Exact closed-form expressions for unitary spin-adapted fermionic singlet double excitation operators

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We derive exact closed-form expressions for the matrix exponential of the anti-Hermitian spin-adapted singlet double excitation fermionic operators. These expressions enable the efficient implementation of such operators within unitary product state frameworks targeting conventional hardware, and allow for the implementation of ansätze that guarantee convergence to specific spin symmetries. Moreover, these exact closed-form expressions might also lay the groundwork for constructing spin-adapted circuits for quantum devices.

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I. INTRODUCTION

With the advent of quantum computing for the use in computational quantum chemistry, the interest in unitary parameterizations for electronic wave functions has risen. Among these parameterizations are the hardware-efficient ansätze[1], qubit ansätze[2,3], qubit-excitation-based ansätze[4–7] and fermionic excitation ansätze[5,7–12]. The fermionic excitation ansätze are among the most chemically motivated ones, since they conserve the number of α and β electrons, ensure the anti-symmetry of the fermionic wave function, and produce an eigenfunction of the z-component of the total spin $\hat{S}_z$. These ansätze are based on generic fermionic excitation operators,

$$\hat{T}^{a_\sigma}_{i_\sigma} = \hat{a}^\dagger_{a_\sigma}\hat{a}_{i_\sigma} \tag{1}$$

$$\hat{T}^{a_\sigma b_\tau}_{i_\sigma j_\tau} = \hat{a}^\dagger_{a_\sigma}\hat{a}^\dagger_{b_\tau}\hat{a}_{j_\tau}\hat{a}_{i_\sigma} \tag{2}$$

$$... \tag{3}$$

with the indices i, j, a, b referring to spatial orbital indices, and σ, τ to the electron spin. Throughout the work, it is assumed that $i, j < a, b$. The anti-Hermitian form of the fermionic operator is given as

$$\hat{G}_J = \hat{T}_J - \hat{T}^\dagger_J \tag{4}$$

with J being a compound index for the indices used in Eqs. (1)–(3). So, for instance $\hat{G}^{a\sigma}_{i\sigma} = \hat{T}^{a_\sigma}_{i_\sigma} - \hat{T}^{a_\sigma\dagger}_{i_\sigma}$. The anti-Hermitian form of the fermionic excitation operators gives rise to a unitary parameterization through a matrix exponentiation,

$$\hat{U}(\theta_J) = \exp\left(\theta_J \hat{G}_J\right) \tag{5}$$

where θ_J is a free real parameter. This anti-Hermitian form in Eq. (4) fulfills the polynomial relation,

$$\hat{G}^3_J = -\hat{G}_J \tag{6}$$

this relationship can be used to write the matrix exponential $\exp\left(\theta\hat{G}_J\right)$ in a closed form,

$$\exp\left(\theta\hat{G}_J\right) = \hat{I} + \hat{G}_J \sin(\theta) + \hat{G}^2_J(1 - \cos(\theta)) \tag{7}$$

The identity in Eq. (7) has been used in previous works[13–17] as well as in an alternative formulation that performs a transformation of a fermionic operator[18]. Utilizing the closed

form in Eq. (7) enables efficient implementation of the unitary form of these fermionic operators and is utilized in codes such as TenCirChem[19] and SlowQuant[20], as well as in recent works aiming for high-performance[21,22] using an equivalent form[14]. In addition, it also enables efficient derivatives through the adjoint differentiation method[23]. For fermionic operators, exact efficient quantum circuits are also known[5,7,12]. A shortcoming of using generic fermionic operators to parametrize the wave function is that they are not guaranteed to produce wave functions that are eigenfunctions of the total spin angular momentum operator $\hat{S}^2$. However, operators that produce wave functions that are eigenfunctions of $\hat{S}^2$ can be constructed and are called spin-adapted operators. Utilizing spin-adapted operators for the wave function parameterization is especially important for multi-state methods such as SS-VQE[24], MC-VQE[25], MORE-ADAPT-VQE[26], variance-VQE[27], and SA-VQE[28] since this allows targeting only states of a specific spin symmetry.

