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Relativistic quantum chemistry on quantum computers

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The past few years have witnessed a remarkable interest in the application of quantum computing for solving problems in quantum chemistry more efficiently than classical computers allow. Very recently, proof-of-principle experimental realizations have been reported. However, so far only the nonrelativistic regime (i.e., the Schrödinger equation) has been explored, while it is well known that relativistic effects can be very important in chemistry. We present a quantum algorithm for relativistic computations of molecular energies. We show how to efficiently solve the eigenproblem of the Dirac-Coulomb Hamiltonian on a quantum computer and demonstrate the functionality of the proposed procedure by numerical simulations of computations of the spin-orbit splitting in the SbH molecule. Finally, we propose quantum circuits with three qubits and nine or ten controlled-NOT (CNOT) gates, which implement a proof-of-principle relativistic quantum chemical calculation for this molecule and might be suitable for an experimental realization.

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Quantum computing [1] is one of the fastest growing fields of computer science. Recent interest in this interdisciplinary field has been fostered by the prospects of solving certain types of problems more effectively than in the classical setting [2,3]. A prominent example is the integer factorization problem where quantum computing offers an exponential speedup over its classical counterpart [2]. However, it is not only cryptography that can benefit from quantum computers. As was first proposed by Feynman [4], quantum computers could in principle be used for *efficient* simulation of another quantum system. This idea, which employs mapping of the Hilbert space of a studied system onto the Hilbert space of a register of quantum bits (qubits), both of them being exponentially large, can in fact be adopted also in quantum chemistry.

Several papers using this idea and dealing with the interconnection of quantum chemistry and quantum computing have appeared in recent years. These cover calculations of thermal rate constants of chemical reactions [5], *nonrelativistic* energy calculations [6–9], quantum chemical dynamics [10], calculations of molecular properties [11], initial-state preparation [12,13], and also proof-of-principle experimental realizations [14–17]. An interested reader can find a comprehensive review in Ref. [18].

An efficient (polynomially scaling) algorithm for calculations of nonrelativistic molecular energies that employs the phase estimation algorithm (PEA) of Abrams and Lloyd [19] was proposed in the pioneering work by Aspuru-Guzik *et al.* [6]. When the ideas of measurement-based quantum computing are adopted [20], the phase estimation algorithm can be formulated in an iterative manner [iterative phase estimation (IPEA)] with only one readout qubit [8,9]. If the phase ϕ ($0 \leq \phi < 1$), which is directly related to the desired energy [9], is expressed in the binary form $\phi = 0.\phi_1\phi_2\dots$,

$\phi_i = \{0,1\}$, one bit of ϕ is measured on the readout qubit at each iteration step. The algorithm is iterated backward from the least significant bits of ϕ to the most significant ones, where the k th iteration is shown in Fig. 1. Not to confuse the reader, \hat{H} in the exponential denotes the Hamiltonian operator, whereas H (in a box) denotes the standard single-qubit Hadamard gate. $|\psi_{\text{system}}\rangle$ represents the part of a quantum register that encodes the wave function of a studied system, R_z is a z -rotation gate whose angle ω_k depends on the results of the previously measured bits [8,9], and parameter τ ensures that $0 \leq \phi < 1$. The PEA always needs an initial guess of the wave function corresponding to the desired energy. This can be either the result of some approximate, polynomially scaling *ab initio* method [7,9], or, as originally proposed by Aspuru-Guzik *et al.* [6], the exact state or its approximation prepared by the adiabatic state preparation (ASP) method.

It is a well-known fact that an accurate description of molecules with heavy elements requires adequate treatment of the relativistic effects [21]. The most rigorous approach [besides quantum electrodynamics (QED), which is presently not feasible for quantum chemical purposes] is the four-component (4c) no-pair formalism. Our work is based on the 4c electronic Dirac-Coulomb Hamiltonian (DCH) in the form

$$\hat{H} = \sum_{i=1}^N [c(\alpha_i \cdot \mathbf{p}_i) + \beta'_i mc^2 - \phi_{\text{nuc}}] + \sum_{i < j} \frac{1}{r_{ij}} + V_{NN}. \quad (1)$$

Dirac matrices appearing in the one-electron part are defined as

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}, \quad \beta' = \beta - I_4, \quad (2)$$

the former in terms of the Pauli spin matrices σ . The DCH is known to cover the major part of the spin-orbit interaction and also scalar relativistic effects. Using this type of Hamiltonian represents no loss of generality for our purposes, since a transition to the Dirac-Coulomb-Breit Hamiltonian [22]

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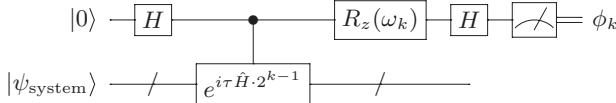


FIG. 1. The k th iteration of the iterative phase estimation algorithm (IPEA). The feedback angle ω_k depends on the previously measured bits.

and the inclusion of the corresponding integrals requires a classically polynomial effort.

