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RESEARCH ARTICLE

Tensor Representation Techniques in post-Hartree Fock Methods: Matrix Product State Tensor Format

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In this proof-of-principle study, we discuss the application of various tensor representation formats and their implications on memory requirements and computational effort for tensor manipulations as they occur in typical post Hartree-Fock methods. A successive tensor decomposition / rank reduction scheme in the matrix product state (MPS) format for the two electron integrals in the AO and MO basis and an estimate of the t_2 amplitudes as obtained from MP2 are described. Furthermore, the AO-MO integral transformation, the calculation of the MP2 energy and the potential usage of tensors in low rank MPS representation for the tensor contractions in CC theory are discussed in detail. We are able to show that the overall scaling of the memory requirements is reduced from the conventional N^4 scaling to approximately N^3 and the scaling of computational effort for tensor contractions in post-HF methods can be reduced to roughly N^4 while the decomposition itself scales as N^5 . While efficient algorithms with low prefactor for the tensor decomposition have yet to be devised, this Ansatz offers the possibility to find a robust approximation with low scaling behaviour with system and basis set size for post Hartree Fock ab initio methods.

Keywords: electronic structure methods, post Hartree-Fock, Configuration Interaction, Coupled Cluster, tensor representation, matrix product state, canonical polyadic product

1. Introduction - Tensor Decomposition Schemes in Quantum Chemistry

First principles electronic structure methods have become powerful tools that find widespread applications in many fields of modern sciences: Computational techniques can be used to interpret the outcome of measurements but they can also be put to creative use in the design of novel systems. The quantum chemical methodology has progressed to the stage where electronic structure methods like density functional theory (DFT) or second-order many-body perturbation theory (MP2) can be routinely applied to large molecular systems (100-200 atoms). [1–3]

From the broad perspective of applied mathematics many of the approximations to reduce the computational effort of quantum chemical methods can directly or indirectly be identified as tensor decomposition techniques of one kind or another. One particularly successful scheme to reduce computational complexity of electronic structure methods is based on the “resolution of the identity” (RI) [4–12] or “density fitting” (DF) approximation. [13–15] These methods have been

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applied since the 1970s in the framework of DFT [16–19] for calculating the Coulomb contribution. Although developed around the same time, the closely related method based on Cholesky Decomposition (CD) has only found its way into electronic structure theory more recently. [20–27] Both, the RI and CD approximations, can be thought of as factorizing expressions of higher dimensional mathematical objects (tensors) into objects of lower dimensionality. Through the decoupling of indices by factorization, the characteristic expensive nested summations occurring in electronic structure theory can be performed as series of summations with lower complexity. Another approach, in which a factorisable form of a multi-dimensional object is used to simplify the calculation has been proposed in the early 90s by Almlöf and Häser: In the Laplace-MP2 the energy denominator is approximated by a factorizing exponential expression. [28–31]

While RI and CD are only special cases which are limited to certain tensors, for example positive semidefinite quantities, a more general approach for representing also the wavefunction parameters of post-HF methods is needed. Methods based on Configuration Interaction (CI) like the hierarchy of Coupled Cluster (CC) methods [32, 33] have evolved into highly efficient tools and their accuracy and robustness has been proven in numerous application studies [33–42]. There, tensor decomposition techniques and low order tensor representations help to reduce the steep scaling of computational costs and also the high memory requirements of these methods. Already in the 1950s Löwdin proposed the usage of natural orbitals in order to achieve enhanced convergence of the CI series and thus to reduce the number of wavefunction parameters. [43–45] This idea has found its way into many modern theories - pair natural orbitals (PNO) [46–48] are used in efficient local approximations [49–52], recently Yang et al. [53–55] proposed the orbital specific virtual approximation (OSV) in the framework of the Pulay Saebø local approximation (non-orthogonal projected atomic orbitals PAO) [56–58] and a series of optimized virtual orbital space methods (OVOS) [59–62] minimizes the size of the virtual space.

While many of the modern truncation schemes rely on the local nature of electron correlation and are often either difficult to control with respect to the achievable accuracy or are not always straightforward to extend to arbitrary kind of electronic structure methods or molecular properties other alternatives have been proposed. General schemes for tensor representations offer new possibilities: Hino et al. describe an ansatz in which the computational effort required for the CCSD(T) method can be reduced by applying an approach related to singular value decomposition (SVD) [63, 64] to the t_3 amplitudes [65, 66]. A new approach termed tensor hypercontraction density fitting (THC-DF) is proposed by Hohenstein et al. [67] decomposing three centre integrals arising in the DF procedure with the CANDECOMP/PARAFAC procedure [64, 68] in order to get a factorized representation of the two electron integrals. These are used to reduce the scaling of second and third order Møller-Plesset perturbation theory to a quartic scaling. [67] We also proposed a similar format using decomposed RI matrices in the canonical polyadic (CP) format [69] as this format arises for contractions of t_2 amplitudes and two electron integrals in the CP representation.

In a recent paper [70], we have suggested the usage of the CP format for the approximation of many body wavefunction parameters and therefore factorizing any of the subsequent tensor contractions that give rise to the steep scaling of computational effort in CC calculations. We have shown that the computational

complexity of any contraction of two tensors scales as $N \cdot d \cdot R_1 \cdot R_2$ with N being the number of orbitals, d the dimensionality of the tensors and R_1, R_2 the expansion length or rank in the CP representation. Numerical examples show, that the rank in the CP format roughly scales with N^2 for two-electron integrals and with N for the amplitudes as obtained in MP2. While the CP format offers several advantages, such as factorization of all dimensions and linear scaling with the order of the tensor, it has also two major disadvantages: Casting the two electron integrals and amplitudes into the CP format is currently very costly, often ill-posed and the resulting expansion length is still high so that a very complex rank reduction algorithm is needed [70]. Furthermore, successive contractions of tensors in a post Hartree Fock method increase the rank of the representation and the product tensors have to be recompressed. Therefore, also alternative tensor formats (like the MPS format) have to be investigated, that can lead to more compact representations and are obtained by more efficient decomposition schemes.

In this work we will focus on the matrix product state (MPS) format in comparison to the canonical polyadic (CP) format and discuss differences and advantages of certain further mathematically based formats in the context of post-HF ab initio methods. The MPS format is sometimes also termed tensor train format (TT) and is identical to the hierarchical tensor format introduced by Hackbusch and Kühn [71] as analyzed by Grasedyck [72] for objects with four dimensions or less (we refer to Ref. 73 for a mathematical description of tensor networks). The MPS format has the great advantage that it can be obtained by successive SVD and can also be seen as an extension to the common RI/DF or CD approximations. It should be noted, that if a decomposed form of the electron density is developed this leads to the DMRG algorithm [74–84], in which various tensor representation formats have been discussed for quite some time. There, the most common format to represent a quantum state is the matrix product state:

$$|\Psi\rangle = \sum_{\sigma_1, \dots, \sigma_L} \mathbf{A}^{\sigma_1} \mathbf{A}^{\sigma_2} \dots \mathbf{A}^{\sigma_{L-1}} \mathbf{A}^{\sigma_L} |\sigma_1, \dots, \sigma_L\rangle. \quad (1)$$

In the following various tensor representation formats are compared from formal perspectives in terms of storage requirement and scaling of computational costs for typical mathematical operations. In Sec. 3 the decomposition of tensors occurring in electronic structure methods into the MPS format is described and in the following section the scaling of the expansion length with increasing system and basis set size is investigated in the context of second order Møller-Plesset perturbation theory.

2. Tensor Representation Techniques

In the comparison of various tensor representation formats we restrict ourselves to examples in four dimensions (tensor order 4) like two electron integrals or t_2 amplitudes, as these are the key components for CI based electronic structure methods. The normal way of representing the two electron integrals, for example, is the indexed based or canonical representation (not to be confused with a canonical orbital-based representation), where each value can be addressed by a specific index tuple. The number of elements that have to be stored and processed can be calculated as N^4 , where N denotes the number of basis functions. If tensors of higher order d are to be treated (like in CI or CC), the number of elements in the tensor increases exponentially to N^d , which is often termed “curse of dimensionality”. [85, 86] To overcome this steep scaling behaviour for high order tensors

