Constructing matrix product operators (MPO) is at the core of the modern density matrix renormalization group and its time dependent formulation. Taking quantum dynamics problem as an example, since the potential energy surface can be very different from molecule to molecule, it may take a lot of time to design and implement a compact MPO to represent the Hamiltonian on a case-by-case basis. In this work, we propose a new generic algorithm to construct the MPO of an arbitrary operator with a sum-of-products form based on the bipartite graph theory. We show that the method has the following advantages: (i) It is automatic in that only the definition of the operator is required; (ii) It is symbolic thus free of any numerical error; (iii) The complementary operator technique can be fully employed so that the resulting MPO is globally optimal for any given order of degrees of freedom; (iv) The symmetry of the system could be fully employed to reduce the dimension of MPO. To demonstrate the effectiveness of the new algorithm, the MPOs of Hamiltonians ranging from the prototypical spin-boson model and Holstein model to the more complicated ab initio
electronic Hamiltonian and the anharmonic vibrational Hamiltonian with sextic force field are constructed. It is found that for the former three cases, our automatic algorithm can reproduce exactly the same MPOs as the optimally manually-designed ones already known in the literature.

1 Introduction

The density matrix renormalization group (DMRG) method originally proposed by White to solve the electronic structure of one-dimensional strongly correlated lattice models has made great progress in quantum chemistry in the last decade and has been widely recognized as a state-of-the-art method for problems with a large active space. In addition to the electronic correlation, DMRG also shows great potential to solve the vibrational correlated problems. More recently, the time dependent (TD) formulation of DMRG called TD-DMRG attracts a lot of attention and quickly emerges as an efficient and “nearly exact” method for quantum dynamics in complex systems. TD-DMRG has been used to simulate the spectroscopy and quantum dynamics, including not only electron dynamics but also electron-vibrational correlated dynamics. TD-DMRG has been demonstrated in a number of models to achieve the same accuracy as the multi-configuration time-dependent Hartree (MCTDH) method which is regarded as the gold standard of the high dimensional quantum dynamics.

The recent rapid advances in quantum chemistry DMRG can be attributed to the formulation of DMRG as matrix product state (MPS) and the corresponding operator could be represented as matrix product operator (MPO). The introduction of MPS and MPO not only establishes a rigorous mathematical foundation of DMRG, but also makes the algorithm more powerful and convenient. Furthermore, it also opens the door to the development of more general tensor network states (TNS) such as tree tensor network states (TTNS) and projected entangled pair states (PEPS). The modern formulation of the DMRG algorithm based on MPS and MPO is usually called the second generation DMRG algorithm.
which could be seamlessly combined with the variational principle to obtain the ground state and the time dependent variational principle to carry out the time propagation.\textsuperscript{21,32} In addition, the exact global arithmetic, such as additions $\Psi_1 + \Psi_2, \hat{O}_1 + \hat{O}_2$ and multiplications $\hat{O}\Psi, \hat{O}_1\hat{O}_2$, are only possible based on MPS and MPO. In this new formulation, the starting point of any DMRG calculation is to construct the MPO representation of the Hamiltonian and all the other required operators. For the same operator, the form of MPO could be completely different as long as the final product is correct. However, a more compact MPO will save computational cost in practice. In order to construct a compact MPO, several methods have been proposed. The most commonly used method in quantum chemistry is to design MPO symbolically (or sometimes called analytically) by hand through inspecting the recurrence relation between neighboring sites.\textsuperscript{33} The so-called complementary operator technique is always fully explored to make the MPO more compact, which is essential to the operators with long-range interactions,\textsuperscript{34} such as the ab initio electronic Hamiltonian. Though usually this method could give the optimal answer by a smart design, it is not automatic in that different operators need a re-design and a re-implementation. The second one is a numerically “top-down” algorithm in which a naive MPO is first constructed and then compressed by the singular value decomposition (SVD) or by removing the linearly dependent terms.\textsuperscript{35} This algorithm is generic and automatic for different operators, while a numerical error is introduced and its effect on the following calculations cannot be well quantified in advance. Apart from this, the time cost spent on the numerical compression is not negligible when the number of terms in the operator is large. The third one which is not widely used in quantum chemistry is to construct a finite-state automaton to mimic the interaction terms in the operator.\textsuperscript{25} The automaton is easy to be constructed for a translationally invariant lattice model with short-range interactions, but becomes extremely complicated for long-range interactions.

Unlike the ab initio electronic Hamiltonian which has the same formula for different systems and thus could be hard-coded in implementation, the Hamiltonian met in the quantum
dynamics problems could be completely different according to the different forms of the potential energy surfaces (PES), including both the simple forms like the spin-boson model and other very complicated forms like the PES with high order Taylor expansions which is widely used to obtain the accurate anharmonic frequency and infrared spectrum.\textsuperscript{36,37} Thus, it is not efficient to use the first method mentioned above to construct MPOs on a case-by-case basis. In addition to the inefficiency, it is also difficult to obtain a globally optimal MPO when the Hamiltonian is very complicated, such as the PES including sextic terms \( \sum_{ijklmn} F_{ijklmn} \hat{q}_i \hat{q}_j \hat{q}_k \hat{q}_l \hat{q}_m \hat{q}_n \) which correlates up to six sites in the DMRG chain.

Since (TD-)DMRG for the high dimensional quantum dynamics has been drawing more and more attention in recent years, it is necessary and desired to have a better MPO construction algorithm which has all the advantages of the methods introduced above: (i) It is generic for all types of factorized operators; (ii) It is automatic, directly from the symbolic operator strings to the MPO; (iii) It gives an optimal MPO. Here, “optimal” means that the MPO is as compact as possible globally in a given order of degrees of freedom (DoF); (iv) It is symbolic thus free of any numerical error. In this work, we propose a new MPO construction algorithm which meets all the four requirements based on the graph theory for a bipartite graph. The remaining sections of this paper are arranged as follows. In section 2, we will present the idea of the new algorithm and the implementation details. In section 3, several typical Hamiltonians are examined ranging from the simple spin-boson model and Holstein model to the more complicated ab initio electronic Hamiltonian and vibrational Hamiltonian with a sextic force field. All the calculations are carried out with our in-house code Renormalizer.\textsuperscript{38} The resulting MPOs are compared with the optimally manually-designed ones reported in the literature.
2 Methodology and Implementation

2.1 MPO and complementary operator technique

The wavefunction ansatz in DMRG is called the matrix product states or tensor train (TT), which is

\[ |\Psi\rangle = \sum_{\{a\},\{\sigma\}} A[1]^{a_1}_{\sigma_1} A[2]^{a_2}_{\sigma_2} \cdots A[N]^{a_N}_{\sigma_N} |\sigma_1 \sigma_2 \cdots \sigma_N\rangle. \]  \hspace{1cm} (1)

For a system of distinguishable particles, \(N\) is the number of DoFs in the system and \(|\sigma_i\rangle\) is the local basis such as the discrete variable representation (DVR) basis for nuclear motion. For electronic systems, \(N\) is the number of orbitals and \(|\sigma_i\rangle\) is the occupation configuration of each orbital (if using spatial-orbital, \(|\sigma_i\rangle = \{|\text{vacuum}\}, |\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle\}; if using spin-orbital, \(|\sigma_i\rangle = \{|\text{vacuum}\}, |\text{occupied}\rangle\}). \(A[i]^{a_{i-1}}_{a_i}\) are the local matrices connected by the indices \(a_i\), which is commonly called (virtual) bond with bond dimension \(M_S\) or denoted as \(|a_i\rangle\). \(\sigma_i\) is called the physical bond with dimension \(d\). One good feature of DMRG is that the accuracy is only determined by the dimension of the virtual bond, and thus could be systematically improved.

