yellow horizontal bars denote the average relative enthalpies. We use a cc-pVTZ basis [70] (204 basis functions) and CASSCF(2,2) natural orbitals, and the flow parameter value $s = 1.0 \times 10^{-2}$ for all six stationary points.

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Appendix A: Symmetry-preserving ansatz for two-configuration wave functions

We exploit spin, particle number and spatial symmetries to construct a hardware-efficient ansatz for two-configuration wave functions. Consider a two electron wave function in a basis of two molecular orbitals $\psi_1, \psi_2$. The singlet ground state in the most general case includes three configurations (bars over the number denote $\beta$ spin orbitals),

$$
\begin{align*}
|\Phi_1\rangle &= |\psi_1\psi_1\rangle, \\
|\Phi_2\rangle &= |\psi_2\psi_2\rangle, \\
|\Phi_3\rangle &= \frac{1}{\sqrt{2}} (|\psi_1\psi_2\rangle - |\psi_2\psi_1\rangle).
\end{align*}
$$

We can remove the contribution of the open-shell configuration $|\Phi_3\rangle$ from the normalized ground-state wave function $|\Psi_0\rangle = C_1'|\Phi_1\rangle + C_2'|\Phi_2\rangle + C_3'|\Phi_3\rangle$ without changing the energy via an orbital rotation

$$
\begin{align*}
|\psi'_1\rangle &= \cos \theta |\psi_1\rangle + \sin \theta |\psi_2\rangle, \\
|\psi'_2\rangle &= \sin \theta |\psi_1\rangle - \cos \theta |\psi_2\rangle,
\end{align*}
$$

where $\tan 2\theta = \frac{\sqrt{C_1'C_2'}}{C_1-C_2}$. We refer interested readers to Ref. [85] (Sec IV.) for detailed discussions on this basis transformation.

For H$_2$, the ground-state wave function expanded in the CASSCF(2,2) orbitals can be accurately described by two closed-shell configurations. While for two transition states in the bicyclobutane $\rightarrow$ trans-butadiene reaction, the open-shell contribution to the wave function cannot be neglected due to strong biradical character (especially for the disrotatory TS). Therefore, we transform...
to the CASSCF(2,2) natural orbital basis, which is mathematically equivalent to enforcing Eq. A2. The ground states of other four stationary points in the pathways are generally well described by a single determinant in the CASSCF(2,2) basis; however, for consistency, we employ CASSCF(2,2) natural orbitals for all computations.

The resulting two-configuration wave function $|\Psi_0\rangle = C_1 |\psi'_1\psi'_2\rangle + C_2 |\psi'_2\psi'_2\rangle$ can be mapped to a one-qubit space

$$
|\psi'_1\psi'_2\rangle \rightarrow |0\rangle, \\
|\psi'_2\psi'_2\rangle \rightarrow |1\rangle,
$$

which leads to the one-qubit wave function ansatz

$$
|\Psi\rangle = C_1 |0\rangle + C_2 |1\rangle.
$$

This state can be prepared by applying to the $|0\rangle$ state a single Y-rotation gate $R_y(t) = e^{-i\frac{\pi}{2}t}$ with one variational parameter $t$, giving $C_1 = \cos \frac{t}{2}$, $C_2 = \sin \frac{t}{2}$.

The Hamiltonian in the one-qubit basis is represented as $H = h_{00}|0\rangle\langle0| + h_{11}|1\rangle\langle1| + h_{10}(|0\rangle\langle1| + |1\rangle\langle0|)$ where $h_{00}$, $h_{11}$, $h_{10}$ are calculated from the one- and two-electron integrals. The Hamiltonian can be decomposed into a weighted sum of single-qubit Pauli operators

$$
H = c_0 + c_z Z + c_x X,
$$

with coefficients given by $c_0 = (h_{00} + h_{11})/2$, $c_z = (h_{00} - h_{11})/2$, $c_x = h_{10}$.

The expectation value of this one-qubit Hamiltonian with respect to $|\Psi\rangle$ has the definite tomography [111, 112] given by

$$
\langle H \rangle_t = a + b \cos t + c \sin t,
$$

The coefficients $a, b, c$ can be found using a three-point Fourier quadrature [111] that requires measuring expectation values for three parameters $t_0$, $t_1$, $t_2$. The corresponding linear equation to solve is:

$$
\begin{bmatrix}
1 & \langle Z \rangle_{t_0} & \langle X \rangle_{t_0} \\
1 & \langle Z \rangle_{t_1} & \langle X \rangle_{t_1} \\
1 & \langle Z \rangle_{t_2} & \langle X \rangle_{t_2}
\end{bmatrix}
\begin{bmatrix}
a \\
b \\
c
\end{bmatrix} =
\begin{bmatrix}
\langle H \rangle_{t_0} \\
\langle H \rangle_{t_1} \\
\langle H \rangle_{t_2}
\end{bmatrix}.
$$

In this work, we use the following three-point Fourier quadrature:

$$
t_0, t_0 - \pi/3, t_0 + \pi/3,
$$

where $t_0$ is arbitrary. For convenience, we use the analytic solution for the optimal angle

$$
t_0 = \arctan 2 \left( \frac{c_x}{c_z} \right).
$$

For the reference preparation (step 2 in Figure 1), we run the VQE algorithm to obtain the 1- and 2-RDMs. These quantities can be measured from the state tomography of the optimal wave function. Table V summarizes the expressions for the 1- and 2-RDM in terms of analytical expressions of the variational parameter $t$ and quantities from direct measurements.

Note that for both the 1- and 2-QDSRG methods, we only need to measure the Pauli $Z$ operator to compute the full 1-RDM and the approximate 2-RDM, while the Pauli $X$ operator only contributes to the non-diagonal components of the two-body reduced density cumulant. Finally, we use the VQE algorithm to estimate the eigenvalue of the DSRG effective Hamiltonian (step 4 in Figure 1).

