List of Figures

1.1	A circuit diagram for quantum phase estimation using three an-	
	cillary qubits. The circuit block labelled with ${ m QFT^{-1}}$ executes	
	the inverse quantum Fourier transformation. When the ancil-	
	lary qubits are in state $ x\rangle$, a controlled rotation $e^{-2\pi i Hx}$ is ap-	
	plied to the main register $ \Psi\rangle$. The ancillary qubits output an	
	eigenvalue of H in binary when being measured in the com-	
	putational basis; meanwhile the main register $ \Psi\rangle$ collapses to	
	the corresponding eigenstate. The circuit diagram is adapted	
	with permission from Rev. Mod. Phys., 92(1):015003, 2020,	
	DOI:10.1103/revmodphys.92.015003. Copyright 2020 Ameri-	
	can Physical Society.	18
1.2	Scheme of the variational quantum eigensolver (VQE)	
	using three qubits. The scheme is reprinted with permis-	
	sion from Rev. Mod. Phys., 92(1):015003, March 2020,	
	DOI:10.1103/revmodphys.92.015003. Copyright 2020 Ameri-	
	can Physical Society.	19
1.3	Schematic of the quantum imaginary time evolution (QITE) al-	
	gorithm	20

2.1	Schematic illustration of the multireference selected quantum	
	Krylov (MRSQK) algorithm. (A) An approximate real-time dy-	
	namics using a single Slater determinant reference (Φ_0) is used	
	to generate a trial state $(\tilde{\Psi})$ (B) Measurements of the deter-	
	minants that comprise the trial state are used to determine the	
	probability of hopping (P_{μ}) to other determinants. This infor-	
	mation is employed to build two new reference states, Φ_1 and	
	Φ_2 . (C) Finally, three real-time evolutions starting from the ref-	
	erences (Φ_0,Φ_1,Φ_2) generate a set of 12 Krylov states ψ_{α} , which	
	are used to diagonalize the Hamiltonian and obtain the energy	
	of the state $\Psi.$	29
2.2	Hadamard test circuit to estimate expectation values of unitary	
	operators with a general form of $\langle ar{0} \hat{U}_{\gamma}^{\dagger}\hat{U}_{\chi} ar{0}\rangle$. Measuring the	
	X , Y operators on the ancillary qubit $ 0\rangle$, one can obtain the	
	mean value of $X+iY=2\left 0\right\rangle \left\langle 1\right $, which equals to $\left\langle X+iY\right\rangle =$	
	$\langle ar{0} \hat{U}_{\gamma}^{\dagger} \hat{U}_{\chi} ar{0} \rangle$	35
2.3	Circuit for applying one controlled $-e^{-it_l\otimes_k\sigma_k}$ operator	36
2.4	The circuit to compute $\langle \Phi_1 e^{-i\Delta t\hat{H}_q} \Phi_1\rangle$ (top) and $\langle \Phi_0 e^{i\Delta t\hat{H}_q} \Phi_1\rangle$	
	(1 · · · · · · · · · · · · · · · · · · ·	
	(bottom) implemented using Qiskit[167]. q[0], q[1] encode	
	basis states for the Hamiltonian, while q[2] is the ancillary	
	basis states for the Hamiltonian, while $q[2]$ is the ancillary	