The spin-adapted (SA) singlet single excitation operator can be written as,

$$^{\mathrm{SA}}\hat{T}_{ai} = \frac{1}{\sqrt{2}}\hat{E}_{ai} \tag{8}$$

with $\hat{E}_{ai} = \hat{a}^\dagger_{a_\alpha}\hat{a}_{i_\alpha} + \hat{a}^\dagger_{a_\beta}\hat{a}_{i_\beta} \equiv (\hat{T}^{a_\alpha}_{i_\alpha} + \hat{T}^{a_\beta}_{i_\beta})$. The corresponding anti-Hermitian spin-adapted singlet single excitation operator $^{\mathrm{SA}}\hat{G}_{ai}$ takes the following form:

$$^{\mathrm{SA}}\hat{G}_{ai} = {}^{\mathrm{SA}}\hat{T}_{ai} - {}^{\mathrm{SA}}\hat{T}^\dagger_{ai} = \frac{1}{\sqrt{2}}\left(\hat{G}^{a_\alpha}_{i_\alpha} + \hat{G}^{a_\beta}_{i_\beta}\right) \tag{9}$$

Using $\left[\hat{G}^{a_\alpha}_{i_\alpha}, \hat{G}^{a_\beta}_{i_\beta}\right] = 0$, allows us to write the matrix exponential in the form,

$$\begin{aligned}
\exp\left(\theta\ {}^{\mathrm{SA}}\hat{G}_{ai}\right) &= \exp\left(\frac{\theta}{\sqrt{2}}\hat{G}^{a_\alpha}_{i_\alpha}\right)\exp\left(\frac{\theta}{\sqrt{2}}\hat{G}^{a_\beta}_{i_\beta}\right) &(10)\\
&= \left\{\hat{I} + \hat{G}^{a_\alpha}_{i_\alpha}\sin\left(\frac{\theta}{\sqrt{2}}\right) + \hat{G}^{a_\alpha 2}_{i_\alpha}\left(1-\cos\left(\frac{\theta}{\sqrt{2}}\right)\right)\right\}\\
&\quad\times\left\{\hat{I} + \hat{G}^{a_\beta}_{i_\beta}\sin\left(\frac{\theta}{\sqrt{2}}\right) + \hat{G}^{a_\beta 2}_{i_\beta}\left(1-\cos\left(\frac{\theta}{\sqrt{2}}\right)\right)\right\} &(11)
\end{aligned}$$

Due to the form of Eq. (11), the spin-adapted singlet single excitation operators can utilize known circuits from the fermionic single excitation operators[5] and lead to a parameter reduction compared to the generic form.

However, contrary to the spin-adapted anti-Hermitian singlet single fermionic excitation operators, the spin-adapted anti-Hermitian singlet double fermionic excitation operators do not decompose into commuting generic fermionic anti-Hermitian operators. Hence, a closed-form expression for the matrix exponential of the spin-adapted singlet double excitation

operators does not take a simple product form similar to the matrix exponential of the spin-adapted singlet single excitation operator in Eq. (11), and an expression for the matrix exponential of the spin-adapted singlet double excitation operators is unknown to date. In the following section, we present exact closed-form expressions for the spin-adapted singlet double fermionic excitation operators. While completing this work, we became aware of the work of Magoulas and Evangelista[29], who derived the closed-form expression for the matrix exponential of the anti- Hermitian form of spin-adapted singlet double fermionic excitations.

II. SPIN-ADAPTED FERMIONIC DOUBLES

The spin-adapted singlet double fermionic excitation operators take the form,[30–32]

$$ {}^{\mathrm{SA}}\hat{T}_{aibj} = \frac{1}{2\sqrt{(1+\delta_{ab})(1+\delta_{ij})}} \left(\hat{E}_{ai}\hat{E}_{bj} + \hat{E}_{aj}\hat{E}_{bi} \right) \tag{12} $$

$$ {}^{\mathrm{SA}}\hat{T}'_{aibj} = \frac{(1-\delta_{ab})(1-\delta_{ij})}{2\sqrt{3}} \left(\hat{E}_{ai}\hat{E}_{bj} - \hat{E}_{aj}\hat{E}_{bi} \right) \tag{13} $$

with Eq. (12) stemming from the intermediate singlet coupling to the singlet double excitation, and Eq. (13) from the intermediate triplet coupling to the singlet double excitation. The intermediate spin-couplings are between the pairs i, j and a, b, with both pairs needing to form an intermediate coupling (singlet or triplet). This gives five different cases, since $\hat{T}'_{aibj}$ is zero if any of the indices are equal,

$$ {}^{\mathrm{SA}}\hat{T}_{aiai} = \frac{1}{2}\hat{E}_{ai}\hat{E}_{ai} \tag{14} $$

$$ {}^{\mathrm{SA}}\hat{T}_{aiaj} = \frac{1}{\sqrt{2}}\hat{E}_{ai}\hat{E}_{aj} \tag{15} $$

$$ {}^{\mathrm{SA}}\hat{T}_{aibi} = \frac{1}{\sqrt{2}}\hat{E}_{ai}\hat{E}_{bi} \tag{16} $$

$$ {}^{\mathrm{SA}}\hat{T}_{aibj} = \frac{1}{2}\left(\hat{E}_{ai}\hat{E}_{bj} + \hat{E}_{aj}\hat{E}_{bi} \right) \tag{17} $$

$$ {}^{\mathrm{SA}}\hat{T}'_{aibj} = \frac{1}{2\sqrt{3}}\left(\hat{E}_{ai}\hat{E}_{bj} - \hat{E}_{aj}\hat{E}_{bi} \right) \tag{18} $$

