

Experimental computations of atomic properties on a superconducting quantum processor

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We experimentally compute relativistic and correlation effects in the atomic properties by using a superconducting qubit processor. Specifically, we compute the relativistic ground-state energies and magnetic-dipole hyperfine structure constants for four Li-like atomic systems ranging from very light to moderately heavy to very heavy in terms of nuclear charge. A symmetry-conserving Bravyi-Kitaev transformation is used to reduce the original six-qubit problem to a four-qubit problem, which is experimentally contrived by reducing the hardware requirement by employing a virtual two-qubit gate. It enables the simulation of four-qubit circuits using two physical qubits with additional circuit evaluations. The ground-state wave functions, required for computing atomic properties, are obtained by using quantum state tomography. Our results show that the averaged relative errors for the ground-state energies are $\approx 0.3 \pm 1\%$. However, for the hyperfine structure constants, the mean values of the relative errors are less than 15%, with their estimated upper bound of relative errors of $\approx \pm 10\%$ (with the exception of $7.2 \pm 47\%$ for neutral ${}^7\text{Li}$). Notably, our results for the hyperfine structure constants exhibit higher sensitivity to errors as compared to energies; a trend which we also confirm through additional numerical simulations.

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I. INTRODUCTION

The achievement of scalable, fault-tolerant computers that can solve classically intractable problems is the holy grail of quantum computing [1,2]. The currently available noisy intermediate-scale quantum (NISQ) computers [3] are an important milestone in the journey towards achieving this goal. These computers are restricted by fairly large error rates and a limited number of qubits among other challenges. Despite these limitations, NISQ devices are being actively explored to harness their maximum quantum computational power and broaden the scope of their applicability [4–10].

NISQ devices prominently utilize hybrid quantum-classical algorithms, specifically tailored for their capabilities,

such as the variational quantum eigensolver (VQE) [11,12]. VQE has gained substantial recognition for its adeptness in approximating molecular ground-state energy, underscoring the practical significance of NISQ devices amid existing quantum hardware limitations. Early VQE applications largely concentrated on computing the ground- and excited-state energies of molecules [13–18]. Atoms and molecules, particularly those with strong electron correlation effects, hold the promise of achieving quantum advantage due to their natural entanglement [19]. There have been significant advances in calculations of a wide range of atomic properties on classical computers in the past two decades [20–22]. Some of these properties are important ingredients in probing new physics beyond the Standard Model of elementary particles [23]. However, ongoing advancements indicate that further progress may eventually require using quantum computers.

The computation of properties beyond energies, such as the hyperfine structure constant is considerably more challenging, especially on quantum hardware, due to its requirement of efficiently capturing physical effects in the near-nuclear regions. Hyperfine interactions are of crucial importance for atomic systems, and they occur in a wide range of physical situations [24]. The present definition of a second is based on the transition between hyperfine levels of the ground state of ${}^{133}\text{Cs}$ atom ($F = 3 \rightarrow F = 4$) [25,26], where F is the total

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angular momentum. Further, the current best optical clocks use the highly forbidden clock transitions $J = 0 \rightarrow J = 0$, which are induced by the hyperfine interactions [27,28], where J represents the total electronic angular momentum. Precise knowledge of hyperfine structures in atomic systems also plays a crucial role in several applications, including cosmology, particularly in the context of the 21-cm line [29], and cold-atom physics [30,31]. An accurate description of hyperfine interactions require precise knowledge of single-particle wave functions in the nuclear region and they can serve as a sensitive test for relativistic and correlation effects in atoms and molecules [32,33].

In this work, we experimentally compute the relativistic ground-state energies and magnetic-dipole hyperfine structure constants of four atomic systems, neutral ^7Li atom and three highly charged ions; Li-like ^{45}Sc , Li-like ^{141}Pr , and Li-like ^{209}Bi , on a superconducting quantum processor. Henceforth, in this work, when ground-state energy and hyperfine structure constant values are mentioned, they refer to the relativistic values of those two atomic properties. We also study the trend of relativistic and correlation effects on the two atomic properties in the above-mentioned atomic systems with increasing nuclear charge. The relativistic effects are captured by employing the relativistic Dirac-Coulomb Hamiltonian, while the electron correlation effects are accounted for by the choice of a suitable ansatz for VQE where the entangling gates facilitate the interorbital interactions. Employing a NISQ technique for simulating large quantum circuits with smaller quantum devices, we implement a virtual two-qubit gate [34,35]. By utilizing the virtual two-qubit gate, we simulate four-qubit circuits using two physical qubits with additional circuit runs. Initially, VQE is implemented on a classical computer to derive the optimized parameters for the ground-state energies of the four systems. Subsequently, the same ansatz is executed on a quantum device with the optimized parameters to compute the expectation values corresponding to the respective ground-state energy and hyperfine structure Hamiltonians. Furthermore, we obtain the ground-state wave functions for the four systems using quantum state tomography (QST).

The rest of the paper is organized as follows. In Sec. II, we review the theory of hyperfine structure constants and discuss the atomic Hamiltonian and its transformation to a qubit Hamiltonian. Section III presents the methodology adopted in this work to obtain the optimized parameters from VQE, which we then utilize to experimentally obtain the ground-state density matrices for the four systems. In Sec. IV, we provide details on the experiment and then present the results obtained from it. In Sec. V, we analyze our experimental results, providing explanations behind the observed trends. These explanations are further corroborated through the numerical simulations. Lastly, in Sec. VI we summarize our work and discuss potential directions for future work.

II. THEORY

A. Hyperfine structure

We begin by considering the relativistic Dirac-Coulomb (DC) Hamiltonian for atomic systems (in SI units)

H_{DC} as

$$H_{\text{DC}} = \sum_i (c\vec{\alpha}_i \cdot \vec{p}_i + \beta_i mc^2) + \sum_i V(\vec{r}_i) + \frac{1}{2} \sum_{i,j \neq i} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \quad (1)$$

where c is the speed of light, $\vec{p}_i$ is the momentum of the i th electron, m is the mass of the electron, e is the electron charge, and $\vec{r}_i$ is the coordinate vector of the i th electron. $\vec{\alpha}_i$ and β_i are the Dirac matrix spinors. The permittivity of a vacuum is represented by ϵ_0 . It is important to consider a nucleus with a finite-size distribution for the computation of properties that are sensitive to physical effects near the nucleus, like the hyperfine interaction. Thus, the electron-nucleus interaction term is given by

$$V(\vec{r}) = -\frac{e}{4\pi\epsilon_0} \int_V \frac{\rho_n(R)}{|\vec{r} - \vec{R}|} d\tau, \quad (2)$$

where ρ_n refers to the volume nuclear charge density (which is a Fermi distribution [36] in our case), with $\vec{r}$ and $\vec{R}$ being the electronic and nuclear coordinates, respectively, and the volume element is denoted by $d\tau$. If we only consider the effect of the nuclear charge and not the higher-order multipoles in the expansion of $\frac{1}{|\vec{r} - \vec{R}|}$, the expression for $V(\vec{r})$ in Eq. (2) reduces to

$$V(\vec{r}) \simeq -\frac{e}{\epsilon_0} \int_0^\infty \frac{\rho_n(R)}{r_>} R^2 dR, \quad (3)$$

where $r_>$ is the radial coordinate which represents the larger of the two values between $|\vec{r}|$ and $|\vec{R}|$, and dR is the radial element. Hereafter, we use atomic units (a.u.), where $e = m = \hbar = 4\pi\epsilon_0 = 1$.

The relativistic hyperfine interaction, which arises due to the interaction of the electron current density and the vector potential due to the nuclear magnetic dipole moment $\vec{\mu}_I$, can be expressed as [37]

$$H_{\text{hf}} = \sum_i \vec{\alpha}_i \cdot \frac{\vec{\mu}_I \times \vec{r}_i}{|\vec{r}_i|^3}, \quad (4)$$

where i refers to the i th electron. We then define an effective hyperfine operator $H_{\text{hf}}^{\text{eff}} = \mathcal{A} \vec{I} \cdot \vec{J}$, where $\mathcal{A}$ is the magnetic-dipole hyperfine structure constant. $\vec{I}$ and $\vec{J}$ are the total nuclear spin and the total electronic angular momenta, respectively. The expression for the expectation values of $H_{\text{hf}}^{\text{eff}}$ satisfies the relation

$$\langle \Psi | H_{\text{hf}}^{\text{eff}} | \Psi \rangle = \langle \Psi | H_{\text{hf}} | \Psi \rangle, \quad (5)$$

where $|\Psi\rangle = |\Psi(JM_J)\rangle \otimes |\Psi(IM_I)\rangle$, J, M_J and I, M_I are the electronic and nuclear quantum numbers, respectively. Keeping in mind that experiments for the measurement of $\mathcal{A}$ are performed in the stretched state, that is, $M_I = I$, and $M_J = J$, from Eq. (5), we obtain

$$\mathcal{A} = \frac{\mu_I}{IJ} \langle \Psi(JJ) | \sum_i \frac{(\vec{r}_i \times \vec{\alpha}_i)_z}{|\vec{r}_i|^3} | \Psi(JJ) \rangle. \quad (6)$$

An alternate but equivalent expression for $\mathcal{A}$ using coupled angular momentum states can be found in the literature [38,39].