We also adopt the no-pair approximation (NPA), widely used in relativistic quantum chemistry [22], in which the N -particle basis of Slater determinants is constructed from positive-energy bispinors only. For a more detailed discussion about the DCH and approximations employed in relativistic quantum chemistry, see the Supplemental Material [23].

The use of a 4c relativistic formalism brings in three major computational difficulties compared to the nonrelativistic case: (1) working with 4c orbitals (bispinors), (2) complex algebra when molecular symmetry is low, and (3) rather large Hamiltonian matrix eigenvalue problems [due to larger mixing of states than in the nonrelativistic (NR) case]. The central objective of this Rapid Communication is to address these problems with regard to an application of a quantum computer and the extension of the quantum full configuration interaction (qFCI) method to the relativistic regime.

We will start the description of the algorithm with a mapping of the relativistic quantum chemical wave function onto a quantum register. The simplest (scalable) NR approach, the direct mapping (DM) [6], assigns each spin orbital one qubit ($|0\rangle$ = unoccupied, $|1\rangle$ = occupied). The relativistic case is similar due to the NPA. Moreover, because of the time-reversal symmetry of the Dirac equation, bispinors occur in degenerate Kramers pairs [22] denoted A and B (in analogy to α and β spins in NR treatments) and the relativistic DM thus corresponds to one qubit for bispinor A and one for B . The 4c character of molecular bispinors therefore does not complicate the approach substantially [note that as in the NR case, the Hartree-Fock (HF) calculation is done on a classical computer and only the exponentially scaling FCI on a quantum one].

The DM is known to be not optimal as it maps the whole Fock space of the system on the Hilbert space of qubits. For this reason, compact mappings from a subspace of fixed-electron-number and spin- or symmetry-adapted wave functions have been proposed [6,7]. However, to the best of our knowledge, general factorization schemes [i.e., algorithms to systematically generate a quantum circuit implementing $\exp(i\tau \hat{H})$] for these mappings have not yet been discovered. In the relativistic case (within NPA), the most convenient compact mapping is based on a subspace of symmetry-adapted functions employing the double-group symmetry.

Assuming the NPA and the empty Dirac picture, the relativistic Hamiltonian has the same second quantized structure as the NR one:

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_s a_r. \quad (3)$$

Notice that (3) represents the spin orbital form of the Hamiltonian which indeed does not assume the time-reversal

symmetry. h_{pq} and g_{pqrs} denote one- and two-electron integrals that are in contrast to the NR ones in general complex. This is in fact not difficult for a quantum computer, since our working environment is a complex vector space of qubits anyway and we do the exponential of a complex matrix even if the Hamiltonian is real (see Fig. 1). After the decomposition of the unitary propagator $[\exp(i\tau \hat{H})]$ to elementary quantum gates (in the case of DM) using the Jordan-Wigner transform [24], one can see that complex molecular integrals require twice as many gates compared to real ones [8], while complex arithmetic on a classical computer requires four times more operations.

The last of the aforementioned difficulties of the 4c formalism is the size of a Hamiltonian matrix eigenvalue problem. This can be inferred from the observation that a significant larger number of integrals in the Hamiltonian (3) will be non-zero due to the lowering of symmetry induced by spin-orbit interaction. The loss of spin symmetry can to some extent be alleviated by consideration of time reversal symmetry. In the Kramers-restricted (KR) approach employed in this work the second-quantized Hamiltonian (3) is expressed in terms of a basis of Kramers pairs, that is, orbital pairs ϕ and $\bar{\phi}$ connected by time reversal. Determinants may be characterized by a pseudo-quantum number $M_K = 1/2(N_A - N_B)$, reflecting the different number of unbarred N_A and barred N_B bispinors. In the non-relativistic limit the Kramers pairs can be aligned with spin partners such that M_K becomes identical to M_S . However, contrary to the NR limit, determinants with different M_K can mix in the presence of spin-orbit interaction. It can be shown (see the Supplemental Material [23]) that the ratio between dimensions of relativistic and nonrelativistic Hamiltonian matrices scales as $O(m^{1/2})$ in the number of molecular orbitals (bispinors).