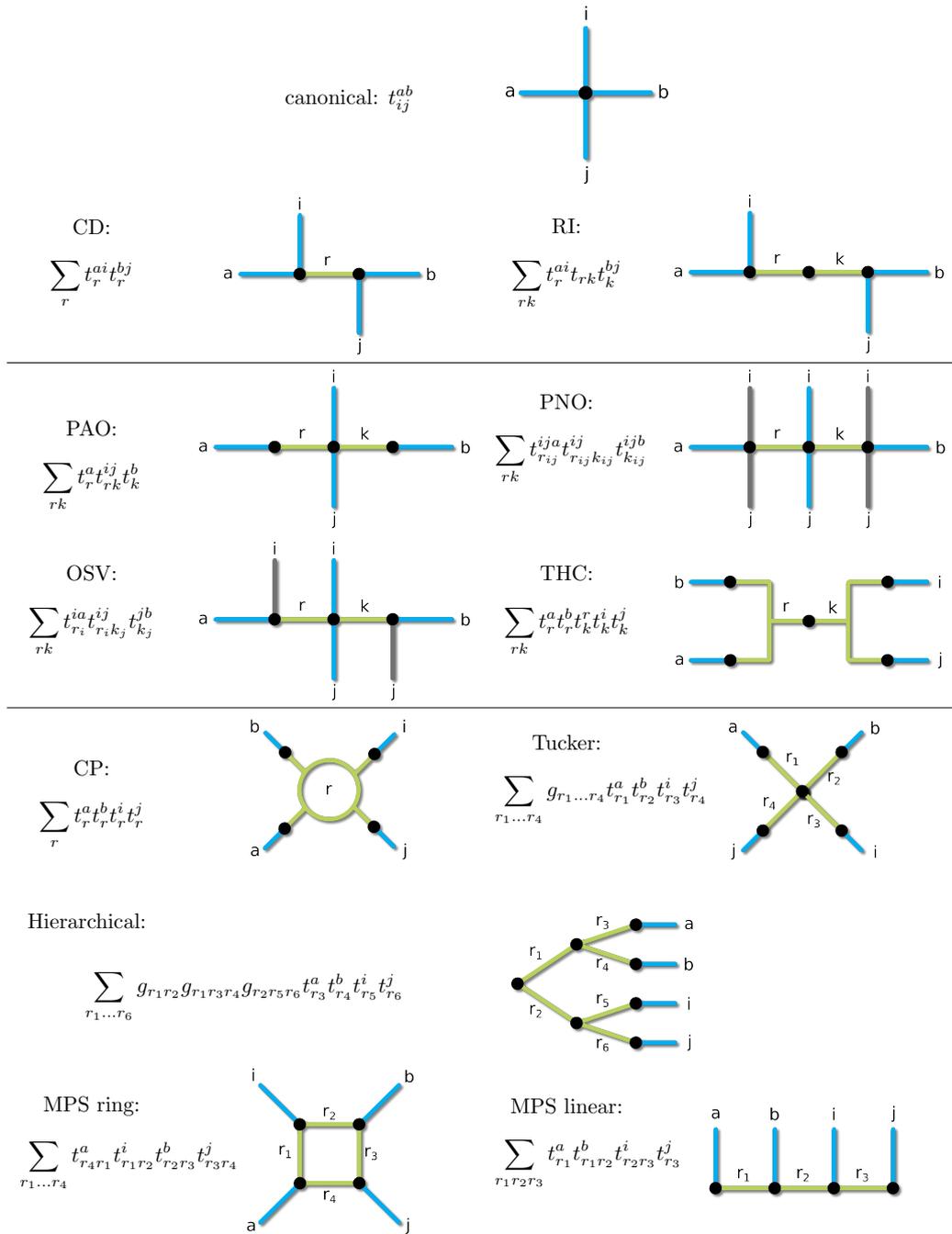


Figure 1. Various tensor formats for tensors of order 4 (for example t_2 amplitudes). Each tensor is denoted as a black dot, external indices are described by blue external lines, while internal summation indices are denoted by green lines between the tensors. It should be noted, that the PNO and OSV approximation are special formats that use specific contractions for different values of i and j . These “auxiliary” indices are denoted in grey. Furthermore, the representation for the CP and THC format are rather schematic (common internal index).

they can be represented in other tensor formats using lower dimensional quantities.

To give a short overview over the presented tensor formats a comparison of the corresponding tensor network graphs is given in Fig. 1. There also the decompositions based on CD, RI, PAO, PNO and OSV are plotted. It should be mentioned, that especially the PAO, PNO and OSV method are special decomposition techniques that rely on physical properties of amplitudes in order

to exploit their sparsity or special locality, while the more mathematical formats are applicable to tensors of general order without knowing anything about the structure or properties of the tensor a priori.

In the following we use the common convention of μ, ν, σ and ρ to denote AO-indices, i, j to denote occupied orbital indices, while a, b denote indices from the virtual orbital space. Virtual summation indices are labeled as e, f , while a summation of occupied indices is denoted with m, n . Orbitals that belong either to the virtual or occupied space are denoted by p, q, r and s . The length of a tensor in one dimension is indicated as N , which is equal to the number of basis functions in the case of two electron integrals in the AO basis for example. Whenever a full tensor is represented and not only a special value for a index tuple the tensor is written in a fracture letter and all sub- or superscripts can be seen as a part of the name to denote the order of dimensions.

2.1. Canonical Polyadic Format (CP)

In the CP format the \mathbf{t}_2 amplitude tensor (t_{ij}^{ab}), for example, can be expressed as a sum of Kronecker products over four so called representing vectors \vec{t}

$$\mathbf{t}_2 = \sum_r^{R_{CP}} \vec{t}_r^{(a)} \otimes \vec{t}_r^{(b)} \otimes \vec{t}_r^{(i)} \otimes \vec{t}_r^{(j)}, \quad (2)$$

where the expansion length R_{CP} is also called rank. It should be noted, that the superscripts in parenthesis do not denote a position in the vector but are rather used to distinguish representing vectors for different dimensions. Furthermore, the representing vector for the first dimension ($\vec{t}^{(a)}$) does not necessarily have to be the same as the vector for the second dimension ($\vec{t}^{(b)}$). In the following the arrow over the representing vectors will be omitted for convenience.

The amount of storage in the CP format highly depends on the rank of the tensor and scales with $\mathcal{O}(N \cdot R_{CP} \cdot d)$. As long as the rank is smaller than $\frac{1}{d}N^{d-1}$ the representation in the CP format has a lower complexity than the full indexed based representation. If a low-rank approximation can be obtained, where the rank is significantly smaller than the given maximal value, the curse of dimensionality is broken, as the scaling is now only linear in the number of dimensions. Furthermore many types of tensor operations such as tensor contractions dealing with high order tensors become favourable in terms of computational costs in a low-rank CP representation [87, 88].

To achieve a representation in the CP format for a given indexed based tensor is not straight forward and decomposition techniques have to be used in order to factorize a tensor into a sum of representing vectors. [87–97] One possibility is to use an extension of the singular value decomposition (SVD) [63] to higher order tensors. However, this is not straightforward and the most common way is to use parallel factor decomposition (PARAFAC) or canonical decomposition (CANDECOMP) [64, 68, 98–100]. These procedures are very complex and can by no means be used as a “black-box” approximation like the SVD for matrices. Also the rank of the tensor may still be large and one can try to minimize the rank by fitting a new tensor $\tilde{\mathbf{t}}_2$ in the CP format with a lower rank K_{CP} up to a given

accuracy ε

$$\|\mathbf{t}_2 - \tilde{\mathbf{t}}_2\| \leq \varepsilon \quad \text{with} \quad \begin{aligned} \mathbf{t}_2 &= \sum_{r=1}^{R_{CP}} \bigotimes_{\lambda=1}^4 t_r^{(\lambda)} \\ \tilde{\mathbf{t}}_2 &= \sum_{k=1}^{K_{CP}} \bigotimes_{\lambda=1}^4 \tilde{t}_k^{(\lambda)}. \end{aligned} \quad (3)$$

For solving this minimization problem there exist different choices like an alternating least square (ALS) scheme [87, 88], a modified Newton method [91, 101] or an accelerated gradient (AG) [70, 102] algorithm. Nevertheless, all these algorithms require highly nonlinear computations and the minimization procedure may possess no solution at all, which makes all close by solutions unstable.

2.2. Tucker Format

The Tucker decomposition uses a form of higher order component analysis to decompose a tensor into a core tensor transformed by a matrix along each dimension [95, 103]. It was first introduced as a tree-mode factor analysis for tensors of order three [103], but later expanded to d -mode principle component analysis also termed higher-order singular value decomposition (HOSVD) [99, 104]. The Tucker decomposition of the fourth-order \mathbf{t}_2 amplitude tensor can be written as

$$\mathbf{t}_2 \approx \sum_{r_1}^{R_1} \sum_{r_2}^{R_2} \sum_{r_3}^{R_3} \sum_{r_4}^{R_4} g_{r_1 r_2 r_3 r_4} \cdot t_{r_1}^{(a)} \otimes t_{r_2}^{(b)} \otimes t_{r_3}^{(i)} \otimes t_{r_4}^{(j)}. \quad (4)$$

It can be seen, that the CP format can be expressed as a special case of the Tucker format where the core tensor g is superdiagonal and all ranks are the same.

The representation in the Tucker format does not break the curse of dimensionality but can reduce the size a tensor if the multilinear rank is smaller than the length for each dimension of the indexed based tensor. Assuming the same length N in all of the dimensions and a constant Tucker rank of R_T for each dimension, the number of elements to store can be decreased to $R_T^4 + 4 \cdot N \cdot R_T$. Here, only the first term shows an exponential scaling with increasing tensor order, while the second term is only linear in the number of dimensions. The great advantage of the Tucker format is the easy and pure algebraic decomposition algorithm that is only based on HOSVD [99, 104]. Furthermore, tensor contractions can be done by evaluation of scalar products of the representing vectors for contracted dimensions, that are used to transform the two corresponding core tensors into a new, common core tensor. Therefore, the ranks do not change and the main algebra can be done with the smaller core tensor. Using a Tucker representation for wavefunction parameters is similar to the PNO approach as a smaller basis is used for the description of the core tensor.