Similar to MPS, any operator \(\hat{O}\) could be expressed as a matrix product operator:\(^{26,33}\)

\[ \hat{O} = \sum_{\{w\},\{\sigma\},\{\sigma'\}} W[1]^{\sigma'_1}_{w_1} W[2]^{\sigma'_2}_{w_2} \cdots W[N]^{\sigma'_N}_{w_{N-1}} |\sigma'_1 \sigma'_2 \cdots \sigma'_N\rangle \langle \sigma_N \sigma_{N-1} \cdots \sigma_1|. \]  \hspace{1cm} (2)

MPO could be constructed by sequential singular value decompositions from the matrix element representation \(O_{\sigma_1' \sigma_2' \cdots \sigma_N' \sigma_1 \sigma_2 \cdots \sigma_N}\) numerically, but it is not practical for a large system since the exact decomposition needs the bond dimension \(M_O\) to increase exponentially, which is \(d^2, d^4, \ldots, d^{N-2}, d^N, d^{N-2}, \ldots, d^2\) if \(N\) is even. In practice, if an operator has a sum-of-
products (SOP) form, MPO is usually first constructed symbolically,

\[
\hat{O} = \sum_{\{z\}} \gamma_{z_1 z_2 \cdots z_N} \hat{z}_1 \hat{z}_2 \cdots \hat{z}_N \tag{3}
\]

\[
= \sum_{\{w\}, \{z\}} W[1]_{w_1} W[2]_{w_1 w_2} \cdots W[N]_{w_{N-1}} \hat{z}_1 \hat{z}_2 \cdots \hat{z}_N \tag{4}
\]

\[
= \sum_{\{w\}} \hat{W}[1]_{w_1} \hat{W}[2]_{w_1 w_2} \cdots \hat{W}[N]_{w_{N-1}}. \tag{5}
\]

In eq (3), \{\hat{z}_i\} represents the elementary operators of each local site such as \{\hat{I}, \hat{p}^2, \hat{x}, \hat{x}^2, \text{etc}\} for a vibrational site or \{\hat{I}, \hat{a}^\dagger, \hat{a}, \hat{a}^\dagger \hat{a}\} for an electronic site. The prefactor \(\gamma_{z_1 z_2 \cdots z_N}\) is commonly very sparse. For example, in the ab initio electronic Hamiltonian, \(\gamma_{z_1 z_2 \cdots z_N} = 0\) if more than four \(\hat{z}_i\) are \(\hat{a}^\dagger\) or \(\hat{a}\). \(\gamma_{z_1 z_2 \cdots z_N}\) could be regarded as the coefficient of \(\hat{O}\) on the operator basis \(\hat{z}_1 \hat{z}_2 \cdots \hat{z}_N\) and its matrix product representation in eq (4) is very similar to an MPS in eq (1). In eq (5), \(\hat{W}[i] = \sum_{\{z_i\}} W[i]_{z_i} \hat{z}_i\) is a matrix composed of some prefactor attached symbolic operators acting locally on site \(i\). From this symbolic MPO, it is easy to obtain the matrix element representation as eq (2) by expanding \(\hat{W}[i]\) on the local basis \(\{|\sigma_i\}\).

From \(\gamma_{z_1 z_2 \cdots z_N}\), if all terms with a nonzero prefactor are extracted, \(\hat{O}\) can also be expressed as

\[
\hat{O} = \sum_{o=1}^{K} \hat{O}[1:N]_o = \sum_{o=1}^{K} (\gamma_o \prod_{i=1}^{N} \hat{z}_i^o). \tag{6}
\]

\(K\) is the number of nonzero terms in total. \(\hat{z}_i^o\) is the local operator of the \(o\)th term at site \(i\) and could be any of the elementary operators in \(\hat{z}_i\). The slice \([1 : N]\) indicates that the operator is from site 1 to site \(N\). The MPO representation of each term \(\hat{O}[1 : N]_o\) in eq (6) has \(M_O = 1\) with \(\hat{W}[i] = \hat{z}_i^o\) and the prefactor \(\gamma_o\) could be attached to any site. The global
arithmetic “add” of any two MPOs (not necessary to have $M_O = 1$) is

$$\gamma_1 \hat{O}[1 : N]_1 + \gamma_2 \hat{O}[1 : N]_2 = \left[ \hat{z}_1 \ 0 \\ 0 \ \hat{z}_1 \right] \left( \prod_{i=2}^{N-1} \left[ \hat{z}_i \ 0 \\ 0 \ \hat{z}_i \right] \right) \left[ \begin{array}{c} \gamma_1 \hat{z}_N \\ \gamma_2 \hat{z}_N \end{array} \right],$$  \hspace{1cm} (7)

which merges the local matrices block-diagonally. Therefore, the naive way to construct MPO of $\hat{O}$ in eq (6) will give $M_O = K$.

A more systematic way to derive MPO is to use the recurrence relation between the neighboring sites. When the system is split between site $i$ and site $i + 1$ into the respective left (L, from site 1 to $i$) and right (R, from site $i + 1$ to $N$) blocks, $\hat{O}$ could be expressed as

$$\hat{O} = \sum_{\alpha_i=1}^{K} \gamma_{\alpha_i} \cdot \hat{O}[1 : i]_{\alpha_i} \otimes \hat{O}[i + 1 : N]_{\alpha_i}$$  \hspace{1cm} (8)

$\hat{O}[1 : i]_{\alpha_i} = \prod_{j=1}^{i} \hat{z}_j^\alpha$ and $\hat{O}[i + 1 : N]_{\alpha_i} = \prod_{j=i+1}^{N} \hat{z}_j^\alpha$ are usually called the normal operators. A recurrence relation between the neighboring $\hat{O}[1 : i - 1]_{\alpha_{i-1}}$ and $\hat{O}[1 : i]_{\alpha_i}$ could be defined as

$$\hat{O}[1 : i]_{\alpha_i} = \sum_{\alpha_{i-1}=1}^{K} \hat{O}[1 : i - 1]_{\alpha_{i-1}} \hat{O}[i]_{\alpha_{i-1}\alpha_i},$$  \hspace{1cm} (9)

