Spin-adapted Matrix Product States and Operators

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Matrix product states (MPSs) and matrix product operators (MPOs) allow an alternative formulation of the density matrix renormalization group algorithm introduced by White. Here, we describe how non-abelian spin symmetry can be exploited in MPSs and MPOs by virtue of the Wigner–Eckart theorem at the example of the spin-adapted quantum chemical Hamiltonian operator.

I. INTRODUCTION

The incorporation of non-abelian symmetries into the density matrix renormalization group (DMRG) algorithm proposed by White is important enhancing both accuracy and computational efficiency. In the context of DMRG, total electronic spin symmetry, which is a non-abelian symmetry induced by the special unitary group SU(2), was first exploited in the interaction round a face (IRF) model by Sierra and Nishino for quantum spin chains. McCulloch and Gulácsı later presented a spin symmetric description in a more versatile way based on a quasi density matrix and studied a broad range of models, including the Fermi–Hubbard model. Their approach was subsequently adopted by Zgid and Nooijen and by Sharma and Chan to formulate a spin-adapted DMRG method for the quantum chemical Hamiltonian. Non-abelian symmetries beyond SU(2) were discussed, for instance, in Refs. and . Note, however, that these more general approaches preclude the application of sum rules for Clebsch–Gordan coefficients only available for SU(2). These sum rules involve the Wigner-6j and Wigner-9j symbols and result in increased numerical efficiency.

Since the emergence of matrix product based DMRG, SU(2) invariant matrix product states (MPSs) and matrix product operators (MPOs) for the Hamiltonian operators of the above mentioned condensed matter models were also described. These systems feature simple Hamiltonian operators with few terms compared to the quantum chemical Hamiltonian. The spin-adaptation of the latter is a non-trivial task because all terms must first be expressed with local operators transforming according to some irreducible representation of SU(2) and subsequently be incorporated into a matrix product structure, requiring additional coupling coefficients.

In previous work, we presented an efficient matrix product operator based formulation of the DMRG algorithm for quantum chemistry, which we denoted second-generation DMRG. In this work, we extend our work to the development of spin-adapted MPSs and MPOs.

In Sec. we briefly introduce the relevant formulae from quantum mechanical angular momentum theory for the spin adaptation of MPSs and MPOs. In Secs. and we demonstrate how these formulae are applied to the construction of spin-adapted MPSs and MPOs, whereas Sec. describes the application of MPOs to MPSs.

II. THE ROLE OF SYMMETRIES

The matrix product state ansatz for a state in a Hilbert space spanned by L spatial orbitals reads

\[ |\psi\rangle = \sum_{\sigma} \sum_{a_1, \ldots, a_{L-1}} M_{a_1}^{\sigma_1} M_{a_1 a_2}^{\sigma_2} \cdots M_{a_{L-1}}^{\sigma_L} |\sigma\rangle, \]

with \(|\sigma\rangle = |\sigma_1, \ldots, \sigma_L\rangle\), and \(\sigma_l = |\uparrow\rangle, |\downarrow\rangle\), which can be interpreted as a configuration interaction (CI) expansion where the CI coefficients are encoded as a product of matrices.

If a Hamiltonian operator possesses global symmetries, we can label its eigenstates with quantum numbers that are the irreducible representations of the global symmetry groups. These labels also apply to the MPS tensors in Eq. and induce a block-diagonal structure. For the special case of total spin symmetry, the Wigner–Eckart theorem applies, which allows us to label the irreducible representations according to total spin (rather than to the spin projection quantum number \(S_z\)) and populate the symmetry blocks with reduced matrix elements.

The effect of spin symmetry adaptation is therefore two-fold. Firstly, MPS tensors assume a block-diagonal structure labeled by quantum numbers. Secondly, these symmetry blocks consist of reduced matrix elements obtained through the Wigner–Eckart theorem.

A. Quantum numbers

We are interested in diagonalizing the non-relativistic electronic Coulomb Hamiltonian

\[ \hat{H} = \sum_{ij} t_{ij} \hat{c}^\dagger_{i\sigma} \hat{c}_{j\sigma} + \frac{1}{2} \sum_{ijkl} V_{ijkl} \hat{c}^\dagger_{i\sigma} \hat{c}^\dagger_{j\sigma'} \hat{c}_{l\sigma} \hat{c}_{k\sigma'} \]

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defined on \( L \) orbitals, referred to as sites. Apart from the total spin, it conserves the particle number and point group symmetry. We can therefore label the eigenstates with the quantum numbers \((S, N, I)\), corresponding to total spin \( S \), number of electrons \( N \), and the irreducible representation \( I \) of the point group of a molecule. According to the Clebsch–Gordan expansion, we find that a composite system consisting of the two representations \( D(S_1, N_1, I_1) \) and \( D(S_2, N_2, I_2) \) decomposes according to

\[
D(S_1, N_1, I_1) \otimes D(S_2, N_2, I_2) = \bigoplus_{S = |S_1 - S_2|} D(S, N_1 + N_2, I_1 \otimes I_2),
\]

where \( I_1 \otimes I_2 \) denotes the application of the point group multiplication table. By employing Eq. \( 3 \), we will later be able to determine the symmetry dependent block structure of the MPS tensors.

### B. Reduced matrix elements

For later reference, we introduce the required formulae for the handling of reduced matrix elements and follow the standard treatment as presented, for example, in the book by Biedenharn and Louck \([10]\).

Due to the fact that MPSs as well as MPOs behave like rank-\( k \) tensor operators, the Wigner–Eckart theorem is the fundamental equation to exploit spin symmetry. It states that the matrix element of the \( m \)-th component \( T^{[k]}_m \) of a rank-\( k \) tensor operator \( T^{[k]} \) is generated from a reduced matrix element multiplied by the Clebsch–Gordan coefficient \( C_{m M m'}^{k j k' j'} \),

\[
\langle j' m' | T^{[k]}_m | j m \rangle = \langle j' | T^{[k]} | j \rangle C_{m M m'}^{k j k' j'}.
\]

The double vertical line denotes Condon and Shortley’s notation for a reduced matrix element, which is independent of any projection quantum number. We further distinguish the reduced matrix elements with bold symbols from their conventional counterparts, a convention that we will follow throughout this work. In the equation above, \( j \) and \( j' \) refer to a spin quantum number (an irreducible \( SU(2) \) representation), \( m, m' \) and \( M \) are projection quantum numbers such as the \( z \)-component of spin if the \( z \)-axis is chosen as the axis of quantization. As the multiplet \( M = -k, \ldots, k \) is determined by a single reduced matrix element, the Wigner–Eckart theorem entails information compression allowing operators to be stored more efficiently.