2.5	Potential energy curve (top) and error (bottom) for symmetric	
	dissociation of linear H ₆ in a STO-6G basis. MRSQK compu-	
	tations use $\Delta t = 0.5$ a.u., three time steps ($s = 3$), and five	
	references ($d=5$) corresponding to 20 Krylov basis states. The	
	number of Trotter steps (m) is indicated in parentheses, while	
	those from exact time evolution are labeled ($m = \infty$)	45
2.6	Potential energy curve (top) and error (bottom) for symmetric	
	dissociation of linear BeH ₂ in a STO-6G basis. MRSQK com-	
	putations use $\Delta t = 2$ a.u., four time steps ($s = 4$), and six	
	references ($d=6$) corresponding to 30 Krylov basis states. The	
	number of Trotter steps (m) is indicated in parentheses, while	
	those from exact time evolution are labeled ($m=\infty$)	47
2.7	Energy error ΔE (in $E_{\rm h}$) as a function of the number of Krylov	
	basis states N of linear H₆ at a bond distance of 1.5 Å	53
2.8	Potential energy curve (top) and energy error (bottom) for sym-	
	metric dissociation of linear H ₆ in STO-6G basis. References in	
	MRSQK were selected using initial QK calculations with $s_0=4$	
	evolutions of the Hartree–Fock determinant and a time step of	
	$\Delta t_0 = 0.25$ a.u. Then the following MRSQK calculations use	
	$\Delta t = 0.5$ a.u., three time steps ($s = 3$), and five references	
	($d=5$) corresponding to 20 Krylov basis states. Two order-	
	ings of Pauli terms are employed for comparison, with nota-	
	tions consistent with that in Table 2.4. The number of Trotter	
	steps (m) is indicated in parentheses, while those from exact	
	time evolution are labeled ($m = \infty$)	54

2.9	Potential energy curve (top) and energy error (bottom) for sym-	
	metric dissociation of linear BeH2 in STO-6G basis. Refer-	
	ences in MRSQK were selected using initial QK calculations	
	with $s_0=3$ evolutions of the Hartree–Fock determinant and	
	a time step of $\Delta t_0 = 0.25$ a.u. Then the following MRSQK cal-	
	culations use $\Delta t = 2.0$ a.u., three time steps ($s = 4$), and five	
	references ($d=6$) corresponding to 30 Krylov basis states. Two	
	orderings of Pauli terms are employed for comparison, with no-	
	tations consistent with that in Table 2.4. The number of Trotter	
	steps (m) is indicated in parentheses	55
2.10	Potential energy curves (in $E_{\rm h}$) of the ground state (1 $^{1}{\rm A}_{g}$) and	
	the first singlet excited state $(2^{1}A_{g})$ for the symmetric disso-	
	ciation of H ₆ computed with the MRSQK method using two	
	reference spaces. All calculations use a STO-6G basis. MRSQK	
	computations use one Trotter step ($m=1$), $\Delta t=0.5$ a.u., three	
	time steps ($s=3$), and five references ($d=4$) corresponding	
	to 16 Krylov basis states	61
2.11	Deviations of vertical excitation energies (in eV) from FCI re-	
	sults of the first singlet excited state (2 $^{1}\mathrm{A}_{g}$) along the symmet-	
	ric dissociation of H_6 computed with the MRSQK method us-	
	ing two reference spaces. All calculations use a STO-6G basis.	
	MRSQK computations use one Trotter step ($m=1$), $\Delta t=0.5$	
	a.u., three time steps ($s=3$), and five references ($d=4$) cor-	
	responding to 16 Krylov basis states	62

3.1	The QDSRG scheme for performing hybrid classical-quantum
	computations on strongly correlated molecules. The computa-
	tion begins with a classical or hybrid orbital optimization (1),
	followed by the preparation of a correlated reference state de-
	fined in the subset of active molecular orbitals (2). This step
	yields the reduced density cumulants $(\tilde{\lambda}_k)$, which are passed to
	a classical DSRG algorithm (3) to produce the effective Hamil-
	tonian $(\bar{H}_{1,2})$ and its expectation value with respect to the ap-
	proximate cumulants $(\langle \bar{H}_{1,2} \rangle_{\tilde{\lambda}_k})$. (4) In the last step, an eigen-
	value of the DSRG effective Hamiltonian is found via a quantum
	algorithm
3.2	The energy error for the H_2 molecule (in mE_h) computed with
	the QLDSRG(2) with various amounts of stochastic noise (σ)
	added to the RDMs. For a given value of σ , the semiopaque cir-
	cles aligned vertically show the distribution of errors from 50
	computations, while the horizontal bars represent the average
	error. All computations use a cc-pVTZ basis [273] and the flow
	parameter value $s=0.5~E_{\rm h}^{-2}$. The energy errors are computed
	with respect to noiseless values. The data are obtained impos-
	ing $\gamma_3 = 0$ in the reconstruction of the approximate three-body