from which the symbolic MPO in eq (5) could be obtained directly with $\hat{W}[i] = \hat{O}[i]$ and again the prefactor $\gamma_{\alpha_i}$ could be attached to any site. This construction gives the same result as the global arithmetic “add” of $K$ MPOs with $M_O = 1$ in eq (7). However, it is apparently not optimal in that some of the interaction terms in eq (8) may share the common operators in the set $\{\hat{O}[1 : i]_{\alpha_i}\}$ or $\{\hat{O}[i + 1 : N]_{\alpha_i}\}$. For example, if $K = 2$ and $\hat{O}[i + 1 : N]_1 \equiv \hat{O}[i + 1 : N]_2$ while $\hat{O}[1 : i]_1 \neq \hat{O}[1 : i]_2$, $\hat{O}[1 : i]_1$ and $\hat{O}[1 : i]_2$ could be summed up with the prefactors to create a complementary operator $\hat{O}[1 : i]_1 = \gamma_1 \hat{O}[1 : i]_1 + \gamma_2 \hat{O}[1 : i]_2$ on the L-block and meanwhile $\hat{O}[i + 1 : N]_2$ is removed from the R-block so that $\hat{O} = \hat{O}[1 : i]_1 \otimes \hat{O}[i + 1 : N]_1$. Thus, $|\alpha_i|$, the number of columns of $\hat{O}[i]$, is reduced
by 1. This example shows that the MPO representation of the same operator is not unique as long as the product result is correct. Generally speaking, to make the MPO compact, if there are redundant operators in \( \{ \hat{O}[i+1 : N]_{o_i} \}(\{ \hat{O}[1 : i]_{o_i} \}) \), the corresponding left (right) complementary operators could be created. This complementary operator technique is of essential importance in constructing MPO for ab initio electronic Hamiltonian by assembling all the 4-index operators \( \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_r a_s \) and 3-index operators \( \sum_{pqr} g_{pqrs} a_p^\dagger a_q^\dagger a_r \) and part of the 2-index operators in one block, reducing \( M_O \) from \( \mathcal{O}(N^4) \) to \( \mathcal{O}(N^2) \). However, the complexity of designing complementary operators comes from that in most Hamiltonian both \( \hat{O}[1 : i]_{o_i} \) and \( \hat{O}[i+1 : N]_{o_i} \) in one interaction term are correlated to other interaction terms. For instance, we add another two terms in the former example, \( \hat{O}[1 : i]_1 \equiv \hat{O}[1 : i]_3 \) and \( \hat{O}[1 : i]_2 \equiv \hat{O}[1 : i]_4 \). In this case, the optimal solution is to create complementary operators \( \hat{O}[i+1 : N]_1 = \gamma_1 \hat{O}[i+1 : N]_1 + \gamma_3 \hat{O}[i+1 : N]_3 \) and \( \hat{O}[i+1 : N]_2 = \gamma_2 \hat{O}[i+1 : N]_2 + \gamma_4 \hat{O}[i+1 : N]_4 \), which will give \( |o_i| = 2 \). While creating the complementary operator \( \hat{O}[1 : i]_1 \) as above will result in \( |o_i| = 3 \). This toy example shows that the design of complementary operators is nontrivial. A typical real example is that when constructing MPO of the ab initio electronic Hamiltonian, a different design strategy of the complementary operators of the 2-index operators within one block will lead to a different \( M_O \) shown in Figure 10 of ref. 33 though all of them are \( \mathcal{O}(N^2) \). Therefore, the key to construct a compact MPO is to design and select the normal and complementary operators smartly at each bond to make the number of retained operators as small as possible. As far as we know, up to now it is still an art to design the complementary operators by hand on a case-by-case basis rather than by a rigorous and automatic procedure.

### 2.2 Novel MPO construction algorithm via bipartite graph theory

We propose to use the theory of bipartite graph to set a rigorous foundation to construct MPO automatically. We first reinterpret the operator selection problem at each bond mentioned in section 2.1 as a minimum vertex cover problem in a bipartite graph and then prove
that the locally optimal solution is also globally optimal.

Figure 1: An example of mapping the operator $\hat{O} = \gamma_{11}\hat{U}_1\hat{V}_1 + \gamma_{12}\hat{U}_1\hat{V}_2 + \gamma_{13}\hat{U}_1\hat{V}_3 + \gamma_{22}\hat{U}_2\hat{V}_2 + \gamma_{32}\hat{U}_3\hat{V}_2 + \gamma_{43}\hat{U}_4\hat{V}_3 + \gamma_{44}\hat{U}_4\hat{V}_4$ to a bipartite graph $G = (U, V, E)$. The vertices represent the non-redundant operators in the L- and R- block. The edges represent the interactions with a nonzero prefactor. The vertices in blue form a minimum vertex cover. The edges in red form a maximum matching.

The non-redundant operator set by removing the duplicated operators in $\{\hat{O}[1 : i_{\alpha}]\}, \{\hat{O}[i + 1 : N]_{\alpha}\}$ of eq (8) are denoted as $U = \{\hat{U}[1 : i]_{\alpha}\}, V = \{\hat{V}[i + 1 : N]_{\alpha}\}$, which are represented as the vertices in Figure 1. Unlike that the interaction pattern is one-to-one between $\{\hat{O}[1 : i_{\alpha}]\}$ and $\{\hat{O}[i + 1 : N]_{\alpha}\}$, it would be one-to-many between $\{\hat{U}[1 : i]_{\alpha}\}$ and $\{\hat{V}[i + 1 : N]_{\alpha}\}$. The $K$ interaction terms are represented as the edges denoted as $E$ each connecting one vertex in $U$ to one vertex in $V$ with a prefactor (weight) $\gamma_{u_i v_i}$. A bipartite graph is often denoted as $G = (U, V, E)$. If the $p$th vertex in $U$ is selected, the corresponding operator $\hat{U}[1 : i]_p$ in the L-block is retained. Meanwhile, the operators $\hat{V}[i + 1 : N]_q$ corresponding to the vertices in $V$ which are linked to $\hat{U}[1 : i]_p$ through edges are multiplied by the prefactor of the certain edge and then are added up to create a new complementary operator in the R-block $\sum_q \gamma_{pq}\hat{V}[i + 1 : N]_q$. The same rule is applied if a vertex in $V$ is selected. Therefore, the minimal number of retained operators in one block which could cover all the $K$ interaction terms is equal to the minimal number of selected vertices in $(U, V)$ which could cover all the edges in $E$ (shown in blue in Figure 1). The latter problem
is called the minimum vertex cover in graph theory. For a bipartite graph described here, Kőnig theorem proves that the number of vertices in the minimum vertex cover is equal to the number of edges in the maximum matching.\textsuperscript{39} A matching is an edge set in which any two edges do not share one vertex. The maximum matching shown in red in Figure 1 is the matching having the maximal number of edges, which could be solved efficiently by the Hungarian algorithm\textsuperscript{40} with complexity $O(nm)$ or the HopcroftKarp algorithm\textsuperscript{41} with complexity $O(\sqrt{nm})$ through finding an augmenting path.\textsuperscript{39} Here, $n$ and $m$ are the total number of vertices and edges in the bipartite graph. Once the maximum matching is found, the vertices in the minimum vertex cover could be obtained easily and the retained operators are optimally selected according to the rules above.

For a DMRG chain with a certain order, the whole procedure to construct the MPO of $\hat{O}$ from site 1 to $N$ (from $N$ to 1 is similar) is summarized as follows.

1. The incoming non-redundant operator set of site $i$ is known as $\{\hat{W}[1 : i−1]_{w_{i−1}}\}$ ($\{\hat{W}[1 : 0]\} = \{1\}$), which are also the outgoing operators of site $i−1$. Commonly, $\{\hat{W}[1 : i−1]_{w_{i−1}}\}$ includes both normal operators and complementary operators. Next, $\{\hat{W}[1 : i−1]_{w_{i−1}}\}$ is multiplied by the local elementary operators $\{\hat{z}_i\}$ on site $i$ to form a non-redundant operator set $\{\hat{U}[1 : i]_{u_i}\} = \{\hat{W}[1 : i−1]_{w_{i−1}}\} \otimes \{\hat{z}_i\}$. The R-block non-redundant operator set is $\{\hat{V}[i+1 : N]_{v_i}\}$, in which all operators are normal operators. Note that for efficiency only the interaction terms with a nonzero prefactor are necessary to be included in the operator sets $\{\hat{U}[1 : i]_{u_i}\}$ and $\{\hat{V}[i+1 : N]_{v_i}\}$. Hence, at this boundary between site $i$ and $i+1$, $\hat{O} = \sum_{u_i,v_i} \gamma_{u_i,v_i} \hat{U}[1 : i]_{u_i} \otimes \hat{V}[i+1 : N]_{v_i}$.