2.3. Hierarchical Tucker or Tensor Train Format

The Hierarchical Tucker format (HT) is a further representation technique commonly used for high order tensors. This format can be obtained by application of SVD on the matrix form of a higher order tensor [71, 105]. For the fourth order \mathbf{t}_2 tensor in a first step the first two dimensions are separated from the last two by

application of SVD. The remaining two submatrices can then again be split into vectors by another SVD. The final result can be written as

$$\mathbf{t}_2 \approx \sum_{r_1}^{R_1} \cdots \sum_{r_6}^{R_6} g_{r_1, r_2} \cdot g_{r_1, r_3, r_4} \cdot g_{r_2, r_5, r_6} \cdot t_{r_3}^{(a)} \otimes t_{r_4}^{(b)} \otimes t_{r_5}^{(i)} \otimes t_{r_6}^{(j)}. \quad (5)$$

Here, the rank R_H can be defined as the maximal rank for all summations in Eqn. 5 and the amount of storage can be calculated to $N \cdot R_H \cdot 4 + (4 - 1) \cdot R_H^3$, which is again linear scaling in the order of the tensor and therefore also breaks the curse of dimensionality. The HT format can also be seen as a compromise between the pure Tucker format and the fully factorized CP format. There exist also some other tensor formats that are related to the Hierarchical format like the Tensor Train (TT) format [106, 107], which can be seen as a special case of the Hierarchical decomposition separating each dimension from the remaining ones.

2.4. Matrix Product State Format

In physics a linear representation also termed Matrix Product State (MPS) format [108] is commonly used in the field of the density matrix renormalization group (DMRG) method [74–76, 82–84]. This representation is somehow similar to the HT or TT format and is also obtained by successive application of SVD to the matrix form of high order tensors. For the t_2 amplitudes the decomposition in the MPS format yields

$$\mathbf{t}_2 \approx \sum_{r_1}^{R_1} \sum_{r_2}^{R_2} \sum_{r_3}^{R_3} t_{r_1}^{(a)} \otimes t_{r_1 r_2}^{(b)} \otimes t_{r_2 r_3}^{(i)} \otimes t_{r_3}^{(j)}. \quad (6)$$

The MPS format therefore does not separate all dimensions, but keeps a link between them in a linear form. For better comparison of ranks between the representation in the MPS format and other formats an effective rank R_{MPS} is defined. For a tensor of order four this effective rank can be calculated as

$$R_{MPS} = \max(R_1, R_3) \cdot R_2. \quad (7)$$

The amount of storage can be approximated as $N \cdot R_{MPS} \cdot 4$, which is again only linear in the order of the tensor and shows a similar scaling as the representation in the CP format with $N \cdot R_{CP} \cdot 4$.

3. Application of MPS Format in Electronic Structure Methods

If the MPS format is to be applied to all tensors that occur in post Hartree-Fock methods, the two electron integrals in the AO basis are a natural starting point for a decomposition as all higher order tensors are derived from them. One way to obtain a representation of the AO two electron integrals in the MPS format is related to the already established RI/DF or CD approximation, that can be seen as an intermediate step towards the MPS format. If the occurring three dimensional quantities $B_X^{\mu\sigma}$ are subject to SVD, a variant of the MPS format arises immediately [69].

$$\begin{aligned}
\langle \mu\sigma | \nu\rho \rangle &\approx \sum_X^{RI} B_X^{\mu\sigma} \tilde{B}_X^{\nu\rho} \\
&\downarrow \text{SVD} \\
&= \sum_L \sum_X \sum_R b_L^\mu b_{LX}^\sigma b_{XR}^\nu b_R^\rho
\end{aligned} \tag{8}$$

Here, X is the index of the auxiliary basis and is usually double the size of the ‘‘outer’’ basis (length of index μ, σ, ν, ρ). Thus, the number of non-zero eigenvalues in the SVD (L and R) should be smaller than twice the basis set size. The decomposition based on RI matrices has not been used in this study but is subject to ongoing research.

Another possibility to separate a full tensor in the MPS format is an algorithm which was described by Vidal [109] and Oseledets [110]. There, a tensor is considered to be its corresponding unfolding matrix and the indices are separated using successively SVD. The Vidal-Algorithm as described in Alg. 1 gives an exact rep-

Algorithm 1 Vidal-algorithm for (d=4)-tensors [109]

$$\begin{aligned}
A^{(0)}(i_1|i_2, i_3, i_4) &:= A(i_1, i_2, i_3, i_4); \\
A^{(0)}(i_1|i_2, i_3, i_4) &\stackrel{\text{SVD}}{\approx} \sum_{r_1=1}^{R_1} a_{r_1}^{(1)}(i_1) \cdot A^{(1)}(r_1, i_2, i_3, i_4); \quad a \\
A^{(1)}(r_1, i_2|i_3, i_4) &\stackrel{\text{SVD}}{\approx} \sum_{r_2=1}^{R_2} \hat{a}^{(2)}(r_1, i_2, r_2) \cdot A^{(2)}(r_2, i_3, i_4); \\
a_{r_1, r_2}^{(2)}(i_2) &:= \hat{a}^{(2)}(r_1, i_2, r_2); \\
A^{(2)}(r_2, i_3|i_4) &\stackrel{\text{SVD}}{\approx} \sum_{r_3=1}^{R_3} \hat{a}^{(3)}(r_2, i_3, r_3) \cdot A^{(3)}(r_3, i_4); \\
a_{r_2, r_3}^{(3)}(i_3) &:= \hat{a}^{(3)}(r_2, i_3, r_3); \\
a_{r_3}^{(4)}(i_4) &:= A^{(3)}(r_3, i_4); \\
\mathfrak{A} &= \sum_{r_1, r_2, r_3} a_{r_1}^{(1)} \otimes a_{r_1, r_2}^{(2)} \otimes a_{r_2, r_3}^{(3)} \otimes a_{r_3}^{(4)};
\end{aligned}$$

^aFrom SVD $\sum_{r_1} a^{(1)}(i_1|r_1) \cdot s(r_1) \cdot b^{(1)}(r_1|i_1, i_2, i_3)$ is received. The singular values are only of importance for the truncation and are included in the second term, $A^{(1)}(r_1, i_2, i_3, i_4) := s(r_1) \cdot b^{(1)}(r_1|i_1, i_2, i_3)$. The first representation vector is directly obtained from the decomposition, $a_{r_1}^{(1)}(i_1) := a^{(1)}(i_1, r_1)$. This holds for the following separations of indices as well.

resentation of the tensor \mathfrak{A} but the eigenvalues obtained from the SVD can also be used to reduce the expansion length. While decomposing the canonical tensor \mathfrak{A} into the MPS format \mathfrak{A}_{MPS} up to a given accuracy ε the following property must hold:

$$\|\mathfrak{A} - \mathfrak{A}_{MPS}\|_F \leq \varepsilon. \tag{9}$$

The subscript F indicates the Frobenius-norm. To reduce the ranks the lowest singular values are truncated in each separation step. During the λ^{th} step with

singular values $s^\lambda(j) < s^\lambda(i)$ for $j > i$ and

$$\sqrt{\sum_{j=r_\lambda+1}^{R_\lambda} (s^\lambda(j))^2} \leq \varepsilon_\lambda = \frac{\varepsilon}{d-1} \quad (10)$$

the rank decreases from R_λ to r_λ holding Eq. (9).

A rank- r matrix can be recovered from a cross of r linearly independent columns and rows, and an arbitrary matrix can be interpolated on the cross entries. Other entries by this cross or pseudo-skeleton approximation are given with errors depending on the closeness of the matrix to a rank- r matrix and as well on the choice of cross, see adaptive cross approximation (ACA) [111]. The ACA algorithm computes a low-rank approximation of a given matrix and is based on the cross approximation method (CA). Let $\mathbf{A} \in \mathbb{R}^{m \times n}$ be a matrix and assume two test matrices $\mathbf{B}_1 \in \mathbb{R}^{m \times r}$ and $\mathbf{B}_2 \in \mathbb{R}^{n \times r}$ are chosen, where for the cross approximation the column vectors are canonical unitary vectors. Assuming that $\mathbf{B}_1^T \mathbf{A} \mathbf{B}_2$ is regular, then the cross approximation \mathbf{A}_r of \mathbf{A} is defined by

$$\mathbf{A}_r = \mathbf{A} \mathbf{B}_2 (\mathbf{B}_1^T \mathbf{A} \mathbf{B}_2)^{-1} \mathbf{B}_1^T \mathbf{A}.$$

With this definition it is easy to see that the interpolation properties

$$\mathbf{B}_1^T \mathbf{A} = \mathbf{B}_1^T \mathbf{A}_r \quad \text{and} \quad \mathbf{A} \mathbf{B}_2 = \mathbf{A}_r \mathbf{B}_2$$

are satisfied. Oseledets and Tyrtshnikov extend this construction to d -dimensional arrays (tensors) [106] and suggest a new interpolation formula in which a d -dimensional array is interpolated on the entries of some TT-cross (tensor-train-cross or matrix product state cross). The total number of entries and the complexity of the interpolation algorithm depend on d linearly, so the approach does not suffer from the curse of dimensionality. The TT-cross approximation is analog to the Vidal-algorithm, that is utilized for this study, but uses the adaptive cross approximation instead of the computational more expensive SVD.