- 3.3 The dissociation curve for the ground-state N_2 computed with the LDSRG(2) and QLDSRG(2). (a) The total energy and (b) the energy error with respect to FCI in units of E_h . Nonparallelism errors (in mE_h) for each method are reported in square brackets. All computations use an active space containing six 2p N atomic orbitals, a cc-pVDZ basis [273], and the flow parameter value s=0.5 E_h^{-2} . The 1-QLDSRG(2)-CCSD data employ natural orbitals and γ_1 from CCSD as the input to the QDSRG computation. All other results employ CASSCF(6,6) orbitals.

3.5	Conrotatory and disrotatory pathways describing the isomer-
	ization of bicyclo[1.1.0]butane (bicyclobutane) to trans-buta-
	1,3-diene ($trans$ -butadiene). The enthalpies in kcal mol $^{-1}$ are
	relative to the reactant for relevant stationary points com-
	puted with the 2-QLDSRG(2) method using one qubit on the
	device ibmq_manila. The black horizontal bars represent the
	2-QLDSRG(2) results obtained with noiseless simulations. The
	device results are shown in parentheses. The semiopaque blue
	circles aligned vertically show the distribution of the relative
	enthalpies from eight experiments (20000 measurements per
	experiment), while the yellow horizontal bars denote the
	average relative enthalpies. We use a cc-pVTZ basis [273] (204
	basis functions) and CASSCF(2,2) natural orbitals, and the
	flow parameter value $s=1.0~E_{\rm h}^{-2}$ for all six stationary points. 97
4.1	Definition of geometrical coordinates, torsion angle $ au$ and pyra-
	midalization angle β utilized in this study. The figure is adapted
	with permission from J. Chem. Phys., 121(23):11614–11624,
	2004, DOI:10.1063/1.1807378. Copyright 2023 American In-
	stitute of Physics
4.2	Two π -like molecular orbitals in the active space for the twisted-
	pyramid conical intersection geometry. The orbitals are opti-
	mized at the CASSCF(2,2)/aug-cc-pVTZ level of theory 116
4.3	Circuit for singlet-restricted ansatz for a CAS(2,2) system 116

4.4 Potential energy curves of the three lowest singlet states along the pyramidalization motion of one CH₂ group computed with (a) SA-DSRG-PT2 [solid lines] and 2-SA-QDSRG-PT2 [asterisks], (b) SA-LDSRG(2) [solid lines], 2-SA-QLDSRG(2) [asterisks], (c) diagonalizing the bare Hamiltonian. Energies are shifted with respect to the ground-state energy of planar geometry calculated using the same method. The vertical dash lines and angle values denote the twisted-pyramid conical intersection geometry at the corresponding computational level.

List of Tables

2.1	Resource estimates for MRSQK calculations with $m=1$ Trotter	
	step approximation on several hydrogen systems in STO-6G ba-	
	sis at the bond length R=1.5 Å. Jordan-Wigner transformation	
	is used to encode the Hamiltonian for all cases in the table 3	8
2.2	Ground-state energies (in $E_{\rm h}$) of H_6 and H_8 at a site-site dis-	
	tance of 1.5 Å using exact time-evolution. Energy and overlap	
	condition number $k(\mathbf{S})$ results are given for a single determi-	
	nant (QK) using N Krylov basis states and $\Delta t = 0.5$. MRSQK	
	results are given for $N=d(s+1)$ Krylov basis states using	
	three steps ($s=3$) and $\Delta t=0.5$ a.u. With N greater than 12	
	states, the condition number for QK does not grow larger than	
	10^{18} . This is likely a result of limitations of double precision	
	arithmetic	1