For setting up the DMRG algorithm with irreducible tensor operators, it will be necessary to calculate the matrix elements of products of tensor operators. If \( S^{[k_1]}_{\mu_1} \) and \( T^{[k_2]}_{\mu_2} \) are rank-\( k_1 \) and rank-\( k_2 \) tensor operators respectively, their product will be given by

\[
[S^{[k_1]}_{\mu_1}] \times [T^{[k_2]}_{\mu_2}] = \sum_{\mu_1 \mu_2} C_{m M m'}^{k j k' j'} S^{[k_1]}_{\mu_1} T^{[k_2]}_{\mu_2}.
\]

To benefit from information compression, we are interested in expressing the reduced matrix element of the above product by reduced matrix elements of the individual factors. By applying the Wigner–Eckart theorem to the product as a whole as well as to the individual elements of \( S^{[k_1]} \) and \( T^{[k_2]} \), one obtains (for a detailed derivation see Ref. \([16]\))

\[
\langle j' || [S^{[k_1]}_{\mu_1}] \times [T^{[k_2]}_{\mu_2}] || j \rangle = (-1)^{j + j' + k_1 + k_2} \times \sum_{j''} \sqrt{(2j'' + 1)(2k + 1)} \left\{ \begin{array}{ccc} j' & k_1 & j'' \\ k_2 & j & k \end{array} \right\}
\]

\[
\times \langle j' || [S^{[k_1]}_{\mu_1}] || j'' \rangle \langle j'' || [T^{[k_2]}_{\mu_2}] || j \rangle
\]

where the quantity in curly brackets is a Wigner-6 symbol.

If \( S^{[k_1]} \) and \( T^{[k_2]} \) act on different spaces, i.e.

\[
S^{[k_1]} = S^{[k_1]} (1) \otimes I_{(2)},
\]

\[
T^{[k_2]} = I_{(1)} \otimes T^{[k_2]} (2),
\]

the summation over the intermediate states \( j'' \) in the coupling law of Eq. \( 4 \) can be eliminated to yield

\[
\langle j' || [S^{[k_1]}_{(1)}] \otimes T^{[k_2]} (2) || j \rangle = \left[ \begin{array}{ccc} j_1 & j_2 & j \\ k_1 & k_2 & k \\ j'_{1'} & j'_{2'} & j' \end{array} \right] \langle j' || [S^{[k_1]}_{(1)}] || j_1 \rangle \langle j_2 || T^{[k_2]} (2) || j_{2'} \rangle,
\]

where \( j_1, j_2 \) means that \( j_1 \) and \( j_2 \) couple according to Eq. \( 5 \) to yield \( j \) and the term in brackets is defined as the product of a Wigner-9j symbol and a normalization factor,

\[
\left[ \begin{array}{ccc} j_1 & j_2 & j \\ k_1 & k_2 & k \\ j'_{1'} & j'_{2'} & j' \end{array} \right] \equiv [(2j_1 + 1)(2j_2 + 1)(2j + 1)(2k + 1)]^{1/2}
\]

\[
\times \left\{ \begin{array}{ccc} \frac{j_1 + j_2 + j'}{2} & \frac{j_1 - j_2 + j'}{2} & \frac{j_1 - j_2 - j'}{2} \\ \frac{j_1 + j_2 - j'}{2} & \frac{j_1 - j_2 - j'}{2} & \frac{j_1 + j_2 + j'}{2} \end{array} \right\}.
\]

In the subsequent sections, examples will be provided of how Eq. \( 5 \) and Eq. \( 4 \) are exploited.

### III. SYMMETRY-ADAPTED MPS

To understand the symmetry properties of the MPS tensors in Eq. \( 1 \), it is important to note that the states

\[
| a_{l-1} \rangle = \sum_{\sigma_1, \ldots, \sigma_{l-1}} M_{a_{l-1} a_{l-2}}^{\sigma_{l-1}} \cdots M_{a_{2} a_{1}}^{\sigma_{1}} \sigma_{1} \cdots \sigma_{l-1}
\]

are defined on the sublattice spanned by \( l - 1 \) sites (spatial orbitals) are mapped by \( M_{a_{l-1} a_{l-2}}^{\sigma_{l-1}} \) to the states

\[
| a_{l} \rangle = \sum_{\sigma_{l}, a_{l-1}} M_{a_{l} a_{l-1}}^{\sigma_{l}} a_{l-1} \otimes \sigma_{l}
\]
on \( l \) sites. For each value of \( \sigma_l \), the MPS tensor \( M^{\sigma_l}_{q_{l-1}^1,a_l} \) therefore behaves like an operator that maps input states to a system enlarged by one site (one orbital), where \( \sigma_l \) labels the local site basis states \( \{|\uparrow\rangle, |\downarrow\rangle\} \), characterized by the quantum numbers

\[
|S, S_z, N, I\rangle = \{0, 0, 2, A_g\}, \frac{1}{2} \frac{1}{2} 1, I\rangle,
\]

\[
\frac{1}{2} \frac{1}{2} 1, I\rangle, |0, 0, 0, A_g\rangle \}.
\]

The operators \( M^{(1)} \) and \( M^{(0)} \) behave like rank-0 tensor operators, while \( M^{(1)} \) and \( M^{(1)} \) are the two \( S_z \) components of a rank-2 tensor operator. According to the Wigner–Eckart theorem, we can therefore calculate the elements of both components from one reduced operator labeled by total spin only, such that the spin-adapted local basis reads

\[
|S, S, N, I\rangle = \{0, 2, A_g\}, \frac{1}{2} 1, I\rangle, |0, 0, A_g\rangle \}.
\]

We now proceed as follows: from the nature of the local basis, we infer the structure of the symmetry blocks for the complete MPS in the following section and apply the Wigner–Eckart theorem to the reduced matrix elements contained in those blocks in Sec. IIIB.