As tensor contractions can increase the rank of the representation (see Sec. 3.4) it is necessary to carry out a recompression procedure in order to minimize the rank and obtain a low rank representation of the product tensor. Only this way the amount of storage and the computational costs for further tensor contractions can be advantageous compared to conventional algorithms. A rank reduction or recompression algorithm dealing with tensors in the MPS format can be obtained as an extension of the Vidal algorithm (c.f. Alg. 1) and is described in Alg. 2 [110, 112]. In a preceding step the MPS tensor is orthonormalized using QR-factorisation to ensure that the truncation property Eq. (9) holds again. Furthermore, one can show that the approximation computed by Vidals algorithm is quasi-optimal [72, 110, 112].

$$\|\mathfrak{A} - \mathfrak{A}_{MPS}\|_F \leq \sqrt{d-1} \inf_{\tilde{\mathfrak{A}}_{MPS} \in \text{MPS}(\mathbb{R})} \|\mathfrak{A} - \tilde{\mathfrak{A}}_{MPS}\|.$$

An important property of the representation in the MPS format is that for the two electron integrals, for example, the MPS format can be defined in different ways depending on the ordering of the indices. There, one can use the standard Dirac

Algorithm 2 MPS recompression algorithm [110]

Orthogonalisation:

$$A^{(d)}(i_d, r_{d-1}) \stackrel{QR}{=} \sum_{r'_{d-1}} Q_d(i_d, r'_{d-1}) R_d(r'_{d-1}, r_{d-1});$$

$$A^{(d)}(i_d, r'_{d-1}) := Q_d(i_d, r'_{d-1});$$

for $\lambda = (d-1)$ **to** 2 **do**

$$A^{(\lambda)}(i_\lambda, r_{\lambda-1}, r'_\lambda) = \sum_{r_\lambda} A^{(\lambda)}(i_\lambda, r_{\lambda-1}, r_\lambda) R_{\lambda+1}^T(r'_\lambda, r_\lambda);$$

$$B^{(\lambda)}(r'_\lambda, i_\lambda, r_{\lambda-1}) := A^{(\lambda)}(i_\lambda, r_{\lambda-1}, r'_\lambda);$$

$$B^{(\lambda)}(r'_\lambda, i_\lambda, r_{\lambda-1}) \stackrel{QR}{=} \sum_{r'_{\lambda-1}} Q_\lambda(r'_\lambda, i_\lambda, r'_{\lambda-1}) R_\lambda(r'_{\lambda-1}, r_{\lambda-1});$$

end for

$$A^{(1)}(i_1, r'_1) = \sum_{r_1} A^{(1)}(i_1, r_1) \cdot R_2^T(r'_1, r_1);$$

SVD:

$$(A^{(1)})^T(i_1, r'_1) \stackrel{SVD}{\approx} \sum_{k_1} U_1(r'_1, k_1) \cdot V_1(k_1, i_1);^b$$

$$a_{k_1}^{(1)}(i_1) := V_1^T(k_1, i_1);$$

for $\lambda = 2$ **to** $(d-1)$ **do**

$$Q_\lambda(r'_\lambda, i_\lambda, k_{\lambda-1}) = \sum_{r'_{\lambda-1}} Q_\lambda(r'_\lambda, i_\lambda, r'_{\lambda-1}) U_{\lambda-1}(r'_{\lambda-1}, k_{\lambda-1});$$

$$Q_\lambda(r'_\lambda | i_\lambda, k_{\lambda-1}) \stackrel{SVD}{\approx} \sum_{k_\lambda} U_\lambda(r'_\lambda, k_\lambda) \cdot V_\lambda(k_\lambda, i_\lambda, k_{\lambda-1});$$

$$a_{k_{\lambda-1}, \lambda}^{(\lambda)}(i_\lambda) := V_\lambda(k_\lambda, i_\lambda, k_{\lambda-1});$$

end for

$$a_{k_{d-1}}^{(d)}(i_d) := \sum_{r'_{\lambda-1}} Q_d(i_d, r'_{d-1}) U_{d-1}(r'_{d-1}, k_{d-1});$$

^bThe SVD is simplified as in Alg. 1: $\sum_k u(r_1, k) \cdot s(k) \cdot v(k, r_2)$; $U(r_1, k) := u(r_1, k) \cdot s(k)$; $V(k, r_2) := v(k, r_2)$

notation and ordering of electron indices

$$\langle \mu\nu | \sigma\rho \rangle = \iint \chi_\mu^*(\mathbf{x}_1) \chi_\nu^*(\mathbf{x}_2) \frac{1}{\|\mathbf{x}_1 - \mathbf{x}_2\|} \chi_\sigma(\mathbf{x}_1) \chi_\rho(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (11)$$

$$= \mathbf{v}_{Dirac} \approx \sum_{r_1}^{R_1} \sum_{r_2}^{R_2} \sum_{r_3}^{R_3} \xi_{r_1}^{(\mu)} \otimes \xi_{r_1, r_2}^{(\nu)} \otimes \xi_{r_2, r_3}^{(\sigma)} \otimes \xi_{r_3}^{(\rho)}, \quad (12)$$

where the electron indices are completely separated from each other. The first and last two representing vectors depend on both electron indices (\mathbf{x}_1 and \mathbf{x}_2) and are connected through the expansion length R_2 so that this type of decomposition can be related to the structure of exchange contributions. Another possibility is the usage of the Mulliken ordering

$$[\mu\nu | \sigma\rho] = \iint \chi_\mu^*(\mathbf{x}_1) \chi_\nu(\mathbf{x}_1) \frac{1}{\|\mathbf{x}_1 - \mathbf{x}_2\|} \chi_\sigma^*(\mathbf{x}_2) \chi_\rho(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 = \langle \mu\sigma | \nu\rho \rangle \quad (13)$$

$$= \mathbf{v}_{Mulliken} \approx \sum_{r_1}^{R_1} \sum_{r_2}^{R_2} \sum_{r_3}^{R_3} \xi_{r_1}^{(\mu)} \otimes \xi_{r_1, r_2}^{(\nu)} \otimes \xi_{r_2, r_3}^{(\sigma)} \otimes \xi_{r_3}^{(\rho)}, \quad (14)$$

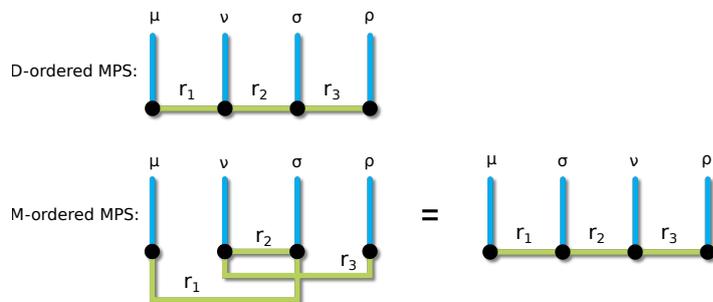


Figure 2. Tensor network representation of MPS format in D- and M-ordering for two electron integrals in the AO basis.

where the first two vectors contain the first electron index, while the last two vectors are associated with the second electron index. This notation can be attributed to the structure of Coulomb interactions as the electron indices are grouped together. Therefore, two different decompositions termed D-ordered MPS (for Dirac) and M-ordered MPS (for Mulliken) are tested. The M-ordered MPS format can also be written in the standard linear form if the original tensor is resorted to match the Dirac notation and a graphical representation of the two decomposition schemes is given in Fig. 2.

3.1. Integral Transformation

If the two electron integrals have been obtained in the MPS format, the next step in post-HF ab-initio methods is the integral transformation into the MO basis

$$v_{rs}^{pq} = \sum_{\mu\sigma\nu\rho} C_{\mu p} C_{\sigma q} C_{\nu r} C_{\rho s} \langle \mu\sigma | \nu\rho \rangle. \quad (15)$$

Using the D-ordered MPS format for the AO integrals this step can be done as

$$\mathbf{v}_{rs}^{pq} = \mathbf{C}^{(\mu,p)} \mathbf{C}^{(\sigma,q)} \mathbf{C}^{(\nu,r)} \mathbf{C}^{(\rho,s)} \sum_{r_1, r_2, r_3} \xi_{r_1}^{(\mu)} \otimes \xi_{r_1, r_2}^{(\sigma)} \otimes \xi_{r_2, r_3}^{(\nu)} \otimes \xi_{r_3}^{(\rho)} \quad (16)$$

$$= \sum_{r_1, r_2, r_3}^{R_1, R_2, R_3} \underbrace{\left(\mathbf{C}^{(\mu,p)} \xi_{r_1}^{(\mu)} \right)}_{:=v_{r_1}^{(p)}} \otimes \underbrace{\left(\mathbf{C}^{(\sigma,q)} \xi_{r_1, r_2}^{(\sigma)} \right)}_{:=v_{r_1, r_2}^{(q)}} \otimes \underbrace{\left(\mathbf{C}^{(\nu,r)} \xi_{r_2, r_3}^{(\nu)} \right)}_{:=v_{r_2, r_3}^{(r)}} \otimes \underbrace{\left(\mathbf{C}^{(\rho,s)} \xi_{r_3}^{(\rho)} \right)}_{:=v_{r_3}^{(s)}} \quad (17)$$

$$= \sum_{r_1, r_2, r_3}^{R_1, R_2, R_3} v_{r_1}^{(p)} \otimes v_{r_1, r_2}^{(q)} \otimes v_{r_2, r_3}^{(r)} \otimes v_{r_3}^{(s)}, \quad (18)$$

by simple matrix-vector multiplications of the coefficient matrices with the corresponding representing vectors. This operation can also be implemented as more efficient matrix-matrix multiplication if the whole set of representing vectors is transformed into the MO basis. The resulting complexity is $\mathcal{O}(N^2 \cdot R_{MPS})$ in the MPS format compared to the conventional AO-MO-integral-transformation including four matrix-matrix products with a complexity of approximately $\mathcal{O}(N^5)$. So the complexity of the integral transformation in the MPS format is lower as long as the effective rank R_{MPS} is lower than N^3 .