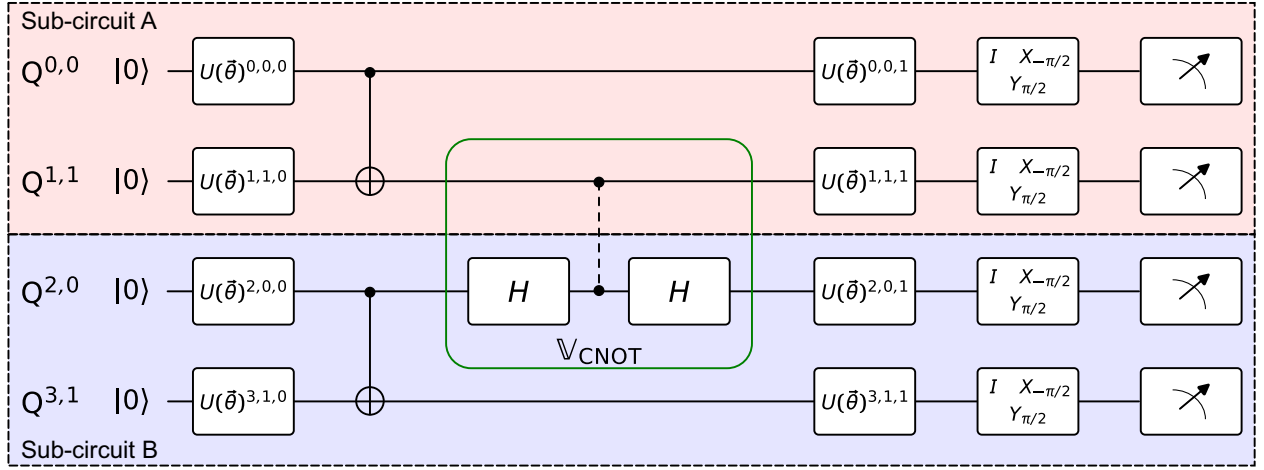


FIG. 1. Quantum circuit for computing ground-state energies and hyperfine structure constants of various electronic systems. The virtual CNOT gate ($\mathbb{V}_{\text{CNOT}}$) is shown in a green box, which is implemented by sandwiching a virtual CZ gate (represented with a dashed line) between two Hadamard gates (H) on the target qubit.

B. Atomic Hamiltonian

The second quantized form of Eq. (1) is given by

$$H = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_s a_r, \quad (7)$$

where $a^\dagger$ and a are the creation and annihilation operators, respectively. The indices p, q, r, s run over the chosen single-particle basis. The coefficients, h_{pq} and g_{pqrs} are one- and two-electron integrals, respectively.

To perform VQE, the electronic Hamiltonian is transformed to a qubit Hamiltonian

$$H_q = \sum_k w_k P_k, \quad (8)$$

where w_k are the real scalar coefficients that depend on h_{pq} and g_{pqrs} . $P_k \in \{I, X, Y, Z\}^{\otimes N}$ is a tensor product of single-qubit Pauli operators on N qubits. In typical fermion-qubit encoding techniques such as Jordan-Wigner transformation (JWT [40]) and Bravyi-Kitaev transformation (BKT [41]), the number of qubits required to encode the wave function equals to the number of spin orbitals in the active space. In this work, we use the 1s, 2s, and 3s orbitals as the active space, which corresponds to a six-qubit problem. However, we adopt a symmetry-conserving BKT (SCBKT [42]) for the wave-function encoding, which allows us to reduce two qubits based on the conservation rule of the numbers of spin-up and spin-down electrons. Note that the two-qubit reduction technique adopted in the SCBKT assumes nonrelativistic atomic calculations in which electron-spin quantum number S becomes a good quantum number. By using the qubit reduction techniques for relativistic atomic calculations as in this study is generally nontrivial. In the present work, however, we consider only s -type orbitals ($j = 1/2$) as the active orbitals, where j is the total angular momentum. In this case the SCBKT is applicable directly to reduce the number of qubits for the wave-function encoding. As discussed below, we also “cut” one CNOT gate and employ a virtual CNOT gate, which allows us to further reduce the number of physical qubits from six in the original problem to two to simulate the

electronic structure of a neutral ^7Li atom and Li-like ions. In the hyperfine integral calculations, we use $g_I \equiv \mu_I/I = 2.17095, 1.35899, 1.71016$, and 0.9134 for neutral ^7Li , Li-like ^{45}Sc , Li-like ^{141}Pr , and Li-like ^{209}Bi , respectively. The μ_I values were taken from the atomic and nuclear data tables provided by Ref. [43]. The hyperfine Hamiltonian H_{hfs}^q in the qubit-operator form contains only one-body terms, and the relevant integrals are generated in a manner similar to that of the one-body part of the qubit Hamiltonian.

III. METHODOLOGY

Figure 1 shows the four-qubit circuit realized by using two physical qubits. The labeling of these qubits is done as $Q^{q,p}$, where q refers to the index of the qubit in the four-qubit circuit and p refers to the index of the physical qubit in the device. Single-qubit operations in the circuit are labeled as $U(\vec{\theta})^{q,p,i}$, where q and p are qubit indices. Moreover, i represents the position of the gate layer in the circuit. The four-qubit circuit can be considered as two subcircuits, labeled as subcircuits A and B in Fig. 1, connected by a two-qubit gate between them. We “cut” this two-qubit gate and employ a virtual two-qubit gate in its place, which allows us to simulate the four-qubit circuit with two physical qubits. We generate a virtual CNOT gate ($\mathbb{V}_{\text{CNOT}}$) between ($Q^{1,1}$ and $Q^{2,0}$) by implementing a virtual CZ gate between the pair of qubits and applying Hadamard (H) gates before and after the virtual CZ gate on the target qubit $Q^{2,0}$. The decomposition of a virtual CZ gate is written as

$$\begin{aligned} \tilde{\text{CZ}} = & \frac{1}{2} \left(\tilde{\mathcal{R}}_Z \left(\frac{\pi}{2} \right) \otimes \tilde{\mathcal{R}}_Z \left(\frac{\pi}{2} \right) \right) + \frac{1}{2} \left(\tilde{\mathcal{R}}_Z \left(-\frac{\pi}{2} \right) \right. \\ & \otimes \tilde{\mathcal{R}}_Z \left(-\frac{\pi}{2} \right) \Big) - \frac{1}{2} \sum_{\alpha_1, \alpha_2} \alpha_1 \alpha_2 \left[\tilde{\Pi}_{\alpha_1 Z} \otimes \tilde{\mathcal{R}}_Z \left((\alpha_2 + 1) \frac{\pi}{2} \right) \right. \\ & \left. \left. + \tilde{\mathcal{R}}_Z \left((\alpha_1 + 1) \frac{\pi}{2} \right) \otimes \tilde{\Pi}_{\alpha_2 Z} \right], \end{aligned} \quad (9)$$

where $\alpha_1, \alpha_2 \in \{-1, +1\}$. The superoperators $\tilde{\mathcal{R}}_Z(\pm\theta)$ and $\tilde{\Pi}_{\pm Z}$ correspond to the operators $\mathcal{R}_Z(\pm\theta) = e^{\pm iZ\theta/2}$ and

$\Pi_{\pm Z} = (I \pm Z)/2$, respectively. $\Pi_{\pm Z}$ represent projection gates, which project the quantum state onto the respective eigenbasis and are nonunitary [34]. The tilde ($\sim$) symbol denotes a superoperator $\tilde{U}$, which corresponds to an operator U . Its action on a density matrix ρ is defined as $\tilde{U}\rho = U\rho U^\dagger$. To implement a virtual CZ gate, five distinct local operations or decomposition operators $\mathcal{D}_k^j$ must be applied to both the control qubit $Q^{1,1}$ and the target qubit $Q^{2,0}$. In $\mathcal{D}_k^j$, the superscript $j \in \{Q^{1,1}, Q^{2,0}\}$ refers to the qubit they are applied to, and the subscript $k \in \{1, 2, 3, 4, 5\}$ refers to the k th decomposition operator in the set $\mathcal{D} \in \{\mathcal{R}_Z(\pi/2), \mathcal{R}_Z(-\pi/2), \Pi_{\pm Z}, I, Z\}$. The projection gates $\mathcal{D}_{k=3}^j = \{\Pi_{\pm Z}\}$ are implemented via mid-circuit measurements. The details of implementing a virtual two-qubit gate experimentally are presented in Ref. [35].

As a first step, we run the VQE algorithm to obtain the optimized parameters $\tilde{\varphi}_{\text{opt}}$ for the circuit shown in Fig. 1, corresponding to the ground-state energies of the four atomic systems. This is performed on a classical computer using the QULACS simulator [44]. We use the hardware-efficient ansatz (HEA) [12] for the VQE, where two layers of single-qubit gates and a layer of actual and virtual two-qubit gates are implemented before measuring the expectation values for the corresponding Hamiltonians for the ground-state energies and hyperfine structure constants, respectively. An initial state $|0000\rangle$ is fed into the VQE algorithm with the initial set of parameters randomly assigned, and “BFGS” [45,46] is used as the optimizer. The VQE convergence results for all the four atomic systems are shown in Fig. 4. After obtaining $\tilde{\varphi}_{\text{opt}}$, we execute the circuit shown in Fig. 1 on a quantum device, using $\tilde{\varphi}_{\text{opt}}$ as the variational parameters to obtain the ground-state wave functions of the four atomic systems. The details of the experimental implementation is presented in Sec. IV.