### Appendix B: Comparisons with the double unitary coupled cluster approach

Here we compare our QDSRG method with the DUCV downfolding technique for the hydrogen molecule and the beryllium atom. In Table VI, we report energies of $\text{H}_2$ at four geometries obtained by diagonalizing the bare, the QDSRG-downfolded, and the DUCV downfolded Hamiltonians in a four-orbital active space, together with the energy errors with respect to the full-space FCI results which use 30 orbitals. We also compute QDSRG energies using different types of orbitals. The DUCV data are taken from Ref. [44]. We observe that for three geometries, all QDSRG computations consistently give less significant energy errors than the DUCV results. For instance, the largest error for the DUCV using RHF orbitals is 7.13 m$E_h$, while the QDSRG shows smaller errors (at most 4.1 m$E_h$). The use of CASSCF orbitals further reduces the maximum QDSRG errors to at most 1.7 m$E_h$.

Tab. VII shows the comparison of the beryllium atom results using active spaces of different sizes and three basis sets. Here we see that the DUCV method introduces errors in the range of 18–30.5 m$E_h$ when 5 or 6 active orbitals are used, and that this error reduced to smaller values (1.8–7.3 m$E_h$) when using 9 active orbitals, while QDSRG results consistently show much smaller energy errors (0.9–4.9 m$E_h$) for all active spaces and basis sets. Notably, the QDSRG downfolding is most effective for the large cc-pVQZ basis, which significantly reduces the

| RDM Element | Analytic Measurement |
|-------------|----------------------|
| $\gamma_1$ | $\cos \frac{t}{2}$ |
| $\gamma_2$ | $\sin \frac{t}{2}$ |
| $|0\rangle$ | $|1\rangle$ |
| $|1\rangle$ | $|0\rangle$ |

TABLE V. Relations between elements of the fermionic 1-RDM ($\gamma_0^0 = \langle a_0^\dagger a_0 \rangle$) and 2-RDM ($\gamma_{ij} = \langle a_i^\dagger a_j \rangle$) and the measured quantities for the one-qubit ansatz. Only nonzero elements are shown; others are zero due to symmetries.}
TABLE VI. Comparison of the energy errors (in mEh) of the QDSRG and the DUCC for the hydrogen molecule at four bond lengths in the cc-pVTZ basis using DSRG flow parameter $s = 0.5 E_h^{-2}$. The size of the active space is denoted in the parenthesis. The energy errors are with respect to the full-space (30-orbital) FCI computations (absolute energies are shown in the first row). The DUCC data are taken from Ref. [44].

| Method (full space) | Orbital Type ($N_{act}$) | 0.8 a.u. | 1.4008 a.u. | 4.00 a.u. | 10.00 a.u. |
|--------------------|--------------------------|----------|-------------|-----------|-----------|
| FCI (full space)   | RHF (30)                 | -1.015729| -1.172455   | -1.014872 | -0.999623 |
| FCI (active space) | RHF (4)                  | 32.729   | 25.755      | 7.872     | 2.523     |
| DUCC               | RHF (4)                  | 7.129    | 4.555       | -0.328    | -1.977    |
| L1-DSRG(2)         | RHF (4)                  | -0.130   | -0.234      | 1.920     | 0.122     |
| 2-QL1-DSRG(2)      | RHF (4)                  | -0.087   | -0.084      | 3.794     | 0.126     |
| 1-QL1-DSRG(2)      | CASSCF(2,2) (4)          | 0.455    | 0.169       | 1.498     | 0.006     |
| 2-QL1-DSRG(2)      | CASSCF(2,2) (4)          | 0.460    | 0.179       | 1.662     | 0.006     |

TABLE VII. Comparison of the energy errors (in mEh) of the QDSRG and the DUCC for the beryllium atom with different basis sets and active spaces. The DSRG flow parameter $s = 2.0 E_h^{-2}$. All computations use RHF orbitals. The energy errors are with respect to the full-space FCI computations (absolute energies are shown in the last column), which use 14, 30, 55 orbitals for cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, respectively. The DUCC data are taken from Ref. [44].

| Method | 5 orbitals  | 6 orbitals  | 9 orbitals  | All orbitals |
|--------|-------------|-------------|-------------|--------------|
| cc-pVDZ | FCI         | 22.242      | 20.575      | 0.493        | -14.617409  |
|         | DUCC        | 19.009      | 18.109      | 1.809        | -14.727409  |
|         | L1-DSRG(2)  | 3.408       | 3.074       | 3.065        | -14.623810  |
|         | 2-QL1-DSRG(2)| 3.430     | 2.974       | 3.074        | -14.623810  |
| cc-pVTZ | FCI         | 34.881      | 33.621      | 7.024        | -14.623810  |
|         | DUCC        | 26.710      | 24.410      | 5.010        | -14.623810  |
|         | L1-DSRG(2)  | 4.199       | 3.202       | 1.216        | -14.623810  |
|         | 2-QL1-DSRG(2)| 4.200     | 3.192       | 2.751        | -14.623810  |
| cc-pVQZ | FCI         | 54.950      | 54.366      | 26.798       | -14.640147  |
|         | DUCC        | 30.547      | 27.547      | 7.347        | -14.640147  |
|         | L1-DSRG(2)  | 4.927       | 4.166       | 0.879        | -14.640147  |
|         | 2-QL1-DSRG(2)| 4.923     | 4.158       | 2.909        | -14.640147  |

energy errors of the active-space FCI results by 50, 50.2, 26 mEh for 5-, 6- and 9-orbital active spaces, while the DUCC method merely gives a reduction of 24, 27, 19 mEh.

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