2. The operators in $\{\hat{U}[1 : i]_{u_i}\}$, $\{\hat{V}[i+1 : N]_{v_i}\}$ and the interactions between them are represented as vertices and edges to form a bipartite graph $G = (U, V, E)$ (see Figure 1). Afterward, the maximum matching and the corresponding minimum vertex cover of this bipartite graph is found with the Hungarian algorithm or the HopcroftKarp algorithm. Next, iterating through each vertex in the minimum vertex cover once:
2.1. If the vertex is the \( p \)th vertex in \( U \), the operator \( \hat{U}[1 : i]_p \) is retained and meanwhile the edges linked to it are removed from the graph.

2.2. If the vertex is the \( q \)th vertex in \( V \), the complementary operator linked through edges to \( \hat{V}[i + 1 : N]_q \) is created and retained, which is \( \hat{U}[1 : i]_q = \sum_p \gamma_{pq} \hat{U}[1 : i]_p \). Meanwhile, the edges are removed.

The reason to remove the edges after each visit is to avoid the double-counting of the interactions. After all the vertices in the minimum vertex cover are visited once, there will be no edge in the graph.

3. The retained operators \( \hat{U}[1 : i]_p \) and \( \hat{U}[1 : i]_q \) together form a new non-redundant operator set \( \{ \hat{W}[1 : i]_{w_i} \} \) in the L-block. It is the outgoing operator set of site \( i \) and meanwhile is the incoming operator set of site \( i + 1 \). After that, with \( \{ \hat{W}[1 : i - 1]_{w_{i-1}} \} \) and \( \{ \hat{W}[1 : i]_{w_i} \} \), the local symbolic MPO \( \hat{W}[i] \) is easy to obtain according to the recurrence relation \( \hat{W}[1 : i] = \hat{W}[1 : i - 1] \hat{W}[i] \). In fact, the local prefactor matrix \( W[i]_{w_{i-1}w_i} \) in \( \hat{W}[i]_{w_{i-1}w_i} = \sum_{z_i} W[i]_{z_i}^{z_i} \hat{z}_i \) is the transformation matrix (reshaped to be \( W[i]_{w_{i-1}z_i,w_i} \)) of operator basis from \( \{ \hat{W}[1 : i - 1]_{w_{i-1}} \} \otimes \{ \hat{z}_i \} \) to \( \{ \hat{W}[1 : i]_{w_i} \} \).

Return back to step 1.

The procedure described above is apparently a locally optimal solution, since the selected operators have already been the minimum vertex cover at each boundary when sweeping from the left to the right. To prove that the locally optimal solution is also globally optimal, we should prove that at each boundary between site \( i \) and \( i + 1 \), the number of edges in the maximum matching (the number of vertices in the minimum vertex cover) is the same no matter whether the operator set of L-block is composed of all normal operators or is composed of both normal operators and complementary operator as \( \{ \hat{W}[1 : i]_{w_i} \} \) according to step 1 to step 3.

Following eq (3), if the coefficient tensor \( \gamma_{z_1z_2\cdots z_N} \) is reshaped as a matrix \( \gamma_i = \gamma_{z_1z_2\cdots z_i,z_{i+1}\cdots z_N} \), it could be regarded as the coefficient matrix of \( \hat{O} \) expanded on the operator basis \( \{ \hat{z}_1 \otimes \cdots \otimes \)
\[ \hat{z}_i \otimes \{ \hat{z}_{i+1} \otimes \cdots \otimes \hat{z}_N \} \] in the operator space. \( \gamma_i \) is called the unfolding matrix of \( \gamma \) in ref 42, whose rank is denoted as \( r_i \) called TT-rank. The bipartite graph \( G[i] = (U[i], V[i], E[i]) \) at the boundary between site \( i \) and site \( i+1 \) is \( U[i] = \{ \hat{z}_1 \otimes \cdots \otimes \hat{z}_i \}, V[i] = \{ \hat{z}_{i+1} \otimes \cdots \otimes \hat{z}_N \}, \) the edges \( E[i] \) has a one-to-one correspondence to the nonzero matrix element in \( \gamma_i \). In the bipartite graph theory, the matrix \( \gamma_i \) could also be regarded as a symbolic bipartite adjacency matrix, for which only that the matrix elements are zero or nonzero is important. Lovász proposed the theorem that the rank of the symbolic adjacency matrix is equal to the number of edges of a maximum matching.\(^{43}\) Therefore, since \( U[i] \) and \( V[i] \) are composed of all normal operators, using the rules described above to select the normal and complementary operators, the ideally minimal number of retained operators at this boundary is equal to \( r_i \), the rank of matrix \( \gamma_i \). In the following, we will prove that sweeping from the left to the right as the procedure above will not change the rank of the adjacency matrix at the same boundary.

Starting from the left at the boundary between site 1 and 2, after the first loop through step 1 to step 3, the coefficient matrix \( \gamma_1 \) is factorized as

\[
\gamma_1 = \gamma_{z_1,z_2 \cdots z_N} = \sum_{w_1} W[1]_{z_1,w_1} C[2:N]_{w_1,z_2,z_3 \cdots z_N} \tag{10}
\]

The matrix \( W[1]_{z_1,w_1} \) is the transformation matrix given in step 3. According to Lovász’s theorem, the dimension of \( w_1, |w_1| \), is equal to \( r_1 \). eq (10) is nothing but a special rank decomposition of matrix \( \gamma_1 \). Hence, both \( W[1] \) (columns are linearly independent) and \( C[2:N] \) (rows are linearly independent) have rank \( r_1 \). Thus,

\[
C[2:N]_{w_1,z_2,z_3 \cdots z_N} = (W[1]^TW[1])^{-1}W[1]^T\gamma_1 = X[1]\gamma_1 \tag{11}
\]

We will show that the unfolding matrices of \( C[2:N] \), which are \( C[2:N]_2 = C[2:N]_{w_1,z_2,z_3 \cdots z_N}, C[2:N]_3 = C[2:N]_{w_1,z_2,z_3,z_4 \cdots z_N}, \cdots, C[2:N]_{N-1} = C[2:N]_{w_1,z_2 \cdots z_{N-1},z_N} \) all
have \( \text{rank}(C[2 : N]_i) = r_i \). Since \( \gamma_i \) has rank \( r_i \), a rank decomposition exists

\[
\gamma_i = \sum_{\beta=1}^{r_i} H_{z_1 \cdots z_i} F_{\beta, z_{i+1} \cdots z_N}
\]

Thus,

\[
C[2 : N]_i = C[2 : N]_{w_1 z_2 \cdots z_i} = X[1]_{w_1 z_1} \gamma_{z_1 z_2 \cdots z_i, z_{i+1} \cdots z_N}
\]

\[
= \sum_{z_1} X[1]_{w_1 z_1} \left( \sum_{\beta=1}^{r_i} H_{z_1 \cdots z_i} F_{\beta, z_{i+1} \cdots z_N} \right)
\]

\[
= \sum_{z_1} \left( \sum_{\beta=1}^{r_i} X[1]_{w_1 z_1} H_{z_1 \cdots z_i} F_{\beta, z_{i+1} \cdots z_N} \right)
\]

\[
= \sum_{\beta=1}^{r_i} M_{w_1 z_2 \cdots z_i} F_{\beta, z_{i+1} \cdots z_N}
\]