### A. Symmetry blocks

We observe that if a subsystem consisting of sites 1 to \( 1 \) is represented by states with quantum numbers \( q_{l-1} \), the system extended to \( l \) sites will be represented by states with quantum numbers \( q_{l-1} \otimes \sigma_l \), where the tensor product for the corresponding representations is defined in Eq. (5) and \( \sigma_l \) labels a local basis state. If we now associate each MPS tensor \( a \) index from Eq. (1) with a quantum number

\[
q_l = (S, N_l, I_l), \quad (13)
\]

each MPS tensor \( M^{\sigma_l}_{q_{l-1}^1,a_l} \) will then be characterized by the symmetry constraint

\[
q_l \in q_{l-1} \otimes \sigma_l, \quad (14)
\]

which partitions the MPS tensor into symmetry blocks, indicated by the extended index \( q_{l-1}^1,a_{l-1};q,a_l \) supplemented with the quantum numbers \( q_{l-1} \) and \( q_l \) and separated by a semicolon for better readability. Since they contain an \( SU(2) \) irreducible representation, the corresponding MPS tensor consists of reduced matrix elements, which we denote by a bold symbol. Note that for an abelian symmetry, e.g., particle number, Eq. (14) simply requires that for each block \( q_{l-1}, q_l \) in \( M^{\sigma_l}_{q_{l-1}^1,a_l} \),

\[
N_l = N_{l-1} + N(\sigma_l) \) holds, where \( N(\sigma_l) \) equals the number of particles in \( \sigma_l \). We deduce that the MPS tensor \( M^{\sigma_l}_{q_{l-1}^1,a_l} \) on site \( l \) is in fact an operator that maps states from the subsystem spanning sites 1 to \( l-1 \) to the subsystem enlarged to site \( l \). We therefore refer to \( q_{l-1}, q_l \) and \( \sigma_l \) as input, output, and operator quantum numbers, respectively.

The sequence of MPS tensors as they appear in Eq. (11) builds up the target state site by site from the vacuum state. Consequently, the quantum numbers appearing in the MPS tensors on opposite ends are the vacuum state and the target state. By choice, we start with the vacuum state on the left hand side and finish with the target state on the right hand side of Eq. (11). The application of the symmetry constraint in Eq. (14) now determines which blocks will appear in the MPS tensors. For \( M^{\sigma_{l}}_{q_0^0} \), we have one block of size 1 denoted by \( q_0 : a_0 = \{0, 0, A_g\} : 1 \} \]

meaning that \( M^{\sigma_{l}}_{q_0^0} \) consists of three 1 \( 1 \) blocks. The MPS tensor on site 2 shares \( q_1 : a_l \) with \( M^{\sigma_{l}}_{q_0^0} \) and the output quantum numbers are

\[
q_2 : a_2 = \{(0, 2, A_g) : 1, (1, I_1) : 1, (0, 0, A_g) : 1\}, \quad (15)
\]

Note that the output quantum number \( q_2 = (0, 2, A_g) \) appears twice in the combination of the input quantum numbers with the local site basis, namely \( q_2 \otimes \sigma_2 = (0, 0, A_g) \otimes (0, 2, A_g) \) and \( (0, 2, A_g) \otimes (0, 0, A_g) \). The two blocks \( q_1 \times q_2 = (0, 0, A_g) \times (0, 2, A_g) \) and \( (0, 2, A_g) \times (0, 0, A_g) \) therefore have a 1 \( 2 \) shape, reflecting the fact that there are two different \( (0, 2, A_g) \) states defined on sites 1 and 2. The continuation of this scheme towards the right leads to exponentially growing block sizes, which must be limited (with the requirement that the output block sizes on site 1 match with the input block sizes on site \( l+1 \)).

We further note that in this way blocks are obtained which do not appear in the set of possible blocks of the reverse process that starts from the right hand side of the MPS by deducing the local basis states from the target quantum number. The correct block structure is therefore obtained from the common subset of the build-up procedure from the left and the decomposition from the right.

### B. Reduced matrix elements

In the previous section, we established that the MPS tensor \( M^{\sigma_l}_{q_{l-1}^1,a_l} \) behaves like a set of two rank-0 and one rank-1 irreducible tensor operator. The application of the Wigner–Eckart theorem to the reduced matrix elements yields

\[
M^{\sigma_l}_{N_{l-1}S_{z,l-1}(k_{l-1}+a_{l-1})}N_{l}S_{z,l}(k_{l}+a_{l}) \]

\[
= M^{\sigma_l}_{q_{l-1}^1,a_l} g_{q_{l-1}^1,a_l}^S S_{z,l-1} m S_{z,l} \] \[= g_{N_{l-1}S_{z,l-1}(k_{l-1}+a_{l-1})}N_{l}S_{z,l}(k_{l}+a_{l}) \]

(17)
where the blocks of the abelian MPS tensor on the left hand side of Eq. (17) are labeled by pairs of the particle number \( N \) and the spin projection \( S_z \). The latter may assume the values

\[
S_{z,l-1} = -S_{l-1}, \ldots, S_{l-1},
\]

\[
S_{z,l} = -S_{l}, \ldots, S_{l},
\]

\[
m = S_{z,l} - S_{z,l-1}.
\]

If \( S_{\sigma_l} \), the spin of the local basis state \( \sigma_l \), is zero, the corresponding Clebsch–Gordan coefficient will be equal to 1. Note that the \( a \) indices are identical on both sides of Eq. (17), meaning that the reduced blocks are transferred as a whole and multiplied by a single Clebsch–Gordan coefficient. In general, there is more than one reduced block on the right hand side of Eq. (17) that transforms into a given block \((N_{l-1}S_{z,l-1}, N_lS_{z,l})\) on the left hand side, such that one has to introduce pairs of row and column offsets \((k_{l-1}, k_l)\) to arrange the reduced blocks in a block-diagonal fashion within the larger \( S_z \) blocks.

Eq. (17) would apply if a spin-adapted MPS with reduced matrix elements had to be transformed to the full matrix elements with abelian particle number and \( S_z \) symmetry, but not to ground state calculations, where the reduced MPS matrix elements are determined by variational optimization.