Here, we implied that $a \neq b$ and $i \neq j$. In the following, we derive the closed form of the unitaries generated by the anti-Hermitian versions of Eqs. (14)–(18) .

A. Case ${}^{\mathrm{SA}}\hat{G}_{aiai}$

This case reduces to a fermionic double excitation operator since $\hat{E}_{ai}\hat{E}_{ai} = 2\hat{T}^{a_\beta a_\alpha}_{i_\beta i_\alpha}$, yielding the anti-Hermitian form of Eq. (14) as,

$$ {}^{\mathrm{SA}}\hat{G}_{aiai} = \hat{G}^{a_\alpha a_\beta}_{i_\alpha i_\beta} \tag{19}$$

This already has the known exact closed-form discussed above (Eq. (7)),

$$\exp\left(\theta\ {}^{\mathrm{SA}}\hat{G}_{aiai}\right) = \hat{I} + {}^{\mathrm{SA}}\hat{G}_{aiai}\sin(\theta) + {}^{\mathrm{SA}}\hat{G}^2_{aiai}(1-\cos(\theta)) \tag{20}$$

Thus, this specific case of spin-adapted singlet double excitations can also utilize known circuits for fermionic operators[5], and is utilized in ansätze using (spin-adapted) singles and pair-doubles[9–12]. For the remaining cases, Eqs. (15)–(18), no such reduction can be made.

B. Case ${}^{\mathrm{SA}}\hat{G}_{aiaj}$ and ${}^{\mathrm{SA}}\hat{G}_{aibi}$

These two cases are the anti-Hermitian versions of the spin-adapted fermionic double excitations operators in Eq. (15) and (16) where two indices match. They can be shown to share the following polynomial relation for powers of the excitation operator,

$$ {}^{\mathrm{SA}}\hat{G}^5_{aiaj} = A\ {}^{\mathrm{SA}}\hat{G}_{aiaj} + B\ {}^{\mathrm{SA}}\hat{G}^3_{aiaj} \tag{21}$$

with $A = -\frac{1}{2}$ and $B = -\frac{3}{2}$. The coefficients A and B were determined by minimization with SLSQP[33] using SciPy[34] together with SlowQuant[20]. SymPy[35] was used as a symbolic backend to verify the equation. Code that performs the minimization and verification can be found in the supplementary information. As the polynomial relation is identical for both ${}^{\mathrm{SA}}\hat{G}_{aiaj}$ and ${}^{\mathrm{SA}}\hat{G}_{aibi}$, the derivation of the closed-form expression will be made only considering ${}^{\mathrm{SA}}\hat{G}_{aiaj}$.

The exponential of an excitation operator can be expanded as

$$\exp\left(\theta\ {}^{\mathrm{SA}}\hat{G}_{aiaj}\right) = \hat{I} + \sum_{k=1}^{\infty}\frac{\theta^k}{k!}\ {}^{\mathrm{SA}}\hat{G}^k_{aiaj} \tag{22}$$

Given that Eq. (21) gives an expression for the fifth-order term as a combination of first and third-order terms, one can recast the matrix exponential in a polynomial form that truncates at the fourth power of ${}^{\mathrm{SA}}\hat{G}_{aiaj}$,

$$\exp\left(\theta\ {}^{\mathrm{SA}}\hat{G}_{aiaj}\right) = \hat{I} + \sum_{n=1}^{4} f_n(\theta)\ {}^{\mathrm{SA}}\hat{G}^n_{aiaj} \tag{23}$$

where the expansion coefficients f_n are polynomial functions of the parameter θ. The explicit expression of $f_n(\theta)$ must be determined and arises from the combination of the $\frac{\theta^k}{k!}$, A, and B factors. Using Eq. (21), let us consider the decomposition of the first and third functions in Eq. (23),

$$f_1(\theta) = \theta + \frac{\theta^5}{5!}A + \frac{\theta^7}{7!}AB + \frac{\theta^9}{9!}(A^2 + AB^2) + ... \tag{24}$$

$$f_3(\theta) = \frac{\theta^3}{3!} + \frac{\theta^5}{5!}B + \frac{\theta^7}{7!}(A + B^2) + \frac{\theta^9}{9!}(2AB + B^3) + ... \tag{25}$$