When employing the DM on a quantum computer, this problem does not occur, since the Hamiltonian (3) then implicitly works with all possible values of M_K . The scaling of the relativistic qFCI method is therefore the same as the NR one, namely, $O(m^5)$ [8,14], where m is the number of molecular orbitals (bispinors).

For numerical tests of the algorithm, we have chosen the SbH molecule whose nonrelativistic ground state ${}^3\Sigma^-$ splits due to spin-orbit effects into $X0^+$ and $A1$. In the approximate λ_ω notation, these states are dominated by $\sigma_{1/2}^2 \pi_{1/2}^2 \pi_{3/2}^0$ and $\sigma_{1/2}^2 \pi_{1/2}^1 \pi_{3/2}^1$ configurations. The splitting is truly of a “molecular nature” as it disappears for dissociated atoms. Its experimental value is $\Delta E_{SO} = 654.97 \text{ cm}^{-1}$ [25].

In all our simulations, we used the Dyall triple-zeta + valence correlating functions, a total of $28s21p15d1f$ for Sb and cc-pVTZ [from the Environmental Molecular Sciences Laboratory (EMSL) basis set library] for H. We, of course, could not manage to simulate the FCI calculations with all electrons in such a large basis. We instead simulated general active-space (GAS) KRCI computations [26] with the occupation constraints shown in Table I giving rise to CI spaces of approximately 29 500 determinants. For a balanced description of both states, we optimized the spinors, taking an average energy expression (two electrons in two Kramers pairs $\pi_{1/2}, \pi_{3/2}$). We worked solely with a compact mapping employing the double-group symmetry (C_{2v}^*), and the exponential of a Hamiltonian was simulated as an n -qubit gate (similarly as in Refs. [6,7,9]). We used the DIRAC program [27]

TABLE I. GAS and occupation constraints for SbH $X0^+$ and A1 state CI calculations. The minimum and maximum number of electrons are accumulated values, applied to this and all preceding GA spaces.

| GAS | Minimum No. of electrons | Maximum No. of electrons | Shell types |
|-----|--------------------------|--------------------------|--|
| I | 0 | 4 | $\sigma_{1/2}, \pi_{1/2}$ |
| II | 2 | 4 | $\pi_{3/2}$ |
| III | 4 | 4 | $\sigma_{1/2}^*, 43$ virtual Kramers pairs |

for calculations of Hamiltonian matrices. The nuclear potential ϕ_{nuc} was generated by finite nuclei using Gaussian charge distributions with exponents chosen according to Ref. [28]. Simulations of qFCI computations were performed with our own C++ code [9]. We ran 17 iterations of the IPEA with the difference between maximum and minimum expected energies equal to $0.5E_H$. We also did not count the least significant binary digit of the phase ϕ to the total success probability (for more details of the algorithm, we refer the reader to our preceding paper [9]). This procedure corresponds to a final energy precision $\approx 3.81 \times 10^{-6} E_H$.

Simulated potential energy curves of both states are shown in Fig. 2. Based on our KRCI setup we obtain a vertical ΔE_{SO} of 617 cm^{-1} . Success probabilities (SPs) of the algorithm with HF initial guesses ($\sigma_{1/2}^2 \pi_{1/2}^2 \pi_{3/2}^0$ for the $X0^+$ state and $\sigma_{1/2}^2 \pi_{1/2}^1 \pi_{3/2}^1$ for A1 one) are presented in Fig. 3. They correspond to the IPEA with the second part of a quantum register (encoding the relativistic quantum chemical wave function) maintained during all iterations (in Ref. [9] denoted as version A). In this case, SPs always lie in the interval $|\langle \psi_{\text{init}} | \psi_{\text{exact}} \rangle|^2 \cdot (0.81, 1)$ [9]. Ground-state SPs confirm that, due to near degeneracies caused by the spin-orbit coupling, relativistic states often have a stronger multireference character than nonrelativistic ones. The upper bound of the SP is less than 0.7 even for the equilibrium geometry, and HF initial guesses can in fact be safely used (SP > 0.5 , amplification of SP by repetitions) only up to $4.8a_0$. The SPs of the A1 state are higher and HF initial guesses can be in a noise-free environment used up to $6a_0$.