IV. SYMMETRY-ADAPTED MPO

We denote the generalization of the MPS concept to MPOs as \( [15, 17] \)

\[
\tilde{W} = \sum_{\sigma, \sigma'} \sum_{b_1, \ldots, b_{L-1}} W_{b_1}^{\sigma_1 \sigma'_1} \cdots W_{b_{L-1}}^{\sigma_{L-1} \sigma'_{L-1}} |\sigma\rangle \langle \sigma'|.
\]

A contraction over the local site indices \( \sigma_l, \sigma'_l \) in \( \sigma, \sigma' \) leads us to define the quantities

\[
\tilde{W}_{b_{i-1} b_i} = \sum_{\sigma_l, \sigma'_l} W_{b_{i-1} b_i}^{\sigma_l \sigma'_l} |\sigma_l\rangle \langle \sigma'_l|,
\]

which are operator-valued matrices; the entries of the \( \tilde{W}_{b_{i-1} b_i} \) matrices are the elementary operators acting on a single site such as the creation and annihilation operators \( \hat{c}_{\sigma} \) and \( \hat{c}_{\sigma} \).

A. Elementary site operators

Elementary site operators are represented by \( 4 \times 4 \) matrices with respect to a basis of \([|\uparrow\rangle, |\downarrow\rangle, |\overline{\uparrow}\rangle, |\overline{\downarrow}\rangle\) \( \rangle \), e.g.,

\[
\hat{c}_\uparrow = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad \hat{c}_\downarrow = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}
\]

and \( \hat{F} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \)

where \( \hat{F} \) represents the fermionic auxiliary operator to describe fermionic anticommutation (see Ref. \( [15] \)). Note that the definition of \( \hat{c}_\uparrow \) contains a minus sign so that \( \hat{c}_\uparrow |\uparrow\rangle = -|\uparrow\rangle \), corresponding to our choice of ordering the \( \uparrow \)-electron before the \( \downarrow \)-electron on a single site.

To those site operators that transform according to an irreducible \( SU(2) \) representation, we may again apply the Wigner–Eckart theorem in Eq. (4). The pairs \( \hat{c}_\uparrow, \hat{c}_\downarrow \), \( \hat{c}_\uparrow, \hat{c}_\downarrow \), for instance, each form the two components of a rank-\( \frac{1}{2} \) tensor operator with reduced matrix elements

\[
\hat{c}_\uparrow = \begin{pmatrix} 0 & -\sqrt{2} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{c} = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix}
\]

with respect to the basis \([|0\rangle, A_g \rangle, |\frac{1}{2}, \frac{1}{2}, I \rangle, |0, 0, A_u \rangle\) \( \rangle \).

The application of Eq. (17) to \( \hat{c}_\uparrow \) and \( \hat{c} \) yields \( \hat{c}_\uparrow, \hat{c}_\downarrow \) and \( \hat{c}, \hat{c} \), respectively.

B. Operator terms

We now turn to the description of the operator terms appearing in the Hamiltonian in Eq. (2). In analogy to the MPS case where an index with associated quantum number \( q_{l-1}, a_{l-1} \) is mapped to \( q_l, a_l \) by calculating the tensor product with the local site occupation \( \sigma_l \), the MPO \( b \) indices of Eq. (19) may be labeled with quantum numbers as well, where the transition from \( b_{l-1} \) to \( b_l \) is mediated through the action of the local site operator located at \( \tilde{W}_{b_{l-1} b_l} \). Introducing the quantum numbers \( p_{l-1} \) and \( p_l \) defined according to Eq. (13), we extend the notation to \( \tilde{W}_{b_{l-1} b_l}^{(k]} \), which associates a (non-abelian) quantum number with each \( b \) index and \( k \) corresponds to the rank of the elementary site operator at the location \( p_{l-1} b_{l-1} ; p_l b_l \). The term

\[
t_{ij} \hat{c}_{\sigma} \hat{c}_{\sigma} = t_{ij} \hat{I}_1 \cdots \hat{c}_{\sigma} \hat{F} \hat{I}_{i+1} \cdots - \hat{c}_{\sigma} \hat{F} \hat{I}_{j+1} \cdots \quad (21)
\]

emerges from the repeated action of the \( \tilde{W}_{p_{l-1} b_{l-1} ; p_l b_l}^{(k]} \) tensors on each site, where the total operator quantum number is encoded in the final \( p_L \) index. We deduce that
the $\tilde{W}_[k]_{p_{i-1} b_{i-1} p b_i}$ tensors behave like rank-$k$ tensor operators, where $k$ equals the rank of the elementary site operator at position $b_{i-1}, b_i$. The Wigner–Eckart theorem 

\[ W_{N_{i-1} S_{i-1} l_{i-1} b_{i-1}; N_i S_i l_i b_i} = W^{\sigma_i \sigma'_i}_{p_{i-1} b_{i-1} p b_i} C^{S_{p_{i-1} k S_{p_i} S_{l_{i-1} m S_{l_i}}} S_{S_i \sigma_i} \mu S_{S_i \sigma_i}}, \tag{22} \]

again with the local quantum numbers

\[ S_{z, l-1} = -S_{p_{i-1}}, \ldots, S_{p_{i-1}}, \]
\[ S_{z, l} = -S_{p_i}, \ldots, S_{p_i}, \]
\[ m = S_{z, l} - S_{z, l-1}, \]
\[ S_{z, \sigma_i} = -S_{\sigma_i'}, \ldots, S_{\sigma_i'}, \]
\[ S_{z, \sigma_i'} = -S_{\sigma_i}, \ldots, S_{\sigma_i}, \]
\[ \mu = S_{\sigma_i} - S_{\sigma_i'}, \]

as before. Note that the symmetry constraint $p_i \in p_{i-1} \otimes k$ applies and, as the Hamiltonian operator is a spin-0 operator, we find that $S_{p_i} = 0$ for each term in Eq. (2).