3.2. Denominator Weighting

In iterative procedures like the evaluation of amplitudes in CC theory, the amplitude update is performed by denominator weighting. In the first iteration, where t_{ij}^{ab} is zero this step takes the form

$$t_{ij}^{ab} = \frac{v_{ij}^{ab}}{-\varepsilon_a - \varepsilon_b + \varepsilon_i + \varepsilon_j} \quad (19)$$

These can be seen as an initial guess for t_2 amplitudes in CC theory and the reduced rank of these MP2 amplitudes can be taken as an estimate of the size of the rank for wavefunction parameter tensors as they are relevant for CC calculations.

The denominator weighting can be carried out starting from decomposed integrals and a decomposed representation of the energy denominator, which is obtained either by Laplace transformation [113] or by approximation with exponential sums [114] and leads to a decomposition into the CP format

$$D_{ij}^{ab} = \frac{1}{-\varepsilon_a - \varepsilon_b + \varepsilon_i + \varepsilon_j} \quad (20)$$

$$= \sum_s^S \omega_s \exp(\alpha_s(-\varepsilon_a - \varepsilon_b + \varepsilon_i + \varepsilon_j)) \quad (21)$$

$$= \sum_s^S \omega_s \underbrace{\exp(-\alpha_s \varepsilon_a)}_{:=\epsilon_s^{(a)}} \underbrace{\exp(-\alpha_s \varepsilon_b)}_{:=\epsilon_s^{(b)}} \underbrace{\exp(\alpha_s \varepsilon_i)}_{:=\epsilon_s^{(i)}} \underbrace{\exp(\alpha_s \varepsilon_j)}_{:=\epsilon_s^{(j)}} \quad (22)$$

$$\mathfrak{D}_{ij}^{ab} = \sum_s^S \epsilon_s^{(a)} \otimes \epsilon_s^{(b)} \otimes \epsilon_s^{(i)} \otimes \epsilon_s^{(j)}. \quad (23)$$

The expansion length s can be chosen according to the desired accuracy of the approximation and the corresponding factors (ω_s and α_s) are taken from Ref. 114. During this study a values of $S = 42$ is used leading to an error in the order of $7.869 \cdot 10^{-12}$ in an interval up to 10^{11} .

With decomposed integrals in the MPS format and the energy denominator in the CP format one can obtain a decomposed representation of the amplitudes

$$t_{ij}^{ab} = v_{ij}^{ab} \mathfrak{D}_{ij}^{ab} \quad (24)$$

$$= \sum_{r_1, r_2, r_3}^{R_1, R_2, R_3} \left(v_{r_1}^{(a)} \otimes v_{r_1, r_2}^{(b)} \otimes v_{r_2, r_3}^{(i)} \otimes v_{r_3}^{(j)} \right) \odot \left(\sum_s^S \epsilon_s^{(a)} \otimes \epsilon_s^{(b)} \otimes \epsilon_s^{(i)} \otimes \epsilon_s^{(j)} \right) \quad (25)$$

$$= \sum_{r_1, r_2, r_3, s}^{R_1, R_2, R_3, S} \left(v_{r_1}^{(a)} \odot \epsilon_s^{(a)} \right) \otimes \left(v_{r_1, r_2}^{(b)} \odot \epsilon_s^{(b)} \right) \otimes \left(v_{r_2, r_3}^{(i)} \odot \epsilon_s^{(i)} \right) \otimes \left(v_{r_3}^{(j)} \odot \epsilon_s^{(j)} \right). \quad (26)$$

In order to maintain the representation in the MPS format the summation over R_1, R_2, R_3 and S have to be merged by multiplication and thus increasing the rank

to $Q_1 = R_1 \cdot S$, $Q_2 = R_2 \cdot S$ and $Q_3 = R_3 \cdot S$.

$$t_{ij}^{ab} = \sum_{q_1, q_2, q_3}^{Q_1, Q_2, Q_3} t_{q_1}^{(a)} \otimes t_{q_1, q_2}^{(b)} \otimes t_{q_2, q_3}^{(i)} \otimes t_{q_3}^{(j)} \quad (27)$$

As the ranks increase during the denominator weighting it is advantageous to recompress the representation of the amplitudes using the reduction algorithm (c.f. Alg. 2).

3.3. MP2 Energy Equation

Having defined amplitudes the MP2 energy can be evaluated according to

$$E_{MP2} = \frac{1}{4} \sum_{efmn} t_{mn}^{ef} v_{mn}^{ef}. \quad (28)$$

Using the decomposed format of the integrals and the amplitudes leads to

$$E_{MP2} = \frac{1}{4} \left(\sum_{q_1, q_2, q_3}^{Q_1, Q_2, Q_3} t_{q_1}^{(e)} \otimes t_{q_1, q_2}^{(f)} \otimes t_{q_2, q_3}^{(m)} \otimes t_{q_3}^{(n)} \right) \left(\sum_{r_1, r_2, r_3}^{R_1, R_2, R_3} v_{r_1}^{(e)} \otimes v_{r_1, r_2}^{(f)} \otimes v_{r_2, r_3}^{(m)} \otimes v_{r_3}^{(n)} \right) \quad (29)$$

$$= \frac{1}{4} \sum_{q_1, q_2, q_3} \sum_{r_1, r_2, r_3} \langle t_{q_1}^{(e)} | v_{r_1}^{(e)} \rangle \cdot \langle t_{q_1, q_2}^{(f)} | v_{r_1, r_2}^{(f)} \rangle \cdot \langle t_{q_2, q_3}^{(m)} | v_{r_2, r_3}^{(m)} \rangle \cdot \langle t_{q_3}^{(n)} | v_{r_3}^{(n)} \rangle, \quad (30)$$

where all successive tensor contractions (tensor products in the MPS format) can be factorized in sequential scalar products. Using an effective rank $Q_{MPS} = \max(Q_1, Q_3) \cdot Q_2$ and $R_{MPS} = \max(R_1, R_3) \cdot R_2$ the overall complexity of evaluating the MP2 energy is approximately

$$\mathcal{O}(N \cdot R_{MPS} \cdot Q_{MPS}). \quad (31)$$

3.4. Tensor Contractions

General tensor contractions as they for example occur in the CC amplitude equations can also be done with tensors in MPS format. In the following, the contraction with the four virtual integral that gives rise to the formal N^6 scaling of CCSD, is discussed as an illustrative example:

$$r_{ij}^{ab} \leftarrow \sum_{ef} t_{ij}^{ef} v_{ef}^{ab}. \quad (32)$$

Having the amplitudes as well as the integrals in a low rank MPS representation this contraction can be written as

$$\mathbf{r}_{ij}^{ab} \leftarrow \left(\sum_{q_1, q_2, q_3}^{Q_1, Q_2, Q_3} t_{q_1}^{(e)} \otimes t_{q_1, q_2}^{(f)} \otimes t_{q_2, q_3}^{(i)} \otimes t_{q_3}^{(j)} \right) \left(\sum_{r_1, r_2, r_3}^{R_1, R_2, R_3} v_{r_1}^{(a)} \otimes v_{r_1, r_2}^{(b)} \otimes v_{r_2, r_3}^{(e)} \otimes v_{r_3}^{(f)} \right) \quad (33)$$

$$= \sum_{q_1, q_2, q_3}^{Q_1, Q_2, Q_3} \sum_{r_1, r_2, r_3}^{R_1, R_2, R_3} \langle t_{q_1}^{(e)} | v_{r_2, r_3}^{(e)} \rangle \cdot \langle t_{q_1, q_2}^{(f)} | v_{r_3}^{(f)} \rangle v_{r_1}^{(a)} \otimes v_{r_1, r_2}^{(b)} \otimes t_{q_2, q_3}^{(i)} \otimes t_{q_3}^{(j)}, \quad (34)$$

so that the contractions over the internal indices are done as scalar products of the corresponding representing vectors. These can also be written as coefficient matrices and the summation over q_1 and r_3 can be performed, as all other representing vectors are independent of these expansion lengths. A single coefficient matrix \mathbf{K} is obtained

$$\mathbf{r}_{ij}^{ab} \leftarrow \sum_{q_2, q_3}^{Q_2, Q_3} \sum_{r_1, r_2}^{R_1, R_2} \left(\sum_{q_1, r_3}^{Q_1, R_3} \mathbf{E}_{q_1, r_2, r_3} \mathbf{F}_{q_1, q_2, r_3} \right) v_{r_1}^{(a)} \otimes v_{r_1, r_2}^{(b)} \otimes t_{q_2, q_3}^{(i)} \otimes t_{q_3}^{(j)} \quad (35)$$

$$= \sum_{q_2, q_3}^{Q_2, Q_3} \sum_{r_1, r_2}^{R_1, R_2} \mathbf{K}_{r_2, q_2} v_{r_1}^{(a)} \otimes v_{r_1, r_2}^{(b)} \otimes t_{q_2, q_3}^{(i)} \otimes t_{q_3}^{(j)}. \quad (36)$$