The difficulty connected with a low success probability for the $X0^+$ state at longer distances can be overcome by

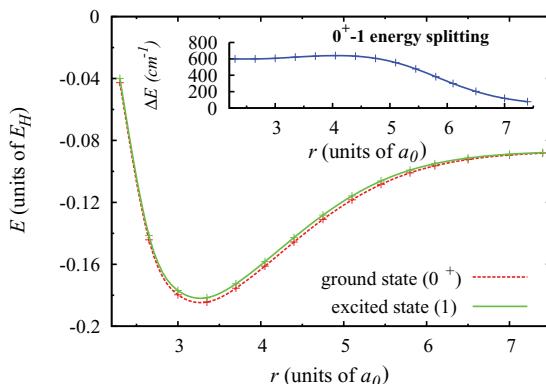


FIG. 2. (Color online) Simulated potential energy curves of ground (0^+) and excited (1) states of SbH, and spin-orbit energy splitting. Absolute energies are shifted by $6481 E_H$.

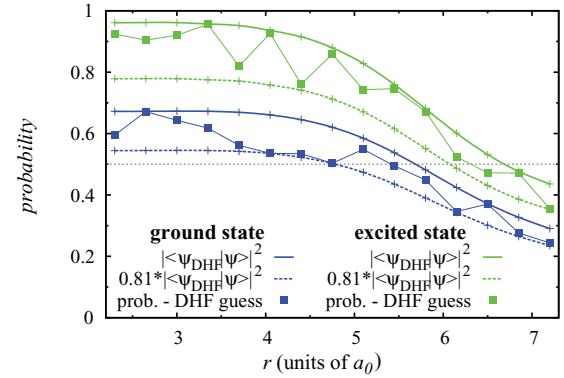


FIG. 3. (Color online) SbH ground- (0^+) and excited- (1) state qFCI success probabilities (SPs) corresponding to HF initial guesses.

the ASP method [6]. In this approach, one slowly varies the Hamiltonian of a quantum register, starting with a trivial one with a known eigenstate and ending with the final exact one in the following simple way:

$$\hat{H} = (1 - s)\hat{H}_{\text{init}} + s\hat{H}_{\text{exact}}, \quad s : 0 \rightarrow 1. \quad (4)$$

If the change is slow enough (depending on the gap between the ground and the first excited state), the register remains in its ground state according to the adiabatic theorem [29]. In our relativistic example, analogously to the nonrelativistic one [6], \hat{H}_{init} is defined to have all matrix elements equal to zero, except H_{11} , which is equal to the (Dirac-)HF energy.

We simulated $X0^+$ qFCI computations with adiabatically prepared states for different internuclear distances; the results are shown in Fig. 4. In this case, for computational reasons, we employed the complete active-space (CAS) KRCI method with a CAS composed of two electrons in the highest occupied ($\pi_{1/2}$) and 45 lowest unoccupied Kramers pairs (corresponding to 2116 determinants). It can be seen that for $t = 1000\hbar E_H^{-1}$, the upper bound of the SP goes safely to unity even for $r = 8a_0$.

Recently, two papers presented the physical implementations of *nonrelativistic* qFCI computations on optical [14] and NMR [15] quantum computers. Correspondingly, we would like to propose two candidates for the *relativistic* computations

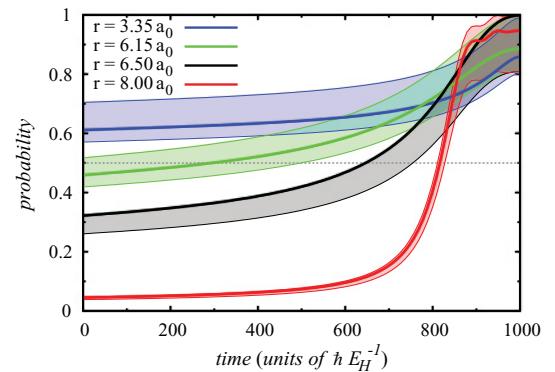


FIG. 4. (Color online) Adiabatic state preparation (ASP) of the SbH ground state (0^+) for different internuclear distances. The solid lines correspond to qFCI success probabilities, and the $|\langle \psi_{\text{ASP}} | \psi_{\text{exact}} \rangle|^2 \cdot (0.81, 1)$ interval is colored (shaded). $1000\hbar E_H^{-1} \approx 10^{-14} \text{ s}$.