We are now in a position to express the terms in Eq. (21) with reduced matrix elements. For this we need $c^{\dagger} \tilde{F}$ in reduced form,

\[ c^{\dagger} \tilde{F} = \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \tag{23} \]

and the coefficients for the reduced elements of the $\tilde{W}_[k]_{p_{i-1} b_{i-1} p b_i}$ tensors. The corresponding Clebsch–Gordan coefficients in Eq. (22) are all equal to 1, except on site $j$ where we find

\[ C^{\frac{1}{2}, \frac{1}{2} 0} = \frac{1}{\sqrt{2}}, \quad C^{\frac{1}{2}, \frac{1}{2} 0} = -\frac{1}{\sqrt{2}}. \tag{24} \]

Consequently, the reduced term

\[ \tau_{ij}^{\frac{1}{2}, \frac{1}{2}} = t_{ij} \sqrt{2} c^{\dagger} \tilde{F} c_j \tag{25} \]

expands to the terms $t_{ij} c^{\dagger}_i \tilde{c}_j$ and $t_{ij} c^{\dagger}_i \tilde{c}_j$. For the $\frac{1}{2}$-case, the minus sign from the expansion of $\tilde{c}$ to $-\tilde{c}$ is balanced by the Clebsch–Gordan coefficient from Eq. (24). Note that since $\tilde{W}_[k]_{p_{i-1} b_{i-1} p b_i}$ in general contains elementary site operators of different ranks, it does not transform irreducibly as a whole. We may only apply the Wigner–Eckart theorem to its elements $b_{i-1}, b_i$ individually. Further examples of reduced terms appearing in the sum of Eq. (2) are given in the appendix.

V. MPS-MPO OPERATIONS

A. Calculations with reduced matrix elements

We can now describe the Hamiltonian in Eq. (2) and its eigenstates with MPOs and MPDs containing reduced matrix elements and that the latter may be transformed with Eq. (4) to the MPOs and MPOs that we are familiar with from DMRG with abelian symmetries. The representation based on reduced matrix elements is more efficient compared to full matrix elements, because there are less elements to store. In order to exploit that fact in a DMRG algorithm, however, we need to be able to directly optimize the reduced elements in an MPO without any intermediate steps involving the full matrix elements.

The decisive equations of a second-generation DMRG implementation [13] are the propagation of the boundaries $L^\mu$ defined by the starting value $L^\mu_{i=1} = 1$ and the recursive relation

\[ L^\mu_{a_i a_i'} = \sum_{a_{i-1}, a_{i-1}'} N^\sigma_{a_i a_{i-1}} W^\sigma_{a_{i-1} b_{i-1} b_{i} a_{i-1}} M^\sigma_{a_{i-1} a_i'}, \tag{26} \]

where the matrices $N^\sigma$ describe a second state

\[ |\phi\rangle = \sum_{\sigma_{a_1 \cdots a_L} L_{a_1 \cdots a_L}} N^\sigma_{a_1 a_2 \cdots a_L} |\sigma\rangle, \tag{27} \]

and the matrix vector multiplication

\[ M^\sigma_{a_{i-1} a_i} = \sum_{a_{i-1} a_{i-1}'} W^\sigma_{a_{i-1} b_{i-1} b_{i} a_{i-1}} M^\sigma_{a_{i-1} a_i'} \mathbb{R}^{b_{i-1} b_i} a_{i-1}' a_i, \tag{28} \]

with the right boundary $\mathbb{R}^{b_i}$ defined in analogy to Eq. (26). Both equations are introduced in our earlier work on second-generation DMRG [13]. It is our goal to calculate the reduced matrix elements of the quantities on the left hand side from the reduced matrix elements of the quantities on the right hand side. Incidentally, the two equations possess the same symmetry properties, i.e., they contain the same number of tensor operators, because $N^\sigma_{a_{i-1} a_i}$ and $\mathbb{R}^{b_{i-1} b_i}$ both behave like a tensor operator whose elements obey Eq. (4). Therefore, we only have to derive one formula for the reduced matrix elements. In Eq. (26), we apply the Wigner–Eckart theorem by substituting each object with the right hand side of Eq. (4), which yields

\[ L^\mu_{q_{i} a_i q_i' a_i'} S_{q_{i} a_i q_i' a_i'} = \sum_{\sigma_{a_i a_i'} q_{i-1} q_{i-1}'} \sum_{\mu_{i-1} \mu_{i-1}'} \left( \frac{\sqrt{2(S_{q_{i} q_{i-1} q_{i-1} a_{i-1}')} (2S_{q_{i} q_{i-1} q_{i-1} a_{i-1}'} + 1)} (2S_{q_{i} q_{i-1} q_{i-1} a_{i-1}'} + 1)} {2S_{q_{i} q_{i-1} q_{i-1} a_{i-1}'} + 1} \right)^{\mu_{i-1} \mu_{i-1}'} \times N^\sigma_{a_i a_i'} q_{i-1} q_{i-1} W^\sigma_{q_{i} q_{i-1} q_{i-1} a_{i-1}'} C^{m_{i-1} m_{i-1} m_{i-1} m_{i-1}'} C^{m_{i-1} m_{i-1} m_{i-1} m_{i-1}'} C^{m_{i-1} m_{i-1} m_{i-1} m_{i-1}'}, \tag{29} \]

\[ \times L^\mu_{q_{i} a_i q_i' a_i'} C^{m_{i-1} m_{i-1} m_{i-1} m_{i-1}'}, \tag{29} \]
Our choice of the normalization factor with the square root ensures that Eq. (29) remains valid for the generation of \( R^b \) from \( R^{b+1} \).

Fortunately, we may simplify the previous equation by employing the relation \( \langle 0 | V_{\nu l}^1 | \nu l \rangle \langle M \rangle = \sum_{\sigma} S_{l \nu} S_{l \mu} C_{M \mu \nu \sigma}^* \) for example, contains nontrivial site operators like \( \hat{c}_{ij} \hat{c}_{ji} \) and \( \hat{c}_{ij}^\dagger \hat{c}_{ji}^\dagger \), which are the \( S_z = 1 \) and \( S_z = -1 \) components of a rank-1 irreducible tensor operator. In reduced form, the matrix elements of these site operators are

\[
\hat{c}_i^\dagger \hat{c}_j^\dagger = \begin{pmatrix}
0 & 0 & 0 \\
0 & \sqrt{3/2} & 0 \\
0 & 0 & 0
\end{pmatrix},
\]