The matrix K can be seen as a connection between the second and the third representing vector and can be used to transform one of these vectors. This way, the final increment to \mathbf{r} is obtained in the MPS format

$$\mathbf{r}_{ij}^{ab} \leftarrow \sum_{r_1, r_2, q_3}^{R_1, R_2, Q_3} \tau_{r_1}^{(a)} \otimes \tau_{r_1, r_2}^{(b)} \otimes \tau_{r_2, q_3}^{(i)} \otimes \tau_{q_3}^{(j)}. \quad (37)$$

For this tensor contraction the rank does not change and the new effective rank is composed of the expansion length from the integrals and the amplitudes. For other types of tensor contractions (contracting different dimensions) this does not necessarily have to be the case. In the M-ordered MPS format this contraction would lead to an increased rank, as two expansion lengths have to be combined in order to obtain the MPS representation of the residual tensor

$$\tilde{\mathbf{r}}_{bj}^{ai} \leftarrow \left(\sum_{q_1, q_2, q_3}^{Q_1, Q_2, Q_3} t_{q_1}^{(e)} \otimes t_{q_1, q_2}^{(i)} \otimes t_{q_2, q_3}^{(f)} \otimes t_{q_3}^{(j)} \right) \left(\sum_{r_1, r_2, r_3}^{R_1, R_2, R_3} v_{r_1}^{(a)} \otimes v_{r_1, r_2}^{(e)} \otimes v_{r_2, r_3}^{(b)} \otimes v_{r_3}^{(f)} \right) \quad (38)$$

$$= \sum_{q_1, q_2, q_3}^{Q_1, Q_2, Q_3} \sum_{r_1, r_2, r_3}^{R_1, R_2, R_3} \langle t_{q_1}^{(e)} | v_{r_1, r_2}^{(e)} \rangle \cdot \langle t_{q_2, q_3}^{(f)} | v_{r_3}^{(f)} \rangle v_{r_1}^{(a)} \otimes t_{q_1, q_2}^{(i)} \otimes v_{r_2, r_3}^{(b)} \otimes t_{q_3}^{(j)}. \quad (39)$$

Table 1. Memory requirement and complexity of operations using different tensor formats. Note that the effective rank in the MPS format R_{MPS} is defined as in Eqn. 7.

| | conventional | CP | MPS |
|--------------------|--------------------|--|--|
| memory | $\mathcal{O}(N^4)$ | $\mathcal{O}(N \cdot R_{CP})$ | $\mathcal{O}(N \cdot R_{MPS})$ |
| transformation | $\mathcal{O}(N^5)$ | $\mathcal{O}(N^2 \cdot R_{CP})$ | $\mathcal{O}(N^2 \cdot R_{MPS})$ |
| MP2 evaluation | $\mathcal{O}(N^4)$ | $\mathcal{O}(N \cdot R_{CP} \cdot Q_{CP})$ | $\mathcal{O}(N \cdot R_{MPS} \cdot Q_{MPS})$ |
| tensor contraction | $\mathcal{O}(N^6)$ | $\mathcal{O}(N \cdot R_{CP} \cdot Q_{CP})$ | $\mathcal{O}(N \cdot R_{MPS} \cdot Q_{MPS})$ |

The summation over q_1 and r_3 can be included into a modification of the second and third representing vector

$$\sum_{q_1}^{Q_1} \langle t_{q_1}^{(e)} | v_{r_1, r_2}^{(e)} \rangle \cdot t_{q_1, q_2}^{(i)} := \bar{t}_{r_1, (r_2, q_2)}^{(i)} \quad (40)$$

$$\sum_{r_3}^{R_3} \langle t_{q_2, q_3}^{(f)} | v_{r_3}^{(f)} \rangle \cdot v_{r_2, r_3}^{(b)} := \bar{v}_{(r_2, q_2), q_3}^{(b)}, \quad (41)$$

and a new expansion parameter $\bar{r}_2 = (r_2, q_2)$ with increased length $\bar{R}_2 = R_2 \cdot Q_2$ is introduced to obtain a representation in the M-ordered MPS format

$$\tilde{t}_{bj}^{ai} \leftarrow \sum_{r_1, \bar{r}_2, q_3}^{R_1, \bar{R}_2, Q_3} v_{r_1}^{(a)} \otimes \bar{t}_{r_1, \bar{r}_2}^{(i)} \otimes \bar{v}_{\bar{r}_2, q_3}^{(b)} \otimes t_{q_3}^{(j)} \quad (42)$$

$$= \sum_{r_1, \bar{r}_2, q_3}^{R_1, \bar{R}_2, Q_3} \tau_{r_1}^{(a)} \otimes \tau_{r_1, \bar{r}_2}^{(i)} \otimes \tau_{\bar{r}_2, q_3}^{(b)} \otimes \tau_{q_3}^{(j)}. \quad (43)$$

The increase in rank is also observed for a representation in the CP format [70] and a rank reduction step is needed after typical tensor contractions.

The complexity for a typical tensor contraction in the MPS format can be approximated as

$$\mathcal{O}(N \cdot R_{MPS} \cdot Q_{MPS}), \quad (44)$$

assuming that the actual expansion length does not differ much for the amplitudes and integrals.

A comparison of memory requirements and scaling of computational effort for integral transformation, MP2 energy evaluation and a typical fourth order tensor contraction over 2 internal indices between the conventional index based representation, the CP and MPS format is given in Tab. 1. Here it can be seen, that both, the CP as well as the MPS format, are linear or quadratic scaling with the rank (or effective rank, respectively) and should be beneficial as long as the ranks are moderate and do not scale with high exponents of N . Therefore, always the effective rank of the MPS format has to be compared to the rank in the CP format. In the following section numerical results for the effective ranks of AO integrals, MO integrals and the t_2 amplitudes as obtained from MP2 are compared. Especially the scaling of ranks with increasing system and basis set size is of interest, as this will determine the overall scaling behaviour of algorithms using tensors in MPS representation.

4. Computational Details

Tensor decompositions are done starting from the full fourth order AO two electron integral tensor computed by the C_{FOUR} program package [115]. The scaling with increasing system size is investigated using a LiH chain using 6-31G basis set [116]. The geometry for LiH monomer was taken from Ref. 117: $R_{LiH} = 159.5$ pm. The chain was build up as a linear chain LiH–LiH–... using a distance of 300 pm between the H-atom of one molecule and the Li-atom of the next. For consistency also an alkyl chain with increasing length is tested using the 6-31G basis set. There an arbitrary geometry is used: $R_{CH} = 108.9$ pm, $R_{CC} = 145.0$ pm, $\theta_{HCH} = \theta_{CCC} = 109.471^\circ$. For a system with increasing basis set size the water molecule ($R_{OH} = 95.72$ pm, $\theta_{HOH} = 104.52^\circ$ [118]) is taken as an example using STO-3G, 6-31G, cc-pVDZ, aug-cc-pVDZ and cc-pVTZ basis set [119]. To estimate the scaling of ranks a function $f(x) = a \cdot x^b$ is fitted in Figures 3–5 by a least squares fit, with a prefactor a and the actual scaling parameter b .