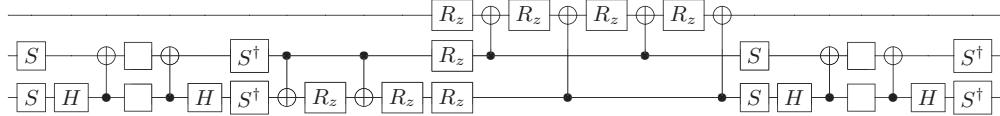


FIG. 5. Scheme of a circuit corresponding to CAS(4,3) calculations on SbH. The empty squares represent generic single-qubit gates. R_z gates are without angle specification. For derivation, details, and all the parameters, see the Supplemental Material [23].

on real quantum computers. Our proposals represent “digital (circuit-based) quantum simulations” (DQSs) as defined by Buluta and Nori [30]. Conceptually different are “analog quantum simulations” (AQSs), where the evolution of a studied quantum system is mapped to be simulated onto the controlled evolution of the quantum simulator. Recently, Gerritsma *et al.* used this approach for the proof-of-principle simulation of a one-dimensional Dirac equation with a single trapped ion [31].

Both of our examples represent calculations of SbH $^3\Sigma^-$ ground-state spin-orbit splitting. Since one has to employ rather large basis sets (triple- ζ quality) to get a meaningful result, they again are not true FCI calculations, but FCI calculations in a limited CAS. The first one corresponds to a CAS composed of two electrons in the highest occupied ($\pi_{1/2}$) and the lowest unoccupied ($\pi_{3/2}$) Kramers pairs [CAS(2,2)]. After the factorization of a Hamiltonian according to the Ω quantum number and taking into account only one of the two degenerate z projections of Ω (for $\Omega = 1$), the size of the CI space is 2 for the ground state (0^+) and 1 for the excited state (1). The excited state is therefore trivial and the calculation of the ground state is in fact a complete analog of the already mentioned NR computations [14,15], because it needs just one qubit for the wave function (two in total). The controlled single-qubit gate can be decomposed using two controlled NOT (CNOT) gates [1]. Calculations with this active space yield an $\Delta E_{\text{SO}} = 509 \text{ cm}^{-1}$ computed at the experimental equilibrium bond distance of $3.255a_0$.

The second example represents a three-qubit experiment (two qubits for the wave function) and employs a CAS composed of four electrons in the $\sigma_{1/2}\pi_{1/2}\pi_{3/2}$ Kramers pairs [CAS(4,3)]. It gives a better value of ΔE_{SO} (518 cm^{-1}) than CAS(2,3) composed of two electrons in the $\pi_{1/2}\pi_{3/2}\sigma_{1/2}^*$ Kramers pairs. After Ω factorization, the CI space of the excited state is three dimensional and that of the ground state is five dimensional. Fortunately, near the equilibrium bond distance, the Hamiltonian matrix of the ground state is to a very good approximation block diagonal (ground-state energy difference of the order μE_H), coupling only three configurations ($\sigma_{1/2}^2\pi_{1/2}^2\pi_{3/2}^0$, $\sigma_{1/2}^2\pi_{1/2}^0\pi_{3/2}^2$, and $\sigma_{1/2}^0\pi_{1/2}^2\pi_{3/2}^2$).

If we take into account only these configurations, both states can be encoded by two qubits.

We used the *quantum Shannon decomposition* (QSD) technique [32] and decomposed the controlled action of a two-qubit $\exp(i\tau \hat{H})$. QSD is known to decompose a generic three-qubit gate with the least number of CNOT gates (20). A minimal number of CNOT gates is very important as their implementations are orders of magnitude more difficult. We found a circuit with nine CNOT gates which is not universal in the sense that the decomposition must be done for all powers of U individually, or a universal ten-CNOT circuit. The structure of this circuit is shown in Fig. 5. The controlled action of the n th power of U is simply done by multiplication of the angles of R_z rotations by n . Details of the decomposition and also all parameters important for a possible experimental realization which correspond to the calculations at an internuclear distance $3.255a_0$ can be found in the Supplemental Material [23]. The proposed experiments are undoubtedly a challenge for different realizations of quantum computation. We regard experimental verification of the usage of HF initial guesses in a realistic noisy environment and also the performance of both versions of IPEA (A and B) proposed in Ref. [9] as very interesting.

In this Rapid Communication, we have presented a quantum algorithm for 4c relativistic FCI energy computations. This algorithm not only achieves an exponential speedup over its classical counterpart, but also has the same cost (in terms of scaling) as its NR analog. We have proved its functionality by numerical simulations of calculations of the spin-orbit splitting in SbH. We have also proposed and designed small-scale experimental realizations of relativistic qFCI computations. Our algorithm can be used as a standalone procedure or as a subroutine of a property algorithm of Kassal *et al.* [11], e.g., for calculations of NMR properties.

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