as the expansion to the full matrix elements [Eq. (31)] confirms, because the operators \( \{ \hat{c}_{ij} \hat{c}_{ji}, \sqrt{2/3} (\hat{n}_{ji} - \hat{n}_{ij}), \hat{c}_{ij}^\dagger \hat{c}_{ji}^\dagger \} \) are obtained. If we now attempt to generate the terms in Eq. (33) from

\[
\tau_{ij}^{[1]} = V_{ijji} \sqrt{3} \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_j \hat{c}_i^\dagger,
\]

where the factor of \( \sqrt{3} \) balances the magnitudes of the Clebsch–Gordan coefficients at site \( j \) from Eq. (22). For example, \( C_{1,10} \), we will find that there are several different possibilities of expanding the term in Eq. (33) to full matrix elements. The sum of all possibilities with a total spin of 0 is

\[
\sum_{\sigma_{ij}, \sigma_{ij}'} \frac{1}{\sqrt{2}} \left( 2S_{ij} + 1 \right) N_{ij}^{\sigma_{ij}} \times W_{\sigma_{ij}, \sigma_{ij}'} S_{ij} S_{ij}^1 \times \frac{1}{\sqrt{2}} \left( 2S_{ij} + 1 \right) \frac{1}{\sqrt{2}} \left( 2S_{ij} + 1 \right) \end{pmatrix} \times \left( \hat{c}_{ij}^\dagger \hat{c}_{ij}^\dagger \hat{c}_{ij} \right)
\]

B. The spin-adapted Hamiltonian

In the previous section, we saw that the two expansion products of the term in Eq. (24) are both contained in the Hamiltonian in Eq. (2). However, this is not always the case. The group of terms

\[
\sum_{\sigma, \sigma'} V_{ijji} \hat{c}_{ij}^\dagger \hat{c}_{ij} \hat{c}_{ij}^\dagger \hat{c}_{ij}^\dagger = - V_{ijji} \left( \hat{n}_{ij} \hat{n}_{ji} + \hat{n}_{ij} \hat{n}_{ji} + \hat{c}_{ij}^\dagger \hat{c}_{ij} \hat{c}_{ij}^\dagger \hat{c}_{ij}^\dagger \right),
\]

for example, contains nontrivial site operators like \( \hat{c}_i \hat{c}_j \) and \( \hat{c}_j^\dagger \hat{c}_i^\dagger \), which are the \( S_z = 1 \) and \( S_z = -1 \) components of a rank-1 irreducible tensor operator. In reduced form, the matrix elements of these site operators are

\[
\hat{c}_i^\dagger \hat{c}_j^\dagger = \begin{pmatrix}
0 & 0 & 0 \\
0 & \sqrt{3/2} & 0 \\
0 & 0 & 0
\end{pmatrix},
\]

as the expansion to the full matrix elements [Eq. (31)] confirms, because the operators \( \{ \hat{c}_i \hat{c}_j, \sqrt{2/3} (\hat{n}_i + \hat{n}_j), \hat{c}_i^\dagger \hat{c}_j^\dagger \} \) are obtained. If we now attempt to generate the terms in Eq. (33) from

\[
\tau_{ij}^{[1]} = V_{ijji} \sqrt{3} \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_j \hat{c}_i^\dagger,
\]

where the factor of \( \sqrt{3} \) balances the magnitudes of the Clebsch–Gordan coefficients at site \( j \) from Eq. (22). For example, \( C_{1,10} \), we will find that there are several different possibilities of expanding the term in Eq. (33) to full matrix elements. The sum of all possibilities with a total spin of 0 is

\[
\sum_{\sigma_{ij}, \sigma_{ij}'} \frac{1}{\sqrt{2}} \left( 2S_{ij} + 1 \right) N_{ij}^{\sigma_{ij}} \times W_{\sigma_{ij}, \sigma_{ij}'} S_{ij} S_{ij}^1 \times \left( \hat{c}_{ij}^\dagger \hat{c}_{ij}^\dagger \hat{c}_{ij} \right)
\]

which does not match Eq. (33). For this reason, we must add a correction of \( -2 \hat{n}_i \hat{n}_j \) to the term in Eq. (33) so that Eq. (33) is reproduced.

We have performed the analysis above for all the terms of the Hamiltonian in Eq. (2), a detailed list is provided in the appendix.

C. Reduced two-site MPS tensors

The variational optimization of two MPS sites at the same time involves the formation of the two-site MPS tensor

\[
P_{\sigma_{ij+1} \sigma_{ij}} = \sum_{\sigma} M_{\sigma_{ij+1} \sigma_{ij}} M_{\sigma_{ij} \sigma_{ij+1}}.
\]

To obtain the reduced elements of \( P \), we follow the description by Wouters et al. \( \psi \) and employ the formula in Eq. (6), which couples two tensor operators and reads

\[
P_{\sigma_{ij+1} \sigma_{ij}} \times \sum_{S_{ij+1}} \sqrt{(S_{ij+1} + 1)(2k + 1)} \left( S_{ij+1} S_{ij} S_{ij+1} S_{ij} S_{ij+1} \right) \times M_{\sigma_{ij+1} \sigma_{ij} \sigma_{ij+1} \sigma_{ij} \sigma_{ij+1}}.
\]
where $k$ runs over the expansion products of $\sigma_l \otimes \sigma_{l+1}$. To split the two-site tensor $P^{\sigma_l \sigma_{l+1}}$ by singular value decomposition into $M^{\sigma_l}$ and $M^{\sigma_{l+1}}$, we first need to back-transform $P^{\sigma_l \sigma_{l+1}}$ into

$$P^{\sigma_l \sigma_{l+1}}_{q_l-1,a_l-1\cdots q_{l+1}a_{l+1}} = M^{\sigma_l}_{q_l-1,a_l-1\cdots q_{l+1}a_{l+1}} M^{\sigma_{l+1}}_{q_l-1,a_l-1\cdots q_{l+1}a_{l+1}},$$