It can be seen that the coefficients of the $\frac{\theta^k}{k!}$ terms are

$$K_1^{[1]} = A, \quad K_2^{[1]} = AB, \quad K_3^{[1]} = A^2 + AB^2, \quad ... \tag{26}$$

$$K_1^{[3]} = B, \quad K_2^{[3]} = A + B^2, \quad K_3^{[3]} = 2AB + B^3, \quad ... \tag{27}$$

Here, the superscript in square parentheses indicates which function the coefficients are associated with, that is $K_n^{[1]}$ is associated with f_1 and $K_n^{[3]}$ is associated with f_3. By combining Eqs. (24)–(27), one obtains the following expressions for the functions,

$$f_1(\theta) = \theta + \sum_{n=1}^{\infty} \frac{\theta^{2n+3}}{(2n+3)!} K_n^{[1]} \tag{28}$$

$$f_3(\theta) = \frac{\theta^3}{3!} + \sum_{n=1}^{\infty} \frac{\theta^{2n+3}}{(2n+3)!} K_n^{[3]} \tag{29}$$

The coefficients in Eq. (26) and Eq. (27) can be seen to follow a recurrence relation,

$$K_n^{[1]} = AK_{n-1}^{[3]} \tag{30}$$

$$K_n^{[3]} = BK_{n-1}^{[3]} + K_{n-1}^{[1]} \tag{31}$$

With the initial condition $K_1^{[1]} = A$ and $K_1^{[3]} = B$. It can be noted that the recurrence relations are linear, and a closed-form solution can be found from the eigenvalues of the matrix equation form of the recurrence relations,

$$\begin{bmatrix} K_n^{[1]} \\ K_n^{[3]} \end{bmatrix} = \begin{bmatrix} 0 & A \\ 1 & B \end{bmatrix} \begin{bmatrix} K_{n-1}^{[1]} \\ K_{n-1}^{[3]} \end{bmatrix} \tag{32}$$

We obtain the following solution,

$$K_n^{[1]} = A(c_1\lambda_1^{n-1} + c_2\lambda_2^{n-1}) \tag{33}$$

$$K_n^{[3]} = c_1\lambda_1^n + c_2\lambda_2^n \tag{34}$$

with λ_1 and λ_2 being the eigenvalues of the coefficient matrix in Eq. (32), and c_1 and c_2 being coefficients determined from the initial condition, found by solving,

$$\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} A\lambda_1^0 & A\lambda_2^0 \\ \lambda_1^1 & \lambda_2^1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \rightarrow \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} A\lambda_1^0 & A\lambda_2^0 \\ \lambda_1^1 & \lambda_2^1 \end{bmatrix}^{-1} \begin{bmatrix} A \\ B \end{bmatrix} \tag{35}$$

The eigenvalues and coefficients are found to be $\lambda_1 = \frac{B-\sqrt{4A+B^2}}{2}$, $\lambda_2 = \frac{B+\sqrt{4A+B^2}}{2}$, $c_1 = \frac{1}{2} - \frac{B}{2\sqrt{4A+B^2}}$ and $c_2 = \frac{1}{2} + \frac{B}{2\sqrt{4A+B^2}}$. By inserting Eq. (33) into Eq. (28) and Eq. (34) into Eq. (29), the functions now take the following form,

$$f_1(\theta) = \theta + \sum_{n=1}^{\infty} \frac{\theta^{2n+3}}{(2n+3)!} \sum_{i=1}^{2} A c_i \lambda_i^{n-1} \tag{36}$$

$$f_3(\theta) = \frac{\theta^3}{3!} + \sum_{n=1}^{\infty} \frac{\theta^{2n+3}}{(2n+3)!} \sum_{i=1}^{2} c_i \lambda_i^{n} \tag{37}$$