We carry out calculations on a classical computer as a reference by taking into consideration all the excitations arising from the electron–electron Coulomb interactions within $1s$, $2s$, and $3s$ orbitals. This is referred to as the complete-active-space configuration-interaction (CAS-CI) calculation, which is the full-CI treatment within a restricted space spanned by all possible configurations that we consider in our work. We denote the CAS-CI values for ground-state energies and hyperfine structure constants for each atomic system as $E^{\text{CAS-CI}}$ and $\mathcal{A}^{\text{CAS-CI}}$, respectively. The Dirac-Hartree-Fock (DHF) configuration is $|(1s)^2(2s)^1(3s)^0\rangle$ (two electrons in $m_j = +1/2$ orbitals and one electron in $m_j = -1/2$), and it is the leading term of the ground-state CAS-CI wave function for all the four atomic systems. In the DHF calculations, we choose Gaussian-type orbitals for our single-particle basis sets. In particular, we choose the universal basis [47] whose i th basis function is given as the Gaussian function

$$g_i(r) = r^{l_i} e^{-\alpha_i r^2}, \quad (10)$$

where l_i is the angular momentum quantum number and α_i is exponent of the Gaussian. The distance from the center of the Gaussian to the origin is given as r . Furthermore, α_i is given as

$$\alpha_i = \alpha_0 \beta^{i-1}, \quad (11)$$

for some constants α_0 and β . Since we truncate our Hilbert space, we carefully choose the values of α_0 and β that still

TABLE I. Parameters of the superconducting transmon qubits used in the experiments: the resonator frequency ω_r , the qubit frequency ω_q , anharmonicity α , energy-relaxation time T_1 , and Hahn-echo time T_{2E} .

Qubit	$\frac{\omega_r}{2\pi}$ (GHz)	$\frac{\omega_q}{2\pi}$ (GHz)	$\frac{\alpha}{2\pi}$ (MHz)	T_1 (μ s)	T_{2E} (μ s)
Q_0	9.956	7.784	−360	21.4	47.2
Q_1	10.155	8.484	−434	27.1	19.1

give the optimal single-particle energies as well as the total energy ($\alpha_0 = 0.0009$ and $\beta = 2.15$). The atomic orbitals are expressed within the basis set as a linear combination of basis functions [48]. We perform DHF calculations using 40 $s_{1/2}$, 39 $p_{1/2}$, 39 $p_{3/2}$, 38 $d_{3/2}$, and 38 $d_{5/2}$ basis functions [49].

The SCBKT reduces two qubits using the information of the number of spin-up and spin-down electrons (the number of electrons occupying $m_j = +1/2$ or $-1/2$ orbitals in our case) being either even or odd. When the VQE is carried out using the HEA in conjunction with the SCBKT, it can converge to odd-electron states other than the three-electron state. This problem is very important for the calculations of Li-like ions because five-electron state is much more stable than the three-electron state we are interested in. To obtain the desired three-electron state in VQE, we introduced a term

$$\eta = C \left(\sum_j a_j^\dagger a_j - n_e \right)^2, \quad (12)$$

which acts as a penalty in the cost function to be minimized. Here, n_e is the number of electrons in the target electronic state and C is a coefficient that controls the strength of the penalty. In this study we used $C = 0, 100, 1000$, and 5000 for neutral ${}^7\text{Li}$, Li-like ${}^{45}\text{Sc}$, Li-like ${}^{141}\text{Pr}$, and Li-like ${}^{209}\text{Bi}$, respectively. The density matrices for the DHF configuration after applying SCBKT for all the four atomic systems, are obtained as $\rho^{\text{DHF}} = |1011\rangle\langle 1011|$. To check the ansatz for the convergence to the CAS-CI values, we run our calculations for all possible configurations of the ansatz by rearranging the positions of the qubits in the calculations (see Appendix A).

IV. EXPERIMENT

For the experiments, we use fixed-frequency superconducting transmon qubits [50]. These qubits are part of a 16-qubit device [51]. The experiments discussed here make use of two of these qubits labeled as Q_0 and Q_1 . The parameters of these qubits are summarized in Table I.

After obtaining $\tilde{\varphi}_{\text{opt}}$ in the VQE on a classical simulator, we execute the circuit shown in Fig. 1 on a quantum device, using $\tilde{\varphi}_{\text{opt}}$ as the variational parameters to obtain the ground-state wave functions of the four atomic systems. The single-qubit operations $U(\vec{\theta})^{q,p,i}$ are implemented as a combination of $\mathcal{R}_Z(\theta)$ and $\mathcal{R}_X(\frac{\pi}{2})$ gates expressed as $U^{q,p,i}(\vec{\theta}) = \mathcal{R}_Z(\theta_1) \times \mathcal{R}_X(\frac{\pi}{2}) \times \mathcal{R}_Z(\theta_2) \times \mathcal{R}_X(\frac{\pi}{2}) \times \mathcal{R}_Z(\theta_3)$, where $\mathcal{R}_A(\pm\theta) = e^{\pm iA\theta/2}$ for an operator A . The average gate fidelities of the single-qubit Clifford gates for Q_0 and Q_1 are evaluated to be 0.9981 ± 0.0006 and 0.9968 ± 0.0002 , respectively, via

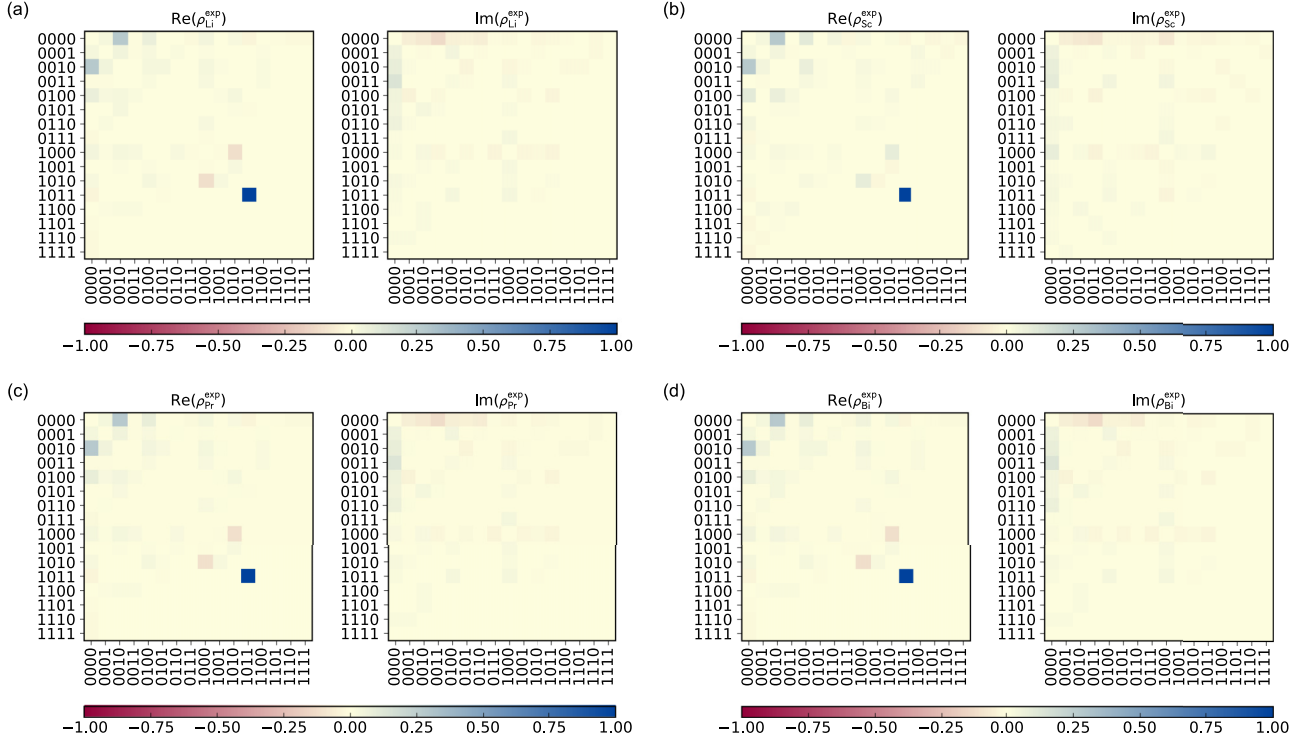


FIG. 2. Quantum state tomography for the considered atomic systems. The experimentally obtained ground-state wave functions of (a) neutral ${}^7\text{Li}$, (b) Li-like ${}^{45}\text{Sc}$, (c) Li-like ${}^{141}\text{Pr}$, and (d) Li-like ${}^{209}\text{Bi}$. Real (imaginary) parts of the density matrices are plotted on the left (right) panels of the figures.

randomized benchmarking [52–54]. Here, we consider real amplitudes ansatz [55], implying rotations around the Y axis, resulting in real amplitudes wavefunction with $\theta_1 = \theta_3 = 0$. This gives rise to one variational parameter per qubit in each single-qubit gate as considered in the circuit shown in Fig. 1. The actual CNOT gates and V_{CNOT} do not have variational parameters. Hence, we obtain $\tilde{\varphi}_{\text{opt}}$ as a set of eight optimized parameters. The implementation of $R_Z(\theta)$ gates are performed through the efficient Z-gate technique in which the rotations around Z axis are performed through the frame changes in the control software [56]. The single-qubit gates are implemented by calibrated shaped microwave pulses [57]. CNOT gates are implemented by cross-resonance (CR) gates [58,59] combined with single-qubit operations. The two-qubit average gate fidelity obtained through interleaved randomized benchmarking is 0.9756 ± 0.0004 .

We obtain the ground-state wave functions of the four atomic systems through quantum state tomography (QST) [60], which requires the measurement of $\{X, Y, Z\}^{\otimes 4}$ observables for the circuit shown in Fig. 1. Since we divide the four-qubit circuit into two subcircuits with each having two physical qubits, we compute the expectation values of the circuit shown in Fig. 1 from the sets of two-qubit circuit expectation values by using Eq. (9). For the measurement of I observable, we always take the outcome to be +1. For each subcircuit and measurement of each observable, we run the circuit 100 000 times, also called as the number of shots N_s , and take the average as the expectation value. For mitigating the initialization errors, we apply a measurement pulse at the beginning of the circuit and postselect only those shots that were measured to be in the ground state initially. For

the measurement-error mitigation, we apply the least-square method in the tensored-matrix mitigation technique [61,62]. Thus, we can obtain the four-qubit density matrices, which we denote as $\{\rho_{\text{Li}}^{\text{exp}}, \rho_{\text{Sc}}^{\text{exp}}, \rho_{\text{Pr}}^{\text{exp}}, \rho_{\text{Bi}}^{\text{exp}}\}$ that refer to the atomic systems, neutral ${}^7\text{Li}$, Li-like ${}^{45}\text{Sc}$, Li-like ${}^{141}\text{Pr}$, and Li-like ${}^{209}\text{Bi}$, respectively. The superscript “exp” denotes the experimentally realized quantum states. The density matrices of the experimentally obtained ground-state wave functions are shown in Fig. 2.