- 2.3 The energy error (in mE_h) of the ground-state (in E_h) of H_6 at a bond distance of 1.5 Å. MRSQK results are given for N=d(s+1) Krylov basis states using three steps (s=3) and $\Delta t=0.5$ a.u. The quantity m indicates the Trotter number. For each value of N, selected configuration interaction (sCI) results were obtained using N determinants with the largest absolute coefficient in the FCI wave function. ADAPT-VQE results show the energy with N cluster amplitudes selected from the pool of spin-adapted generalized singles/doubles. All energy errors are computed with respect to the FCI energy ($-3.020198\ E_h$). . .
- 2.4 Ground-state energies (in $E_{\rm h}$) of H₆ at a bond distance of 1.5 Å computed with MRSQK using different term orderings. MRSQK calculations use N=d(s+1) Krylov basis states with three steps (s=3) and $\Delta t=0.5$ a.u. m indicates the Trotter number. Subscripts denote different ordering type of Pauli terms in the qubit Hamiltonian after the Trotterization. **OF**: OpenFermion's default QubitOperator ordering; **JW**: terms are sorted in the descending order based on the magnitude of coefficients after *Jordan-Wigner* transform (Pauli term with largest magnitude goes first); **sq**: terms are sorted in the descending order based on the magnitudes of amplitudes of fermion operators in the second quantized form of the Hamiltonian (the group of terms from the fermion operator with the largest amplitude go first). **rand**: Pauli terms are shuffled randomly after Jordan-Wigner

transform.

44

m limit. The data in parentheses show deviations from the FCI result ($\epsilon = \Delta E_{\rm MRSQK} - \Delta E_{\rm FCI}$, unit in eV). The best estimate of each reference space is indicated in bold type.

60

state energy obtained using the same values for N and m (as

reported in Table 2.3). Note that we take the Trotter approxi-

mation with m=100 as a good approximation to the infinite

- 2.7 Statistical evaluation for deviations of vertical excitation energies (in eV) along the dissociation of H₆ as shown in Figure 2.11. The mean absolute error (MAE, in eV) is estimated as an arithmetic average of the absolute errors over 28 geometries. The nonparallelism error (NPE, in eV) is defined as the difference between the largest and smallest excitation energy deviation from the FCI vertical excitation energy along the symmetric dissociation curve.
- 3.1 The energy error for the H_2 molecule (in mE_h) computed with the LDSRG(2) and QLDSRG(2) methods. All computations use a cc-pVTZ basis [273] and the flow parameter value s=0.5 E_h^{-2} . The energy errors are computed with respect to full configuration interaction (FCI) energies (in E_h) reported in the last row of the table. For the LDSRG(2), the expectation value of the energy is designated with " $\langle \bar{H}_{1,2} \rangle$," while the lowest eigenvalue is indicated with "eig. $\bar{H}_{1,2}$." For the QDSRG methods, we report two sets of data. Those labeled " $\gamma_3=0$ " use an approximate three-body cumulant reconstructed from $\tilde{\lambda}_1$ and $\tilde{\lambda}_2$. The results for line M employ CCSD natural orbitals and the one-body relaxed CCSD reduced density matrix as input to the QDSRG procedure.

3.2	Spectroscopic constants for the ground state $(X^{1}\Sigma_{g}^{+})$ of N_{2}	
	from the dissociation curves in Figure 3.3. The data in paren-	
	theses show deviations from FCI results. All LDSRG(2) and	
	QLDSRG(2) computations as well as literature results listed	
	here use the cc-pVDZ basis	88
3.3	Adiabatic singlet-triplet splittings ($\Delta E_{ m ST}=E_{ m T}-E_{ m S}$) in kcal	
	mol^{-1} of <i>para</i> -benzyne computed with the LDSRG(2) and QLD-	
	SRG(2) in the cc-pVTZ basis [273] with the flow parameter	
	value $s=1.0~E_{\rm h}^{-2}$. The data in parentheses show the difference	
	with respect to the experimental value of $\Delta E_{\rm ST}$ (in kcal mol ⁻¹).	
	All LDSRG(2) and QLDSRG(2) results include a zero-point vi-	
	brational energy (ZPVE) correction equal to $+0.30$ kcal mol ⁻¹	
	(see Ref. [289]). The geometries are taken from Ref. [290].	
	We use CASSCF(2,2) optimized orbitals for all computations of	
	the singlet state and ROHF orbitals for the triplet state. For	
	the LDSRG(2), the expectation value of the energy is desig-	
	nated with " $\langle \bar{H}_{1,2} \rangle$ ", while the lowest eigenvalue is indicated	
	with "eig. $\bar{H}_{1,2}$ ". For the QDSRG methods, we report two sets	
	of data. Those labeled " $\gamma_3=0$ " use an approximate three-body	
	cumulant reconstructed from approximate $\tilde{\lambda}_1$ and $\tilde{\lambda}_2$. All liter-	
	ature results listed here for comparison use the same cc-pVTZ	
	hasia	01