One can identify these sums to take the closed form,

$$\sum_{n=1}^{\infty} \frac{\theta^{2n+3}}{(2n+3)!} \lambda_i^{n-m} = \frac{1}{\lambda_i^{3/2+m}} \left(\sinh\left(\theta\sqrt{\lambda_i}\right) - \theta\sqrt{\lambda_i} - \frac{\left(\theta\sqrt{\lambda_i}\right)^3}{3!} \right) \tag{38}$$

with $m = 1$ for the f_1 case and $m = 0$ for the f_3 case. Inserting Eq. (38) into Eqs. (36) and (37) yields,

$$f_1(\theta) = \theta + \sum_{i=1}^{2} \frac{A c_i}{\lambda_i^{5/2}} \left(\sinh\left(\theta\sqrt{\lambda_i}\right) - \theta\sqrt{\lambda_i} - \frac{\left(\theta\sqrt{\lambda_i}\right)^3}{3!} \right) \tag{39}$$

$$f_3(\theta) = \frac{\theta^3}{3!} + \sum_{i=1}^{2} \frac{c_i}{\lambda_i^{3/2}} \left(\sinh\left(\theta\sqrt{\lambda_i}\right) - \theta\sqrt{\lambda_i} - \frac{\left(\theta\sqrt{\lambda_i}\right)^3}{3!} \right) \tag{40}$$

Since the eigenvalues λ_i are all negative, one can use that $\sinh(\mathrm{i}x) = \mathrm{i}\sin(x)$. Further inserting $\lambda_1 = \frac{B-\sqrt{4A+B^2}}{2}$, $\lambda_2 = \frac{B+\sqrt{4A+B^2}}{2}$, $c_1 = \frac{1}{2} - \frac{B}{2\sqrt{4A+B^2}}$, $c_2 = \frac{1}{2} + \frac{B}{2\sqrt{4A+B^2}}$, $A = -\frac{1}{2}$, and $B = -\frac{3}{2}$, these expressions reduce to,

$$f_1(\theta) = \sum_{i=1}^{2} k_i^{(1)} \sin\left(\theta S_i\right) \tag{41}$$

$$f_3(\theta) = \sum_{i=1}^{2} k_i^{(3)} \sin\left(\theta S_i\right) \tag{42}$$

with real coefficients S_i and $k_i^{(n)}$ given in Table I. As it can be noted, all powers in θ have canceled out.

TABLE I. Values of coefficients in Eq. (45).

n	$k_n^{(1)}$	$k_n^{(3)}$	$k_n^{(2)}$	$k_n^{(4)}$	S_n
1	-1	-2	1	2	1
2	$2\sqrt{2}$	$2\sqrt{2}$	-4	-4	$\frac{\sqrt{2}}{2}$

Carrying out a similar derivation for the even terms in Eq. (23), we find

$$f_2(\theta) = \sum_{i=1}^{2} k_i^{(2)} (\cos(\theta S_i) - 1) \tag{43}$$

$$f_4(\theta) = \sum_{i=1}^{2} k_i^{(4)} (\cos(\theta S_i) - 1) \tag{44}$$

This yields the final closed-form expression for ${}^{\mathrm{SA}}\hat{G}_{aiaj}$ and ${}^{\mathrm{SA}}\hat{G}_{aibi}$,

$$\begin{aligned} \exp\left(\theta\ {}^{\mathrm{SA}}\hat{G}_{aiaj}\right) = \hat{I} &+ \sum_{n=1}^{2} \left(k_n^{(1)}\ {}^{\mathrm{SA}}\hat{G}_{aiaj} + k_n^{(3)}\ {}^{\mathrm{SA}}\hat{G}^3_{aiaj}\right) \sin(\theta S_n) \\ &+ \sum_{n=1}^{2} \left(k_n^{(2)}\ {}^{\mathrm{SA}}\hat{G}^2_{aiaj} + k_n^{(4)}\ {}^{\mathrm{SA}}\hat{G}^4_{aiaj}\right) (\cos(\theta S_n) - 1) \end{aligned} \tag{45}$$

An alternative route of deriving similar expressions has been proposed by Izmaylov et al.[36] Explicit expressions for the powers of ${}^{\mathrm{SA}}\hat{G}_{aiaj}$ can be found in the work of Magoulas and Evangelista.[29] The closed-form expression for $\exp\left(\theta\ {}^{\mathrm{SA}}\hat{G}_{aibi}\right)$ is identical to that of $\exp\left(\theta\ {}^{\mathrm{SA}}\hat{G}_{aiaj}\right)$ but with ${}^{\mathrm{SA}}\hat{G}_{aiaj}$ replaced by ${}^{\mathrm{SA}}\hat{G}_{aibi}$.