By using the experimentally obtained expectation values of $\{X, Y, Z\}^{\otimes 4}$ observables from the QST experiments, we use the relevant Pauli strings to compute the ground-state energies E^{exp} and hyperfine structure constants $\mathcal{A}^{\text{exp}}$ by using Eq. (8) as

$$E^{\text{exp}} = \langle H_q \rangle = \sum_k w_k \langle P_k \rangle_{\text{exp}}, \quad (13)$$

$$\mathcal{A}^{\text{exp}} = \langle H_{\text{hfs}}^q \rangle = \sum_l w_l^{\text{hfs}} \langle P_l \rangle_{\text{exp}}, \quad (14)$$

where w_k and w_l^{hfs} are the real coefficients corresponding to the ground-state energy and hyperfine structure constant Hamiltonians, respectively. The relative errors from the values obtained in the CAS-CI are defined as

$$\Delta_r^E = \frac{E^{\text{exp}} - E^{\text{CAS-CI}}}{E^{\text{CAS-CI}}}, \quad (15)$$

$$\Delta_r^{\mathcal{A}} = \frac{\mathcal{A}^{\text{exp}} - \mathcal{A}^{\text{CAS-CI}}}{\mathcal{A}^{\text{CAS-CI}}}, \quad (16)$$

respectively. The results are presented in Fig. 3. Here, we calculate the error bars as follows. For each qubit, we

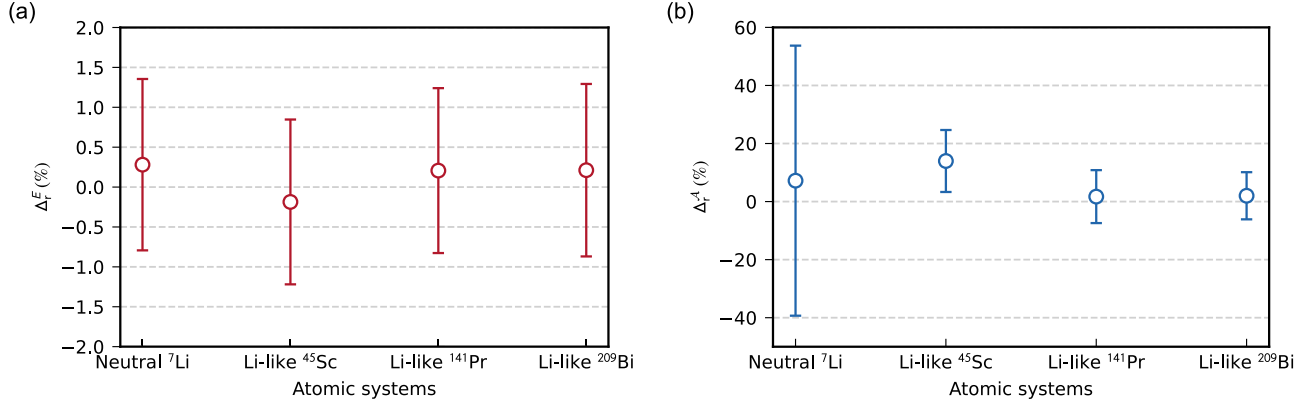


FIG. 3. Relative errors of the experimentally obtained parameters with respect to the reference values from the CAS-CI calculations. (a) Relative error for the ground-state energies, Δ_r^E . (b) Relative error for the ground-state hyperfine structure constants Δ_r^A .

construct the transition matrix and then determine error margins for ground-state energies and hyperfine structure constants. To estimate these uncertainties, we calculate the upper bound on errors for each expectation value [63] within each subcircuit. The error bound δ is expressed as

$$\delta = \frac{\Upsilon}{\sqrt{N_s}}, \quad (17)$$

where Υ is defined as

$$\Upsilon = \prod_{i=\{0,1\}} \frac{1 + |\kappa_i - \chi_i|}{1 - \kappa_i - \chi_i}, \quad (18)$$

with i representing the index of each physical qubit. κ and χ are the readout error rates describing $0 \rightarrow 1$ and $1 \rightarrow 0$ error transition probabilities, respectively. Refer to Appendix B for further details. It is important to note that these error bars represent the upper bounds of the relative errors in the calculated ground-state energy and hyperfine structure constant values. This occurs when the expectation values of all the Hamiltonian terms are consistently overestimated or underestimated. However, in practice, the actual relative errors are significantly smaller, as overestimations and underestimations tend to partially cancel each other out. The averaged relative errors for the ground-state energies Δ_r^E are $\approx 0.3 \pm 1\%$. The mean values of the relative errors for the hyperfine structure constants Δ_r^A are $< 15\%$, with their upper bound of relative errors around 10% (with the exception of $7.2 \pm 47\%$ for neutral ${}^7\text{Li}$). This observed higher upper bound of relative error in the ground-state hyperfine structure constants compared to the ground-state energies aligns with the expectations, given the first's inherent higher sensitivity to errors. Further discussion about the obtained results is presented in Sec. V.

We conduct a comparative analysis between the absolute values of our experimental results for the ground-state energies and hyperfine structure constants of the four systems and the corresponding DHF and CAS-CI values computed on a classical computer, as detailed in Tables IV and V, respectively. Additionally, in Table V, we incorporate the results of spectroscopic experiments pertaining to the ground-state hyperfine structure constants [64–67], designated as “REX” to denote reference experiments. The observation that

the ground-state energies as well as the hyperfine structure constants increase sharply as we move from the lightest, neutral ${}^7\text{Li}$ atom, to the heaviest, Li-like ${}^{209}\text{Bi}$, reflects the increasing atomic number Z of the nucleus (and therefore the increase in relativistic effects). In fact, our results in Tables IV and V show that the hyperfine structure constant of the heaviest system considered is larger than the lightest one by over five orders of magnitude. Our hardware results reflect this expected trend. See Appendix C for the details.

V. DISCUSSION

The obtained experimental results, as presented in Fig. 3, show higher upper bounds of relative errors in the ground-state hyperfine structure constants compared to the ground-state energies. Because the upper bounds of the relative errors are calculated by summing the standard deviations of the expectation values of each Hamiltonian term, they become larger when the sum of the absolute values of the coefficients in the qubit Hamiltonian [$|w_k|$ and $|w_k^{\text{hfs}}|$ in Eqs. (13) and (14) for ground-state energies and hyperfine structure constants, respectively] is large. To investigate the trend of the upper bounds of the relative errors theoretically, we calculate the $L1$ norms of the Hamiltonians scaled by their respective CAS-CI values, which can be expressed as

$$\Gamma_q = \frac{\|H_q\|}{|E^{\text{CAS-CI}}|} = \frac{\sum_k |w_k|}{|E^{\text{CAS-CI}}|}, \quad (19)$$

$$\Gamma_{\text{hfs}}^q = \frac{\|H_{\text{hfs}}^q\|}{\mathcal{A}^{\text{CAS-CI}}} = \frac{\sum_l |w_l^{\text{hfs}}|}{\mathcal{A}^{\text{CAS-CI}}}, \quad (20)$$

where Γ_q and Γ_{hfs}^q are the scaled $L1$ norms of the ground-state energy and hyperfine structure constant Hamiltonians, respectively. The calculated Γ_q and Γ_{hfs}^q , respectively, are summarized in Table II. We confirm that the upper bounds of relative errors in Fig. 3 are approximately proportional to the $L1$ norms, and Γ_{hfs}^q is more than one order larger than Γ_q for all the four systems. The magnitude of Γ_{hfs}^q also explains why the upper bound of relative error of the ground-state hyperfine structure constant of neutral ${}^7\text{Li}$ is larger than that of other Li-like ions.

The large Γ_{hfs}^q values can be explained by the nature of the hyperfine Hamiltonian. In the hyperfine Hamiltonian, the

TABLE II. $L1$ norms of the ground-state energy Hamiltonian (Γ_q) and hyperfine structure constant Hamiltonian (Γ_{hfs}^q) scaled by their respective CAS-CI values.

System	Γ_q	Γ_{hfs}^q
Neutral ${}^7\text{Li}$	1.244	55.249
Li-like ${}^{45}\text{Sc}$	1.224	20.278
Li-like ${}^{141}\text{Pr}$	1.217	18.062
Li-like ${}^{209}\text{Bi}$	1.217	16.426

spin-up ($m_j = 1/2$) and spin-down ($m_j = -1/2$) electrons contribute to the hyperfine structure constant with the same magnitude but opposite signs. Therefore, when both the spin-up and spin-down orbitals are occupied, their contributions to the hyperfine structure constant cancel out completely. In the atomic systems being investigated, the contribution to the hyperfine structure constant from the $1s$ orbital is very small because the ground-state wave function can be well approximated by the Dirac-Fock electron configuration. However, experiments with superconducting quantum devices show an insufficient cancellation of these contributions from the $1s_{\text{up}}$ and $1s_{\text{down}}$ spin orbitals, due to hardware noises and errors. Note that the $|w_{\text{hfs}}^i|/\mathcal{A}^{\text{CAS-CI}}$ values with $P_i = ZIII$, which describes the contribution of the $1s_{\text{up}}$ spin-orbital to the hyperfine structure constant are 20.57, 4.48, 3.70, and 3.18 for neutral ${}^7\text{Li}$, Li-like ${}^{45}\text{Sc}$, Li-like ${}^{141}\text{Pr}$, and Li-like ${}^{209}\text{Bi}$, respectively. Lighter elements are more affected by the insufficient cancellation of contributions from the spin-up and spin-down electrons.