(39)

corresponding to the bare matrix-matrix product of $M^{\sigma_l}$ and $M^{\sigma_{l+1}}$. It is given by

$$P^{\sigma_l \sigma_{l+1}}_{q_l-1,a_l-1\cdots q_{l+1}a_{l+1}} = (-1)^{S_{q_l}+S_{q_{l+1}}+S_{q_{l+1}}+S_{q_l}} \times \sum_k \sqrt{(S_{q_l}+1)(2k+1)} \left\{ \frac{S_{q_{l+1}}}{S_{\sigma_l}} \frac{S_{q_l}}{S_{\sigma_{l+1}}} \right\} \times P^{\sigma_l \sigma_{l+1}}_{q_l-1,a_l-1\cdots q_{l+1}a_{l+1}},$$

(40)

A singular value decomposition yields

$$P^{\sigma_l \sigma_{l+1}}_{q_l-1,a_l-1\cdots q_{l+1}a_{l+1}} \to \sum_{q_l} U^{\sigma_l}_{q_l-1,a_l-1\cdots q_{l+1}a_{l+1}} V^{\sigma_{l+1}}_{q_l},$$

(41)

after which we can set $M^{\sigma_l} = U$, $M^{\sigma_{l+1}} = S \cdot V$ when sweeping towards the right and $M^{\sigma_{l+1}} = S \cdot V$, $M^{\sigma_l} = U$ during a left sweep. Note that, compared to Ref. [18], we do not apply any normalization factor in Eq. (41).

D. Reduced two-site MPO tensors

The calculation of the reduced matrix elements of the two-site MPO tensor

$$\tilde{V}^{\sigma_l \sigma_{l+1} \sigma'_l \sigma'_{l+1}}_{b_{l-1}b_l; b'_{l+1}b'_{l+2}} = \sum_{b'_l} \tilde{W}^{\sigma_l \sigma'_{l+1}}_{b_{l-1}b'_l} \tilde{W}^{\sigma_{l+1} \sigma'_{l+1}}_{b'_l b_{l+2}}$$

(42)

requires the application of Eq. (19) in analogy to the two-site MPS tensor case to couple the matrix $b$ indices and Eq. (20) to form the tensor product of two elementary site operators acting on separate spaces. In summary, we obtain

$$\tilde{V}^{\sigma_l \sigma_{l+1} \sigma'_l \sigma'_{l+1}}_{p_{l-1}b_{l-1}; p_{l+1}b_{l+1}} = (-1)^{S_{p_{l-1}}+S_{p_{l+1}}+k_1+k_2} \times \sum_{p_l} \sqrt{(S_{p_l}+1)(2k_1+1)} \left\{ \frac{S_{p_{l+1}}}{k_2} \frac{k_1}{S_{p_{l-1}}} \right\} \times \tilde{W}^{\sigma_l \sigma'_{l+1}}_{p_{l-1}b_{l-1}; p_{l}b_{l}} \tilde{W}^{\sigma_{l+1} \sigma'_{l+1}}_{p_{l}b_{l}; p_{l+1}b_{l+1}},$$

(43)

We emphasize, that Eq. (43) remains valid after an exchange of $M$ with $P$ and $W$ with $V$.

VI. NUMERICAL EXAMPLE

For illustration purposes, we compare our spin- and non-spin-adapted implementations in QCMaquis [15] at the example of the dioxygen molecule and consider the lowest-lying singlet state $1^1\Delta_g$, which is the first excited state above the triplet ground state $3\Sigma_g^+$. For our calculations, we employed a cc-pVTZ basis set [19] and correlated all 16 electrons in all 60 orbitals (full configuration interaction). For this homonuclear diatomic, we had to adopt the highest non-abelian point group symmetry, i.e., $D_{2h}$, offered by the MoLCA program [20] and therefore could not consider the proper point group $D_{sch}$. In our $D_{2h}$ calculations, the triplet ground state is in irreducible representation $B_{1g}$, whereas the singlet state transforms as $A_g$ (except for the spin-contaminated calculation for $S_z=0$, for which we chose $C_1$). We compare with CCSD(T) data obtained with the same basis set from the NIST computational chemistry comparison and benchmark database [21]. In fact, we selected the optimized CCSD(T) internuclear distances also for the DMRG calculations (see Table I).

| Method                  | $E_{el}(1^1\Delta_g)$ / $E_H$ |
|-------------------------|--------------------------------|
| DMRG(16,60), $S_z=0$, $m=1000$ | -150.147 369                  |
| DMRG(16,60), $S_z=0$, $m=1000$ | -150.114 826                  |
| DMRG(16,60), $S_z=1$, $m=2000$ | -150.116 789                  |
| DMRG(16,60), $S_z=1$, $m=4000$ | -150.117 657                  |
| DMRG(16,60), $S_z=0$, $m=1000-4000$, extr. | -150.118 164 |
| CCSD(T)=FULL [21]        | -150.105 829                  |
| Method                  | $E_{el}(3\Sigma_g^+)$ / $E_H$ |
|-------------------------|--------------------------------|
| DMRG(16,60), $S_z=1$, $m=1000$ | -150.151 163                  |
| DMRG(16,60), $S_z=1$, $m=2000$ | -150.153 533                  |
| DMRG(16,60), $S_z=1$, $m=4000$ | -150.154 643                  |
| DMRG(16,60), $S_z=1$, $m=1000-4000$, extr. | -150.155 142 |
| CCSD(T)=FULL [21]        | -150.153 620                  |

The non-spin-adapted energy of -150.147 369 $E_H$ for the singlet state in $C_1$ point group symmetry with $S_z=0$ converged to the triplet state. Hence, the singlet state will not be accessible with a non-spin-adapted algorithm, if point group symmetry is not enforced. In the $D_{sch}$ subgroup of $D_{2h}$, the two $1^1\Delta_g$ components reduce to $A_g$ and $B_{1g}$ symmetry (the $z$ axis is along the internuclear axis) so that considering point group symmetry would allow one to select which state is optimized. With the spin-adapted algorithm we may set the total spin $S$ equal to zero and describe the singlet state correctly, even if point group symmetry is not enforced.

For comparison with coupled-cluster results, we extrapolated a series of DMRG calculations with a varying number of renormalized block states $m$ comprising $m=1000 - 4000$ to calculate the singlet energy. A conservative estimate of the accuracy is 0.5 $mE_H$ given by
the difference between the extrapolated value and the best variational result with $m = 4000$. In Table I we also include results from the triplet ground-state calculation for comparison.