Therefore, \( \text{rank}(C[2 : N]_i) \leq r_i \). On the other hand, if \( \text{rank}(C[2 : N]_i) < r_i \),

\[
\gamma_i = \sum_{w_1} W[1]_{z_1, w_1} C[2 : N]_{w_1 z_2 z_3 \cdots z_N}
\]

\[
= \sum_{w_1} W[1]_{z_1, w_1} \left( \sum_{\beta=1}^{\text{rank}(C[2 : N]_i)} M_{w_1 z_2 \cdots z_i} F_{\beta, z_{i+1} \cdots z_N} \right)
\]

\[
= \sum_{\beta=1}^{\text{rank}(C[2 : N]_i)} \left( \sum_{w_1} W[1]_{z_1, w_1} M_{w_1 z_2 \cdots z_i} F_{\beta, z_{i+1} \cdots z_N} \right)
\]

\[
= \sum_{\beta=1}^{\text{rank}(C[2 : N]_i)} H_{z_1 \cdots z_i, \beta} F_{\beta, z_{i+1} \cdots z_N}
\]

The decomposition is contradictory to that the rank of \( \gamma_i \) is \( r_i \). Thus, \( \text{rank}(C[2 : N]_i) = r_i \). The symbolic bipartite adjacency matrix between site 2 and 3 is \( C[2 : N]_2 \), which has rank \( r_2 \). \( C[2 : N]_2 \) could be further symbolically decomposed by finding the maximum matching
and then the transformation matrix in step 3:

\[
C[2 : N]_2 = \sum_{w_2=1}^{r_2} W[2]_{w_1 z_2, w_2} C[3 : N]_{w_2, z_3 \cdots z_N}
\] (15)

The process can be continued by induction. This whole proof is very similar to Theorem 2.1 of ref 42. The difference is that the equality \( \text{rank}(C[i : N]_j) = r_j \ (j \geq i) \) always holds. The proof above could be intuitively understood from the fact that the rank of the coefficient matrix between two sub-systems will not change after sequential linear combinations of the basis in each sub-system as long as the new basis is linearly independent. Therefore, after sweeping from the left to the boundary between site \( i \) and \( i+1 \), since the rank of the bipartite adjacency matrix \( C[i : N]_i \) is \( r_i \), the minimal number of retained operators is the same as the case that all normal operators are retained without any combination (complementary operators). As a result, the locally optimal solution is also globally optimal. It is worth noting that in ref 35, the ideal rank \( r_i \) of MPO at the \( i \)th bond is expected to be approached by numerical SVD compression, deparallelization and delinearization, but it is not guaranteed because of the numerical error. But here, it is guaranteed symbolically via the bipartite graph theory.

Several other advantages of the novel algorithm are that (i) The sparsity of MPO is fully maintained, which could be used to reduce the computational cost during the tensor contraction in DMRG single state or time evolution algorithms. (ii) The symmetry could be directly implemented by attaching the good quantum numbers on each normal and complementary operator. (iii) The algorithm not only works for MPO construction, but also works for MPS construction if the wavefunction in the Fock space representation has already been known. For the same reason, the obtained MPS is the most compact one to represent the wavefunction exactly.

Finally, it should be mentioned that for a system in which the interaction pattern is inhomogeneous, the order of DoFs will affect the size of MPO. It is still unclear whether
there is an algorithm which could efficiently find out a specific order with the minimal MPO. However, in our opinion, this problem is less of a priority than the widely known ordering problem with respect to the accuracy of DMRG calculation.

3 Results

In this section, we will demonstrate the effectiveness of the new algorithm by constructing the MPOs of Hamiltonians ranging from the simple spin-boson model and Holstein model to the more complicated ab initio electronic Hamiltonian and vibrational Hamiltonian with a sextic force field.

3.1 Spin-boson model and Holstein model

The spin-boson model (expressed in the first quantization formalism in eq (16)) describes a two-level system coupled with a harmonic bath, which is widely used to investigate the quantum dissipation.

\[
\hat{H}_{\text{SBM}} = \epsilon \hat{\sigma}_z + \Delta \hat{\sigma}_x + \frac{1}{2} \sum_i (\hat{p}_i^2 + \omega_i^2 \hat{q}_i^2) + \hat{\sigma}_z \sum_i c_i \hat{q}_i
\] (16)

Holstein model (expressed in the second quantization formalism in eq (17)) is also a widely used electron-vibrational coupling model to describe the charge transport, energy transfer and spectroscopy of molecular aggregates.\cite{17,21,46,47} It could be regarded as a group of two-level systems as the spin-boson model coupled with each other through coupling constant $J_{ij}$.

\[
\hat{H}_{\text{Holstein}} = \sum_i \varepsilon_i a_i^\dagger a_i + \sum_{i \neq j} J_{ij} a_i^\dagger a_j + \sum_{in} \omega_{in} b_i^\dagger b_i + \sum_{in} \omega_{in} g_{in} a_i^\dagger a_i (b_i^\dagger + b_i)
\] (17)

Both of the two models are often adopted to benchmark the quantum dynamics methods. We put the two models in the same section because spin-boson model could be re-
garded as a one-site Holstein model with an additional interstate coupling $\Delta$ and thus the MPOs of them are very similar. We test a spin-boson model with 100 discrete modes and the order is $[\text{spin}, v_1, v_2 \cdots, v_{100}]$. We also test two Holstein models with 20 electronic sites and both of them have two vibrational modes of each electronic site but the former only has one-dimensional nearest-neighbor electronic hopping while the latter has long-range hoppings between any two electronic sites. The order of the Holstein model is $[e_1, v_{1,1}, v_{1,2}, e_2, v_{2,1}, v_{2,2}, \cdots, e_{20}, v_{20,1}, v_{20,2}]$. The MPO bond dimension $M_O$ versus the bond index is shown in Figure 2. The reference results (blue line) are based on a manually-designed strategy, in which the normal operators for the electronic coupling terms are switched to the complementary operators $\hat{P}_j = \sum_i J_{ij} a_i$ and $\hat{P}_j^\dagger = \sum_i J_{ij} a_i^\dagger$ after passing the middle electronic site. The details are provided in the appendix in our former work, which is believed to be near-optimal for the two models (from the results shown below, it is optimal except at the first bond for the Holstein model.).

For the spin-boson model shown in Figure 2a, $M_O$ is a constant independent of system size because $\hat{W}[1 : i] = \{\hat{H}[1 : i], \hat{\sigma}_z, \hat{I}\}$ where $\hat{H}[1 : i]$ is the complete Hamiltonian from site 1 to $i$. The new automatic algorithm gives exactly the same result as the manually-designed one. For the Holstein model shown in Figure 2b and 2c, $M_O$ is independent of the number of the electronic site when the electronic coupling is one-dimensional nearest-neighbor coupling, while it is linearly dependent on the number of the electronic site if the long-range hopping is allowed. The new automatic algorithm gives the same results as the manually-designed ones except at the first bond, where the new algorithm gives one less bond dimension. This minor difference comes from that the manually-designed strategy gives $\hat{W}[1] = \{\varepsilon_1 a_1^\dagger a_1, a_1^\dagger a_1, a_1^\dagger, a_1, \hat{I}\}$ while the automatic algorithm gives $\hat{W}[1] = \{a_1^\dagger a_1, a_1^\dagger, a_1, \hat{I}\}$ and the local energy of the first site $\varepsilon_1 a_1^\dagger a$ is considered in $\hat{W}[2]_{0,0} = \varepsilon_1 \hat{I}$. Though this small improvement will not make a noticeable difference on the actual computational cost, it is clear to demonstrate that since the new algorithm is globally optimal, it could find out the redundancy which will be neglected sometimes with the common manually-designed
strategy.

