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Atomic-batched tensor decomposed two-electron repulsion integrals

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We present a new integral format for 4-index electron repulsion integrals, in which several strategies like the Resolution-of-the-Identity (RI) approximation and other more general tensor-decomposition techniques are combined with an atomic batching scheme. The 3-index RI integral tensor is divided into sub-tensors defined by atom pairs on which we perform an accelerated decomposition to the canonical product (CP) format. In a first step, the RI integrals are decomposed to a high-rank CP-like format by repeated singular value decompositions followed by a rank reduction, which uses a Tucker decomposition as an intermediate step to lower the prefactor of the algorithm. After decomposing the RI sub-tensors (within the Coulomb metric), they can be reassembled to the full decomposed tensor (RC approach) or the atomic batched format can be maintained (ABC approach). In the first case, the integrals are very similar to the well-known tensor hypercontraction integral format, which gained some attraction in recent years since it allows for quartic scaling implementations of MP2 and some coupled cluster methods. On the MP2 level, the RC and ABC approaches are compared concerning efficiency and storage requirements. Furthermore, the overall accuracy of this approach is assessed. Initial test calculations show a good accuracy and that it is not limited to small systems. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4979571>]

I. INTRODUCTION

Quantum chemical methods for calculating the electronic structure of atoms and molecules have become a viable tool in the study of chemical phenomena. They can nowadays be applied to relatively large systems with around hundred atoms, but still most methods suffer from the so-called curse of dimensionality. The computational costs for algebraic operations on tensors emerging from the underlying working equations show a steep scaling with the molecular size and also the storage requirements can quickly become a bottleneck.

For several years, scientists have tried to find approximations that circumvent the curse of dimensionality in order to make calculations on large systems feasible. From a mathematical point of view, many of these attempts can be seen as low-rank tensor approximations. For instance, in the very popular Resolution-of-the-Identity (RI) approximation^{1–4} or the closely related Cholesky Decomposition (CD) technique,^{5–8} 4th-order tensors are factorized into an expression, where only 3rd and 2nd-order tensors appear. This already paves the way for much more efficient implementations. For MP2 speed ups by a factor 100 are realistic when using the RI approximation. Additionally, recent work employs projected atomic orbitals (PAOs),^{9,10} orbital specific virtuals (OSVs),¹¹ and pair natural orbitals (PNOs)^{12,13} together with factorizations of the wave function correlation amplitudes for obtaining very efficient algorithms.^{14–20}

All these approximations are based on physical motivations, but can still be identified as tensor factorizations. Noting this, one has to realize that the field of tensor factorizations is very broad and one might get additional insight by taking a more general mathematical view on it. In a general introduction to tensor decomposition, one usually starts with the work of Hitchcock²¹ and the later application of tensor decomposition techniques by Tucker,^{22,23} Carroll and Chang,²⁴ and Harshman²⁵ in the context of psychometrics. Over the last 10 years, tensor-decomposition techniques made their way into different fields like data mining,^{26,27} neuroscience,²⁸ or signal processing²⁹ to only mention few areas. Also in the field of quantum chemistry, this more general view became attractive. Recently Benedikt *et al.*^{30,31} studied the use of the Canonical decomposition (CP) in the context of electronic structure theory and Godtliebsen *et al.*^{32,33} studied the use of CP-decomposed tensors in vibrational coupled cluster. Furthermore, Martinez and co-workers established the Tensor hypercontraction (THC) format for the two-electron integrals, which arises if CP-decomposed 3-index integrals in the RI approximation are used.^{34–36} The THC format enables a reduction of the scaling of, for example, MP2, MP3, and CC2 to $\mathcal{O}(\mathcal{N}^4)$, where $\mathcal{N}$ is a measure of the system size. In their first publication, Martinez and co-workers obtained the THC format by performing a CP decomposition of the 3-index integrals in the RI approximation.³⁴ Due to the high computational cost of this step, they later switched to a grid-based approach and a least-squares procedure giving rise to LS-THC.³⁵ In Ref. 37, they could show that for a polynomial basis and certain grids, this procedure can be exact, which is not guaranteed for a CP-decomposition-based method in those cases. However, in most quantum chemical methods, a non-polynomial basis is used, and therefore a black-box approach that does not rely on grids

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is desirable. In this paper, we present an alternative approach and keep an alternating-least-squares algorithm for the decomposition of the 3-index integrals to the CP format (CP-ALS), which removes the necessity of preoptimized grids and paves the way for more black-box approaches. We achieve this by not treating the full integral tensor, but sub-tensors defined by atom pairs on which we perform an accelerated CP-ALS procedure. Afterwards one can recombine the decomposed sub-tensors to the full decomposed tensor or stay in an atomic-batched framework and adapt the existing working equations to this format. In this work, we follow both strategies on the MP2 level and compare them with respect to storage requirements and efficiency. After the present manuscript was submitted for publication, an article by Song and Martinez was published on LS-THC-SOS-MP2 which also takes up the idea of an atom-based decomposition and local THC in order to lower the scaling for the formation of the THC factorization (inversion of the THC metric).³⁸ In contrast to our work, they stay in the LS-THC framework using a grid approach and furthermore they use in their atomic decomposition larger blocks of atom groups.

The paper is structured as follows: First, we will give a short summary of the important tensor factorizations and show different routes towards a THC-like format for two-electron repulsion integrals. For one of these routes, we introduce the atomic batching scheme to make a CP decomposition on the large 3-index integrals feasible. Afterwards we show which ranks we obtain and how accurate and fast our new method is.

II. THEORY

A. Tensors and canonical decomposition

In general, a tensor is the representation of d -dimensional data, where the number of dimensions is referred to as the order of a tensor. In the context of tensors, the dimensions are also known as ways or modes. A zeroth-order tensor is a scalar, a first-order tensor is a vector, and a second-order tensor is a matrix. Tensors of order three and higher are then referred to as higher order tensors. As scalars, vectors, and matrices, they can be represented as d -dimensional arrays, where for each set of indices a certain value is stored,

$$X(i_1, i_2, \dots, i_d) = \text{value}. \quad (1)$$

Although this representation is quite intuitive, it has also some disadvantages. Even if the data are sparse, many negligible values have to be stored, where the storage requirements show a steep $\mathcal{O}(n^d)$ scaling with the order d assuming the same number of entries n for each mode. Besides the unfavorable storage requirements, the costs for algebraic operations show a steep scaling with increasing dimensionality as well. But one has not to rely on the array-based representation. Many of the mentioned problems can be solved by using the so-called low-rank representations. One of the simplest approaches is the canonical decomposition, which is in the literature also referred to as CANDECOMP and PARAFAC (parallel factors).^{21,24,25} Using the CP format, a tensor $\mathcal{X} \in \mathbb{R}^{n_i \times n_j \times \dots \times n_d}$ is factorized into a weighted sum of direct products of vectors

representing each mode,

$$\mathcal{X} = \sum_r \omega_r \mathbf{a}_r^{(1)} \otimes \mathbf{a}_r^{(2)} \dots \otimes \mathbf{a}_r^{(d)} \quad (2)$$

or showing the indices explicitly

$$X_{i,j,\dots,d} = \sum_r \omega_r a_{ir}^{(1)} a_{jr}^{(2)} \dots a_{dr}^{(d)}, \quad (3)$$

where R is the rank of the representation. The minimal R , which makes the factorization exact, is known as the rank of the tensor $\mathcal{X}$.

Without losing generality, we will in the following absorb the weighting factor ω_r in one of the mode vectors. The storage requirements depend heavily on the rank and scale for a d -order tensor with lengths n_i for mode i with $R \cdot \sum_i n_i$ data elements to be stored. Assuming that all n_i are the same less data compared to the array-based representation has to be stored, if the rank falls below $\frac{1}{d}n^{d-1}$. Besides the storage requirements, also many algebraic operations like contractions can be done with a reduced operation count.

For the 2-dimensional case, the singular value decomposition (SVD) offers a clear route to obtain a factorization in the CP format. Unfortunately no unique procedure is known for tensors of arbitrary order $d \geq 3$. Most schemes try to fit a tensor in the CP format $\mathcal{X}(\lambda)$ depending on parameters λ_i and a given rank R to the target tensor minimizing the Frobenius norm of the difference tensor,

$$\min_{\lambda} \|\mathcal{X} - \mathcal{X}(\lambda)\|. \quad (4)$$

This is often done in an alternating least squares (ALS) fashion: From all mode matrices $\mathbf{a}_r^{(i)}$, which are the set of vectors for a given mode, only one is optimized at a time while the others are fixed. The minimization then reduces to a least-squares fit problem. If one mode matrix is optimized, the next one will be optimized while the others are fixed. This procedure is repeated until convergence. An algorithm to find the CP decomposition with the lowest possible rank for a given accuracy starts usually with a low rank CP tensor of a given rank (say 1), performs the CP-ALS algorithm, and then increases the rank until the difference norm falls below a given threshold. In an ideal world, this procedure should converge when the fit is 100%, but unfortunately different fits can be arbitrarily close which causes numerical difficulties and the algorithm is slowly convergent and even not guaranteed to converge at all. In the following, this kind of algorithm is referred to as FindBestCPALS algorithm.

B. Tucker decomposition

An alternative representation of a tensor is given by the Tucker decomposition, in which a higher order component analysis is used to decompose the target tensor $\mathcal{X}$ into a core tensor β transformed by a matrix along each mode.^{22,23} It was first shown for third-order tensors $\in \mathbb{R}^{n_i \times n_j \times n_k}$,

$$X_{ijk} = \sum_{r_1}^{R_1} \sum_{r_2}^{R_2} \sum_{r_3}^{R_3} \beta_{r_1 r_2 r_3} U_{ir_1}^{(1)} U_{jr_2}^{(2)} U_{kr_3}^{(3)}, \quad (5)$$

but is easily extendable to the d -order case. If the core tensor is super-diagonal and all ranks are the same $R_1 = R_2 = R_3$, the CP format can be seen as a special case of a Tucker decomposition.

The Tucker format does not circumvent the curse of dimensionality since the core tensor is of the same order as the original tensor, but if it can be sufficiently compressed, then it is possible to achieve savings concerning the storage requirements. For a d -order tensor with lengths n_i and ranks R_i for each mode, the storage is given as $\prod_i^d R_i + \sum_i^d n_i R_i$. Furthermore algebraic operations can be done much more efficiently if they are performed on the smaller core tensor. This philosophy is, for example, already extensively pursued in the Pair Natural Orbital (PNO) representation,³⁹ which gained a lot of interest in the last years¹⁵ and can be seen as a kind of Tucker decomposition, where the integrals and amplitudes are projected down to a smaller subspace. An attractive feature of the Tucker format is that there are pure algebraic decomposition algorithms available based on higher order SVD (HOSVD), which can be applied in a black box manner and with a guaranteed accuracy.

Besides the CP and Tucker format, also other common factorizations like the hierarchical singular value decomposition of tensors⁴⁰ or the tensor train decomposition⁴¹ are present in the literature, but since they are not relevant for our current work we limit ourselves to the given description of common tensor decompositions. Nevertheless we will in the following comment on additional factorizations, but in contrast to the already mentioned they are very tailored to quantum chemistry and not well known in other scientific disciplines.

C. RI approximation as a route towards further decompositions

In many QM codes, the so-called Resolution-of-the-identity (RI) approximation¹⁻³ is used to accelerate the evaluation and processing of 4-index electron repulsion integrals (ERIs) in MP2⁴ and HF/DFT calculations. This approximation is in principle a tensor decomposition of the 4th-order integral tensor into a sum of products of 2 and 3-index integrals,

$$(\mu\nu|\kappa\lambda) \approx \sum_{PQ} I_{\mu\nu}^P [J]_{PQ}^{-1} I_{\kappa\lambda}^Q, \quad (6)$$

where we introduced the following short hand notations for the 2 and 3-index integrals:

$$I_{\mu\nu}^P = (\mu\nu|P) = \int \int \phi_\mu(r_1) \phi_\nu(r_1) \frac{1}{r_{12}} \phi_P(r_2) dr_1 dr_2, \quad (7)$$

$$J_{PQ} = (P|Q) = \int \int \phi_P(r_1) \frac{1}{r_{12}} \phi_Q(r_2) dr_1 dr_2. \quad (8)$$

For J_{PQ} , the so-called Coulomb metric is used. Alternatively, also the overlap metric

$$S_{PQ} = (PQ) = \int \int \phi_P(r_1) \phi_Q(r_2) dr_1 dr_2 \quad (9)$$

can be used which gives three (in fact two different) choices to express the ERI as

$$(\mu\nu|\kappa\lambda) \approx \sum_{PQ} (\mu\nu P) [S]_{PQ}^{-1} I_{\kappa\lambda}^Q, \quad (10)$$

$$(\mu\nu|\kappa\lambda) \approx \sum_{PQ} I_{\mu\nu}^P [S]_{PQ}^{-1} (Q\kappa\lambda), \quad (11)$$

or

$$(\mu\nu|\kappa\lambda) \approx \sum_{PQ} \sum_{RS} (\mu\nu P) [S]_{PQ}^{-1} [J]_{QR} [S]_{RS}^{-1} (S\kappa\lambda), \quad (12)$$

where $(\mu\nu P)$ are three center overlap integrals

$$(\mu\nu P) = \int \phi_\mu(r_1) \phi_\nu(r_1) \phi_P(r_1) dr_1. \quad (13)$$

However from these three choices, in fact, only the last one (Eq. (12)) is viable. The first two integral forms are not symmetric and might cause difficulties due to possible complex eigenvalues. The overlap metric especially in the last form has the advantage that the quantities involved are potentially easier to compute, but from the early work of Dunlap *et al.*² and Vahtras *et al.*,³ it is known that the errors introduced can be two orders of magnitude larger than compared to the Coulomb metric. Later Manby⁴² realized that the Coulomb metric is superior, because using the operator's own metric is equivalent to a robust resolution-of-the-identity, which guarantees that the error in the energy is quadratic in the error in the fitted density. In principle, this also opens a way to obtain the same accuracy using the overlap metric. In the robust RI approximation, we can write the ERI using the overlap metric as

$$(\mu\nu|\kappa\lambda) \approx \sum_{PQ} (\mu\nu P) [S]_{PQ}^{-1} I_{\kappa\lambda}^Q + \sum_{PQ} I_{\mu\nu}^P [S]_{PQ}^{-1} (Q\kappa\lambda) - \sum_{PQ} \sum_{RS} (\mu\nu P) [S]_{PQ}^{-1} [J]_{QR} [S]_{RS}^{-1} (S\kappa\lambda). \quad (14)$$

Though this recovers the accuracy of the Coulomb metric, it is computationally the most demanding since it requires the evaluation of all quantities from the Coulomb and overlap metric.