The higher sensitivity of $\mathcal{A}^{\text{exp}}$ to errors is also confirmed from the numerical simulations [68] of the ground-state energies and hyperfine structure constants with depolarizing errors [60] and shot noise. The details are given in Appendix D. We find that the ground-state hyperfine structure constants are more sensitive to errors than the ground-state energies, as also seen in the experiments. According to our numerical simulations, the standard deviation of the relative errors of the ground-state energy for 100 independent simulations is less than 0.001% when we perform 10^5 shots, while that of ground-state hyperfine structure constants is less than 2% (see Fig. 5). Again, we emphasize that the error bars in Fig. 3 represent upper bounds on the relative errors, and the standard deviation of the energies and hyperfine structure constants obtained from 100 repetitions of the numerical simulations are smaller than the upper bound.

VI. CONCLUSION

In this work, we experimentally computed relativistic and correlation effects in the ground-state energies and magnetic-dipole hyperfine structure constants of atomic systems on a superconducting quantum processor. We considered four atomic systems; neutral ${}^7\text{Li}$ and its three isoelectronic ions that are intermediate, heavy, and very heavy in terms of atomic number Z . After reducing the number of qubits from six to four via the symmetry-conserving Bravyi-Kitaev transformation, we further reduced the hardware requirement by simulating the four-qubit circuit with two physical qubits by implementing a virtual two-qubit gate. The hyperfine structure

values are highly sensitive to errors; we also found that from the experimental results. While computing expectation values with less errors were important to evaluate the energy values, generating precise wave functions was equally important to explore other atomic properties such as hyperfine structure constants. We experimentally demonstrated the importance of relativistic and correlation effects in atomic systems by carrying out computations of ground-state energies and more strikingly, ground-state hyperfine structure constants, of light, medium-heavy, and very heavy atomic systems (where relativistic effects dominate). It is worth adding here that there is a huge space that can be explored using NISQ techniques such as virtual two-qubit gates, hybrid quantum-classical algorithms, and quantum error mitigation which can pave a way to compute many other significant physical properties and phenomena.

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APPENDIX A: DIFFERENT ANSATZ CONFIGURATIONS

We check the ansatz employed in the circuit shown in Fig. 1 to ensure convergence to the CAS-CI values. Taking the example of neutral ${}^7\text{Li}$, we investigate the dependence of our calculations on all the possible arrangements of the entangling gates in the ansatz. For this purpose, we rearrange the ordering of the Hamiltonian and calculated each arrangement 100 times with randomly prepared initial parameters. In the notation used in Table III, the arrangement [0,1,2,3], for example, refers to CNOT gates connecting qubits 0 and 1, 1 and 2, and 2 and 3, where the first member in the pair refers to the control qubit and the latter the target qubit. The value p_s refers to the probability of successful convergence to the CAS-CI value for a given arrangement. As we see in Table III, the arrangements converge to the CAS-CI values albeit with different probabilities p_s . Therefore, we chose the default arrangement [0,1,2,3] for all the four atomic systems in the experiments, for simplicity. The VQE convergence results to the corresponding CAS-CI values for all the four atomic systems under the [0,1,2,3] arrangement are shown in Fig. 4.

APPENDIX B: QUBIT READOUT CHARACTERIZATION

To compute the transition probability matrix A , we start by initializing the qubit in the ground state $|0\rangle$ and applying a

TABLE III. Results from different arrangements of entangling gates for our choice of ansatz for neutral ^7Li .

Ordering	p_s	$E^{\text{CAS-Cl}}$ (Hartree)	$\mathcal{A}^{\text{CAS-Cl}}$ (Hartree)
[0, 1, 2, 3]	0.96	-7.433469 ± 0.000035	$(6.586025 \pm 0.025077) \times 10^{-8}$
[0, 1, 3, 2]	0.99	-7.433463 ± 0.000049	$(6.587089 \pm 0.025077) \times 10^{-8}$
[0, 2, 1, 3]	0.97	-7.433455 ± 0.000033	$(6.586633 \pm 0.025685) \times 10^{-8}$
[0, 2, 3, 1]	1.0	-7.433465 ± 0.000037	$(6.584809 \pm 0.025989) \times 10^{-8}$
[0, 3, 1, 2]	1.0	-7.433466 ± 0.000033	$(6.587697 \pm 0.024925) \times 10^{-8}$
[0, 3, 2, 1]	1.0	-7.433467 ± 0.000036	$(6.586785 \pm 0.026749) \times 10^{-8}$
[1, 0, 2, 3]	0.92	-7.433451 ± 0.000040	$(6.585569 \pm 0.022189) \times 10^{-8}$
[1, 0, 3, 2]	1.0	-7.433456 ± 0.000057	$(6.587393 \pm 0.031916) \times 10^{-8}$
[1, 2, 0, 3]	0.89	-7.433442 ± 0.000058	$(6.588153 \pm 0.032524) \times 10^{-8}$
[1, 2, 3, 0]	1.0	-7.433464 ± 0.000042	$(6.591800 \pm 0.023709) \times 10^{-8}$
[1, 3, 0, 2]	1.0	-7.433460 ± 0.000027	$(6.588609 \pm 0.023557) \times 10^{-8}$
[1, 3, 2, 0]	0.98	-7.433456 ± 0.000038	$(6.588001 \pm 0.023405) \times 10^{-8}$
[2, 0, 1, 3]	0.96	-7.433455 ± 0.000038	$(6.582833 \pm 0.023405) \times 10^{-8}$
[2, 0, 3, 1]	1.0	-7.433451 ± 0.000048	$(6.586025 \pm 0.020214) \times 10^{-8}$
[2, 1, 0, 3]	0.99	-7.433459 ± 0.000054	$(6.582073 \pm 0.025989) \times 10^{-8}$
[2, 1, 3, 0]	1.0	-7.433467 ± 0.000039	$(6.582529 \pm 0.024469) \times 10^{-8}$
[2, 3, 0, 1]	1.0	-7.433461 ± 0.000058	$(6.580401 \pm 0.025533) \times 10^{-8}$
[2, 3, 1, 0]	0.98	-7.433462 ± 0.000038	$(6.585265 \pm 0.022949) \times 10^{-8}$
[3, 0, 1, 2]	0.99	-7.433470 ± 0.000044	$(6.583593 \pm 0.026445) \times 10^{-8}$
[3, 0, 2, 1]	0.98	-7.433453 ± 0.000049	$(6.583441 \pm 0.024621) \times 10^{-8}$
[3, 1, 0, 2]	0.98	-7.433450 ± 0.000043	$(6.581921 \pm 0.023405) \times 10^{-8}$
[3, 1, 2, 0]	0.92	-7.433457 ± 0.000039	$(6.589216 \pm 0.022493) \times 10^{-8}$
[3, 2, 0, 1]	0.94	-7.433447 ± 0.000058	$(6.589824 \pm 0.030093) \times 10^{-8}$
[3, 2, 1, 0]	0.99	-7.433462 ± 0.000040	$(6.583289 \pm 0.022341) \times 10^{-8}$

$\mathcal{R}_X(\pi/2)$ gate. This is followed by two successive measurement pulses to determine the qubit's final state. Our aim is to calculate the probability of detecting the qubit in a particular state after it has been prepared in a specific initial state. The resulting transition probability matrix A is defined as

$$A = \begin{bmatrix} 1 - \kappa_i & \chi_i \\ \kappa_i & 1 - \chi_i \end{bmatrix}, \quad (\text{B1})$$

where κ_i represents the probability of incorrectly assigning a measurement outcome of 1 when the qubit is initially prepared in the state $|0\rangle$ (i.e., a $0 \rightarrow 1$ error), and χ_i is the probability of incorrectly assigning a measurement outcome of 0 when the qubit is prepared in the state $|1\rangle$ (i.e., a $1 \rightarrow 0$ error). Here, i denotes the index of the qubit under consideration.

For Q_0 , we obtain $\kappa_0 = 0.2075 \pm 0.0174$ and $\chi_0 = 0.2149 \pm 0.0174$. For Q_1 , we find $\kappa_0 = 0.0634 \pm 0.0126$ and $\chi_0 = 0.1086 \pm 0.0126$, respectively. The average readout assignment fidelity $\mathcal{F}_{a_i}$ for each qubit is defined as

$$\mathcal{F}_{a_i} = \frac{1}{2}(2 - \kappa_i - \chi_i). \quad (\text{B2})$$

TABLE IV. Results for the ground-state energies of the four atomic systems. E^{DHF} , $E^{\text{CAS-Cl}}$, and E^{exp} correspond to the DHF, CAS-Cl, and experimental values of the ground-state energies, respectively.

System	E^{DHF} (Hartree)	$E^{\text{CAS-Cl}}$ (Hartree)	E^{exp} (Hartree)
Neutral ^7Li	-7.433513	-7.433516	-7.454386 ± 0.079829
Li-like ^{45}Sc	-477.8354	-477.8357	-476.9458 ± 4.9361
Li-like ^{141}Pr	-4056.999	-4057.000	-4065.379 ± 41.928
Li-like ^{209}Bi	-8551.218	-8551.219	-8569.309 ± 92.423

APPENDIX C: ENERGY AND HYPERFINE STRUCTURE CONSTANT VALUES

We list the ground-state energies and hyperfine structure constants results for all the four atomic systems in Tables IV and V, respectively. In Table V, we also included the results from spectroscopy experiments performed for the four atomic systems; neutral ^7Li atom [64], Li-like ^{45}Sc [65], Li-like ^{141}Pr [66], and Li-like ^{209}Bi [67]. These data serve the purpose of showing the importance of relativistic effects in atomic systems as their atomic number Z increases, and the absolute values of the quantities of interest in this work.