Figure 2: The bond dimension $M_O$ versus the bond index in (a) spin-boson model with 100 discrete vibrational modes. (b) Holstein model of 20 electronic sites with only one-dimensional electronic coupling and each electronic site has two vibrational modes. (c) same as (b) except with arbitrary long-range electronic couplings. The reference results (blue line) are based on the manually-designed complementary operator strategy provided in our former work.\(^{17}\)

3.2 Ab initio electronic Hamiltonian

The second Hamiltonian considered is the ab initio electronic Hamiltonian, in which up to 4 sites are interacted. Thus it is much more complicated than the spin-boson model and Holstein model. With spin-orbitals, the Hamiltonian is written as

$$
\hat{H}_{el} = \sum_{p,q=1}^{N} h_{pq}a_{p}^{\dagger}a_{q} + \frac{1}{2} \sum_{p,q,r,s=1}^{N} v_{pqrs}a_{p}^{\dagger}a_{r}^{\dagger}a_{q}a_{s} = \sum_{p,q=1}^{N} h_{pq}a_{p}^{\dagger}a_{q} + \sum_{p<q,r<s}^{N} g_{pqrs}a_{p}^{\dagger}a_{q}^{\dagger}a_{r}a_{s} \quad (18)
$$

where the two-electron integral $v_{pqrs}$ is $(ps|qr)$ in chemist’s notation. The second equality with $g_{pqrs} = v_{pqrs} - v_{qprs} = v_{pqrs} - v_{pqsr}$ takes advantage of the symmetry in $v_{pqrs}$.

Firstly, we introduce the optimal manually-designed strategy to construct the MPO of ab initio electronic Hamiltonian. For more implementation details, please refer to ref \(^{33}\). For convenience, $\hat{H}_{el}$ is divided into three components. The first part is $\hat{H}_1 = \hat{H}_L + \hat{H}_R$, in which $\hat{H}_L$ and $\hat{H}_R$ are respectively the full Hamiltonian of the orbitals in the L-block and R-block. In fact, $\hat{H}_L$ and $\hat{H}_R$ could be regarded as the complementary operators of identity operator.
\(\hat{I}_R\) and \(\hat{I}_L\) in the R-block and L-block, reducing \(O(N^4)\) normal operators to 1 complementary operator. Apparently, \(\hat{H}_1\) has \(M_{O,1} = 2\) at each bond. The second part with two fermionic creation or annihilation (elementary) operators in each block is written as

\[\hat{H}_2 = \sum_{pqr<s} -g_{pLQRRLS}(a_{pL}^\dagger a_{qR}) (a_{qR}^\dagger a_{sL}) + g_{pLQLRSR}(a_{pL}^\dagger a_{qL}^\dagger) (a_{qR} a_{sR}) + g_{PRQRLSRL}(a_{qL} a_{sL}) (a_{pR}^\dagger a_{qR}^\dagger) \tag{19}\]

The optimal strategy to design the complementary operator depends on the number of orbitals denoted as \(n_L\) and \(n_R\) in each block. For instance, if \(n_L > n_R\), the complementary operators of the first term in eq \(19\) is \(\hat{P}_{qs} = \sum_{pr} -g_{pLQRRLS}(a_{pL}^\dagger a_{rL})\), which have \(n_R^2\) terms in total. Therefore, the ideally minimal bond dimension is \(M_{O,2} = \min(n_L^2, n_R^2) + 2 \cdot \min(n_L(n_L - 1)/2, n_R(n_R - 1)/2)\). The third part with one creation or annihilation operator in one block and three in the other is commonly written as

\[
\hat{H}_3 = \sum_p a_{pL}^\dagger \left( \sum_q \frac{1}{2} h_{pLQR} a_{qR} + \sum_{qrs} g_{pLQRRLS}(a_{qR}^\dagger a_{rL} a_{sR}) \right) \\
+ \sum_r a_{rL} \left( \sum_s -\frac{1}{2} h_{sRL} a_{sR}^\dagger + \sum_{pqrs} g_{PRQRLS}(a_{pR}^\dagger a_{qR}^\dagger a_{rL} a_{sR}) \right) \\
+ \sum_q \left( \sum_{pq} -\frac{1}{2} h_{QRPL} a_{pL} + \sum_{pqrs} g_{PLQLRS}(a_{pL}^\dagger a_{rL} a_{sL}) \right) a_{qR}^\dagger \\
+ \sum_s \left( \sum_{pq} \frac{1}{2} h_{RLSR} a_{rL}^\dagger + \sum_{pqrs} g_{PRQRSL}(a_{pL}^\dagger a_{qL}^\dagger a_{rL}) \right) a_{sR} \tag{20}\]

The terms in the parentheses are the complementary operators which should be firstly summed up. This kind of complementary operators is used to construct MPO of ab initio electronic Hamiltonian, as it greatly reduces \(M_{O,3}\) from \(O(N^3)\) to \(O(N)\). However, it is only near-optimal because near the boundary of the chain, such as near the leftmost site there are more 1-index operators in the R-block than 3-index operator in the L-block and
thus the optimal way to construct the complementary operator at this boundary is

\[
\hat{H}_3 = \sum_p a^\dagger_{pl} \left( \sum_q h_{plqr} a_{qr} + \sum_{qrs} g_{plqr^rs} a^\dagger_{qr} a_{sr} \right) \\
+ \sum_r a_{rl} \left( \sum_s -h_{srl} a^\dagger_{sr} + \sum_{pqrs} g_{pqrlsr} a^\dagger_{pr} a^\dagger_{qr} a_{sr} \right) \\
+ \sum_{prs} a^\dagger_{pl} a_{rl} a_{sl} \left( \sum_q g_{plqlsr} a^\dagger_{qr} \right) \\
+ \sum_{pqrs} a^\dagger_{pl} a^\dagger_{ql} a_{rl} \left( \sum_s g_{plqlsr} a_{sr} \right)
\]  

(21)

It is similar at the bond near the rightmost boundary of the chain. Therefore, the minimal \(M_{O,3}\) equals \(2 \cdot \min(n_L^2(n_L - 1)/2, n_R) + 2 \cdot \min(n_L, n_R^2(n_R - 1)/2)\). It is clear that \(M_{O,2}\) contributes most to the total \(M_O = M_{O,1} + M_{O,2} + M_{O,3}\), and thus this improvement of \(M_{O,3}\) is rarely considered. But it could be considered automatically with our new algorithm.

Adding up the contributions of the three components, the largest bond dimension always lies in the middle of the chain, which is \(M_{O,\text{max}} = 2(\frac{N}{2})^2 + 3(\frac{N}{2}) + 2\).