The auxiliary basis is generally 3–4 times larger than the orbital basis. However, it can be reduced in specific cases. Taking up ideas of the natural-orbital expansion and SVD, Kállay introduced a rank-reduction algorithm for the auxiliary basis, which relies on a single adjustable parameter.⁴³ However, this approach does not lower the scaling and it was shown that especially for highly accurate methods like CCSD(T), only a small compression of the auxiliary basis is possible without significantly affecting the accuracy.

Having the 4-index integrals in a decomposed form enables routes for well-defined further decompositions we want to comment on. If the RI approximation is employed and we obtained a CP decomposed expression for the 3-index integrals (*vide infra*), it is quite easy to obtain an expression for the 4-index integrals in the CP format itself or to arrive at the THC format,^{34,35} which can be seen as an intermediate step in the conversion to the CP format. To get such an expression, the $[J^{-1}]_{PQ}$ matrix can be casted to a CP-like format by applying a SVD,

$$[J^{-1}]_{PQ} \approx \sum_{r_x}^{R_x} \bar{U}_{Pr_x}^J \bar{V}_{Qr_x}^J, \quad (15)$$

where we absorbed the singular values $\sigma^{1/2}$ into the vectors, which is indicated by the bar over the singular vectors. Assuming 3-index integrals in CP format,

$$I_{\mu\nu}^P \approx \sum_r^R W_{\mu r}^{(1)} W_{\nu r}^{(2)} W_{Pr}^{(3)}, \quad (16)$$

the 4-index integrals can be written as

$$(\mu\nu|\kappa\lambda) \approx (\mu\nu|\kappa\lambda)_{\text{RI}} = \sum_{PQ} \left(\sum_{r_1}^{R_1} W_{\mu r_1}^{(1)} W_{\nu r_1}^{(2)} W_{P r_1}^{(3)} \right) \left(\sum_{r_x}^{R_x} \bar{U}_{P r_x}^J \bar{V}_{Q r_x}^J \right) \times \left(\sum_{r_2}^{R_2} W_{\kappa r_2}^{(1)} W_{\lambda r_2}^{(2)} W_{Q r_2}^{(3)} \right). \quad (17)$$

The sums can be rearranged to

$$(\mu\nu|\kappa\lambda)_{\text{RI}} = \sum_{r_1}^{R_1} \sum_{r_2}^{R_2} \sum_{r_x}^{R_x} \left(\sum_P W_{P r_1}^{(3)} \bar{U}_{P r_x}^J \right) \times \left(\sum_Q \bar{V}_{Q r_x}^J W_{Q r_2}^{(3)} \right) W_{\mu r_1}^{(1)} W_{\nu r_1}^{(2)} W_{\kappa r_2}^{(1)} W_{\lambda r_2}^{(2)}, \quad (18)$$

and a summation over P and Q yields

$$(\mu\nu|\kappa\lambda)_{\text{RI}} = \sum_{r_1}^{R_1} \sum_{r_2}^{R_2} \sum_{r_x}^{R_x} P_{r_1 r_x} Q_{r_x r_2} W_{\mu r_1}^{(1)} W_{\nu r_1}^{(2)} W_{\kappa r_2}^{(1)} W_{\lambda r_2}^{(2)}. \quad (19)$$

Only $P_{r_1 r_x}$ and $Q_{r_x r_2}$ depend on r_x . If we perform the summation, we introduce a new coefficient matrix, the combination matrix $M_{r_1 r_2}$, which combines the expansion lengths R_1 and R_2 ,

$$(\mu\nu|\kappa\lambda)_{\text{RI}} = \sum_{r_1}^{R_1} \sum_{r_2}^{R_2} M_{r_1 r_2} W_{\mu r_1}^{(1)} W_{\nu r_1}^{(2)} W_{\kappa r_2}^{(1)} W_{\lambda r_2}^{(2)}. \quad (20)$$

This is quite similar to the THC format, in which in the notation of the authors,³⁴ a 4-index integral is represented as

$$(\mu\nu|\kappa\lambda) \approx \sum_{\bar{P}\bar{Q}} X_{\mu}^{\bar{P}} X_{\nu}^{\bar{P}} Z^{\bar{P}\bar{Q}} X_{\kappa}^{\bar{Q}} X_{\lambda}^{\bar{Q}}, \quad (21)$$

where here the over-bar indicates that $\bar{P}$ and $\bar{Q}$ do not refer to the auxiliary basis, but a different (larger) one. $Z^{\bar{P}\bar{Q}}$ is the analogue of the combination matrix and $X_{\mu}^{\bar{P}}$ are the mode matrices from the CP decomposition. In their first derivation, which yielded PF-THC (PARAFAC THC), Hohenstein *et al.*³⁴ also started from CP-decomposed 3-index integrals, but instead of using the Coulomb metric, they used the overlap metric. In our notation, their Z-Matrix/combination matrix can be expressed as

$$M_{r_1 r_2} \approx \sum_{PQRS} W_{P r_1} [S]_{PQ}^{-1} [J]_{QR} [S]_{RS}^{-1} W_{S r_2}. \quad (22)$$

The expression for the combination matrix in later incarnations of THC (for example, LS-THC) differs and also the use of the overlap metric is avoided. Since the Coulomb metric offers a better accuracy,³ we also follow this strategy in our CP-based approach towards a THC-like factorization. The drawback is that using the overlap metric the 3-index integrals should be more sparse and lower ranks for the CP decomposition are more likely. In a follow-up work, we will compare both choices in more detail. In order not to confuse the THC integrals in our work with that of Hohenstein *et al.*³⁴ in their first paper, we refer this choice as Coulomb-PF-THC or C-PF-THC since we used the Coulomb metric instead of the overlap metric. Furthermore we want to note that the THC format can be seen

as an intermediate step to convert the 4-index integrals into the CP format,

$$(\mu\nu|\kappa\lambda)_{\text{RI}} = \sum_r^{R_1 \cdot R_2} \bar{W}_{\mu r}^{(1)} \bar{W}_{\nu r}^{(2)} \bar{W}_{\lambda r}^{(3)} \bar{W}_{\kappa r}^{(4)}, \quad (23)$$

where the weighting factors again are absorbed into the vectors. For the $\bar{W}_r$ vectors, the W_r vectors are simply copied for r_1 or r_2 and one is multiplied with the entries of the combination matrix $M_{r_1 r_2}$. In THC-like formats, the storage requirements depend heavily on the size of $M_{r_1 r_2}$ and can be given as $R_1 \cdot R_2 + 2 \cdot R_1 \cdot N_{\text{bas}} + 2 \cdot R_2 \cdot N_{\text{bas}}$ or $R_1 \cdot (R_2 + 1)/2 + 2 \cdot R_1 \cdot N_{\text{bas}} + 2 \cdot R_2 \cdot N_{\text{bas}}$ if some permutational symmetry is exploited. The requirements scale therefore quadratically with the ranks obtained.

An alternative route towards a CP-like format of 4-index integrals with the aid of the RI approximation is to write the ERI as

$$(\mu\nu|\kappa\lambda)_{\text{RI}} = \sum_Q B_{\mu\nu}^Q B_{\kappa\lambda}^Q \quad (24)$$

with the intermediates

$$B_{\mu\nu}^Q = \sum_P I_{\mu\nu}^P J_{PQ}^{-1/2}, \quad (25)$$

where $J_{PQ}^{-1/2}$ can be computed as Cholesky decomposition of J_{PQ} . If we are now performing a SVD on the B intermediate, we obtain

$$B_{\mu\nu}^Q = \sum_k^K \bar{U}_{\mu k}^{B,Q} \bar{V}_{\nu k}^{B,Q}, \quad (26)$$

with $K \leq N_{\text{aux}}$ and where the bar indicates that the singular values as $\sigma^{1/2}$ have been absorbed into the singular vectors. With this the ERI can be cast in the CP format as

$$(\mu\nu|\kappa\lambda)_{\text{RI}} = \sum_Q^K \sum_{k_X} \bar{U}_{\mu k_X}^{B,Q} \bar{V}_{\nu k_X}^{B,Q} \sum_{k_Y} \bar{U}_{\kappa k_Y}^{B,Q} \bar{V}_{\lambda k_Y}^{B,Q} = \sum_r^R W_{\kappa 1}^{(1)} W_{\nu r}^{(2)} W_{\kappa r}^{(3)} W_{\lambda r}^{(4)}, \quad (27)$$

where R is $N_{\text{aux}} \cdot K^2$. In the best case scenario, K quickly becomes independent of the system size and then the rank increases linearly with the number of auxiliary functions. In the worst case scenario, K is equal to the number of basis functions (N_{bas}) and the ranks therefore increase cubically with system size. Let us compare these findings to the first shown route, where we expect in the ideal case a quadratic scaling. There we got that the rank equals $R = R_1 \cdot R_2$, where R_1 and R_2 are the ranks of the 3-index integrals. We know that for 3-order tensors $\mathcal{X} \in \mathbb{R}^{I \times J \times K}$, the (theoretical) maximum rank is bounded by $\min(IJ, IK, JK)$; this leads to an upper bound as

$$R_1 \leq N_{\text{bas}}^2 \quad (28)$$

and results in the worst case scenario to a $\mathcal{O}(N^4)$ scaling of the ranks. In the best and worst case scenario, the second route seems therefore to be superior. However a central point of our work is the combination with a batching scheme driven by atom indices, which will be discussed in detail in a subsidiary part. Applying this scheme the argumentation turns exactly the opposite way around as shown later.

1. Comment on the size of the combination matrix

Martinez and co-workers report that the dimension of the combination matrix is a few multiples of the fitting basis³⁴ and also we observe that it can become quite large compared to the fitting basis (*vide infra*). Of course for an efficient implementation, it should be as small as possible. So naturally the question arises if there are ways to judge the size of the combination matrix. From Equation (22), where we compare the combination matrix with the original PF-THC formalism³⁴ and Equation (19), it is obvious that the number of non-vanishing singular values of the combination matrix is bound by the size of the fitting basis. The combination matrix is obtained by performing a SVD on the matrix J_{PQ} and then one index is transformed to a large basis and the transformed singular vectors are again combined. This implies that the combination matrix is in general much larger than it has to be and that it combines expansion lengths, which contain some redundancies. Although this problem is evident, there is no straight forward way to avoid it. This dilemma will be of concern in ongoing research.

D. Casting the 3-index integrals into CP format

For the procedure sketched above, it is necessary to have the 3-index integrals $I_{\mu\nu}^Q$ in CP format. With the help of SVDs on the sub-matrices $(Q\mu)$ defined by the basis function index ν as it is sketched in Algorithm 1, there exists a well-defined route to obtaining a high-rank CP representation without fitting the tensor. In spirit it shares some similarities with the rank-reduction algorithm of Kállay for RI integrals in Ref. 43, but our method is performed on blocks of the integral tensor and does not require to substitute the SVD of the 3 index integrals by an eigen decomposition of $W_{PQ} = \sum_{\mu\nu} B_{\mu\nu}^P B_{\mu\nu}^Q$. The here presented procedure is quite simple and the error is easily controllable by the threshold for the SVDs T_{SVD} . The disadvantage of the procedure is the high rank, which scales with the number of basis functions N_{bas} . In the worst case scenario, we can expect a rank of $N_{\text{bas}} \cdot N_{\text{bas}}$, but for large systems many singular values for the auxiliary AO sub-blocks will be zero. Nevertheless the rank has to be reduced after the RI-SVD decomposition to allow storage savings and efficient implementations. For this purpose we use the algorithm depicted in Algorithm 2, which is our adaption of the C2T/T2C algorithm of Khoromskij and Khoromskaia.^{44,45}

The main idea of the algorithm is to combine the CP format with the Tucker format. A target tensor $\mathcal{X} \in \mathbb{R}^{n_1 \times n_2 \times n_3}$ in the CP format

Algorithm 1. Initial casting of 3-index integrals in CP format by SVD guided scheme.

```

for  $\nu = 1, \dots, N_{\text{bas}}$  do
  • Copy Auxiliary-AO blocks for  $\nu$  to  $A_{Q\mu}$ 
  • do a SVD on slice:  $\mathbf{A} = \mathbf{U} \cdot \Sigma \cdot \mathbf{V}^T$ 
  • Use rows in  $\mathbf{U}$  and columns in  $\mathbf{V}^T$  as mode vectors.
  • For the AO index which defines the slices use unit vectors,
    where the index  $\nu$  is encoded and then absorb the singular value
    in it.
end for
  • Do a rank reduction by the code in 2 or CP-recompression.