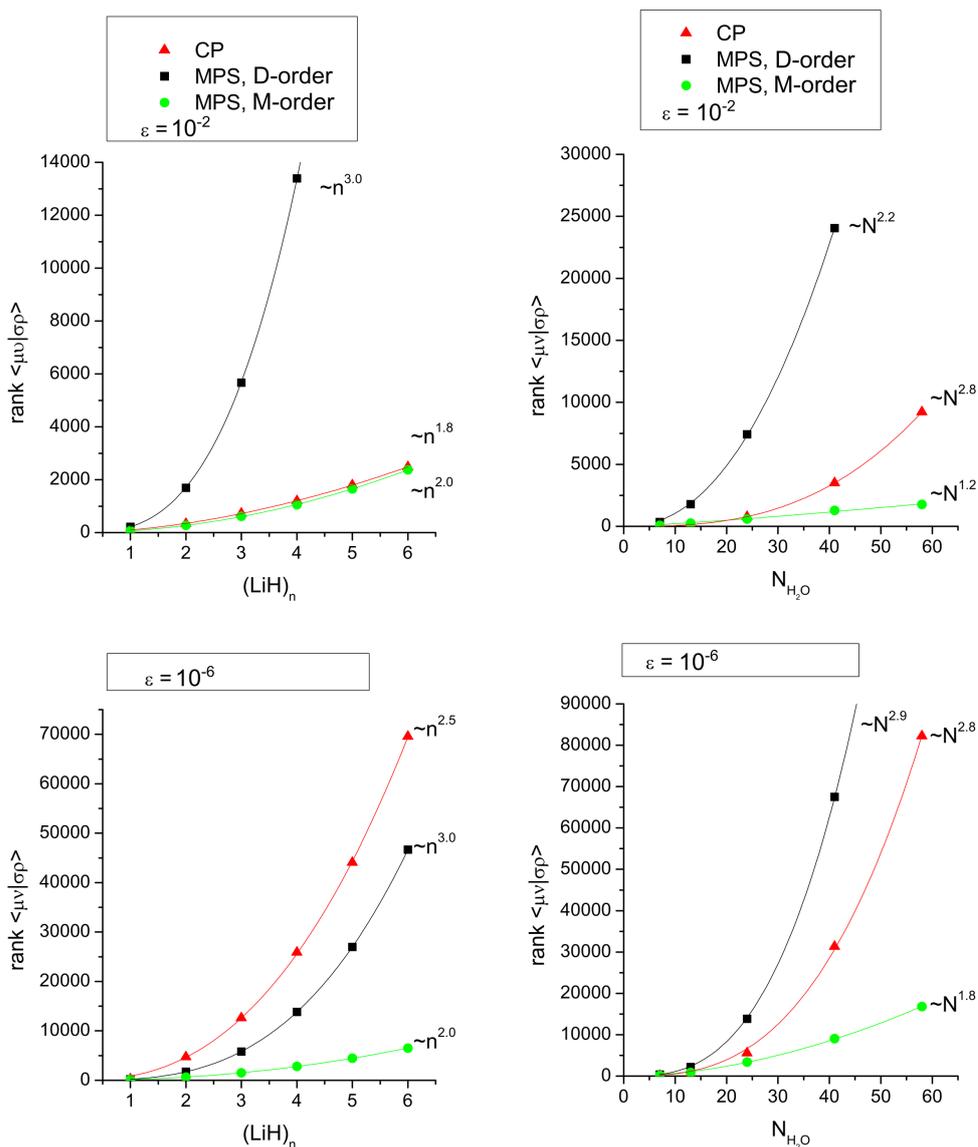
5. Numerical Results

If a tensor decomposition in a certain format is to be used in post-HF ab-initio method two aspects are important for a practicable solution: First, the expansion length in the decomposed has to be modest and secondly, the algorithm to cast or generate a tensorial quantity in the decomposed format has to have tolerable computational effort. Furthermore, the format has to yield a separable representation that allows for a reduction of scaling in the final algorithm by factorization of the contractions in MBPT, CC or CI like schemes.

In contrast to the CP format, the MPS format can be generated efficiently from the RI/DF quantities or by decomposing the full fourth order AO integral tensor using a very robust scheme based on SVD as shown in Sec. 3. However, as different algorithms for casting tensors into the MPS format or different orderings of indices in the full tensor representation may yield different ranks, numerical tests are necessary. For this purpose, two electron integrals for a variety of test systems have been decomposed and the ranks are truncated by a threshold for the eigenvalues of the SVD, so that only important eigenvectors are regarded for the representation (c.f. Alg. 1). The scaling of the effective ranks R_{MPS} with system size (n) or basis set size (N) determines the overall scaling of memory requirements and computational complexity for tensor manipulations in the decomposed format.

Fig. 3 shows the scaling behaviour of effective MPS ranks in comparison to the CP rank for the AO two electron integrals in LiH chains and water with different basis sets using approximation parameters $\varepsilon = 10^{-2}$ and $\varepsilon = 10^{-6}$. For the LiH chains the D-ordered MPS format exhibits a scaling of the effective rank of $n^{3.0}$ for both applied thresholds, which leads to a scaling of the storage amount with n^4 and therefore nothing is gained compared to the conventional tensor treatment. The M-ordered MPS format has a much lower scaling of the effective ranks with system size in the order of n^2 . Compared to the representation in the CP format only the high accuracy approximation ($\varepsilon = 10^{-6}$) has a lower scaling of ranks with increasing chain length and also the fitted prefactor is much lower than for the CP representation.

For an increasing number of basis functions in the water molecule the CP-format scales approximately $\mathcal{O}(N^{2.8})$ for each threshold so that, for example, the memory

(a) $(LiH)_n$ -chain using 6-31G basis set(b) H_2O with N basis functions, using STO-3G, 6-31G, cc-pVDZ, aug-cc-pVDZ and cc-pVTZ basis setFigure 3. Scaling of effective ranks in MPS format compared to ranks in CP format (taken from Ref. 70) for AO two electron integrals with system size n and number of basis functions N , respectively.

requirements to store the tensor are approximately the same as for the full 4 dimensional quantity. In the MPS format the scaling can be lower, especially if the larger threshold ($\varepsilon = 10^{-2}$) is used, where the D-ordered MPS effective rank scales as $N^{2.2}$ and the M-ordered MPS rank as $n^{1.2}$, respectively. It should be noted that despite the low scaling of ranks for the D-ordered MPS format the fitted prefactor is still very large compared to the ranks of the higher scaling CP representation. For the more accurate approximation the scaling in the MPS format increases slightly compared to the constant scaling for integrals in CP format.

Generally the effective ranks of the M-ordered MPS representation and CP ranks do not differ much, especially for lower accuracy and smaller systems. For smaller accuracy threshold values, the ranks in the MPS format with M-ordering

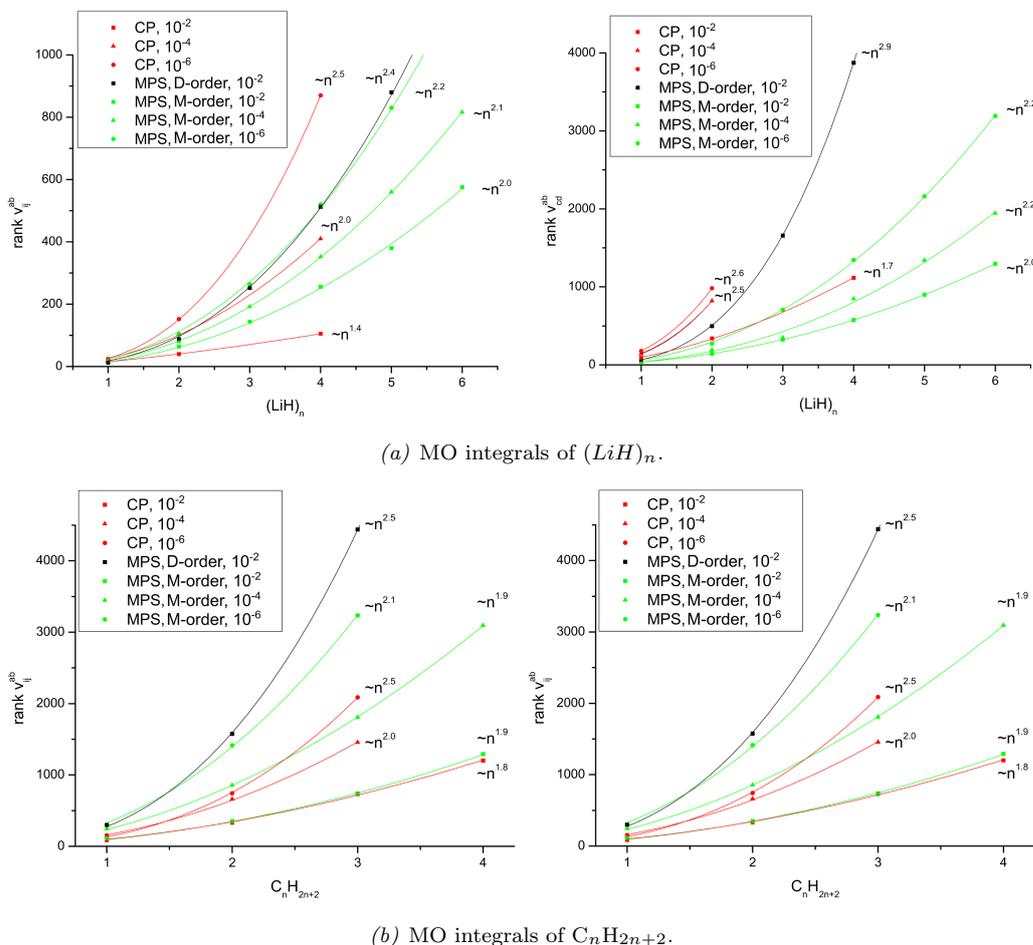


Figure 4. Scaling of ranks (effective ranks in the case of MPS format) for various types of MO integrals in $(LiH)_n$ and C_nH_{2n+2} using the 6-31G basis set. The ranks for the CP representation are taken from Ref. 70.

are smaller than the corresponding ranks in the CP format, leading to a more compact representation in terms of storage and computational effort in further manipulations.

In Fig. 4 results for different types of MO integrals for a lithium-hydride chain and a growing alkyl chain are shown. The ranks are obtained from a decomposition of the canonical transformed MO integrals taken from CFour using the Vidal algorithm (see Alg. 1) truncating the rank depending on the size of the eigenvalues for the successive SVDs. Another possibility is to use the AO integrals in the MPS format, where the ranks are already reduced and to perform the AO-MO transformation as described in Sec. 3.1. There the rank stays the same upon transformation but one can try to reduce the ranks for the MO integrals further using the reduction algorithm (c.f. Alg. 2). This way, similar ranks as for the direct decomposition of the MO integrals are obtained.