APPENDIX D: EFFECT OF NOISES ON THE GROUND-STATE ENERGY AND HYPERFINE STRUCTURE CONSTANTS

To check the effect of depolarizing noise and shot noise on the energies and hyperfine structure constants, we carry out numerical simulations in the presence of single-qubit depolarizing error channel $\mathcal{D}_\lambda$, whose action on an initial state ρ is

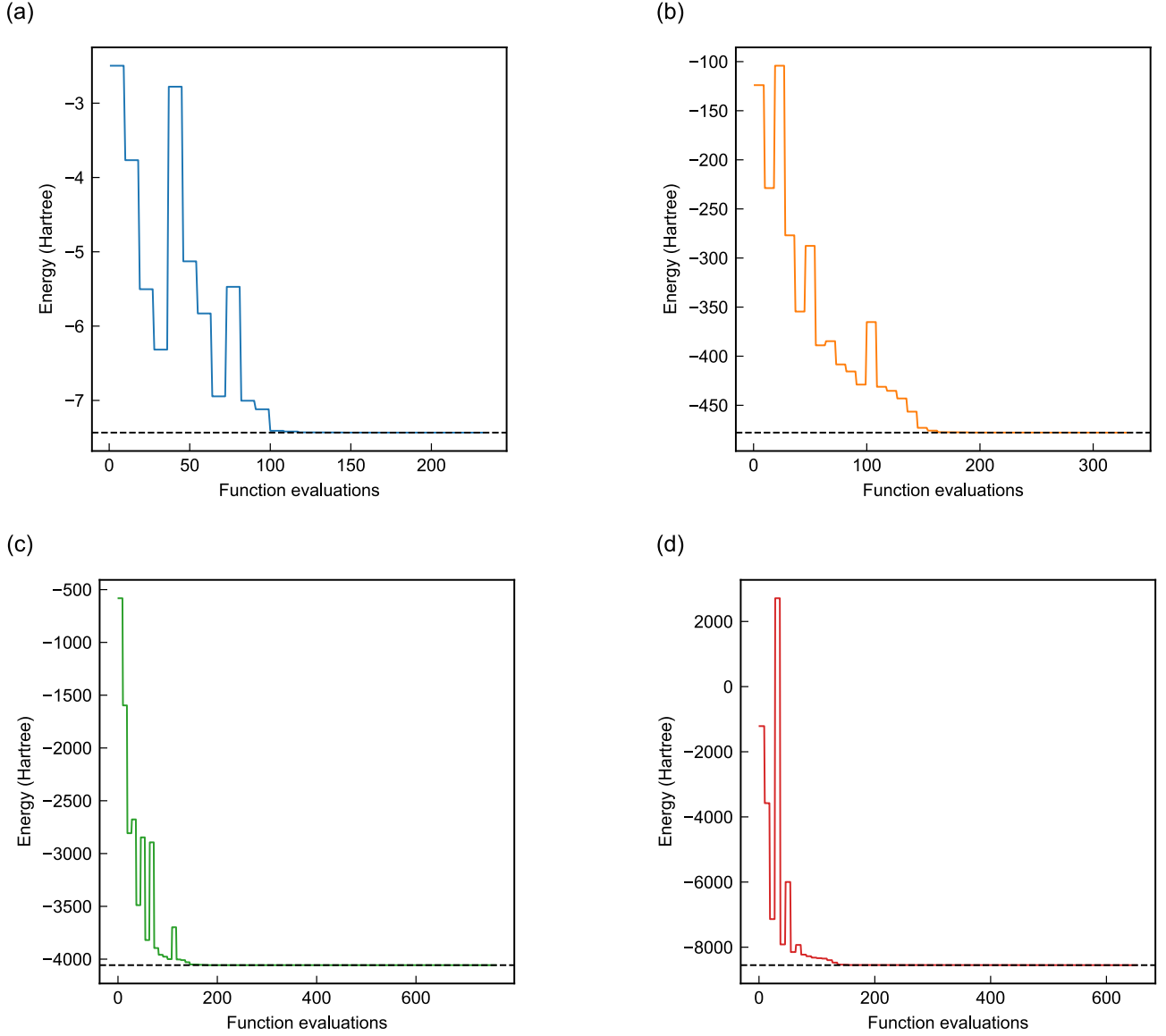


FIG. 4. VQE optimization for the ground-state energies. (a)–(d) Ground-state energy convergence for neutral ${}^7\text{Li}$, Li-like ${}^{45}\text{Sc}$, Li-like ${}^{141}\text{Pr}$, and Li-like ${}^{209}\text{Bi}$, respectively. The calculations are performed by using QULACS simulator. In each figure, the dashed horizontal line refers to the CAS-CI value of the ground-state energy.

given as

$$\mathcal{D}_\lambda(\rho) = (1 - \lambda)\rho + \frac{\lambda}{3}(X\rho X + Y\rho Y + Z\rho Z), \quad (\text{D1})$$

where λ is the probability of occurrence of an error. To capture the influences of the specified error sources, we assume that our quantum circuit is capable of generating the CAS-CI

TABLE V. Results for the ground-state hyperfine structure constants of the four atomic systems. $\mathcal{A}^{\text{DHF}}$, $\mathcal{A}^{\text{CAS-CI}}$, and $\mathcal{A}^{\text{exp}}$ correspond to the DHF, CAS-CI, and experimental values of the ground-state hyperfine structure constants, respectively. $\mathcal{A}^{\text{REX}}$ denotes the reference experimental results for the ground-state hyperfine structure constants, which are obtained through spectroscopic measurements of energy levels in atom and ions [64–67].

System	$\mathcal{A}^{\text{DHF}}$ (Hartree)	$\mathcal{A}^{\text{CAS-CI}}$ (Hartree)	$\mathcal{A}^{\text{exp}}$ (Hartree)	$\mathcal{A}^{\text{REX}}$ (Hartree)
Neutral ${}^7\text{Li}$	6.4816×10^{-8}	6.5871×10^{-8}	$(6.1128 \pm 3.0410) \times 10^{-8}$	$(6.1059 \pm 0.0000) \times 10^{-8}$
Li-like ${}^{45}\text{Sc}$	1.8884×10^{-4}	1.9022×10^{-4}	$(2.1680 \pm 0.1973) \times 10^{-4}$	$(2.2785 \pm 0.0294) \times 10^{-4}$
Li-like ${}^{141}\text{Pr}$	6.0338×10^{-3}	6.0525×10^{-3}	$(6.1561 \pm 0.5276) \times 10^{-3}$	$(7.2212 \pm 0.0441) \times 10^{-3}$
Li-like ${}^{209}\text{Bi}$	2.6634×10^{-2}	2.6704×10^{-2}	$(2.7239 \pm 0.2128) \times 10^{-2}$	$(3.0134 \pm 0.0955) \times 10^{-2}$

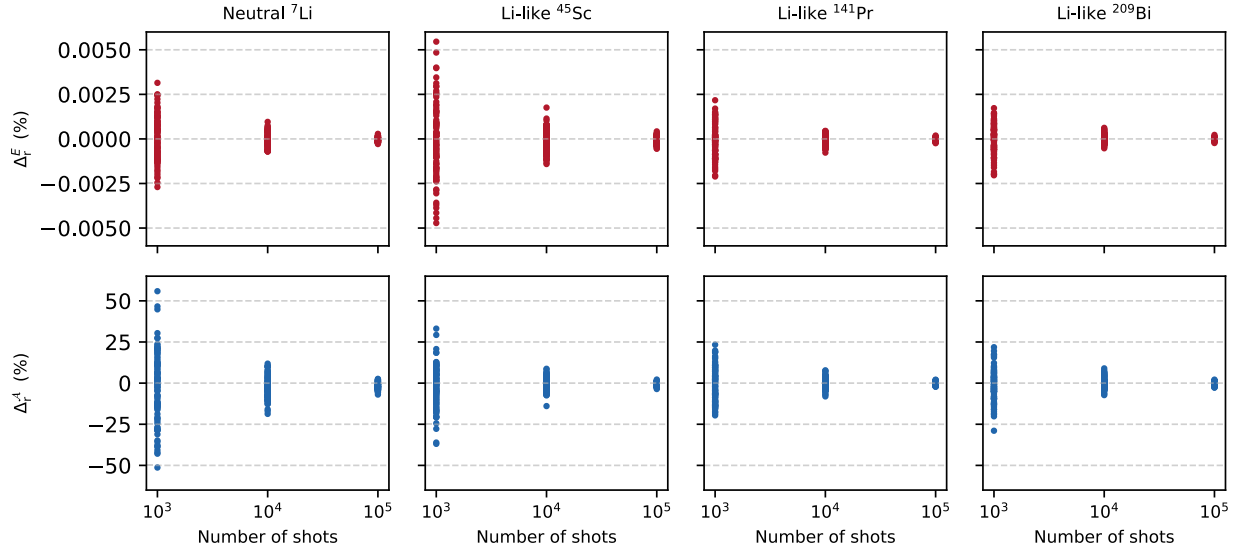


FIG. 5. Relative error from the reference values. Relative errors of the ground-state energies Δ_r^E and hyperfine structure constants Δ_r^A obtained from numerical simulations with Pauli error channels.

wave function and all quantum gates can be executed without noise. The depolarizing error channel is introduced before the measurement in which Pauli- X , Y , and Z gates are applied with the same probability $\lambda/3 = 0.001$. In the calculation of the expectation values we do not employ Pauli grouping, and the number of shots for the computation of each Pauli string is set to be 10^3 , 10^4 , and 10^5 . The simulations are performed 100 times for each computational condition. The

relative errors of ground-state energies and hyperfine structure constants are plotted in Fig. 5. We can see from Fig. 5 that the averaged relative errors of the ground-state energies are much smaller than that of ground-state hyperfine structure constants. Among the results of the hyperfine structure constants for all the four atomic systems (bottom row of Fig. 5), we can see that the standard deviation is largest for neutral ${}^7\text{Li}$. Both of these trends are in line with the experimental results.