```

Algorithm 2. Rank reduction for d order tensors.

```

Input: High rank tensor  $\mathcal{T}_{in}^{CP} \in \mathbb{R}^{n_1 \times n_2 \times \dots \times n_d}$  in CP format
  • Calculate truncated SVD of the mode matrices of  $\mathcal{T}_{in}^{CP}$ :
  •  $\mathbf{W}^{(k)} = \mathbf{U}^{(k)} \Sigma^{(k)} (\mathbf{V}^{(k)})^T$ 
  •  $\mathbf{U}^{(k)} \in \mathbb{R}^{n_k \times R_k}$ ,  $\Sigma^{(k)} \in \mathbb{R}^{R_k \times R_k}$  and  $\mathbf{V} \in \mathbb{R}^{R_k \times R}$ 
for  $i = 1, \dots, n_{\text{maxiter}}$  do
  • Project the mode matrices:  $\tilde{\mathbf{W}} = (\mathbf{U}^{(k)})^T \mathbf{W}^{(k)}$ ,  $\tilde{\mathbf{W}} \in \mathbb{R}^{R_k \times R}$ 
for  $k = 1, \dots, d$  do
  • Construct partially projected tensor:  $\tilde{\mathcal{T}}^k = \sum_r R_{\text{high}} \tilde{\mathbf{W}}_r^{(1)} \otimes \dots \otimes \mathbf{W}_r^{(k)} \otimes \dots \otimes \tilde{\mathbf{W}}_r^{(d)}$ 
  • Reshape  $\tilde{\mathcal{T}}^{(k)}$  into a matrix  $\mathbf{M} \in \mathbb{R}^{n_k \times (\prod_{j \neq k} R_j)}$ 
  • Calculate truncated SVD of the matrix unfolding:
     $\mathbf{M} = \tilde{\mathbf{U}}^{(k)} \tilde{\Sigma}^{(k)} (\tilde{\mathbf{V}}^{(k)})^T$ 
  • Update the subspace:  $\mathbf{U}^{(k)} \leftarrow \tilde{\mathbf{U}}^{(k)}$ 
end for
end for
  • Obtain converged projected mode matrices:  $\tilde{\mathbf{W}}^{(k)} = (\mathbf{U}^{(k)})^T \mathbf{W}^{(k)}$ 
  • Construct core tensor in CP format:  $\beta = \sum_r R_{\text{high}} \tilde{\mathbf{W}}_r^{(1)} \otimes \tilde{\mathbf{W}}_r^{(2)} \dots \otimes \tilde{\mathbf{W}}_r^{(d)}$ 
  • Tucker tensor is now given as:  $\mathcal{T}^{\text{Tucker}} = \beta \times_1 \tilde{\mathbf{U}}^{(1)} \times_2 \tilde{\mathbf{U}}^{(2)} \dots \times_d \tilde{\mathbf{U}}^{(d)}$ 
  • Recompress core tensor using CP-ALS:  $\beta_{r_1 r_2 \dots r_d} = \sum_r R_{\text{low}} \mathbf{b}_r^{(1)} \otimes \mathbf{b}_r^{(2)} \dots \otimes \mathbf{b}_r^{(d)}$ 
  • Set the mode matrices of  $\mathcal{T}_{out}^{CP}$  to  $\mathbf{W}_{i_k r}^{(k)} \leftarrow \sum_{r_k} R_k \tilde{\mathbf{U}}_{i_k r_k}^{(k)} \mathbf{b}_{r_k}^{(k)}$ 
Output:  $\mathcal{T}_{out}^{CP}$  with low rank  $R_{\text{low}}$ 

```

$$X_{n_1 n_2 n_3} = \sum_r^{R_{\text{high}}} W_{n_1 r}^{(1)} W_{n_2 r}^{(2)} W_{n_3 r}^{(3)} \quad (29)$$

is with a HOOI⁴⁶-like procedure converted into the Tucker format

$$X_{n_1 n_2 n_3} = \sum_{r_1 r_2 r_3} \beta_{r_1 r_2 r_3} \tilde{U}_{n_1 r_1}^{(1)} \tilde{U}_{n_2 r_2}^{(2)} \tilde{U}_{n_3 r_3}^{(3)}. \quad (30)$$

The optimized side matrices $\tilde{U}_{n_i r_i}$ are obtained in an ALS manner, which is repeated n_{maxiter} times. Initial tests show that a small number of iterations, e.g., 5–10, is sufficient.

After obtaining the tensor in the Tucker format, the core tensor β is decomposed into the CP format

$$X_{n_1 n_2 n_3} = \sum_{r_1 r_2 r_3} \left(\sum_r^{R_{\text{low}}} b_{r_1 r}^{(1)} b_{r_2 r}^{(2)} b_{r_3 r}^{(3)} \right) \tilde{U}_{n_1 r_1}^{(1)} \tilde{U}_{n_2 r_2}^{(2)} \tilde{U}_{n_3 r_3}^{(3)}. \quad (31)$$

The rank of the core tensor R_{low} equals then the rank of the output vector in the CP format and (hopefully) enabled a reduction,

$$X_{n_1 n_2 n_3} = \sum_r^{R_{\text{low}}} \sum_{r_1} b_{r_1 r}^{(1)} \tilde{U}_{n_1 r_1}^{(1)} \sum_{r_2} b_{r_2 r}^{(2)} \tilde{U}_{n_2 r_2}^{(2)} \sum_{r_3} b_{r_3 r}^{(3)} \tilde{U}_{n_3 r_3}^{(3)}, \quad (32)$$

$$X_{n_1 n_2 n_3} = \sum_r^{R_{\text{low}}} \tilde{W}_{n_1 r}^{(1)} \tilde{W}_{n_2 r}^{(2)} \tilde{W}_{n_3 r}^{(3)}. \quad (33)$$

Deviating from the algorithm presented in Refs. 44 and 45, we never construct the core tensor in the array-based format, but keep it in the CP format and apply the CP-ALS algorithm on this quantity. This has the advantage that some computational steps can be done in a more efficient way exploiting the CP format. To distinguish between the standard CP-ALS algorithm, we name this procedure CP-recompression.

FIG. 1. Graphical representation of the rank reduction algorithm. The tensor in CP format is projected down to a subspace via the Tucker decomposition and all operations are then performed on the smaller core tensor to lower the prefactor of the CP-ALS algorithm. After a lower rank is found, the tensor is projected back to the full space.

The essence of the algorithm is sketched in Fig. 1. In order to lower the prefactor of the CP-ALS algorithm, the large tensor is projected down to a smaller sub-space via Tucker decomposition and the CP-ALS/recompression step is performed on the core tensor.

The accuracy of the conversion to the Tucker format can be controlled by the thresholds for the SVDs T_{SVD} meaning including all $\sigma_i \geq T_{\text{SVD}}$. Based on an error bound for the conversion of a CP tensor to a Tucker tensor,⁴⁴

$$\|\mathcal{X} - \mathcal{X}^{\text{Tucker}}\| \leq \|\omega\| \sum_{l=1}^d \left(\sum_{k=R_l+1}^{\min(n_l, \prod_{j \neq l} R_j)} \sigma_{lk}^2 \right)^{1/2}, \quad (34)$$

the SVD threshold can be chosen in a self-adapting approach. In the upper equation, d is the order of the tensor and R_l the selected subset of the full possible rank for a given mode l , and σ_{lk} refer to the cut out singular values. The sum is bounded by the number of possible singular values of the matrix unfolding of the partially projected tensor ($\min(n_l, \prod_{j \neq l} R_j)$). The factor in front $\|\omega\|$ is $\|\omega\| = \sqrt{\sum_i^R \omega_i^2} = \sqrt{R}$, where ω_i are the weighting factors for the mode vectors and in our case always one since we absorbed them into one of the vectors.

If a maximal allowed error T_{err} is chosen, T_{SVD} can be selected according to this. For each mode, the error bound is tested if more and more singular values are neglected. If T_{err}/d is reached, T_{SVD} is set just below the current singular value. For all modes the selected T_{SVD} thresholds are compared and the smallest one is chosen. For a general algorithm it might be interesting to explore the possibilities to use for each mode a different threshold, but in our specific case this is not of interest since mainly the singular values of the mode belonging to the auxiliary functions are truncated.

A potential weak point of the algorithm is the construction of the matrix unfolding which is likely to be of the same order/size as the original tensor. This problem will be addressed in the next paragraph when the atomic batching is introduced.

E. Atomic-batched build of the 3-index integrals

Performing the rank reduction algorithm or using a conventional FindBestCPALS algorithm to the full set of 3-index integrals is not practical due to the large prefactor of a CP-ALS procedure and was one reason why Martinez and co-workers^{34,35} moved from a CP-ALS algorithm to a grid based approach to obtain the ERIs in the THC format. In their procedure, which is called least-squares tensor hypercontraction (LS-THC), the THC format is generated by a least-squares renormalization of a spatial quadrature over the r_{12}^{-1} operator.³⁵ Although this strategy is quite successful, it also has some disadvantages. One needs for example specialized grids to ensure a certain overall accuracy. In the initial implementation, the grids were mainly tailored towards MP2 and are less accurate in, for example, CCSD calculations because different classes of MO integrals arise in this case. A black box approach to obtain the (C-PF-)THC format without relying on empirical knowledge is clearly favorable.

We therefore follow a different route to make the generation of integrals in the (C-PF-)THC format (and thereby CP format) feasible by modifying the algorithm to obtain the integrals. To lower the prefactor, while accepting a probably larger output rank, we perform the RI-SVD decomposition followed by the rank reduction on sub-blocks of the integral tensor, which are given by all basis functions belonging to a certain atom. This approach is similar to split and merge techniques described in other algorithms to make a CP decomposition feasible on large tensors.⁴⁷ In contrast to the approach in Ref. 47, no sampling/heuristics are required to identify appropriate sub-tensors since these are given by the block structure of the integrals. We also emphasize from the outset that this approach reduces a large task to many smaller tasks being well suited for parallelization. In order not to confuse with the earlier mentioned PF-THC or C-PF-THC and since we also take up equally portions of additional ideas like the C2T/T2C algorithm as well as an atomic batching scheme, we introduce two new and simpler terms: By the RC approach, we mean that the RI approximation using the Coulomb metric is invoked, and that for each atom pair, the 3-index integrals are decomposed to a high rank CP-like format by repeated SVDs followed by a rank reduction by means of the C2T/T2C algorithm. Afterwards the decomposed sub-tensors are reassembled to the full decomposed tensor. On the other hand, the ABC approach denotes the atomic batched partition. Obviously, analogous RO and ABO methods are obtainable when using the overlap metric. We note that the RC format is in the end equivalent to the THC format, but differs in the construction, meaning RC integrals and THC integrals are different approximations to the exact ERIs.

The algorithms used to obtain the RC and ABC integral formats only differ in the last step and remain the same for the decomposition steps, but they yield different kinds of working equations (*vide infra*). Most of the equations presented so far stay valid, but one has to be aware of additional indices referring to atoms A, B, and C. In a loop of atom pairs, we read in blocks associated to a given atom pair

$$I_{\mu^A \nu^B}^Q = (Q | \mu^A \nu^B) \quad (35)$$

and perform the decomposition

$$I_{\mu^A \nu^B}^{Q,CP} = \sum_{r^{AB}} W_{\mu^A r^{AB}}^{AB,(1)} W_{\nu^A, r^{AB}}^{AB,(2)} W_{Q r^{AB}}^{AB,(3)} \quad (36)$$

with RI-SVD followed by a rank reduction with the C2T/T2C algorithm. We only restrict the basis function of the orbital basis to be centered at the atom pairs. The auxiliary functions are not restricted since the not required contributions will be cut out by the Tucker decomposition. In this scheme, we exploit for each atom pair the permutational symmetry of the AO basis functions ($Q|\mu^A \nu^B\rangle = (Q|\nu^B \mu^A\rangle)$ to use our decomposition algorithm for each pair only once. The 4-index integrals can now be assembled for each atom quadruple $\{A, B, C, D\}$ in a THC-like format

$$(\mu^A \nu^B | \kappa^C \lambda^D) = \sum_{r^{AB}} \sum_{r^{CD}} M_{r^{AB} r^{CD}}^{ABCD} W_{\mu^A r^{AB}}^{AB,(1)} W_{\nu^B r^{AB}}^{AB,(2)} \times W_{\kappa^C r^{CD}}^{CD,(1)} W_{\lambda^D r^{CD}}^{CD,(2)}. \quad (37)$$

At this point one can stay in the atomic batched framework (ABC) or reassemble the CP decomposed sub-tensors for the 3-index integrals to form the whole integral tensor by summation of the CP sub-tensors (RC). As already mentioned, both strategies shall be followed and compared. To assemble the full 3-index integral tensor, we use the block structure of the AO basis. The obtained mode matrices correspond to sub-blocks of the full AO basis mode matrices with zeroes before or after the sub-block as sketched in Fig. 2. A standard CP-ALS algorithm on the full 3-index integral tensor would scale as $\mathcal{O}(N_{\text{aux}} \cdot N_{\text{bas}}^2 \cdot R)$, where N_{aux} is the number of auxiliary functions, N_{bas} the number of basis functions, and R the rank. However, the atomic batched decomposition in combination with the Tucker decomposition reduces this in the asymptotic limit to quadratic scaling costs, $\mathcal{O}(N_{\text{atom}}^2 N_{\text{aux}}^{\text{local}} \cdot (N_{\text{bas}}^{\text{atom}})^2 \cdot R_{\text{atom}})$, since due to the Tucker decomposition the core tensor does not increase with system size at some point and therefore the locally assigned auxiliary basis functions $N_{\text{aux}}^{\text{local}}$ become constant in addition to the rank of the sub-tensor R_{atom} and the number of basis function at an atom pair $(N_{\text{bas}}^{\text{atom}})^2$, which are constant anyway. Therefore the costs are only determined by the number of performed CP-ALS decompositions, which scale quadratically with the number of atoms.