C. Case ${}^{\mathrm{SA}}\hat{G}_{aibj}$

Now we turn to the anti-Hermitian version of Eq. (17), i.e., the case with four unique indices coming from the intermediate singlet coupling. Here, the polynomial relation becomes

$${}^{\mathrm{SA}}\hat{G}^9_{aibj} = A\ {}^{\mathrm{SA}}\hat{G}_{aibj} + B\ {}^{\mathrm{SA}}\hat{G}^3_{aibj} + C\ {}^{\mathrm{SA}}\hat{G}^5_{aibj} + D\ {}^{\mathrm{SA}}\hat{G}^7_{aibj} \tag{46}$$

with $A = -\frac{1}{4}$, $B = -\frac{15}{8}$, $C = -\frac{35}{8}$ and $D = -\frac{15}{4}$. Following the same procedure as the previous cases gives the closed-form expression as

$$\begin{aligned}\exp\left(\theta\ {}^{\mathrm{SA}}\hat{G}_{aibj}\right) = \hat{I} + \sum_{n=1}^{4}\Big(&k_n^{(1)}\ {}^{\mathrm{SA}}\hat{G}_{aibj} + k_n^{(3)}\ {}^{\mathrm{SA}}\hat{G}^3_{aibj} \\ &+ k_n^{(5)}\ {}^{\mathrm{SA}}\hat{G}^5_{aibj} + k_n^{(7)}\ {}^{\mathrm{SA}}\hat{G}^7_{aibj}\Big)\sin\left(S_n\theta\right) \\ + \sum_{n=1}^{4}\Big(&k_n^{(2)}\ {}^{\mathrm{SA}}\hat{G}^2_{aibj} + k_n^{(4)}\ {}^{\mathrm{SA}}\hat{G}^4_{aibj} \\ &+ k_n^{(6)}\ {}^{\mathrm{SA}}\hat{G}^6_{aibj} + \ k_n^{(8)}\ {}^{\mathrm{SA}}\hat{G}^8_{aibj}\Big)\left(\cos\left(S_n\theta\right) - 1\right)\end{aligned} \tag{47}$$

with the coefficients given in Table II.

TABLE II. Values of coefficients in Eq. (47).

n	$k_n^{(1)}$	$k_n^{(3)}$	$k_n^{(5)}$	$k_n^{(7)}$	$k_n^{(2)}$	$k_n^{(4)}$	$k_n^{(6)}$	$k_n^{(8)}$	S_n
1	$\frac{2}{3}$	$\frac{13}{3}$	$\frac{22}{3}$	$\frac{8}{3}$	-$\frac{2}{3}$	$-\frac{13}{3}$	$-\frac{22}{3}$	$-\frac{8}{3}$	1
2	$-\frac{\sqrt{2}}{42}$	$-\frac{\sqrt{2}}{6}$	$-\frac{\sqrt{2}}{3}$	$-\frac{4\sqrt{2}}{21}$	$\frac{1}{42}$	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{4}{21}$	$\sqrt{2}$
3	$-\frac{8\sqrt{2}}{3}$	$-\frac{44\sqrt{2}}{3}$	$-\frac{52\sqrt{2}}{3}$	$-\frac{16\sqrt{2}}{3}$	$\frac{16}{3}$	$\frac{88}{3}$	$\frac{104}{3}$	$\frac{32}{3}$	$\frac{\sqrt{2}}{2}$
4	$\frac{128}{21}$	$\frac{64}{3}$	$\frac{64}{3}$	$\frac{128}{21}$	$-\frac{256}{21}$	$-\frac{128}{3}$	$-\frac{128}{3}$	$-\frac{256}{21}$	$\frac{1}{2}$

D. Case ${}^{\mathrm{SA}}\hat{G}'_{aibj}$

The spin-adapted double that comes from the intermediate triplet excitation with four unique indices, Eq. (18), has the polynomial relation,

$${}^{\mathrm{SA}}\hat{G}'^{11}_{aibj} = A\ {}^{\mathrm{SA}}\hat{G}'_{aibj} + B\ {}^{\mathrm{SA}}\hat{G}'^{3}_{aibj} + C\ {}^{\mathrm{SA}}\hat{G}'^{5}_{aibj} + D\ {}^{\mathrm{SA}}\hat{G}'^{7}_{aibj} + E\ {}^{\mathrm{SA}}\hat{G}'^{9}_{aibj} \tag{48}$$

with $A = -\frac{1}{48}$, $B = -\frac{113}{288}$, $C = -\frac{587}{288}$, $D = -\frac{613}{144}$ and $E = -\frac{11}{3}$. The closed-form expression is obtained using the same procedure as above,