3.4	The errors of 2-QLDSRG(2) energies in mE_h (with respect to
	FCI energies) along the H ₂ dissociation curve (Figure 3.4). For
	results from the ibm_lagos device, we show the unsigned aver-
	age energy errors and standard deviations (in $\mathrm{m}E_{\mathrm{h}}$). Unsigned
	energy errors below 1 m $E_{\rm h}$ are highlighted in bold type 95
3.5	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 interme-
	diate, the transition state connecting gauche-butadiene and
	trans-butadiene, and the trans-butadiene product. We use the
	cc-pVTZ basis [273] (204 basis functions) and CASSCF(2,2)
	natural orbitals, and the flow parameter value $s=1.0~E_{\rm h}^{-2}.$
	All results include zero-point vibrational energy (ZPVE) cor-
	rections taken from Ref. [303]. The OMR3-DMC and CC(t;3)
	results also use the cc-pVTZ basis. The differences of values
	(in kcal mol^{-1}) with respect to the experimental data for the
	conrotatory transition state and trans-butadiene are shown in
	parentheses; values within 1 kcal mol ⁻¹ deviation are indicated
	in bold type
3.6	Summary of the number of qubits required for the full-space
	and QDSRG computations that use large basis sets in this study. 104

3.7	The relations between the elements of the fermionic 1-RDM
	$(\gamma_q^p=\langle a_p^\dagger a_q \rangle)$ and 2-RDM $(\gamma_{rs}^{pq}=\langle a_p^\dagger a_q^\dagger a_s a_r \rangle)$ and the measured
	quantities for the one-qubit ansatz. Only nonzero elements are
	shown; others are zero due to symmetries. $ C_1 ^2 = \langle \Psi 0 \rangle \langle 0 \Psi \rangle$
	and $ C_2 ^2=\langle\Psi 1\rangle\langle 1 \Psi angle$ are obtained from projective measure-
	ments [50, 320] of the optimized state in the computational
	basis; $\langle X \rangle$ is the expectation value of the Pauli X operator 107
3.8	A comparison of the energy errors (in $\mathrm{m}E_\mathrm{h}$) of the QDSRG and
	the DUCC for the H ₂ molecule at four bond lengths in the cc-
	pVTZ basis using DSRG flow parameter $s=0.5~E_{\rm h}^{-2}$. The size
	of the active space is denoted in parentheses. The energy errors
	are with respect to the full-space (30-orbital) FCI computations
	[absolute energies (in $E_{\rm h}$) are shown in the first row]. The
	DUCC data are taken from Ref. [237]
3.9	A comparison of the energy errors (in $mE_{\rm h}$) of the QDSRG and
	the DUCC for the Be atom with different basis sets and active
	spaces. The DSRG flow parameter $s=2.0~E_{\rm h}^{-2}$. All computa-
	tions use RHF orbitals. The energy errors are with respect to
	the full-space FCI computations [absolute energies (in $E_{ m h}$) are
	shown in the last column], which use 14, 30 and 55 orbitals
	for the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, respectively.
	The DUCC data are taken from Ref. [237]

4.1	Excitation energies (in eV) of the three lowest singlet states of
	the twisted-pyramid conical intersection geometry, The excita-
	tion energies are computed with respect to the ground-state
	energy of planar geometry (Franck-Condon point) calculated
	at the corresponding computational level