After introducing the atomic batching, we want to come back to a few issues raised during the discussion so far. We showed two schemes to obtain the CP format of the 3-index integrals and argued that scheme 2 has potentially the benefit of a lower rank. So why do we not use this approach? The answer is that the argumentation turns around if atomic batching is used. If only the basis functions at atom pairs are considered for $I_{\mu^A \nu^B}^Q, B_{\mu^A \nu^B}^Q$, we get for scheme 1 in the worst case ranks

FIG. 2. Graphical representation of the relation between atomic batched and full tensors.

Algorithm 3. Atomic batched build of 3-index integrals.

```

Init rank:  $R = 0$ 
for  $AB = 1, \dots, N_{\text{AtomPairs}}$  do
  • Get integral block  $I_{\mu^A \nu^B}^Q = (Q|\mu^A \nu^B)$  with no restriction on  $Q$ 
  • Perform RI-SVD decomp. on  $I_{\mu^A \nu^B}^Q$  using  $\nu^B$  to define the sub
    matrices. (code 1) The pair list is sorted such that  $N_{\text{bas}}^B$  is always
    smaller or equal to  $N_{\text{bas}}^A$  in order to ensure the lowest possible
    initial rank.
  • Perform rank reduction step with C2T/T2C algorithm. (code 2)
  • Optionally, for RC: Patch local CP tensor  $I_{\mu^A \nu^B}^{Q,CP}$  of rank  $R_{\text{loc}}$ 
    onto full one  $I_{\mu^A \nu^B}^{Q,CP}$ 
end for

```

scaling with $N_{\text{atom}}^2 \cdot (N_{\text{bas}}^{\text{atom}})^4$, where $N_{\text{bas}}^{\text{atom}}$ are the number of basis functions centered at an atom and N_{atom} the number of atoms. This is likely better than $N_{\text{atom}}^2 \cdot N_{\text{aux}} \cdot (N_{\text{bas}}^{\text{atom}})^2$ what we get from scheme 2 since the number of auxiliary functions N_{aux} scales linearly with the system size.

Another issue raised was that we build in the C2T/T2C algorithm the matrix unfolding in the array-based representation and this could easily become a storage bottleneck. Here we note that the atomic batching lifts this problem since only small pieces of the full tensor are considered and the Tucker format efficiently screens out the non-required parts of the auxiliary functions so that the size for the matrix unfolding is small even in the unpacked array-based format.

1. Dependence on molecular size

Far distant pairs of atoms, they carry less important information for the energy calculation and therefore need less tight thresholds for the CP-ALS fit T_{CP} (unit E_h). After extensive numerical tests, we came up with a simple relation, which chooses T_{CP} as a function of the distance between the centers of the basis functions. The user selects an initial $T_{\text{CP}}^{\text{in}}$, which is applied to the diagonal pairs and used to calculate the threshold that is used,

$$T_{\text{CP}}(r_{AB}) = \min(T_{\text{CP}}^{\text{in}} + 0.10 \cdot r_{AB} \cdot T_{\text{CP}}^{\text{in}}, T_{\text{CP}}^{\text{in}} \cdot 10) \quad (38)$$

for all other pairs, where r_{AB} is the distance between the atomic centers A and B . In this way, the importance of a pair is better reflected without introducing too large errors.

F. Laplace transformation

Aiming now at exploring the performance of our approximate scheme in the context of MP2, not only the integrals but also the energy denominator is required to be in the CP or a similar format. One can of course build the array-based energy-denominator tensor and then decompose it with the CP-ALS algorithm, but with means of the Laplace-transformation techniques there exists a route towards a CP-like format for the denominator in a fast black box approach yielding an expansion with only few terms. The idea goes back to Almlöf and Häser,⁴⁸ who replaced the energy denominator by an equivalent Laplace-transformed expression, which is then evaluated using numerical quadrature,

$$\frac{1}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j} = \Delta_{ij}^{ab} \approx \sum_{z=1}^{n_{\text{lap}}} \omega_z \exp(-t_z \cdot (\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j)). \quad (39)$$

This has a very similar structure to the CP format and we obtain

$$\Delta_{ij}^{ab} \approx \sum_{z=1}^{n_{\text{lap}}} \omega_z a_{az}^{(1)} a_{iz}^{(2)} a_{bz}^{(3)} a_{jz}^{(4)}. \quad (40)$$

The number of required Laplace points n_{lap} is usually quite small 4–8 and does not depend on the molecular size but the range of the orbital energies. To obtain the Laplace factorization of the denominator, we use an algorithm similar to that described in Ref. 48.

G. Calculation of the MP2 energy

The MP2 energy expression

$$E_{\text{MP2}} = - \sum_{ab} \sum_{ij} (ai|bj) [2(ai|bj) - (bi|aj)] \Delta_{ij}^{ab} \quad (41)$$

can be partitioned in a Coulomb-like contribution

$$E_{\text{MP2-J}} = - \sum_{ab} \sum_{ij} 2(ai|bj)(ai|bj)\Delta_{ij}^{ab} \quad (42)$$

and an exchange-like contribution

$$E_{\text{MP2-K}} = \sum_{ab} \sum_{ij} (ai|bj)(bi|aj)\Delta_{ij}^{ab}. \quad (43)$$

Invoking the RC/THC format and CP format for the energy denominator leads to

$$\begin{aligned} E_{\text{MP2-J}}^{\text{RC}} &\approx E_{\text{MP2-J}}^{\text{RC}} = -2 \sum_{ab} \sum_{ij} \sum_{r_1 r_2} W_{ar_1}^{(1)} W_{ir_1}^{(2)} W_{br_2}^{(1)} W_{jr_2}^{(2)} M_{r_1 r_2} \\ &\times \sum_{r_3 r_4} W_{ar_3}^{(1)} W_{ir_3}^{(2)} W_{br_4}^{(1)} W_{jr_4}^{(2)} M_{r_3 r_4} \\ &\times \sum_z \omega_z a_{az}^{(1)} a_{iz}^{(2)} a_{bz}^{(3)} a_{jz}^{(4)}. \end{aligned} \quad (44)$$

Depending on whether we reassemble the sub-tensors to the full decomposed 3-index integral tensors or stayed in the atomic batched framework, we have two routes towards the Coulomb-like contribution. If we reassemble the tensor, we follow the work of Hohenstein *et al.*³⁴ and group all factor and mode matrices with the same MO index,

$$\begin{aligned} E_{\text{MP2-J}}^{\text{RC}} &= -2 \sum_{ab} \sum_{ij} \sum_{r_1 r_2 r_3 r_4 z} \omega_z \left(W_{ar_1}^{(1)} W_{ar_3}^{(1)} a_{az}^{(1)} \right) \\ &\times \left(W_{ir_1}^{(2)} W_{ir_3}^{(2)} a_{iz}^{(2)} \right) \left(W_{br_2}^{(1)} W_{br_4}^{(1)} a_{bz}^{(3)} \right) \\ &\times \left(W_{jr_2}^{(2)} W_{jr_4}^{(2)} a_{jz}^{(4)} \right) M_{r_1 r_2} M_{r_3 r_4}, \end{aligned} \quad (45)$$

$$E_{\text{MP2-J}}^{\text{RC}} = -2 \sum_{r_1 r_2 r_3 r_4 z} \omega_z {}^C A_{zr_1 r_3} {}^C I_{zr_2 r_4} {}^C A_{zr_2 r_4} {}^C I_{zr_1 r_3} M_{r_1 r_2} M_{r_3 r_4} \quad (46)$$

with the intermediates listed in Table I together with their operation count. Defining shortcuts via the Hadamard product gives then

$$E_{\text{MP2-J}}^{\text{RC}} = -2 \sum_{r_1 r_2 r_3 r_4 z} \omega_z {}^C E_{zr_1 r_3} {}^C E_{zr_2 r_4} M_{r_1 r_2} M_{r_3 r_4} \quad (47)$$

and if the transformation with the combination matrices **M** is carried out, one obtains

$$E_{\text{MP2-J}}^{\text{RC}} = -2 \sum_{r_1 r_4 z} \omega_z {}^C \bar{E}_{zr_1 r_4} {}^C \bar{E}_{zr_4 r_1}. \quad (48)$$

The operation count for all steps is shown in Table I.

If we use the atomic batched framework, it is important to note that for a given quadruple, the combination matrix can be split into two matrices which only depend on a pair of atoms,

$$M_{r^{AB} r^{CD}}^{ABCD} = \sum_{PQ} W_{P^{AB}}^{AB,(3)} J_{PQ}^{-1} W_{Q^{CD}}^{CD,(3)}. \quad (49)$$

If one performs a SVD on J_{PQ}^{-1} and absorbs $\sigma^{1/2}$ in the singular vectors, we obtain accordingly

$$M_{r^{AB} r^{CD}}^{ABCD} = \sum_k^K \bar{U}_{r^{AB} k}^{M,AB} \bar{V}_{r^{CD} k}^{M,CD}. \quad (50)$$

Plugging this into the Coulomb energy expression gives

$$\begin{aligned} E_{\text{MP2-J}}^{\text{ABC}} &= -2 \sum_z \omega_z \sum_{ABCD} \sum_{A'B'C'D'} \sum_{r^{AB}} \sum_{r^{A'B'}} \sum_{r^{CD}} \sum_{r^{C'D'}} {}^C E_{zr^{AB} r^{CD}}^{ABCD} \\ &\times {}^C E_{zr^{A'B'} r^{C'D'}}^{A'B'C'D'} \sum_{k_1} \bar{U}_{r^{AB} k_1}^{M,AB} \bar{V}_{r^{A'B'} k_1}^{M,A'B'} \sum_{k_2} \bar{U}_{r^{CD} k_2}^{M,CD} \bar{V}_{r^{C'D'} k_2}^{M,C'D'}. \end{aligned} \quad (51)$$

See Table I for intermediates. Note that there MO indices with atom labels indicate that they only refer to AO transformed with the coefficients at a particular atom,

$$W_{r p^A}^{(i)} = \sum_{\mu^A} C_{\mu^A p^A} W_{r^{AB} \mu^A}^{(i)}. \quad (52)$$

With

$${}^C F_{zr^{CD} k}^{CD} = \sum_{AB} \sum_{r^{AB}} {}^C E_{zr^{AB} r^{CD}}^{ABCD} \bar{U}_{r^{AB} k}^{M,AB} \quad (53)$$

and since the right and left singular vectors are identical for symmetric matrices (**U** = **V**), we obtain for the energy expression

$$\begin{aligned} E_{\text{MP2-J}}^{\text{ABC}} &= -2 \sum_z \omega_z \sum_{CD} \sum_{C'D'} \sum_{r^{CD}} \sum_{r^{C'D'}} {}^{RCD} {}^{R'C'D'} \\ &\times \sum_{k_1} {}^C F_{zr^{CD} k_1}^{CD} {}^C F_{zr^{C'D'} k_1}^{C'D'} \sum_{k_2} \bar{U}_{r^{CD} k_2}^{M,CD} \bar{V}_{r^{C'D'} k_2}^{M,C'D'}, \end{aligned} \quad (54)$$

$$E_{\text{MP2}}^{\text{ABC}} = -2 \sum_z \omega_z \sum_{CD} \sum_{C'D'} \sum_{k_1} \sum_{k_2} {}^C \bar{F}_{zk_2 k_1}^{CD} {}^C \bar{F}_{zk_2 k_1}^{C'D'}. \quad (55)$$

After showing the working equations for both routes, it is important to discuss the formal scaling. For that purpose, we will assume for the sake of simplicity that the reassembled rank *R* scales linearly with the system size. Then the most time consuming step is the construction of the ${}^C \bar{E}_{zr_1 r_4}$ intermediates which scales with $\mathcal{O}(\mathcal{N}^3)$. In the atomic batched scheme, the most expensive step is the formation of the intermediates ${}^C A_{zr^{AB} r^{CD}}^{ABCD}$ and ${}^C I_{zr^{AB} r^{CD}}^{ABCD}$ where we contract over the MO indices. Here we have $\mathcal{O}(R_{\text{atom}}^2 \cdot N_{\text{vir}} \cdot n_{\text{lap}} \cdot N_{\text{atom}}^4)$ scaling of the operation count. R_{atom} and n_{lap} are independent of the system size yielding the well-known $\mathcal{O}(\mathcal{N}^5)$ scaling for MP2. However we note that the operation count scales with the fourth power of the number of atoms, which is usually a small number. Furthermore in extended systems, it should be possible to neglect atom quadruples, where the centers are far apart and furthermore the ranks for distant atom pairs are

TABLE I. Summary of intermediates used in the MP2 energy computation for the RC (upper half) and ABC (lower half) approaches. In the ABC approach, atom labels on MO indices are used to make clear that the mode matrices were only multiplied with the MO coefficients for the particular atom. R refers to the rank, N_{bas} to the number of basis functions, N_p to a generic MO index, N_{vir} and N_{oct} to active virtual and occupied MOs, and n_{lap} to the Laplace points. The subscript atom is used to point out atom-centered quantities and the label N_{atom} indicates the number of atoms.