Table I clearly shows that the non-spin-adapted ($S_z = 0$) result is too low in energy, whereas the correct, spin-adapted electronic energy of the singlet state is higher by about 0.033 $E_H$. The former actually converged toward the triplet state, but the energy for this state is not fully converged as a comparison with the converged triplet ground-state DMRG(16,60)[4000] energy in Table I shows. Note also that the CCSD(T) results are higher in energy than the corresponding DMRG results because this coupled-cluster model restricts the excitation operators to double substitutions with perturbatively corrected triples. The (adiabatic) singlet-triplet gap is 125.5 kJ/mol with CCSD(T) and 97.1 kJ/mol with DMRG (for $m=4000$ as well as for the extrapolated result). The experimental result for this gap is 94.7 kJ/mol and therefore in very good agreement with the DMRG result. Note, however, that we do not include any vibrational corrections in our results.

\[ c^\dagger = \begin{pmatrix} 0 & -\sqrt{2} & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{c} = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix} \quad (44) \]

\[ \hat{n} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{c}^\dagger \hat{c}^{[1]} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \sqrt{3/2} & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (45) \]

\[ \hat{c}^\dagger \hat{n} = \begin{pmatrix} 0 & -\sqrt{2} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{n} \hat{c} = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (46) \]

\[ \hat{p}^\dagger = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{p} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad (47) \]

Reduced Hamiltonian terms

The definition of the two-electron integrals according to the notation in Ref. \[22\] reads

\[ V_{ijkl} = \int d^3r d^3r' \phi_i^*(r) \phi_k^*(r') V(|r - r'|) \phi_j(r) \phi_l(r'), \quad (48) \]

and exhibits the permutation symmetries

\[ V_{ijkl} = V_{klij} = V^*_{jilk} = V^*_{klij}, \quad (49) \]

which give rise to equivalence classes of index permutations that share the same two-electron integral. We partition the Hamiltonian in Eq. (2) according to these equivalence classes described in Table III. The format for the one- and two-electron integrals described in Ref. \[22\] only lists unique integral values. Therefore, the second column of Table III contains the terms for all permutations given in the first column. Note, that in the first column of Table III only half of the possible two-electron index permutations are listed in order to cancel the factor $1/2$ in Eq. (2).

VII. CONCLUSIONS

Here, we developed a formalism for the incorporation of non-abelian spin symmetry into second-generation DMRG, which is a purely MPO-based formulation of the DMRG algorithm for quantum chemistry described in Ref. \[15\]. The MPO concept allows one to clearly separate the operator from the contraction formula in which the operator is applied to a wave function. We can therefore achieve spin adaptation for all the building blocks consisting of elementary site-operators, the matrix product basis, and the contraction formula in Eq. (31) individually. This modularity facilitates a flexible implementation, which was then applied to dioxygen as a numerical example.

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APPENDIX

For reference purposes, we provide the complete list of reduced matrix elements implemented in QCMAQUIS to represent the Hamiltonian in Eq. (2).

Reduced elementary site operators

Local basis: \{0, 2, A_y, |1, \frac{1}{2}, I>, |0, 0, A_y\}.
TABLE II. Terms of the Hamiltonian partitioned into one- and two-electron equivalence classes.

| integral | terms | reduced |
|----------|-------|---------|
| $t_{ii}$ | $\sum_\sigma \hat{c}_{i\sigma} \hat{c}_{i\sigma}$ | $\hat{n}$ |
| $t_{ij} = t_{ji}$ | $\sum_\sigma \hat{c}_{i\sigma} \hat{c}_{j\sigma}$ $\frac{1}{\sqrt{2}} [\hat{c}_{i\uparrow} \hat{c}_{j\uparrow} - \hat{c}_{i\downarrow} \hat{c}_{j\downarrow}]$ | $\hat{c}_{i\sigma} \hat{c}_{j\sigma}$ |
| $V_{ii}$ | $\hat{n}_i \hat{n}_j$ | $d_i$ |
| $V_{ij} = V_{ji}$ | $\sum_{\sigma,\sigma'} \hat{c}_{i\sigma} \hat{c}_{j\sigma'} \hat{n}_{\sigma'}$ | $\sqrt{2} [\hat{c}_{i\uparrow} \hat{n}_{\downarrow} \hat{c}_{j\downarrow} - \hat{c}_{i\downarrow} \hat{n}_{\uparrow} \hat{c}_{j\uparrow}]$ |
| $V_{ijkl} = V_{ijkl}$ | $\hat{n}_{\sigma'} \hat{n}_{\sigma''}$ | $\hat{n}_i \hat{n}_j$ |
| $V_{ijkl} = V_{ijlk}$ | $\hat{c}_{i\sigma} \hat{c}_{j\sigma'} \hat{c}_{k\sigma''} \hat{c}_{l\sigma'''}$ | $\hat{c}_{i\sigma} \hat{c}_{j\sigma'} \hat{c}_{k\sigma''} \hat{c}_{l\sigma'''}$ |
| $V_{ijkl} = V_{ijlk}$ | $\hat{c}_{i\sigma} \hat{c}_{j\sigma'} \hat{c}_{k\sigma''} \hat{c}_{l\sigma'''}$ | $\sum_{\sigma,\sigma'} \hat{c}_{i\sigma} \hat{c}_{j\sigma'} \hat{c}_{k\sigma''} \hat{c}_{l\sigma'''}$ | see Table III |

TABLE III. continued from Table II, lower right. Reduced Hamiltonian terms for the case $i \neq j \neq k \neq l$.

| integral | terms | reduced |
|----------|-------|---------|
| $V_{ijkl}$ | $\sum_{\sigma,\sigma',\sigma''} \hat{c}_{i\sigma} \hat{c}_{j\sigma'} \hat{c}_{k\sigma''} \hat{c}_{l\sigma'''}$ | $\alpha \hat{c}_{i\sigma} \hat{c}_{j\sigma'} \hat{c}_{k\sigma''} \hat{c}_{l\sigma'''} + \beta \hat{c}_{i\sigma} \hat{c}_{j\sigma'} \hat{c}_{i\sigma} \hat{c}_{j\sigma'} + \gamma \hat{c}_{i\sigma} \hat{c}_{j\sigma'} \hat{c}_{k\sigma''} \hat{c}_{l\sigma'''}$ |

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