$$\begin{aligned}\exp\left(\theta\ {}^{\mathrm{SA}}\hat{G}'_{aibj}\right) = \hat{I} + \sum_{n=1}^{5}\Big(&k_n^{(1)}\ {}^{\mathrm{SA}}\hat{G}'_{aibj} + k_n^{(3)}\ {}^{\mathrm{SA}}\hat{G}'^{3}_{aibj} + k_n^{(5)}\ {}^{\mathrm{SA}}\hat{G}'^{5}_{aibj} \\ &+ k_n^{(7)}\ {}^{\mathrm{SA}}\hat{G}'^{7}_{aibj} + k_n^{(9)}\ {}^{\mathrm{SA}}\hat{G}'^{9}_{aibj}\Big)\sin\left(S_n\theta\right) \\ + \sum_{n=1}^{5}\Big(&k_n^{(2)}\ {}^{\mathrm{SA}}\hat{G}'^{2}_{aibj} + k_n^{(4)}\ {}^{\mathrm{SA}}\hat{G}'^{4}_{aibj} + k_n^{(6)}\ {}^{\mathrm{SA}}\hat{G}'^{6}_{aibj} \\ &+ k_n^{(8)}\ {}^{\mathrm{SA}}\hat{G}'^{8}_{aibj} + k_n^{(10)}\ {}^{\mathrm{SA}}\hat{G}'^{10}_{aibj}\Big)\left(\cos\left(S_n\theta\right) - 1\right)\end{aligned} \tag{49}$$

with the coefficients given in Table III.

TABLE III. Values of coefficients in Eq. (49).

n	$k_n^{(1)}$	$k_n^{(3)}$	$k_n^{(5)}$	$k_n^{(7)}$	$k_n^{(9)}$	$k_n^{(2)}$	$k_n^{(4)}$	$k_n^{(6)}$	$k_n^{(8)}$	$k_n^{(10)}$	S_n
1	$\frac{\sqrt{2}}{1150}$	$\frac{11\sqrt{2}}{690}$	$\frac{133\sqrt{2}}{1725}$	$\frac{16\sqrt{2}}{115}$	$\frac{48\sqrt{2}}{575}$	$-\frac{1}{1150}$	$-\frac{11}{690}$	$-\frac{133}{1725}$	$-\frac{16}{115}$	$-\frac{48}{575}$	$\sqrt{2}$
2	$\frac{8\sqrt{2}}{5}$	$\frac{404\sqrt{2}}{15}$	$\frac{308\sqrt{2}}{3}$	$\frac{608\sqrt{2}}{5}$	$\frac{192\sqrt{2}}{5}$	$-\frac{16}{5}$	$-\frac{808}{15}$	$-\frac{616}{3}$	$-\frac{1216}{5}$	$-\frac{384}{5}$	$\frac{\sqrt{2}}{2}$
3	$-\frac{54\sqrt{3}}{25}$	$-\frac{171\sqrt{3}}{5}$	$-\frac{2718\sqrt{3}}{25}$	$-\frac{576\sqrt{3}}{5}$	$-\frac{864\sqrt{3}}{25}$	$\frac{162}{25}$	$\frac{513}{5}$	$\frac{8154}{25}$	$\frac{1728}{5}$	$\frac{2592}{25}$	$\frac{\sqrt{3}}{3}$
4	$-\frac{16\sqrt{3}}{75}$	$-\frac{56\sqrt{3}}{15}$	$-\frac{1192\sqrt{3}}{75}$	$-\frac{112\sqrt{3}}{5}$	$-\frac{192\sqrt{3}}{25}$	$\frac{32}{75}$	$\frac{112}{15}$	$\frac{2384}{75}$	$\frac{224}{5}$	$\frac{384}{25}$	$\frac{\sqrt{3}}{2}$
5	$\frac{432\sqrt{3}}{115}$	$\frac{2952\sqrt{3}}{115}$	$\frac{1368\sqrt{3}}{23}$	$\frac{6192\sqrt{3}}{115}$	$\frac{1728\sqrt{3}}{115}$	$-\frac{2592}{115}$	$-\frac{17712}{115}$	$-\frac{8208}{23}$	$-\frac{37152}{115}$	$-\frac{10368}{115}$	$\frac{\sqrt{3}}{6}$

E. Wave function parameter reduction

The most prominent application of our finding is for fermionic excitation methods, such as fUCC[17,37,38] and fermionic-ADAPT[8] that can now be efficiently implemented in state vector simulators in a spin-adapted formalism that guarantees convergence to the correct spin symmetry. As using spin-adapted operators is equivalent to being in the space of configuration state functions instead of the space of determinants, the number of parameters is reduced accordingly. As an example, we here consider parameterization of a factorized unitary coupled cluster expansion to singles and doubles.