Intermediates	Operation count
$W_{rp}^{(i)} = \sum_{\mu} C_{\mu p} W_{r\mu}^{(i)}$	$\mathcal{O}(R \cdot N_{\text{bas}} \cdot N_p)$
${}^C A_{zr_1 r_3} = \sum_a W_{ar_1}^{(1)} W_{ar_3}^{(1)} a_{az}^{(1)}$	$\mathcal{O}(R^2 \cdot N_{\text{vir}} \cdot n_{\text{lap}})$
${}^C I_{zr_1 r_3} = \sum_i W_{ir_1}^{(2)} W_{ir_3}^{(2)} a_{iz}^{(2)}$	$\mathcal{O}(R^2 \cdot N_{\text{oct}} \cdot n_{\text{lap}})$
${}^C E_{zr_1 r_3} = {}^C A_{zr_1 r_3} {}^C I_{zr_1 r_3}$	$\mathcal{O}(R^2 \cdot n_{\text{lap}})$
${}^C \bar{E}_{zr_1 r_4} = \sum_{r_3} {}^C E_{zr_1 r_3} M_{r_3 r_4}$	$\mathcal{O}(R^3 \cdot n_{\text{lap}})$
${}^X A_{jbr_2} = W_{br_2}^{(1)} W_{jr_2}^{(2)}$	$\mathcal{O}(R \cdot N_{\text{vir}} \cdot N_{\text{oct}})$
${}^X B_{jbr_1} = \sum_{r_2} M_{r_1 r_2} {}^X A_{jbr_2}$	$\mathcal{O}(R^2 \cdot N_{\text{vir}} \cdot N_{\text{oct}})$
${}^X E_{jzr_1 r_3} = \sum_b a_{bz} W_{br_3}^{(1)} {}^X B_{jbr_1}$	$\mathcal{O}(R^2 \cdot N_{\text{vir}} \cdot N_{\text{oct}} \cdot n_{\text{lap}})$
${}^X G_{zr_1 r_3} = \sum_i a_{iz} W_{ir_1}^{(2)} W_{ir_3}^{(2)}$	$\mathcal{O}(R^2 \cdot N_{\text{oct}} \cdot n_{\text{lap}})$
${}^X H_{zr_1 r_3} = \sum_j a_{jz} {}^X E_{jzr_1 r_3} {}^X G_{zr_1 r_3}$	$\mathcal{O}(R^2 \cdot N_{\text{oct}} \cdot n_{\text{lap}})$
$W_{rp^A}^{(i)} = \sum_{\mu^A} C_{\mu^A p^A} W_{r\mu^A}^{(i)}$	$\mathcal{O}(R_{\text{atom}} \cdot N_{\text{bas}}^{\text{atom}} \cdot N_p)$
${}^C A_{zrABrCD}^{ABCD} = \sum_a W_{a^A rAB}^{ABCD,(1)} W_{a^C rCD}^{ABCD,(1)} a_{az}^{(1)}$	$\mathcal{O}(R_{\text{atom}}^2 \cdot N_{\text{vir}} \cdot n_{\text{lap}} \cdot N_{\text{atom}}^4)$
${}^C I_{zrABrCD}^{ABCD} = \sum_i W_{i^A rAB}^{ABCD,(2)} W_{i^C rCD}^{ABCD,(2)} a_{iz}^{(2)}$	$\mathcal{O}(R_{\text{atom}}^2 \cdot N_{\text{oct}} \cdot n_{\text{lap}} \cdot N_{\text{atom}}^4)$
${}^C E_{zrABrCD}^{ABCD} = {}^C A_{zrABrCD}^{ABCD} {}^C I_{zrABrCD}^{ABCD}$	$\mathcal{O}(R_{\text{atom}}^2 \cdot n_{\text{lap}} \cdot N_{\text{atom}}^4)$
${}^C F_{zrCDk}^{CD} = \sum_{AB} \sum_{rAB} {}^C E_{zrABrCD}^{ABCD} \bar{U}_{rABk}^{M,AB}$	$\mathcal{O}(N_{\text{atom}}^4 \cdot n_{\text{lap}} \cdot R_{\text{atom}}^2 \cdot K)$
${}^C H_{zrCDk}^{CD} = \sum_{AB} \sum_{rAB} {}^C E_{zrABrCD}^{ABCD} \bar{V}_{rABk}^{M,AB}$	$\mathcal{O}(N_{\text{atom}}^4 \cdot n_{\text{lap}} \cdot R_{\text{atom}}^2 \cdot K)$
${}^C \bar{F}_{z^2 k_1 k_2}^{CD} = \sum_{rCD} {}^C F_{zrCDk_1}^{CD} \bar{U}_{rCDk_2}^{M,CD}$	$\mathcal{O}(K^2 \cdot n_{\text{lap}} \cdot R_{\text{atom}})$
${}^X A_{j^D b^C rCD}^{CD} = W_{b^C rCD}^{CD,(1)} W_{j^D rCD}^{CD,(2)}$	$\mathcal{O}(N_{\text{atom}}^2 \cdot R_{\text{atom}} \cdot N_{\text{vir}} \cdot N_{\text{oct}})$
${}^X E_{k_1 j^D b^C}^{CD} = \sum_{rCD} {}^X A_{j^D b^C rCD}^{CD} \bar{V}_{rCDk_1}^{M,CD}$	$\mathcal{O}(N_{\text{atom}}^2 \cdot R_{\text{atom}} \cdot K)$
${}^X E_{k_1 j^D b^C}^{CD} = \sum_{CD} {}^X E_{k_1 j^D b^C}^{CD}$	$\mathcal{O}(N_{\text{atom}}^2 \cdot R_{\text{atom}} \cdot K)$
${}^X E_{zjrABk_1}^{AB} = \sum_b {}^X E_{k_1 j^A b^A} W_{b^A rAB}^{AB,(1)} a_{bz}$	$\mathcal{O}(N_{\text{atom}}^2 \cdot R_{\text{atom}} \cdot n_{\text{lap}} \cdot N_{\text{oct}} \cdot K \cdot N_{\text{vir}})$
${}^X F_{zjrABrCD}^{ABCD} = \sum_{k_1} {}^X E_{zjrABk_1}^{AB} \bar{U}_{rCDk_1}^{M,CD}$	$\mathcal{O}(N_{\text{atom}}^4 \cdot R_{\text{atom}}^2 \cdot n_{\text{lap}} \cdot N_{\text{oct}} \cdot K)$
${}^X G_{zrABrCD}^{ABCD} = \sum_i W_{i^A rAB}^{AB,(2)} W_{i^C rCD}^{CD,(2)} a_{iz}^{(2)}$	$\mathcal{O}(N_{\text{atom}}^4 \cdot R_{\text{atom}}^2 \cdot N_{\text{oct}} \cdot n_{\text{lap}})$
${}^X H_{zrABrCD}^{ABCD,(1)} = \sum_j {}^X F_{jrABrCD}^{ABCD,(1)} {}^X F_{jrCDrAB}^{CDAB,(1)} a_{jz}^{(4)}$	$\mathcal{O}(N_{\text{atom}}^4 \cdot R_{\text{atom}}^2 \cdot N_{\text{oct}} \cdot n_{\text{lap}})$

smaller so that the operation count for such pairs is smaller as well.

Next we take a look at the exchange term and follow for the RC format initially the work by Hohenstein *et al.*,³⁴

$$\begin{aligned}
 E_{\text{MP2-K}}^{\text{RC}} \approx E_{\text{MP2-K}}^{\text{RC}} &= \sum_{r_1 r_2} W_{ar_1}^{(1)} W_{ir_1}^{(2)} W_{br_2}^{(1)} W_{jr_2}^{(2)} M_{r_1 r_2} \\
 &\times \sum_{r_3 r_4} W_{br_3}^{(1)} W_{ir_3}^{(2)} W_{ar_4}^{(1)} W_{jr_4}^{(2)} M_{r_3 r_4} \\
 &\times \sum_z \omega_z a_{az}^{(1)} a_{iz}^{(2)} a_{bz}^{(3)} a_{jz}^{(4)}. \quad (56)
 \end{aligned}$$

In a first step, some of the factor matrices are combined

$${}^X A_{jbr_2} = W_{br_2}^{(1)} W_{jr_2}^{(2)} \quad (57)$$

and afterwards transformed with the corresponding combination matrix $\mathbf{M}$ to yield

$${}^X B_{jbr_1} = \sum_{r_2} M_{r_1 r_2} {}^X A_{jbr_2}. \quad (58)$$

Now the following intermediates can be calculated

$${}^X E_{jzr_1 r_3} = \sum_b a_{bz} W_{br_3}^{(1)} {}^X B_{jbr_1}, \quad (59)$$

$${}^X G_{zr_1 r_3} = \sum_i a_{iz} W_{ir_1}^{(2)} W_{ir_3}^{(2)}, \quad (60)$$

$${}^X H_{zr_1 r_3} = \sum_j a_{jz} {}^X E_{jzr_1 r_3} {}^X E_{jzr_1 r_3}. \quad (61)$$

The energy expressions become with these intermediates

$$E_{\text{MP2-K}} \approx \sum_{r_1 r_2 z} \omega_z {}^X G_{zr_1 r_3} {}^X H_{zr_1 r_3}. \quad (62)$$

Again we consider the atomic batched partition as well and start from the expression,

$$E_{\text{MP2-K}} \approx E_{\text{MP2-K}}^{\text{ABC}} = \sum_{ABCD} \sum_{A'B'C'D'} \sum_{ab} \sum_{ij} \sum_{r^{AB}} \sum_{r^{CD}} \sum_{r^{A'B'}} \sum_{r^{C'D'}} \sum_z W_{a^A r^{AB}}^{AB,(1)} W_{i^B r^{AB}}^{AB,(2)} W_{b^C r^{CD}}^{CD,(1)} W_{j^D r^{CD}}^{CD,(2)} M_{r^{AB} r^{CD}}^{ABCD} \\ \times W_{b^{A'} r^{A'B'}}^{A'B',(1)} W_{i^{B'} r^{A'B'}}^{A'B',(2)} W_{a^{C'} r^{C'D'}}^{C'D',(1)} W_{j^{D'} r^{C'D'}}^{C'D',(2)} M_{r^{A'B'} r^{C'D'}}^{A'B'C'D'} \omega_z a_{az}^{(1)} a_{iz}^{(2)} a_{bz}^{(3)} a_{jz}^{(4)}, \quad (63)$$

where again on MO indices it is indicated that it only refers to AO transformed with the coefficients at a particular atom. Then we combine one set of intermediates with a common rank index

$${}^X A_{j^D b^C r^{CD}}^{CD} = W_{b^C r^{CD}}^{CD,(1)} W_{j^D r^{CD}}^{CD,(2)} \quad (64)$$

and plug in the SVD decomposed expression for the combination matrix,

$$E_{\text{MP2-K}}^{\text{ABC}} = \sum_{ABCD} \sum_{A'B'C'D'} \sum_{ab} \sum_{ij} \sum_{r^{AB}} \sum_{r^{CD}} \sum_{r^{A'B'}} \sum_{r^{C'D'}} \sum_z W_{a^A r^{AB}}^{AB,(1)} W_{i^B r^{AB}}^{AB,(2)} {}^X A_{j^D b^C r^{CD}}^{CD} \sum_{k_1} \bar{U}_{r^{AB} k_1}^{M,AB} \bar{V}_{r^{CD} k_1}^{M,CD} W_{b^{A'} r^{A'B'}}^{A'B',(1)} W_{i^{B'} r^{A'B'}}^{A'B',(2)} {}^X A_{j^{D'} a^{C'} r^{C'D'}}^{C'D'} \\ \times \sum_{k_2} \bar{U}_{r^{A'B'} k_2}^{M,A'B'} \bar{V}_{r^{C'D'} k_2}^{M,C'D'} \omega_z a_{az}^{(1)} a_{iz}^{(2)} a_{bz}^{(3)} a_{jz}^{(4)}. \quad (65)$$

We contract the V intermediates along the rank index,

$${}^X E_{j^D b^C k_1}^{CD} = \sum_{r^{CD}} {}^X A_{j^D b^C r^{CD}}^{CD} \bar{V}_{r^{CD} k_1}^{M,CD} \quad (66)$$

and carry out the summation over CD and $C'D'$,

$$E_{\text{MP2-K}}^{\text{ABC}} = \sum_{AB} \sum_{A'B'} \sum_{ab} \sum_{ij} \sum_{r^{AB}} \sum_{r^{A'B'}} \sum_z \sum_{k_1} \sum_{k_2} W_{a^A r^{AB}}^{AB,(1)} W_{i^B r^{AB}}^{AB,(2)} {}^X E_{j^D b^C k_1}^{CD} \bar{U}_{r^{AB} k_1}^{M,AB} W_{b^{A'} r^{A'B'}}^{A'B',(1)} W_{i^{B'} r^{A'B'}}^{A'B',(2)} {}^X E_{j^{D'} a^{C'} k_2}^{C'D'} \bar{U}_{r^{A'B'} k_2}^{M,A'B'} \omega_z a_{az}^{(1)} a_{iz}^{(2)} a_{bz}^{(3)} a_{jz}^{(4)}. \quad (67)$$

In a next step, we contract over the virtual indices,

$$E_{\text{MP2-K}}^{\text{ABC}} = \sum_{AB} \sum_{A'B'} \sum_{ij} \sum_{r^{AB}} \sum_{r^{A'B'}} \sum_z \sum_{k_1} \sum_{k_2} \omega_z {}^X E_{zj^D r^{A'B'} k_1}^{A'B',(1)} W_{i^B r^{AB}}^{AB,(2)} \bar{U}_{r^{AB} k_1}^{M,AB} {}^X E_{zj^D r^{A'B'} k_2}^{A'B',(1)} W_{i^{B'} r^{A'B'}}^{A'B',(2)} \bar{U}_{r^{A'B'} k_2}^{M,A'B'} a_{iz}^{(2)} a_{jz}^{(4)}. \quad (68)$$