With the new automatic MPO construction algorithm, the antisymmetry of fermions is considered by introducing the Jordan-Wigner transformation\(^{48}\) for the elementary creation and annihilation operators.\(^6\)\(^{31}\)

\[
|\text{vacuum}\rangle = |\alpha\rangle \\
|\text{occupied}\rangle = |\beta\rangle \\
\]

(22)

(23)

\[
a^\dagger_j = \prod_{i=1}^{j-1} \sigma_z[i] \times \sigma_- [j] \\
a_j = \prod_{i=1}^{j-1} \sigma_z[i] \times \sigma_+ [j]
\]

(24)

(25)

Figure 3a shows the maximal \(M_O\) of systems with 10 to 70 spin-orbitals and Figure 3b shows \(M_O\) at each bond of a 50 spin-orbitals system. The correctness of the MPOs obtained
Figure 3: (a) The maximal MPO bond dimension $M_{O,\text{max}}$ of ab initio electronic Hamiltonian with different number of spin-orbitals. The blue curve $M_{O,\text{max}} = 2\left(\frac{N}{2}\right)^2 + 3\left(\frac{N}{2}\right) + 2$ is the optimal result from the manually-designed complementary operator strategy (see text for details). The red circles are the results obtained from the new automatic MPO construction algorithm. (b) The MPO bond dimension $M_O$ at each bond of ab initio electronic Hamiltonian of a 50 spin-orbitals system.
from the new automatic algorithm has been verified by checking the residue \( \| \text{MPO}_1 - \text{MPO}_2 \| = 0 \) with respect to the MPOs developed by Li et al. in ref \(^6\) and implemented in package QCMPO.\(^{49}\) The obtained \( M_O \) at each bond and \( M_{O,\text{max}} \) (red asterisks) exactly matches what the optimally manually-designed strategy described above would give (blue circles), except at the first bond where the new automatic algorithm gives \( M_O = 4 \) and 
\[ \hat{W}[1] = [\sigma_- \sigma_+, \sigma_z \sigma_-, \sigma_z \sigma_+, \hat{I}] \]
while the manually-designed strategy gives \( M_O = 5 \) and 
\[ \hat{W}[1] = [h_{11} \sigma_- \sigma_+, \sigma_- \sigma_+, \sigma_z \sigma_- \sigma_z, \sigma_z \sigma_+, \hat{I}] \]. The reason is the same as that in the case of Holstein models.

In addition, in Figure 3b, \( M_O \) versus the bond index is symmetric as expected and the kink at the bond index 5 and 45 is due to the switch of the complementary operators from eq (21) to eq (20), indicating that the new algorithm could really find out the optimal solution.

The MPO obtained from the new automatic algorithm is also verified through calculating the ground state energy of water with 6-31g basis with different \( M_S \), which is shown in Figure 4. The structure of \( \text{H}_2\text{O} \) in the Cartesian coordinates is \( \text{O}(0,0,-0.0644484) \), \( \text{H}(\pm0.7499151, 0, 0.5114913) \) in Angstroms. The electron integral and the reference full configuration interaction (FCI) result are calculated by PySCF.\(^{50}\) The error of ground state energy with \( M_S = 800 \) is less than \( 1 \times 10^{-6} \) \( E_h \).

![Figure 4: The error of the ground state energy of H2O with 6-31g basis calculated by MPO based DMRG algorithm with different MPS bond dimension \( M_S \). The two-site algorithm is adopted to optimize the ground state MPS. The reference is the FCI energy \( E_{\text{FCI}} = -76.11969704 \) \( E_h \). The MPO is obtained from the new automatic MPO construction algorithm.](image)
3.3 Ab initio anharmonic potential energy surface with a sextic force field

The third example considered is the anharmonic vibrational Hamiltonian. With the Born-Oppenheimer approximation, solving the nuclear Schrödinger equation on high accurate ab initio potential energy surface is very important to obtain the anharmonic frequency and infrared spectrum.\textsuperscript{36,37,51} Herein we use the following vibrational Hamiltonian on normal coordinates, which neglects the Coriolis term and the Watson correction term in the Watson’s Hamiltonian.\textsuperscript{37}

\begin{equation}
\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial q_i^2} + V(\{q\}) \tag{26}
\end{equation}

\begin{equation}
V(\{q\}) = V_0 + \frac{1}{2} \sum_i \omega_i^2 q_i^2 + \frac{1}{3!} \sum_{ijk} F_{ijk} q_i q_j q_k + \frac{1}{4!} \sum_{ijkl} F_{ijkl} q_i q_j q_k q_l + \frac{1}{5!} \sum_{ijklm} F_{ijklm} q_i q_j q_k q_l q_m + \cdots \tag{27}
\end{equation}

$V(\{q\})$ is the analytical PES with high order Taylor expansion around the equilibrium geometry. Akin to the electronic structure theory, there are a series of methods at different hierarchical levels to solve the anharmonic vibrational Hamiltonian including vibrational self consistent field (VSCF), vibrational perturbation theory (VPT), vibrational configuration interaction (VCI), vibrational coupled cluster (VCC) and multi-reference approaches.\textsuperscript{37,52–55} MCTDH combined with the improved relaxation algorithm\textsuperscript{56} is another efficient method to obtain eigenstates of vibrational Hamiltonian. Recently, DMRG and TTNS have also been proposed to solve the anharmonic vibrational problem.\textsuperscript{10–12,29} We note that two methods have been used to construct MPO of vibrational Hamiltonian. In ref\textsuperscript{10} a compact MPO is constructed by SVD compression and in ref\textsuperscript{11} a symbolic MPO is constructed in the second quantization formalism as the electronic Hamiltonian.\textsuperscript{31} If high order potential terms are considered, the construction of the MPO of eq (26) could be even more complicated than the ab initio electronic Hamiltonian in section 3.2. To demonstrate the effectiveness
and efficiency of the new MPO construction algorithm, we choose the widely studied C\textsubscript{2}H\textsubscript{4} molecule\textsuperscript{11,53,57,58} and calculate the lowest nine eigenstates to obtain the zero point energy and the first eight fundamental frequencies with the state-averaged DMRG method (SA-DMRG). Using more sophisticated excited state algorithms\textsuperscript{12,59,60} in DMRG to target the high-lying excited states accurately is beyond the scope of the current work. The PES of C\textsubscript{2}H\textsubscript{4} used here is a sextic force field on normal coordinates as eq (27) from PyPES library\textsuperscript{57} which is an adaptation of the PES constructed at CCSD(T) level with quadruple-zeta basis on internal coordinates.\textsuperscript{61} The constant $V_0$ is set to 0 for simplicity. Since C\textsubscript{2}H\textsubscript{4} at equilibrium geometry has D\textsubscript{2h} point group symmetry, there are only 2644 nonzero potential terms in the Hamiltonian otherwise it would be 18485 terms. Figure 5 shows the MPO bond di-

![Figure 5: The MPO bond dimension $M_O$ versus bond index of C\textsubscript{2}H\textsubscript{4} described by an ab initio sextic force field with or without considering D\textsubscript{2h} point group symmetry.](image-url)

mension at each bond of the vibrational Hamiltonian of C\textsubscript{2}H\textsubscript{4} with or without considering the point group symmetry. The 12 vibrational DoFs within the DMRG chain are arranged according to their harmonic frequencies $\omega_i$. With point group symmetry, the largest MPO bond dimension is reduced from 112 to 77, which will reduce the computational cost spent in the DMRG static state or the time evolution calculations. Because the construction is automatic rather than by hand, the gain by utilizing symmetry to reduce the size of MPO is for free. For the same reason, for Hamiltonian where there are negligible terms, it would
be efficient to use the current algorithm to construct MPO by pre-screening of the prefactors. To demonstrate the correctness of the MPO, the zero point energy and the first eight fundamental frequencies calculated with different $M_S$ are listed in Table 1. The local basis for each DoF is the lowest 6 harmonic eigenbasis. For comparison, VCI(8) results with up to octuple excitation for the same PES are also listed. Table 1 shows that the convergence has already been reached within 1 cm$^{-1}$ with only $M_S = 50$ in the SA-DMRG calculation.