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- [1] P. W. Shor, Polynomial-time algorithms for prime factorization and discrete logarithms on a quantum computer, *SIAM Rev.* **41**, 303 (1999).
 - [2] A. Montanaro, Quantum algorithms: An overview, *npj Quantum Inf.* **2**, 15023 (2016).
 - [3] J. Preskill, Quantum computing in the NISQ era and beyond, *Quantum* **2**, 79 (2018).
 - [4] 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, *Rev. Mod. Phys.* **94**, 015004 (2022).
 - [5] A. Callison and N. Chancellor, Hybrid quantum-classical algorithms in the noisy intermediate-scale quantum era and beyond, *Phys. Rev. A* **106**, 010101 (2022).
 - [6] F. Arute, K. Arya, R. Babbush, D. Bacon, J. C. Bardin, R. Barends, R. Biswas, S. Boixo, F. G. S. L. Brandao, D. A. Buell, B. Burkett, Y. Chen, Z. Chen, B. Chiaro, R. Collins, W. Courtney, A. Dunsworth, E. Farhi, B. Foxen, A. Fowler *et al.*, Quantum supremacy using a programmable superconducting processor, *Nature (London)* **574**, 505 (2019).
 - [7] H.-S. Zhong, H. Wang, Y.-H. Deng, M.-C. Chen, L.-C. Peng, Y.-H. Luo, J. Qin, D. Wu, X. Ding, Y. Hu, P. Hu, X.-Y. Yang, W.-J. Zhang, H. Li, Y. Li, X. Jiang, L. Gan, G. Yang, L. You, Z. Wang *et al.*, Quantum computational advantage using photons, *Science* **370**, 1460 (2020).
 - [8] Y. Wu, W.-S. Bao, S. Cao, F. Chen, M.-C. Chen, X. Chen, T.-H. Chung, H. Deng, Y. Du, D. Fan, M. Gong, Cheng Guo, Chu Guo, S. Guo, L. Han, L. Hong, H.-L. Huang, Y.-H. Huo, L. Li, N. Li *et al.*, Strong quantum computational advantage using a superconducting quantum processor, *Phys. Rev. Lett.* **127**, 180501 (2021).
 - [9] Q. Zhu, S. Cao, F. Chen, M.-C. Chen, X. Chen, T.-H. Chung, H. Deng, Y. Du, D. Fan, M. Gong, Cheng Guo, Chu Guo, S. Guo, L. Han, L. Hong, H.-L. Huang, Y.-H. Huo, L. Li, N. Li, S. Li *et al.*, Quantum computational advantage via 60-qubit 24-cycle random circuit sampling, *Sci. Bull.* **67**, 240 (2022).
 - [10] T. M. Graham, Y. Song, J. Scott, C. Poole, L. Phuttitarn, K. Jooya, P. Eichler, X. Jiang, A. Marra, B. Grinkemeyer, M. Kwon, M. Ebert, J. Cherek, M. T. Lichtman, M. Gillette, J. Gilbert, D. Bowman, T. Ballance, C. Campbell, E. D. Dahl *et al.*, Multi-qubit entanglement and algorithms on a neutral-atom quantum computer, *Nature (London)* **604**, 457 (2022).
 - [11] A. Peruzzo, J. McClean, P. Shadbolt, M.-H. Yung, X.-Q. Zhou, P. J. Love, A. Aspuru-Guzik, and J. L. O'Brien, A variational eigenvalue solver on a photonic quantum processor, *Nat. Commun.* **5**, 4213 (2014).
 - [12] A. Kandala, A. Mezzacapo, K. Temme, M. Takita, M. Brink, J. M. Chow, and J. M. Gambetta, Hardware-efficient variational quantum eigensolver for small molecules and quantum magnets, *Nature (London)* **549**, 242 (2017).

- [13] P. J. J. O'Malley, R. Babbush, I. D. Kivlichan, J. Romero, J. R. McClean, R. Barends, J. Kelly, P. Roushan, A. Tranter, N. Ding, B. Campbell, Y. Chen, Z. Chen, B. Chiaro, A. Dunsworth, A. G. Fowler, E. Jeffrey, E. Lucero, A. Megrant, J. Y. Mutus *et al.*, Scalable quantum simulation of molecular energies, *Phys. Rev. X* **6**, 031007 (2016).
- [14] A. Kandala, K. Temme, A. D. Corcoles, A. Mezzacapo, J. M. Chow, and J. M. Gambetta, Error mitigation extends the computational reach of a noisy quantum processor, *Nature (London)* **567**, 491 (2019).
- [15] P. J. Ollitrault, A. Kandala, C.-F. Chen, P. K. Barkoutsos, A. Mezzacapo, M. Pistoia, S. Sheldon, S. Woerner, J. M. Gambetta, and I. Tavernelli, Quantum equation of motion for computing molecular excitation energies on a noisy quantum processor, *Phys. Rev. Res.* **2**, 043140 (2020).
- [16] Y. Nam, J.-S. Chen, N. C. Pisenti, K. Wright, C. Delaney, D. Maslov, K. R. Brown, S. Allen, J. M. Amini, J. Apisdorf, K. M. Beck, A. Blinov, V. Chaplin, M. Chmielewski, C. Collins, S. Debnath, K. M. Hudek, A. M. Ducore, M. Keesan, S. M. Kreikemeier *et al.*, Ground-state energy estimation of the water molecule on a trapped-ion quantum computer, *npj Quantum Inf.* **6**, 33 (2020).
- [17] T. E. O'Brien, G. Anselmetti, F. Gkritis, V. E. Elfving, S. Polla, W. J. Huggins, O. Oumarou, K. Kechedzhi, D. Abanin, R. Acharya, I. Aleiner, R. Allen, T. I. Andersen, K. Anderson, M. Ansmann, F. Arute, K. Arya, A. Asfaw, J. Atalaya, J. C. Bardin *et al.*, Purification-based quantum error mitigation of pair-correlated electron simulations, *Nat. Phys.* **19**, 1787 (2023).
- [18] S. Guo, J. Sun, H. Qian, M. Gong, Y. Zhang, F. Chen, Y. Ye, Y. Wu, S. Cao, K. Liu, C. Zha, C. Ying, Q. Zhu, H.-L. Huang, Y. Zhao, S. Li, S. Wang, J. Yu, D. Fan, D. Wu *et al.*, Experimental quantum computational chemistry with optimised unitary coupled cluster ansatz, *Nat. Phys.* **20**, 1240 (2024).
- [19] Z. Huang and S. Kais, Entanglement as measure of electron-electron correlation in quantum chemistry calculations, *Chem. Phys. Lett.* **413**, 1 (2005).
- [20] B. K. Sahoo and B. P. Das, Relativistic normal coupled-cluster theory for accurate determination of electric dipole moments of atoms: First application to ^{199}Hg atom, *Phys. Rev. Lett.* **120**, 203001 (2018).
- [21] N. Yamanaka, B. K. Sahoo, N. Yoshinaga, T. Sato, K. Asahi, and B. P. Das, Probing exotic phenomena at the interface of nuclear and particle physics with the electric dipole moments of diamagnetic atoms: A unique window to hadronic and semi-leptonic CP violation, *Eur. Phys. J. A* **53**, 54 (2017).
- [22] S. G. Porsev, K. Beloy, and A. Derevianko, Precision determination of electroweak coupling from atomic parity violation and implications for particle physics, *Phys. Rev. Lett.* **102**, 181601 (2009).
- [23] V. A. Dzuba, J. C. Berengut, V. V. Flambaum, and B. Roberts, Revisiting parity nonconservation in cesium, *Phys. Rev. Lett.* **109**, 203003 (2012).
- [24] M. Kaur, R. Nakra, B. Arora, C.-B. Li, and B. K. Sahoo, Accurate determination of energy levels, hyperfine structure constants, lifetimes and dipole polarizabilities of triply ionized tin isotopes, *J. Phys. B: At. Mol. Opt. Phys.* **53**, 065002 (2020).
- [25] L. Essen and J. V. L. Parry, An atomic standard of frequency and time interval: A Caesium resonator, *Nature (London)* **176**, 280 (1955).
- [26] N. Ramsey, History of atomic clocks, *J. Res. Natl. Bur. Stand.* **88**, 301 (1983).
- [27] A. D. Ludlow, M. M. Boyd, J. Ye, E. Peik, and P. O. Schmidt, Optical atomic clocks, *Rev. Mod. Phys.* **87**, 637 (2015).
- [28] K. Beloy, M. I. Bodine, T. Bothwell, S. M. Brewer, S. L. Bromley, J.-S. Chen, J.-D. Deschênes, S. A. Diddams, R. J. Fasano, T. M. Fortier, Y. S. Hassan, D. B. Hume, D. Kedar, C. J. Kennedy, I. Khader, A. Koepke, D. R. Leibbrandt, H. Leopardi, A. D. Ludlow, W. F. McGrew *et al.*, Frequency ratio measurements at 18-digit accuracy using an optical clock network, *Nature (London)* **591**, 564 (2021).
- [29] D. Vrbanc, Exploring the Epoch of Reionization with the 21 cm line, Ph.D. thesis, Ludwig-Maximilians-Universität München (2019).
- [30] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, Observation of Bose-Einstein condensation in a dilute atomic vapor, *Science* **269**, 198 (1995).
- [31] K. B. Davis, M. O. Mewes, M. R. Andrews, N. J. van Druten, D. S. Durfee, D. M. Kurn, and W. Ketterle, Bose-Einstein condensation in a gas of sodium atoms, *Phys. Rev. Lett.* **75**, 3969 (1995).
- [32] B. K. Sahoo, R. K. Chaudhuri, B. P. Das, H. Merlitz, and D. Mukherjee, Application of relativistic coupled-cluster theory to heavy atomic systems with strongly interacting configurations: Hyperfine interactions in $^{207}\text{Pb}^+$, *Phys. Rev. A* **72**, 032507 (2005).
- [33] M. Abe, G. Gopakumar, M. Hada, B. P. Das, H. Tatewaki, and D. Mukherjee, Application of relativistic coupled-cluster theory to the effective electric field in YbF, *Phys. Rev. A* **90**, 022501 (2014).
- [34] K. Mitarai and K. Fujii, Constructing a virtual two-qubit gate by sampling single-qubit operations, *New J. Phys.* **23**, 023021 (2021).
- [35] A. P. Singh, K. Mitarai, Y. Suzuki, K. Heya, Y. Tabuchi, K. Fujii, and Y. Nakamura, Experimental demonstration of a high-fidelity virtual two-qubit gate, *Phys. Rev. Res.* **6**, 013235 (2024).
- [36] R. Hofstadter, H. R. Fichter, and J. A. McIntyre, High-energy electron scattering and nuclear structure determinations, *Phys. Rev.* **92**, 978 (1953).
- [37] T. P. Das, *Relativistic Quantum Mechanics of Electrons*, 1st ed. (Harper & Row, New York, 1973).
- [38] I. P. Grant, *Relativistic Quantum Theory of Atoms and Molecules: Theory and Computation*, 1st ed. (Springer, New York, 2007), p. 461.
- [39] B. K. Sahoo, Coupled-Cluster Theory of Parity Non-Conservation in Atoms, Ph.D. thesis, Indian Institute of Astrophysics (2006).
- [40] P. Jordan and W. E., Über das Paulische Äquivalenzverbot, *Z. Phys.* **47**, 631 (1928).
- [41] J. T. Seeley, M. J. Richard, and P. J. Love, The Bravyi-Kitaev transformation for quantum computation of electronic structure, *J. Chem. Phys.* **137**, 224109 (2012).
- [42] S. Bravyi, J. M. Gambetta, A. Mezzacapo, and K. Temme, Tapering off qubits to simulate fermionic Hamiltonians, *arXiv:1701.08213*.