As can be seen from Fig. 4 the effective rank of the D-ordered MPS format scales very high with increasing system size and is in the order of $n^{2.4}$ to $n^{2.9}$ even for the large threshold of 10^{-2} . As the effective ranks are even larger for smaller values of ϵ these results are omitted in Fig. 4. For the M-ordered MPS format the scaling is much lower and also does not depend much on the given accuracy threshold and is in the order of $N^{2.0 \pm 0.2}$. In comparison, the scaling of ranks in

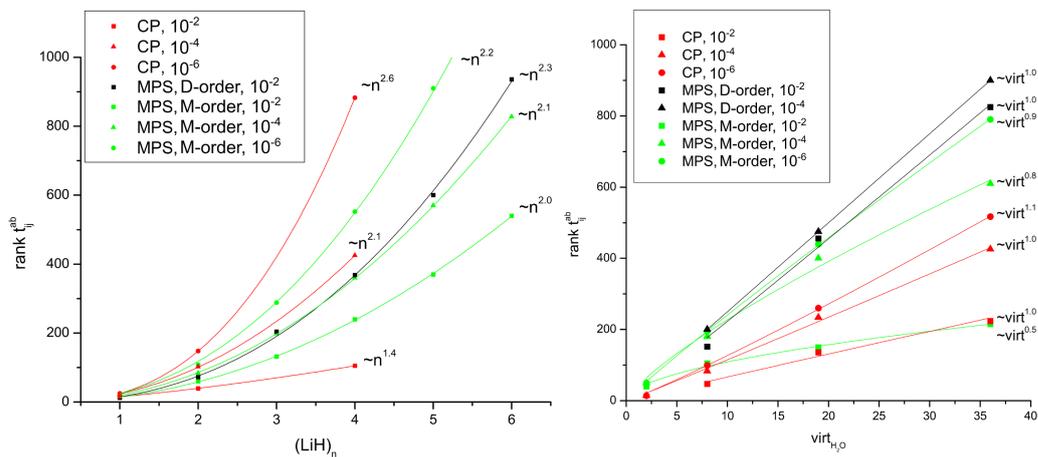


Figure 5. t_2 -amplitudes of $(LiH)_n$ and H_2O . The CP data are from Benedikt et al. [70].

the CP format has a strong dependence on the ε value and is between $n^{1.4}$ to $n^{2.6}$. There are also no large differences between the two tested systems (weakly interacting LiH chain and growing alkyl chain).

For the MO integrals the effective ranks in the D-ordered MPS format and the reduced ranks for a CP representation are comparable and sometimes almost the same. Only for the largest threshold ($\varepsilon = 10^{-2}$) the CP format has smaller ranks and can also exhibit a better scaling with increasing system size. Thus, the D-ordered MPS format is apparently not well suited as a low rank approximation for the MO integral tensor, as the ranks and also the scaling with increasing system size are too large. A similar behaviour can be observed if the scaling with increasing basis set size is considered.

As presented in Sec. 3.2 it is possible to obtain a first guess for the representation of CC t_2 amplitudes by weighting the MO integrals in MPS format with the energy denominator. Fig. 5 shows the scaling of the reduced t_2 amplitudes as obtained from MP2 using the reduced MPS representation of the integrals and the CP representation of the denominator. Here, for the M-ordered as well as the D-ordered MPS format a scaling of ranks with system size of $n^{2.1 \pm 0.2}$ for all tested accuracies is obtained. So the actual scaling is almost independent of the chosen reduction threshold. However, the representation rank in the CP format depends much stronger on the accuracy of the approximation. For the value of $\varepsilon = 10^{-4}$ the actual ranks in the CP and M-ordered MPS format do not differ much. For increasing basis set size the scaling of the amplitude tensor is almost linear for all tested tensor formats and can be even sublinear for lower accuracies in the M-ordered MPS format.

One can summarize that the scaling of effective ranks in the M-ordered MPS format for different fourth order tensors is in the order of n^2 for increasing system size. Especially for the wavefunction parameters (t_2 amplitudes) even a sublinear scaling with increasing basis set size can be achieved. The actual ranks are often similar to the ranks obtained for a representation in the CP format and only for $\varepsilon = 10^{-2}$ the CP representation has lower ranks. The D-ordered MPS format often exhibits much larger scaling than the M-ordered format and therefore is not well suited for a low rank representation of the presented tensors. There, the actual ranks are often too large so that, for example, the memory requirements are almost

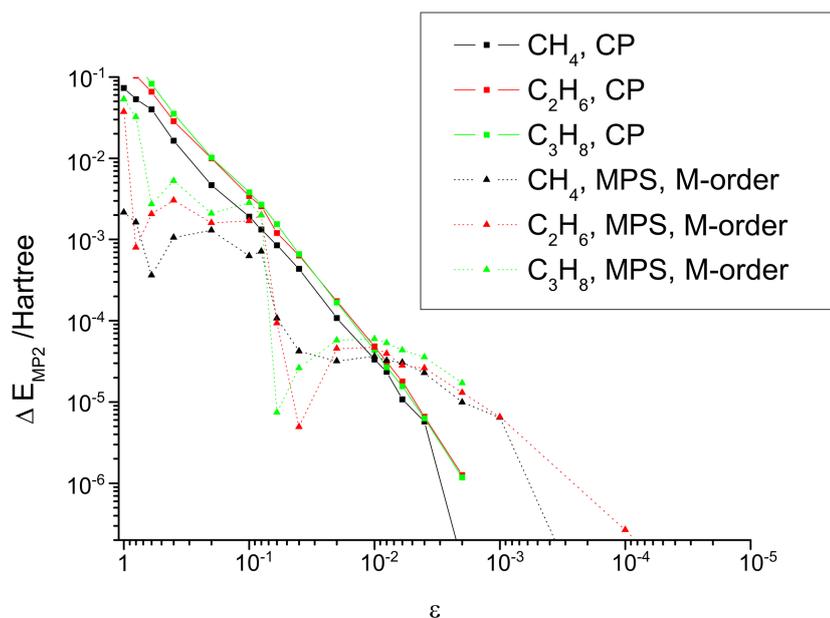


Figure 6. Absolute error in MP2 energy depending on the ε -threshold. The CP data are from Benedikt et al. [70].

the same or even larger than for the canonical index based representation.

In order to correlate the approximation error (in Frobenius norm) with an actual error in the calculated energy the MP2 correlation energy is calculated as described in Sec. 3.3 using decomposed integrals and the already weighted amplitude tensor. Fig. 6 shows the absolute error in the MP2-energy in dependence of the chosen threshold ε . There, the MO integrals are approximated from the full fourth order tensor, while the amplitudes are calculated by weighting the decomposed amplitudes with the denominator in CP representation. The actual error in the MP2 correlation energy calculated from the M-ordered MPS representation are not so smooth compared to calculations in CP format but the results are still comparable. From $\varepsilon = 1$ to $\varepsilon = 10^{-2}$ the M-ordered MPS-format shows better but fluctuating results, while for lower threshold values ($\varepsilon < 10^{-2}$) the CP-format tends to be more accurate. Nevertheless, it is still possible to reach mHartree-accuracy with a threshold between 10^{-1} to 10^{-2} for both formats. At $\varepsilon = 10^{-3}$ the approximation using the CP format reaches μ Hartree-accuracy while a threshold of $\varepsilon = 10^{-4}$ is needed for the same accuracy with the M-ordered MPS-format.

6. Conclusion

In this proof-of-principle study, we applied a successive tensor decomposition and rank reduction scheme in the MPS format to the two electron integrals in the AO and MO basis and an estimate of the CC t_2 amplitudes as obtained from MP2 for a series of small molecular systems. The effective ranks in the M-ordered MPS format exhibit low scaling with increasing system and basis set size in the order of n^2 to n . Especially for the wavefunction parameters linear scaling with increasing basis set size is obtained using the M-ordered MPS representation in a low rank approximation. However, the D-ordered MPS format exhibits much higher scaling and therefore is less suited for the effective treatment of higher order tensors in electronic structure methods. Only the low scaling of effective ranks in

the M-ordered MPS format leads to a decrease in the memory requirements by approximately one order of magnitude (N^3-N^2) compared to the conventional tensor storage. This is also the scaling that one would expect for the AO integrals for larger systems taking the decay of long ranged Coulomb interactions into account.

Furthermore the computational complexity of tensor manipulations can be decreased: A tensor contraction over two internal indices between the integrals and the amplitudes scales with the product of the two effective ranks of the MPS representation leading to an overall scaling of approximately N^4 . For these tensor contractions the actual ranks in the MPS format may increase depending on the type of contraction and on the permutation of indices in the representation. In principle different types of contractions would be necessary for different M-ordered MPS formats to avoid an increase of the ranks. However, this would require the conversion between different permuted formats during successive tensor operations. On the other hand, one can try to find a single permuted format that is convenient for all contractions but leads to an increased rank for some operations. The increased rank can then be reduced by application of the reduction algorithm so that the tensor is processed in a low rank representation.

Therefore, an iterative procedure dealing with higher order tensors in a low rank representation, like the solution of the amplitude equations in CC methods, can be divided into four steps: First, quantities like two electron integrals and Fock-matrix elements are decomposed into a low rank tensor representation and then all tensor contractions for the definition of a residual value can be done in this tensor format. In between different contractions one either can convert the tensor format so that the ranks for the following contraction stay the same or use a common MPS permutation and reduce increased ranks with the reduction algorithm. Afterwards, the wavefunction parameters can be updated and the next iteration starts. As a consequence the general structure of iterative algorithms has to be adapted if tensors in a low rank representation are used.

The described procedure is similar to the proposed algorithms using tensors in CP representation [69, 70] yielding also a similar scaling of the memory requirements and computational effort with increasing system size. Nevertheless, the MPS format has the great appeal that the decomposition and rank reduction is based on a straightforward algorithm using SVD, while rank reduction in the CP format includes non linear computations and may not find a low rank approximation at all. Therefore, a low rank MPS representation is perfectly suited for usage in high level post HF calculations. In conclusion one can say, that tensor decomposition techniques show the potential to break the curse of dimensionality and lead to a new generation of electronic structure methods based on low rank tensor representation as only the physical necessary content of a tensor is processed. In fact, a detailed analysis shows that DMRG is related to tensor decomposition schemes as currently discussed in applied mathematics. [76, 80, 120]

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