Table 1: The zero point energy (ZPE) and the first eight fundamental frequencies of $\text{C}_2\text{H}_4$ calculated by state-averaged DMRG.

| harmonic | SA-DMRG $M_S = 20$ | SA-DMRG $M_S = 50$ | SA-DMRG $M_S = 100$ | VCI(8)$^a$ |
|----------|-------------------|-------------------|-------------------|----------|
| ZPE      | 11164.45          | 11012.19          | 11011.67          | 11011.64 |
| $1$      | 824.97            | 820.83            | 820.06            | 820.12   |
| $2$      | 950.19            | 927.55            | 926.41            | 926.49   |
| $3$      | 966.39            | 942.64            | 941.75            | 941.82   |
| $4$      | 1050.81           | 1018.24           | 1017.53           | 1017.62  |
| $5$      | 1246.76           | 1222.61           | 1222.21           | 1222.35  |
| $6$      | 1369.38           | 1348.48           | 1342.30           | 1342.01  |
| $7$      | 1478.48           | 1447.10           | 1438.66           | 1438.32  |
| $8$      | 1672.57           | 1630.50           | 1623.28           | 1622.94  |

$^a$ the VCI(8) results are from ref 57,58. VCI(8) means that up to 8 modes could be excited in the CI calculation.

Finally, we briefly discuss the computational scaling when using the MPO based DMRG algorithms. When dealing with the ab initio electronic Hamiltonian, it has been pointed out that directly treating the MPO as a dense matrix will result in an incorrect scaling $O(N^5)$ compared to $O(N^4)$ of the original DMRG algorithm in which only the renormalized operator matrix is retained. Herein for the vibrational Hamiltonian with sextic force field, the same problem will arise. The $M_{O,\text{max}}$ of $\hat{H}$ with the number of vibrational modes is shown in Figure 1 (blue curve). For $\hat{H}$, $M_{O,\text{max}} = \frac{1}{48}N^3 + \frac{3}{8}N^2 + \frac{5}{3}N + 2$ when $N$ is even. The leading term $O(N^3)$ comes from the 3-index normal operators in each block and the prefactor is $\binom{N}{3}/3$. When calculating the expectation value $\langle \Psi | \hat{H} | \Psi \rangle$ or optimizing the ground state, the cost spent in each blocking process is $O(N^6)$, because the size of each local matrix in MPO is $O(N^3) \times O(N^3)$. Hence, the total cost after each sweep is $O(N^7)$.
However, with the original DMRG algorithm, the bottleneck in the blocking process is to contract the 3-index normal operators $q_i q_j q_k$ in the L-block (R-block) and 1-index operator $q_l$ in the center site to the complementary operator of $q_m q_n$ in the R-block (L-block), which is $\hat{P}_{mn} = \sum_{ijkl} F_{ijklmn} q_i q_j q_k q_l$, with a local computational scaling $O(N^5)$ and in total $O(N^6)$ in one sweep. To recover the correct scaling in the MPO based algorithm, two approaches have been proposed. One is to fully employ the sparsity of MPO when contracting tensors. The other method is to split the total $\hat{H}$ into a sum of $\hat{H}_i$, $\hat{H}_i = \sum_{i=1}^N \hat{H}_i$, where

$$\hat{H}_i = -\frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \frac{V_0}{N} + \frac{1}{2} \omega_i^2 q_i^2 + \frac{1}{3!} \sum_{jkl} F_{ijkl} q_i q_j q_k q_l + \frac{1}{4!} \sum_{jkl} F_{ijkl} q_i q_j q_k q_l + \frac{1}{5!} \sum_{jklm} F_{ijklm} q_i q_j q_k q_l q_m q_n.$$  

(28)

Figure 6: The maximal MPO bond dimension $M_{O,\text{max}}$ of the vibrational Hamiltonian $\hat{H}$ in eq (26) (blue circle) and $\hat{H}_i$ in eq (28) (red star) versus the number of modes. The blue curve $\frac{1}{48} N^3 + \frac{1}{2} N^2 + \frac{5}{3} N + 2$ exactly fits the $M_{O,\text{max}}$ of $\hat{H}$. The two black dashed curves $\frac{1}{4} N^2$ and $\frac{1}{2} N^2$ indicate the scaling of $M_{O,\text{max}}$ of $\hat{H}_i$ is $O(N^2)$ and the prefactor is between $\frac{1}{4}$ and $\frac{1}{2}$.

For $\hat{H}_i$ with index $i$ fixed, the maximal 5-free-index operator will give an MPO with $M_{O,\text{max}} = O(N^2)$. The red curve in Figure 6 shows $M_{O,\text{max}}$ of $\hat{H}_i$ with the number of modes. The prefactor of the leading term is between $\frac{1}{4}$ and $\frac{1}{2}$. If all the $N$ sub-MPOs are added up according to eq (7), the total MPO of $\hat{H}$ will be recovered with the same scaling of the
bond dimension $\mathcal{O}(N^3)$ but with a larger prefactor. The advantage to introduce $\hat{H}_i$ is that the contraction of $\hat{H}$ could be first divided into contractions of $\hat{H}_i$ and then sum them up together. Even though the MPO of $\hat{H}_i$ is treated as a dense matrix, the computational scaling in the blocking process is $\mathcal{O}(N^4)$ for each of them and the total $N$ MPOs will result in $\mathcal{O}(N^5)$. Therefore, this “sum of MPO” algorithm not only recovers the correct computational scaling but also is easy to be parallelized.

4 Conclusion

In this work, we propose a new generic algorithm for the construction of matrix product operator of any operator with a sum-of-products form based on the bipartite graph theory. The most important feature of the algorithm is that it could translate the operator expression to the MPO representation automatically. Therefore, it is very useful for the current (TD-)DMRG methods to be easily extended to more problems described by different Hamiltonians, such as different potential energy surfaces in quantum dynamics. The idea of the new algorithm is to map the complementary operator selection problem to a minimum vertex cover problem in a bipartite graph, which could be elegantly solved by several well-established algorithms to get a locally optimal solution. We also prove that the constructed MPO is globally optimal. In addition, the new algorithm is symbolic and the sparsity of the Hamiltonian is fully preserved, which could be utilized to reduce the computational cost when contracting the tensors. We demonstrate the effectiveness and efficiency of the new algorithm by constructing MPOs ranging from the simple spin-boson model, Holstein model to the more complicated ab initio electronic Hamiltonian, and vibrational Hamiltonian with ab initio sextic force field. In all of the examples, the new algorithm performs well in that it could find out the small redundancy in the near-optimal manually-designed MPO and it could take advantage of the symmetry to reduce the dimension of MPO. Finally, we expect that the generalization of the current graph-based algorithm for MPS/MPO or TT to other
tensor network states/operators would be interesting in the future.

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**Supporting Information Available**

The following files are available free of charge.

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Graphical TOC Entry

\[
\hat{\sigma} = \sum_{\alpha=1}^{K} \phi_{\alpha} \prod_{\beta=1}^{K} \sigma_{\beta}
\]