Afterwards contraction over the k indices and the index i yields

$$E_{\text{MP2-K}}^{\text{ABC}} = \sum_{AB} \sum_{A'B'} \sum_j \sum_{r^{AB}} \sum_{r^{A'B'}} \sum_z \\ \times \omega_z {}^X F_{jr^{A'B'} r^{AB}}^{A'B'AB,(1)} {}^X F_{jr^{A'B'} r^{AB}}^{ABA'B',(1)} G_{zr^{AB} r^{A'B'}}^{ABA'B'} a_{jz}^{(4)}. \quad (69)$$

As one last step, we introduce the intermediate,

$${}^X H_{zr^{AB} r^{A'B'}}^{ABA'B',(1)} = \sum_j {}^X F_{jr^{AB} r^{A'B'}}^{ABA'B',(1)} {}^X F_{jr^{A'B'} r^{AB}}^{A'B'AB,(1)} a_{jz}^{(4)} \quad (70)$$

to write the exchange-like energy as

$$E_{\text{MP2-K}}^{\text{ABC}} = \sum_{AB} \sum_{A'B'} \sum_{r^{AB}} \sum_{r^{A'B'}} \sum_z \omega_z {}^X H_{zr^{AB} r^{A'B'}}^{ABA'B',(1)} {}^X G_{zr^{AB} r^{A'B'}}^{ABA'B'}. \quad (71)$$

Like for the Coulomb-like contribution, it is important to discuss the operation count. Using the RC format, the ${}^X E_{jzr_1 r_3}$ intermediate shows the steepest scaling with $\mathcal{O}(N^4)$ assuming again that R scales linearly with the system size, which is in reality not completely fulfilled (*vide infra*). Exploiting the ABC format, the most time consuming intermediate is the ${}^X F_{zj^D r^{AB} r^{CD}}^{ABCD}$ intermediate, where a formal operation

count of $\mathcal{O}(N^6)$ is required. But as for the Coulomb-like contribution, it contains a N_{atom}^4 part and due to the CP decomposition the operation count for large distant pairs/quadruples is smaller and in the asymptotic limit reduced to $\mathcal{O}(N^2)$ giving also the possibility for a $\mathcal{O}(N^4)$ scaling evaluation of the exchange-like contribution. Furthermore the formation of the intermediate contains the contraction over an auxiliary index. At the moment this is not restricted, but as the work by different groups concerning local density fitting shows, it should be possible to restrict the fitting domains so that the scaling is further reduced.^{15,49} Often robust density fitting is employed to reduce the error due to the local fitting domains. Recently Merlot *et al.*⁵⁰ showed that robust density fitting does not ensure semi-positive definiteness and that in local schemes this can lead to nonphysical results. In Ref. 50 it was demonstrated how to lift this pitfall by introducing a scheme to add further auxiliary function to the local basis. However, this again can increase the computational costs significantly. Therefore Hollmann *et al.* showed a scheme, where this problem is alleviated by including exact integrals for the matrix elements of the basis functions at semidiagonal atom blocks.⁵¹ Furthermore it can be accurate enough to use standard density fitting as shown in the work of Ihrig *et al.*⁵² or in a different context by Schmitz *et al.*¹⁸ Since the main aim of this work is to explore a new integral format and to assess its accuracy, the introduction of local density fitting remains for future work. Furthermore the current approach can be enhanced using localized occupied orbitals giving the possibility to exploit the locality in a more rigorous way. Since the energy denominator is replaced by an equivalent Laplace-transformed expression, it is not necessary to use iterative solvers for the MP1 amplitudes, but it is only required to calculate MO integrals which depend on the Laplace grid points.

III. TECHNICAL DETAILS

The RC-MP2 and ABC-MP2 calculations were performed with the Midas program package.⁵³ For the 3-index RI integrals, we used a local development version of the TURBOMOLE program package,⁵⁴ which was also used to perform the required Hartree-Fock, RI-MP2, and MP2 reference

calculations using the dscf,⁵⁵ ricc2,⁵⁶ and mpgrad⁵⁷ modules. We used the correlation consistent cc-pVXZ and aug-cc-pVXZ basis set families^{58–60} with $X = D, T, Q$ which we will abbreviate as XZ and aXZ, together with the optimized auxiliary basis sets from Ref. 61.

IV. RESULTS AND DISCUSSION

A. Obtained ranks after reassembling

Since we generate the RC representation using an incremental scheme driven by pairs of atoms, one could expect that the total rank after assembling the ranks for each pairs increases at least quadratically with molecular size, since the untruncated pair lists increase quadratically. But it is however possible to truncate the pair lists to solve this issue since in the asymptotic limit the number of non-negligible pairs increases non-quadratically with molecular size. But at the moment, we do not impose an *a priori* restriction to the pair lists. Long distant pairs contain less information and it is therefore more likely that they can be represented using a lower rank. If the decay is fast enough, an *ad hoc* restriction of the pair list is not required since the CP decomposition takes care of this. To investigate this further, we performed calculations on a chain of hydrocarbons in the DZ basis. In Table II the ranks of the RC format and the error due to the decomposition relative to the RI-MP2 reference are given as well as the RI error for comparison (the difference between the MP2 and RI-MP2 energy). Although here solely the RC error is given, it only differs by the ABC error by numerical noise so that all conclusions are transferable. For the calculation, we ensured that the error in the difference norm of the fitted and target tensor is below 10^{-3} ($T_{\text{CP}}^{\text{in}} = 10^{-3} E_h$), $5 \cdot 10^{-3}$ ($T_{\text{CP}}^{\text{in}} = 5 \cdot 10^{-3} E_h$), or 10^{-2} ($T_{\text{CP}}^{\text{in}} = 10^{-2} E_h$). On the first look, this seems to be a quite harsh approximation, but is sufficiently accurate (*vide infra*) and in accordance with the work of Benedikt *et al.*,^{30,31} who also studied the usage of low rank tensor decompositions in post-HF methods.

For $T_{\text{CP}}^{\text{in}} = 10^{-3} E_h$, the RC/ABC error is always below the RI error which indicates that there is no decline in accuracy in comparison to RI-MP2. Also in the case for $T_{\text{CP}}^{\text{in}} = 5 \cdot 10^{-3} E_h$ and $T_{\text{CP}}^{\text{in}} = 10^{-2} E_h$, the RC error is still of comparable size as

TABLE II. RI as well as RC error for alkane chains using the DZ basis. Additionally the assembled ranks in the RC format are listed.

Molecule	$\Delta_{\text{RI}} (E_h)$	$T_{\text{CP}} = 10^{-3} E_h$		$T_{\text{CP}} = 5 \cdot 10^{-3} E_h$		$T_{\text{CP}} = 10^{-2} E_h$	
		$\Delta_{\text{RC}}(E_h)$	R	$\Delta_{\text{RC}}(E_h)$	R	$\Delta_{\text{RC}}(E_h)$	R
CH ₄	$-4.97 \cdot 10^{-5}$	$-2.03 \cdot 10^{-5}$	893	$-1.34 \cdot 10^{-6}$	762	$-6.16 \cdot 10^{-6}$	685
C ₂ H ₆	$-7.52 \cdot 10^{-5}$	$-6.09 \cdot 10^{-6}$	2 344	$4.75 \cdot 10^{-5}$	1 918	$-9.10 \cdot 10^{-5}$	1 721
C ₃ H ₈	$-9.66 \cdot 10^{-5}$	$-3.45 \cdot 10^{-5}$	4 245	$3.97 \cdot 10^{-5}$	3 406	$8.95 \cdot 10^{-5}$	3 015
C ₄ H ₁₀	$-1.21 \cdot 10^{-4}$	$-2.25 \cdot 10^{-5}$	6 376	$3.27 \cdot 10^{-5}$	5 115	$2.89 \cdot 10^{-4}$	4 520
C ₅ H ₁₂	$-1.45 \cdot 10^{-4}$	$-1.92 \cdot 10^{-5}$	8 846	$1.69 \cdot 10^{-4}$	7 056	$5.54 \cdot 10^{-4}$	6 367
C ₆ H ₁₄	$-1.70 \cdot 10^{-4}$	$1.45 \cdot 10^{-6}$	11 408	$1.63 \cdot 10^{-4}$	9 304	$8.81 \cdot 10^{-4}$	8 361
C ₇ H ₁₆	$-1.95 \cdot 10^{-4}$	$-1.02 \cdot 10^{-5}$	13 975	$2.43 \cdot 10^{-4}$	11 395	$1.38 \cdot 10^{-3}$	10 196
C ₈ H ₁₈	$-2.20 \cdot 10^{-4}$	$-1.02 \cdot 10^{-5}$	16 789	$4.41 \cdot 10^{-4}$	13 787	$1.35 \cdot 10^{-3}$	12 532
C ₉ H ₂₀	$-2.45 \cdot 10^{-4}$	$-1.93 \cdot 10^{-6}$	19 428	$4.41 \cdot 10^{-4}$	15 776	$1.51 \cdot 10^{-3}$	14 607
C ₁₀ H ₂₀	$-2.70 \cdot 10^{-4}$	$3.28 \cdot 10^{-6}$	23 072	$4.66 \cdot 10^{-4}$	18 117	$1.90 \cdot 10^{-3}$	15 852

the RI error and still allows sub-millihartree accuracy. As observed in several THC implementations, e.g., Ref. 34, the RI error is in most cases of opposite sign as the RC error which might cause some error cancellation. The ranks in our initial implementation are still large but further analysis shows that the ranks increase only as $N_{\text{carb}}^{1.412}$, $N_{\text{carb}}^{1.392}$, and $N_{\text{carb}}^{1.395}$ for $T_{\text{CP}}^{\text{in}} = 10^{-3} E_h$, $T_{\text{CP}}^{\text{in}} = 5 \cdot 10^{-3} E_h$, and $T_{\text{CP}}^{\text{in}} = 10^{-2} E_h$, respectively. Since the powers are very close, one can conclude that the scaling does not differ much for different thresholds. Only the prefactor is increased, but this conclusion might change if larger systems are considered, since then more and more atom pairs will be screened out completely. So far this is observed starting from C_6H_{14} , where depending on the threshold one or two pairs are discarded. For $\text{C}_{10}\text{H}_{20}$ then 15 pairs with the loose threshold are cut out and 10 with the tight one. We note that the RC and ABC format might give rise for an intuitive tool to understand the interaction in large molecules on an atomistic level. For example, as the integrals, the wave function amplitudes can be casted in a similar format. This then allows for analysis purposes to do a SVD on each combination matrix, which should indicate the relative importance of the correlation of electrons at the contributing atom quadruples.

The large ranks are only a problem for the RC format. If the ABC format is used, the ranks for all pairs are sufficiently small and no bottlenecks concerning storage or operation count emerge.

1. Rank prediction

In our initial implementation, we started each tensor fitting with a rank-1 tensor and then proceeded with a Find-BestCPALS algorithm, where tensors of larger and larger ranks are fitted to the target tensor. To accelerate this procedure by reducing the number of required rank increments, we searched for a way to predict the final rank based on some easy to calculate quantities. Using a small test containing the alkane chains in the DZ basis and additionally the first five dimers in the S66 set in the aDZ basis, we studied the dependence with a simple model. The final rank R of a sub-block should be proportional to the information the tensor contains, which is in our case the number of electrons n_{el} and the size of the target tensor, e.g., the number of basis functions n_{bas} . The number of electrons was in a first version left out, but helped to enhance the correlation a bit. Additionally the rank should be anti-proportional to the interatomic distance r_{AB} . Combining these quantities yields the simple relation

$$R \propto \frac{(n_{\text{el}}^A + n_{\text{el}}^B) \cdot n_{\text{bas}}^A n_{\text{bas}}^B}{r_{AB}}. \quad (72)$$

FIG. 3. Dependence of the ranks to the functions in Eqs. (72) and (73).

For the diagonal pairs $A = B$, a slightly different model due to a singularity at $r_{AB} = 0$ has to be used,

$$R \propto n_{\text{el}}^A \cdot (n_{\text{bas}}^A)^2. \quad (73)$$

To test how well the predictions perform, they are plotted for the test set in Fig. 3 against the final rank. A correlation is clearly observable. However the correlation for the diagonal pairs is a bit more systematic. Moreover the plot reveals that a sub-tensor belonging to a diagonal pair can be compressed further than a sub-tensor of comparable size belonging to a non-diagonal pair. One can argue that in the diagonal case, less information is contained in the tensor and the clearer trend indicates that the structure of the tensor enables an easier fitting. In the diagonal case, the 3-index integral describes the Coulomb interaction of the basis functions at one center with the auxiliary functions, which is likely easier to describe than the interaction of two centers with auxiliary functions.

For the non-diagonal pairs, the distribution can be quite broad, but the correlation is good enough to enhance the Find-BestCPALS algorithm by predicting a better starting rank. The effect of this enhanced prediction shall be illustrated with Table III, where for the first 5 dimers in the S66 set,⁶² the total number of CP-ALS iterations is shown using the aDZ basis. With exception of the Water-MeOH dimer, the number of iterations could be significantly reduced especially for the larger complexes 04 and 05, which directly leads to a more efficient implementation. In both cases, we used random start guesses for the mode matrices and increased the initial rank by a rank increment of one, if the error was still too large. For the rank increment, we fitted the rank-1 tensor to the difference between the target tensor and the current representation and used the current rank + rank increment as guess for a new representation.

TABLE III. Number of CP-ALS iterations accumulated for all pairs using the initial code and the distant dependent rank prediction. As an example, the first 5 dimers of the S66 test set are chosen using the aDZ basis.