- [43] N. J. Stone, Table of nuclear magnetic dipole and electric quadrupole moments, *At. Data Nucl. Data Tables* **90**, 75 (2005).
- [44] Y. Suzuki, Y. Kawase, Y. Masumura, Y. Hiraga, M. Nakadai, J. Chen, K. M. Nakanishi, K. Mitarai, R. Imai, S. Tamiya, T. Yamamoto, T. Yan, T. Kawakubo, Y. O. Nakagawa, Y. Ibe, Y. Zhang, H. Yamashita, H. Yoshimura, A. Hayashi, and K. Fujii, Qulacs: A fast and versatile quantum circuit simulator for research purpose, *Quantum* **5**, 559 (2021).
- [45] J. Nocedal and S. Wright, in *Numerical Optimization*, 2nd ed., Springer Series in Operations Research and Financial Engineering (Springer, New York, 2006).
- [46] P. Virtanen, R. Gommers, T. E. Oliphant, M. Haberland, T. Reddy, D. Cournapeau, E. Burovski, P. Peterson, W. Weckesser, J. Bright, S. J. van der Walt, M. Brett, J. Wilson, K. J. Millman, N. Mayorov, A. R. J. Nelson, E. Jones, R. Kern, E. Larson, C. J. Carey *et al.*, SciPy 1.0: Fundamental algorithms for scientific computing in Python, *Nat. Methods* **17**, 261 (2020).
- [47] K. G. Dyall, I. P. Grant, and S. Wilson, The Dirac equation in the algebraic approximation. II. Extended basis set calculations for hydrogenic atoms, *J. Phys. B: At. Mol. Phys.* **17**, 1201 (1984).
- [48] S. Battaglia, D. Bouet, A. Lecoq, S. Evangelisti, N. Faginas-Lago, T. Leininger, and A. Lombardi, Distributed Gaussian orbitals for molecular calculations: Application to simple systems, *Mol. Phys.* **118**, 1615646 (2020).
- [49] S. Huzinaga, Basis sets for molecular calculations, *Comput. Phys. Rep.* **2**, 281 (1985).
- [50] J. Koch, T. M. Yu, J. Gambetta, A. A. Houck, D. I. Schuster, J. Majer, A. Blais, M. H. Devoret, S. M. Girvin, and R. J. Schoelkopf, Charge-insensitive qubit design derived from the cooper pair box, *Phys. Rev. A* **76**, 042319 (2007).
- [51] S. Tamate, Y. Tabuchi, L. Szikszai, K. Kusuyama, K. Zuo, Z. Yan, A. Badrutdinov, Y. Hishida, W. Qiu, H. Terai, G. Fujii, K. Makise, N. Watanabe, H. Nakagawa, M. Fujino, M. Ukibe, W. Mizubayashi, K. Kikuchi, and Y. Nakamura, Scalable packaging design for large-scale superconducting quantum circuit, *Bull. Am. Phys. Soc.* **66**, C30.9 (2021), <https://meetings.aps.org/Meeting/MAR21/Session/C30.9>.
- [52] E. Knill, D. Leibfried, R. Reichle, J. Britton, R. B. Blakestad, J. D. Jost, C. Langer, R. Ozeri, S. Seidelin, and D. J. Wineland, Randomized benchmarking of quantum gates, *Phys. Rev. A* **77**, 012307 (2008).
- [53] J. Emerson, R. Alicki, and K. Życzkowski, Scalable noise estimation with random unitary operators, *J. Opt. B: Quantum Semiclass.* **7**, S347 (2005).
- [54] E. Magesan, J. M. Gambetta, and J. Emerson, Scalable and robust randomized benchmarking of quantum processes, *Phys. Rev. Lett.* **106**, 180504 (2011).
- [55] Q. D. Team, RealAmplitudes-Qiskit 0.31.0 documentation (2021), <https://docs.quantum.ibm.com/api/qiskit/qiskit.circuit.library.RealAmplitudes>.
- [56] D. C. McKay, C. J. Wood, S. Sheldon, J. M. Chow, and J. M. Gambetta, Efficient Z gates for quantum computing, *Phys. Rev. A* **96**, 022330 (2017).
- [57] E. Lucero, J. Kelly, R. C. Bialczak, M. Lenander, M. Mariantoni, M. Neeley, A. D. O'Connell, D. Sank, H. Wang, M. Weides, J. Wenner, T. Yamamoto, A. N. Cleland, and J. M. Martinis, Reduced phase error through optimized control of a superconducting qubit, *Phys. Rev. A* **82**, 042339 (2010).
- [58] C. Rigetti and M. Devoret, Fully microwave-tunable universal gates in superconducting qubits with linear couplings and fixed transition frequencies, *Phys. Rev. B* **81**, 134507 (2010).
- [59] S. Sheldon, E. Magesan, J. M. Chow, and J. M. Gambetta, Procedure for systematically tuning up cross-talk in the cross-resonance gate, *Phys. Rev. A* **93**, 060302(R) (2016).
- [60] M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information: 10th Anniversary Edition* (Cambridge University Press, Cambridge, England, 2010).
- [61] M. R. Geller and M. Sun, Toward efficient correction of multiqubit measurement errors: Pair correlation method, *Quantum Sci. Technol.* **6**, 025009 (2021).
- [62] P. D. Nation, H. Kang, N. Sundaresan, and J. M. Gambetta, Scalable mitigation of measurement errors on quantum computers, *PRX Quantum* **2**, 040326 (2021).
- [63] S. Bravyi, S. Sheldon, A. Kandala, D. C. McKay, and J. M. Gambetta, Mitigating measurement errors in multiqubit experiments, *Phys. Rev. A* **103**, 042605 (2021).
- [64] A. Beckmann, K. D. Böklen, and D. Elke, Precision measurements of the nuclear magnetic dipole moments of ${}^6\text{Li}$, ${}^7\text{Li}$, ${}^{23}\text{Na}$, ${}^{39}\text{K}$, and ${}^{41}\text{K}$, *Z. Phys.* **270**, 173 (1974).
- [65] M. Lestinsky, E. Lindroth, D. A. Orlov, E. W. Schmidt, S. Schippers, S. Böhm, C. Brandau, F. Sprenger, A. S. Terekhov, A. Müller, and A. Wolf, Screened radiative corrections from hyperfine-split dielectronic resonances in lithiumlike scandium, *Phys. Rev. Lett.* **100**, 033001 (2008).
- [66] P. Beiersdorfer, E. Träbert, G. V. Brown, J. Clementson, D. B. Thorn, M. H. Chen, K. T. Cheng, and J. Sapirstein, Hyperfine splitting of the $2s_{1/2}$ and $2p_{1/2}$ levels in Li- and Be-like ions of ${}^{141}\text{Pb}$, *Phys. Rev. Lett.* **112**, 233003 (2014).
- [67] P. Beiersdorfer, A. L. Osterheld, J. H. Scofield, J. R. Crespo López-Urrutia, and K. Widmann, Measurement of QED and hyperfine splitting in the $2s_{1/2}$ - $2p_{3/2}$ X-Ray transition in Li-like ${}^{209}\text{Bi}^{80+}$, *Phys. Rev. Lett.* **80**, 3022 (1998).
- [68] QISKIT contributors, QISKIT: An open-source framework for quantum computing (2023), <https://doi.org/10.5281/zenodo.8190968>.