TABLE IV. Number of variational parameters using factorized unitary coupled cluster singles doubles and spin-adapted factorized unitary coupled cluster singles doubles for different system sizes. The top row is referring to the size of the active space in the notation (number of electrons, number of spatial orbitals).

	(2,2)	(4,4)	(6,6)	(8,8)	(10,10)	(12,12)	(14,14)	(16,16)
fUCCSD	3	26	117	360	875	1818	3381	5792
SA-fUCCSD	2	14	54	152	350	702	1274	2144

In Table IV, the number of variational parameters for different sizes for fUCCSD and SA-fUCCSD expansions can be seen. The reduction of the number of parameters becomes about 60% for the larger systems and goes towards a 66% reduction asymptotically. Another direct benefit of using spin-adapted operators is that the number of operators to measure

in an iteration of a fermionic-ADAPT will also be reduced, equivalent to the parameter reduction for a fUCCSD.

F. State vector implementation performance

In order to quantify the performance enhancement of the closed form expressions, the analytical expressions found in Eqs. (45), (47), and, (49) have been implemented and compared to the matrix exponentiation from SciPy[34], specifically the `scipy.sparse.linalg.expm_multiply`[39,40] functionality. Both of the implementations avoid constructing the matrix form of the fermionic operators, and use SlowQuant[20] as a backend to calculate the matrix-free operator state vector product. The specific implementations can be seen in the supplementary information.

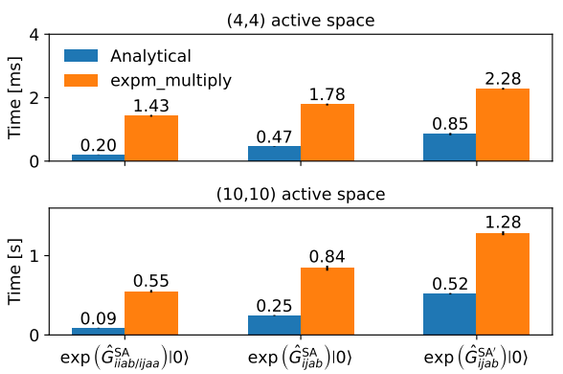

FIG. 1. The mean execution time of applying an operator to the state-vector, the black bars are +/- the standard deviation based on 100 runs. The test systems are a (4,4) active-space system and a (10,10) active-space system, where the state vector is initialised to all ones. The timings were performed on an 11th Gen Intel(R) Core(TM) i5-11600K 3.90GHz.

The execution speed of applying an anti-Hermitian spin-adapted excitation operator to a state vector has been tested for a small system, (4,4) active space, and a large system, (10,10) active space, using both the implementation based on the analytical expressions and an implementation based on SciPy. The timings can be seen in Fig. 1, with both system sizes showing the same trend. The analytical expressions give a speed-up of a factor of 6-7 for the operator utilizing Eq. (45), a factor of ∼3.5 for the operator utilizing Eq. (47), and, a speed-up of a factor of ∼2.5 for the operator utilizing Eq. (49), when compared to the im-

plementation using `expm_multiply`. Using the analytical expressions for the operators thus provides a significant speed-up when targeting classical hardware. Having the analytical expressions also allows for other types of implementations, like the tree-based implementation from Chen et al.[14]

III. CONCLUSION

In this work, exact closed-form expressions have been derived for unitary spin-adapted fermionic double excitation operators. We show that these closed form expressions can be utilized for an efficient implementation of these operators in unitary product state codes that target conventional hardware or state vector simulations for quantum emulation. Further, as spin-adapted operators strictly operate in the space of configuration state functions, an asymptotic parameter reduction of 66% can be obtained for the fUCCSD wave function. Moreover, our findings might also provide guidance about how to construct circuits for spin-adapted double excitation operators on quantum hardware. This will be part of future research.

IV. SUPPLEMENTARY MATERIAL

In the supplementary material we have provided code that determines the coefficients A, B, C, D, and, E for the Eqs. (21), (46), and, (48) in the file `determining_the_coefficients.ipynb`. Code that symbolically verifies the validity of Eqs. (21), (46), and, (48) in the file `checking_eq_21_46_48.ipynb`. An implementation of Eqs. (45), (47), and, (49), as well their corresponding `expm_multipliy` implementation, in the file `timings.ipynb`. At last the used version of SlowQuant is also provided.

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DATA AVAILABILITY

The data that supports the findings of this study are available within the article and its supplementary material.

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