	01 Water-Water	02 Water-MeOH	03 Water-MeNH2	04 Water-Peptide	05 MeOH-MeOH
Initial	462 689	444 615	390 586	244 883	151 327
New	183 220	407 068	201 021	85 525	61 433

B. Distribution of the SVD thresholds

Since the SVD thresholds for the conversion of the CP to the Tucker format are selected by an error bound, it is interesting to take a look at the distribution of the chosen thresholds. Figure 4 shows a distribution of the automatically selected thresholds for the C2T/T2C algorithm when a maximal error of 10^{-5} in the norm is allowed. Mostly values for T_{SVD} around $10 \cdot T_{\text{err}}$ are selected, but the histograms also reveal that there are cases where T_{SVD} must be selected substantially smaller (close to numerical zero). Thus it is evident that the error bound based selection is the preferred choice for the algorithm since otherwise there is a danger to neglect important parts of the target tensor.

C. Accuracy

To assess the accuracy of our method, we carried out calculations on the S22 sub-set and the larger S66 super-set for weak intermolecular interactions (Ref. 62) and calculated errors relative to MP2 results (without RI approximation). For that purpose, we took a look at the uncorrected and counterpoise corrected energies in the DZ, TZ, and aDZ basis varying the threshold for the decomposition $T_{\text{CP}}^{\text{in}}$. For the calculations, a threshold of $T_{\text{CP}}^{\text{in}} = 10^{-3} E_h$ and $T_{\text{CP}}^{\text{in}} = 10^{-4} E_h$ was used.

Already for small test cases, it turned out that $T_{\text{CP}}^{\text{in}} = 10^{-2} E_h$ is too loose for the diffuse aDZ basis, although the results for the alkane chains using the DZ basis did not fully indicate this. The overall statistic is depicted in Table IV and in the [supplementary material](#) a more detailed overview can be found. For the non-diffuse DZ and TZ basis, the errors for the not counterpoise corrected energies are typical below 1 kJ/mol for both thresholds. For $T_{\text{CP}}^{\text{in}} = 10^{-4} E_h$, it is mostly below 0.1 kJ/mol and therefore insignificant. We note that for the not diffuse DZ and TZ basis $T_{\text{CP}}^{\text{in}} = 10^{-3} E_h$ is sufficiently accurate, but this is not the case for the diffuse aDZ basis set. Here at least $T_{\text{CP}}^{\text{in}} = 10^{-4} E_h$ is required, but then the results are in most cases nearly spot on. However for dimers 17 and 22, the errors for the counterpoise corrected energies are then still above 0.1 kJ/mol for this basis.

From the sign of the mean error (MEAN), it can be seen that due to the ABC error in most cases the binding energy is a bit underestimated for the calculations without counterpoise correction and a bit overestimated when using a counterpoise correction. For the RI error this behavior is less evident, but since it is roughly 1–2 orders of magnitude smaller than the ABC error, it is also nearly meaningless to give a general conclusion on the sign since we are clearly below the intrinsic accuracy of MP2.

FIG. 4. Distribution of the selected T_{SVD} for the dimers 02, 03, 04, and 05 from the S66 set in the aDZ basis.

TABLE IV. RI- and ABC-error statistics in kJ/mol for the different basis sets and thresholds T_{CP}^{in} for interaction energies with and without counterpoise correction for the S22 set. If data for the S66 super-set are available, the values are given in parentheses.

	MEAN	MAD
Δ_{RI}/DZ	0.012 (−0.008)	0.012 (0.017)
$\Delta_{ABC}/DZ T_{CP}^{in} = 10^{-3} E_h$	−0.008 (−0.079)	0.112 (0.246)
$\Delta_{ABC}/DZ T_{CP}^{in} = 10^{-4} E_h$	0.003 (−0.071)	0.102 (0.128)
Δ_{RI}^{corr}/DZ	0.004 (0.007)	0.006 (0.042)
$\Delta_{ABC}^{corr}/DZ T_{CP}^{in} = 10^{-3} E_h$	0.060 (0.051)	0.207 (0.404)
$\Delta_{ABC}^{corr}/DZ T_{CP}^{in} = 10^{-4} E_h$	0.023 (−0.039)	0.228 (0.155)
Δ_{RI}/aDZ	0.000	0.006
$\Delta_{ABC}/aDZ T_{CP}^{in} = 10^{-3} E_h$	−0.693	1.160
$\Delta_{ABC}/aDZ T_{CP}^{in} = 10^{-4} E_h$	−0.079	0.082
Δ_{RI}^{corr}/aDZ	−0.003	0.008
$\Delta_{ABC}^{corr}/aDZ T_{CP}^{in} = 10^{-3} E_h$	0.035	0.428
$\Delta_{ABC}^{corr}/aDZ T_{CP}^{in} = 10^{-4} E_h$	−0.019	0.071
Δ_{RI}/TZ	−0.007	0.009
$\Delta_{ABC}/TZ T_{CP}^{in} = 10^{-3} E_h$	−0.168	0.171
$\Delta_{ABC}/TZ T_{CP}^{in} = 10^{-4} E_h$	−0.081	0.161
Δ_{RI}^{corr}/TZ	−0.003	0.004
$\Delta_{ABC}^{corr}/TZ T_{CP}^{in} = 10^{-3} E_h$	−0.015	0.149
$\Delta_{ABC}^{corr}/TZ T_{CP}^{in} = 10^{-4} E_h$	−0.040	0.211

For the TZ and aDZ basis, only results for the smaller S22 sub-set are presented, but from the results for the DZ basis, one can conclude that the mean absolute deviations might increase by a factor of two if the larger test set is considered. The increase is still in an acceptable range. Since the larger test set also includes several larger dimers and the energy and therefore the error in the energy is an extensive property, this behavior is not unexpected. Also for the RI error we see an increase, although it is less strong.

For the not counterpoise corrected interactions energies, the mean absolute error (MAD) goes in all cases down when the CP threshold is tightened, although the effect might not be strong. For the counterpoise corrected energies, this does not hold in all cases. Here the looser threshold profits from some error cancellation, which is lost for the tighter threshold and a further improvement is then only possible by further tightening the CP threshold.

D. Potential-energy surfaces

A further important point to address is whether the ABC framework enables smooth potential surfaces and how tight the CP threshold has to be chosen to ensure it. In order to investigate this further, the distance from the equilibrium structure of the water–water dimer was continuously increased. Figure 5 shows the energy curves for the DZ, TZ, and QZ basis for

FIG. 5. Energy of the water–water dimer depending on the distance of the monomers for different basis sets and T_{CP}^{in} thresholds. Additionally the energy difference relative to the RI-MP2 curve is plotted.

RI-MP2 and ABC-MP2 for different $T_{\text{CP}}^{\text{in}}$ thresholds. Interesting is the very close agreement for the TZ basis. Here the dependence on the threshold is less strong. However for the DZ and QZ bases, using $T_{\text{CP}}^{\text{in}} = 10^{-2} E_h$ leads to small kinks in the curves. In general, the agreement is better for short distances. For longer distances, the RI-MP2 and ABC-MP2 curves separate more. For the DZ basis, the ABC-MP2 energy is slightly above the RI-MP2 one and for the QZ basis below. Besides this, look at total energy curves, it is interesting to examine the geometric dependence on the energy difference between RI-MP2 and ABC-MP2. It is depicted in Figure 5(d). In this plot, kinks are more evident and can also be observed for smaller thresholds than $T_{\text{CP}}^{\text{in}} = 10^{-2} E_h$. Again for the TZ basis, the curve is quite smooth. For the DZ and QZ bases, the curves are a bit less smooth but improve strongly when the CP threshold is set tighter. In conclusion, a bumpy behavior is found to the extent that the thresholds are not tight enough, as will be the case for most such thresholds. As the thresholds are tightened, the curves become smoother and follows the reference closer.

E. Storage savings

One point we did not investigate so far, but which is of crucial importance is the storage requirements compared to the conventional 4-index integrals. For that purpose we take again a look at the calculation for the alkane chains, but now using the DZ as well as the TZ basis and the CP threshold $T_{\text{CP}}^{\text{in}} = 10^{-3} E_h$. To compare the storage we use the 8-fold symmetry of the AO integrals in the conventional case. For RC we exploit that the combination matrix can be stored in packed format, which is required in combination with the mode matrices for the AO indices of the 3-index integrals to represent the 4-index integrals. In contrast, we do not need the combination matrix in the ABC format. Here we can calculate the needed sub-blocks on the fly via the mode matrix for the auxiliary index and the SVD of J_{PQ}^{-1} , both of which we do not need to store in the RC case. In our current implementation, we store for the ABC as well as the RC format the AO mode matrices as the patched mode matrices of the full tensor. This implies that for ABC we store unused zeros, but for the initial implementation which is meant to compare RC and ABC a common storage scheme for the mode matrices is more convenient. Nevertheless this implies that minor further savings are possible, but not exploited.

Table V lists the storage requirements in megabytes (MB) for the three cases for increasingly larger alkane chains. For the RC format the picture is a bit mixed. Here for the TZ basis in all cases a reduction can be observed, but for the DZ

TABLE V. Storage requirements in megabytes (MB) for the packed AO integrals and the ABC format using different basis sets and a CP threshold of $T_{\text{CP}}^{\text{in}} = 10^{-3} E_h$.

	AO		RC		ABC	
	DZ	TZ	DZ	TZ	DZ	TZ
C ₃ H ₈	43	1 588	74	1257	10	67
C ₄ H ₁₀	120	4 358	165	2615	19	125
C ₅ H ₁₂	272	9 752	316	4703	32	206
C ₆ H ₁₄	536	19 061	523	7670	49	311

FIG. 6. Wall time of RC-MP2 and ABC-MP2 calculations on alkane chains in the aDZ basis. Besides the total wall time also the parts for the CP decomposition and the evaluation of the Coulomb-like (J) and exchange-like (K) energy contribution are depicted.

basis not for the given system sizes. But this likely only holds for the current studied system sizes, which are not that large. Going beyond C₆H₁₄ also savings in the DZ basis are possible. Nevertheless for molecules like C₅H₁₂ and C₆H₁₄ savings in the TZ basis between 40% and 80% are possible.

Turning the look at the ABC format the picture becomes much clearer. Since in this case the storage of the combination matrix is avoided (on disk as well as in memory) by replacing it with the mode matrices for the auxiliary index and the SVD of J_{PQ}^{-1} , the overall storage requirements are significantly reduced. In fact we observe for each molecule a reduction. For the small DZ basis the savings are with 10%–50% still moderate but for the TZ basis in all cases a reduction of over 90% can be observed. The low storage requirements are obviously a major advantage of the ABC format. For example, the C₆H₁₄ integrals in the TZ basis take less space than the DZ integrals in either AO or RC format.

F. Timings

After considering the accuracy and the dependence of the accumulated ranks with molecular size, it is important to take a deeper look at the computational efficiency. At the moment only the ABC and RC approaches shall be compared with each other. A comparison with efficient and tuned RI-MP2 implementations is at the moment not of interest since the CP decomposition alone is for most systems more costly and the code is not tuned for absolute speed yet. Although the decomposition has due to the atomic batching a formal $\mathcal{O}(N^2)$ scaling, it has a huge prefactor and will dominate. ABC-MP2 can on a single core not compete with RI-MP2, but we see a potential for parallelization and in particular we want to apply this

TABLE VI. Fitted power laws for the wall time (s) for the 3 major contributions as obtained in the calculations for the RC and ABC approaches.

	CP	E(J)	E(K)
RC	$10^{2.69} N_{\text{bas}}^{1.37}$	$10^{0.29} N_{\text{bas}}^{4.15}$	$10^{0.55} N_{\text{bas}}^{4.00}$
ABC	$10^{2.69} N_{\text{bas}}^{1.37}$	$10^{0.05} N_{\text{bas}}^{3.94}$	$10^{-0.02} N_{\text{bas}}^{4.61}$

FIG. 7. Percentage to the overall costs in Wall time for the CP decomposition, calculation of the energy contributions, and the remaining steps in the aDZ basis using $T_{CP}^m = 10^{-3} E_h$.

approach to higher correlated levels of theory in the future. For the analysis, the Wall time of the ABC-MP2 and RC-MP2 calculation on alkane chains in the aDZ basis shall be analyzed. In Fig. 6 they are plotted on a double logarithmic plot. To extract the scaling we fitted the data to a power law of the form $10^A \times N_{carb}^B$. The fitted expressions are listed in Table VI. In this plot, the total Wall time, the time for the CP decomposition, and the energy calculation are shown. For small molecules the CP decomposition dominates, but around C_6H_{14} the calculation of the energy takes over. It is evident from the plot that the energy calculation has a much steeper scaling than the decomposition step, which shows an effective scaling of $\mathcal{O}(N^{1.37})$. For RC-J and ABC-J, respectively, an effective scaling of $\mathcal{O}(N^{4.15})$ and $\mathcal{O}(N^{3.94})$ is observed, while for RC-K and ABC-K, the scaling is $\mathcal{O}(N^{4.00})$ and $\mathcal{O}(N^{4.60})$. Although for ABC-MP2 we can expect at worst a $\mathcal{O}(N^6)$ scaling, it shows a smaller effective scaling. For distant pairs a smaller rank is obtained and therefore the operation count for distant pairs is reduced, which leads to the effective sub- $\mathcal{O}(N^5)$ scaling.

Exploiting the ABC format the Coulomb-like contribution can be evaluated much faster than in the RC format. The current algorithm design is in principle flexible enough to switch between RC and ABC representations in one run in order to use the most efficient approach for each contribution. As previously mentioned, the ABC implementation can also be improved in several ways.

Complementary to these findings, Figure 7 shows pie charts with the percentage of the total Wall time spent on the

CP decomposition, the energy calculation, and the remaining steps for some dimers from the S66 set in the aDZ basis. Besides dimer 04 in all cases, the CP decomposition and therefore the generation of the ABC format still dominate, but it is evident that the energy calculation and especially the evaluation of the exchange-like contribution take over for larger systems. Furthermore it shows that no other steps besides the CP decomposition and the energy calculation take significant time.

V. OUTLOOK AND CONCLUSION

We demonstrated a new integral format for two-electron integrals which combines several techniques like the RI approximation and CP and Tucker tensor decompositions with an atomic batching scheme. The format has strong similarities to the THC format, but no grids and therefore less empirical knowledge is required to perform the needed CP decomposition in a feasible amount of time. This is achieved by constructing the decomposed integrals in a batched way, where the full integral tensor is split up into small sub-tensors, which are decomposed by an accelerated CP-ALS algorithm. In a first step, the 3-index integrals are cast into a CP format with high rank using a procedure with the repeated SVDs. Having the integrals already in the CP format enables the use of a recompression CP-ALS algorithm, which exploits the computational savings due to the CP format. The recompression algorithm is additionally enhanced by using a Tucker

decomposition as an intermediate step. The tensor is converted to the Tucker format and the recompression algorithm is applied to the smaller core tensor, where the core tensor is still in CP format. Afterwards the sub-tensors can be reassembled to the full set and form the RC format, where we use the extension R to point out that the sub-tensors are reassembled and the C to indicate that the Coulomb metric for the 3-index integrals was used. A second alternative is to not reassemble the sub-tensors, but to stay in the atomic batched format given rise to the ABC format. The storage requirements in the ABC format are significantly reduced in comparison to the conventional storage of AO integrals and also the RC format. Even for small molecules, the ABC integrals allow a reduction of over 90% in the TZ basis. If an atomic batching scheme is used in a reformulation of the MP2 equations, this gives rise to a potentially $\mathcal{O}(N^6)$ scaling algorithm while in RC at most $\mathcal{O}(N^4)$ scaling costs can be expected. On the first look, this seems unfavorable, but this formal scaling contains a quartic scaling with the number of atoms. This is usually a small number and furthermore the CP decomposition of the 3-index integrals per atom pair already reduce formal scaling since for distant pairs lower ranks are obtained. When going to larger systems, some pairs will even be screened out completely. For alkane chains in the aDZ basis, indeed a sub- $\mathcal{O}(N^5)$ scaling was observed. Furthermore it is possible to combine the rate determining step with local density fitting techniques to reduce the scaling further and to remove this potential issue.

For model systems it could be shown that the ranks in the reassembled RC format increase only as $N^{1.40}$ with the system size without any *a priori* truncation of atom-pair lists. The ranks of the sub-tensors show a good dependence on the data they are containing and the distance of the atom pairs, which enabled us to improve the rank prediction and save iterations in the CP-ALS algorithm. Concerning the accuracy, the RC/ABC error for total energies can be set below the RI error so that virtually no loss in accuracy can be expected. For a small test set for weak intermolecular interactions, it was shown that the errors for interaction energies could easily be controlled to be below 1 kJ/mol, but diffuse basis sets need more caution than non-augmented bases.

First profiling shows that only for smaller systems the decomposition to the ABC/RC format is the major time-consuming step, which shows an effective scaling of $\mathcal{O}(N^{1.37})$, and for larger systems the energy calculations start to dominate which shows in our test cases for RC an effective scaling of $\mathcal{O}(N^{4.15})$ for the Coulomb-like part and $\mathcal{O}(N^{4.00})$ for the exchange-like contribution was observed. Exploiting the ABC format the effective scaling for the Coulomb part is $\mathcal{O}(N^{3.94})$ and $\mathcal{O}(N^{4.61})$ for the exchange part. In ongoing work this part can be accelerated by means of local density-fitting approximations.

The reassembled ranks in the RC format are still quite large, but so far we applied only some modifications to the underlying CP-ALS recompression algorithm. A faster convergence and smaller output ranks may be possible with improved starting guesses. The atomic-batched construction opens here the route to, for instance, pre-tabulate guesses for certain atom types. Nevertheless the large accumulated

ranks are not a problem for the ABC format since the ranks per pair are reasonably small. To divide a large problem into lots of smaller pieces might pave the way for efficient parallelization strategies. Since the data per atom pair are quite small no large communication overhead should be expected.

In ongoing research, we want to apply the RC and especially the ABC format to higher-level methods. Furthermore, a deeper comparison between the RC format and a RO format using the overlap metric will be made.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for a more detailed overview of the ABC and RI errors evaluated for the S66 set.

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- ¹J. L. Whitten, *J. Chem. Phys.* **58**, 4496 (1973).
- ²B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, *J. Chem. Phys.* **71**, 3396 (1979).
- ³O. Vahtras, J. Almlöf, and M. W. Feyereisen, *Chem. Phys. Lett.* **213**, 514 (1993).
- ⁴F. Weigend and M. Häser, *Theor. Chem. Acc.* **97**, 331 (1997).
- ⁵S. Wilson, *Comput. Phys. Commun.* **58**, 71 (1990).
- ⁶I. Røeggen and E. Wisløff-Nilssen, *Chem. Phys. Lett.* **132**, 154 (1986).
- ⁷N. H. F. Beebe and J. Linderberg, *Int. J. Quantum Chem.* **12**, 683 (1977).
- ⁸H. Koch, A. S. de Mers, and T. B. Pedersen, *J. Chem. Phys.* **118**, 9481 (2003).
- ⁹S. Saebø and P. Pulay, *Chem. Phys. Lett.* **113**, 13 (1985).
- ¹⁰S. Saebø and P. Pulay, *Annu. Rev. Phys. Chem.* **44**, 213 (1993).
- ¹¹J. Yang, G. K.-L. Chan, F. R. Manby, M. Schütz, and H.-J. Werner, *J. Chem. Phys.* **136**, 144105 (2012).
- ¹²W. Meyer, *Int. J. Quantum Chem.* **5**, 441 (1971).
- ¹³R. Ahlrichs, F. Driessler, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.* **62**, 1235 (1975).
- ¹⁴M. Schütz and H.-J. Werner, *J. Chem. Phys.* **114**, 661 (2001).
- ¹⁵A. Hansen, D. G. Liakos, and F. Neese, *J. Chem. Phys.* **135**, 214102 (2011).
- ¹⁶B. Helmich and C. Hättig, *J. Chem. Phys.* **135**, 214106 (2011).
- ¹⁷C. Krause and H.-J. Werner, *Phys. Chem. Chem. Phys.* **14**, 7591 (2012).
- ¹⁸G. Schmitz, B. Helmich, and C. Hättig, *Mol. Phys.* **111**, 2463 (2013).
- ¹⁹C. Riplinger and F. Neese, *J. Chem. Phys.* **138**, 034106 (2013).
- ²⁰C. Riplinger, B. Sandhoefer, A. Hansen, and F. Neese, *J. Chem. Phys.* **139**, 134101 (2013).
- ²¹F. L. Hitchcock, *J. Math. Phys.* **6**, 164 (1927).
- ²²L. R. Tucker, *Psychometrika* **31**, 279 (1966).
- ²³L. R. Tucker, in *Problems in Measuring Change*, edited by C. W. Harris (University of Wisconsin Press, Madison, WI, 1963), pp. 122–137.
- ²⁴J. D. Carroll and J.-J. Chang, *Psychometrika* **35**, 283 (1970).
- ²⁵“Foundations of the PARAFAC procedure: Models and conditions for an ‘explanatory’ multimodal factor analysis,” *UCLA Working Papers in Phonetics*, Vol. 16, 1970, pp. 1–84 (University Microfilms, Ann Arbor, Michigan, No. 10,085).
- ²⁶E. Acar, S. A. Çamtepe, M. S. Krishnamoorthy, and B. Yener, “Modeling and multiway analysis of chatroom tensors,” in *Intelligence and Security Informatics: IEEE International Conference on Intelligence and Security Informatics, ISI 2005, Atlanta, GA, USA, May 19-20, 2005. Proceedings*, edited by P. Kantor, G. Muresan, F. Roberts, D. D. Zeng, F.-Y. Wang,

- H. Chen, and R. C. Merkle (Springer Berlin Heidelberg, Berlin, Heidelberg, 2005), pp. 256–268.
- ²⁷L. Omberg, G. H. Golub, and O. Alter, *Proc. Natl. Acad. Sci. U. S. A.* **104**, 18371 (2007), <http://www.pnas.org/content/104/47/18371.full.pdf>.
- ²⁸E. Martinez-Montes, P. A. Valdés-Sosa, F. Miwakeichi, R. I. Goldman, and M. S. Cohen, *NeuroImage* **22**, 1023 (2004).
- ²⁹L. D. Lathauwer and J. Vandewalle, *Linear Algebra Appl.* **391**, 31 (2004).
- ³⁰U. Benedikt, A. A. Auer, M. Espig, and W. Hackbusch, *J. Chem. Phys.* **134**, 054118 (2011).
- ³¹U. Benedikt, K.-H. Böhm, and A. A. Auer, *J. Chem. Phys.* **139**, 224101 (2013).
- ³²I. H. Godtliessen, B. Thomsen, and O. Christiansen, *J. Phys. Chem. A* **117**, 7267 (2013).
- ³³I. H. Godtliessen, M. B. Hansen, and O. Christiansen, *J. Chem. Phys.* **142**, 024105 (2015).
- ³⁴E. G. Hohenstein, R. M. Parrish, and T. J. Martínez, *J. Chem. Phys.* **137**, 044103 (2012).
- ³⁵E. G. Hohenstein, R. M. Parrish, C. D. Sherrill, and T. J. Martínez, *J. Chem. Phys.* **137**, 221101 (2012).
- ³⁶C. Song and T. J. Martínez, *J. Chem. Phys.* **144**, 174111 (2016).
- ³⁷R. M. Parrish, E. G. Hohenstein, N. F. Schunck, C. D. Sherrill, and T. J. Martínez, *Phys. Rev. Lett.* **111**, 132505 (2013).
- ³⁸C. Song and T. J. Martínez, *J. Chem. Phys.* **146**, 034104 (2017).
- ³⁹C. Edmiston and M. Krauss, *J. Chem. Phys.* **45**, 1833 (1966).
- ⁴⁰L. Grasedyck, *SIAM J. Matrix Anal. Appl.* **31**, 2029 (2010).
- ⁴¹I. V. Oseledets, *SIAM J. Sci. Comput.* **33**, 2295 (2011).
- ⁴²F. R. Manby, *J. Chem. Phys.* **119**, 4607 (2003).
- ⁴³M. Kállay, *J. Chem. Phys.* **141**, 244113 (2014).
- ⁴⁴B. N. Khoromskij and V. Khoromskaia, *SIAM J. Sci. Comput.* **31**, 3002 (2009).
- ⁴⁵V. Khoromskaia and B. N. Khoromskij, *Phys. Chem. Chem. Phys.* **17**, 31491 (2015).
- ⁴⁶L. D. Lathauwer, B. D. Moor, and J. Vandewalle, *SIAM J. Matrix Anal. Appl.* **21**, 1324 (2000).
- ⁴⁷E. E. Papalexakis, C. Faloutsos, and N. D. Sidiropoulos, “Parcube: Sparse parallelizable tensor decompositions,” in *Machine Learning and Knowledge Discovery in Databases: European Conference, ECML PKDD 2012, Bristol, UK, September 24–28, 2012. Proceedings, Part I*, edited by P. A. Flach, T. De Bie, and N. Cristianini (Springer Berlin Heidelberg, Berlin, Heidelberg, 2012), pp. 521–536.
- ⁴⁸M. Häser and J. Almlöf, *J. Chem. Phys.* **96**, 489 (1992).
- ⁴⁹H.-J. Werner, F. R. Manby, and P. J. Knowles, *J. Chem. Phys.* **118**, 8149 (2003).
- ⁵⁰P. Merlot, T. Kjrgaard, T. Helgaker, R. Lindh, F. Aquilante, S. Reine, and T. B. Pedersen, *J. Comput. Chem.* **34**, 1486 (2013).
- ⁵¹D. S. Hollman, H. F. Schaefer, and E. F. Valeev, *J. Chem. Phys.* **140**, 064109 (2014).
- ⁵²A. C. Ihrig, J. Wierfink, I. Y. Zhang, M. Ropo, X. Ren, P. Rinke, M. Scheffler, and V. Blum, *New J. Phys.* **17**, 093020 (2015).
- ⁵³O. Christiansen, I. H. Godtliessen, E. M. Gras, W. Györfy, M. B. Hansen, M. B. Hansen, J. Kongsted, E. L. Klinting, C. König, S. A. Losilla, D. Madsen, N. K. Madsen, P. Seidler, K. Sneskov, M. Sparta, B. Thomsen, D. Toffoli, and A. Zoccante, “Midascpp (Molecular Interactions, Dynamics and Simulation Chemistry Program Package in C++)” (2016), www.chem.au.dk/midas.
- ⁵⁴“TURBOMOLE V6.6 2014, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007, available from <http://www.turbomole.com>.”
- ⁵⁵R. Ahlrichs, M. Bär, H. Horn, and C. Kölmel, *Chem. Phys. Lett.* **162**, 165 (1989).
- ⁵⁶C. Hättig and F. Weigend, *J. Chem. Phys.* **113**, 5154 (2000).
- ⁵⁷F. Haase and R. Ahlrichs, *J. Comput. Chem.* **14**, 907 (1993).
- ⁵⁸C. W. J. Bauschlicher, S. R. Langhoff, and P. R. Taylor, *J. Chem. Phys.* **88**, 2540 (1988).
- ⁵⁹D. E. Woon and T. H. J. Dunning, *J. Chem. Phys.* **98**, 1358 (1993).
- ⁶⁰T. H. J. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- ⁶¹F. Weigend, A. Köhn, and C. Hättig, *J. Chem. Phys.* **116**, 3175 (2002).
- ⁶²J. Rezac, K. E. Riley, and P. Hobza, *J. Chem. Theory Comput.* **7**, 2427 (2011).