THE INTEGRAL- AND INTERMEDIATE-SCREENED COUPLED-CLUSTER METHOD

L.K. Sørensen*

Department of Chemistry - Ångström Laboratory, Uppsala University, S-75105 Uppsala, Sweden

E-mail: lasse.kraghsorensen@kemi.uu.se

Abstract

We present the formulation and implementation of the integral- and intermediate-screened coupled-cluster method (ISSCC). The IISCC method gives a simple and rigorous integral and intermediate screening (IIS) of the coupled-cluster method and will significantly reduces the scaling for all orders of the CC hierarchy exactly like seen for the integral-screened configuration-interaction method (ISCI). The rigorous IIS in the IISCC gives a robust and adjustable error control which should allow for the possibility of converging the energy without any loss of accuracy while retaining low or linear scaling at the same time. The derivation of the IISCC is performed in a similar fashion as in the ISCI where we show that the tensor contractions for the nested commutators are separable up to an overall sign and that this separability can lead to a rigorous IIS. In the nested commutators the integrals are screened in the first tensor contraction and the intermediates are screened in all successive tensor contractions. The rigorous IIS will lead to linear scaling for all nested commutators for large systems in a similar way as seen for the ISCI. The reduced scaling can in this way be obtained without any range dependent parameter for the interaction, unlike other low scaling methods and is therefore also suitable for charge separated systems. It is expected that the IISCC, just like the ISCI, can

*To whom correspondence should be addressed
use dramatically larger orbital spaces combined with large CC expansions as compared with traditional CC methods. Due to the size extensive nature of the CC method the IISCC should not only be applicable to few electron systems but also to large molecular system unlike the ISCI. The IISCC can here either be used as a stand alone method or combined with other linear scaling approaches like the fragmentation method or other methods which introduces a range dependent interaction screening. Three different ways to obtain IIS for the CC method is shown and the algorithm for two of these are shown and discussed. The first algorithm is very similar to the regular CC method where intermediates are collected and an IIS is used for every tensor contraction. In the second method all contractions in the nested commutators are performed in a single step. Here an IIS is used before every multiplication with the amplitudes for a cluster operator which will effectively remove the vast majority of all multiplications with the amplitudes.

1 Introduction

The coupled-cluster method (CC) originally introduced in nuclear physics by Coester and Kümmel\(^1,2\) and some years later picked up by Čížek, Paldus and Shavitt\(^3,4\) started in the late 70s to early 80s to replace the configuration-interaction method (CI)\(^5–7\) as the workhorse in accurate quantum chemistry calculations. The replacement was quite obvious since the non-linear wave function ansatz of the CC method gives a significantly more compact representation of the wave function in comparison to linear ansatz in CI. The success of the CC method in accurately capturing the correlation energy is largely connected to the ability to include important disconnected correlation effects already at the CCSD level. The CC ansatz is therefore still the most efficient wave function parameterization known for capturing the dynamic electron correlation effects. Here the CCSD(T) method\(^8\) has become known as the "golden standard" for closed shell systems near the equilibrium geometry in quantum chemistry due to the methods ability to accurately capture the triple excitations perturbatively and quadruples via disconnected correlation effects.

Due to the steep scaling of wave function methods the size of the systems for which the standard
CC method is applicable is limited. A great deal of work has therefore been placed on a large scale parallelization of the CCSD and CCSD(T) equations which either seeks to reduce the memory requirement or communication between nodes while still trying to have an efficient code. While the massive parallelization of the CC equations enables the ability of calculating slightly larger systems in a reasonably time the fundamental problem of the steep scaling cannot be overcome simply by the use of more computational power alone and a different strategy, which reduces the scaling, for very large systems is therefore needed.

During the last decade the interest in CC methods with reduced or linear scaling has therefore grown significantly. These methods all in some way relies on long range screening in local orbitals as proposed by Pulay. The integral- and intermediate-screened coupled-cluster method (IISCC), as proposed here, will also rely on local orbitals for an improved reduced scaling but unlike all other methods will not introduce domains in order to achieve a range dependent screening. The IISCC method will instead follow the integral screening (IS) of the recently proposed integral-screened configuration-interaction method (ISCI) which introduces a simple and rigorous IS by looping over the integral indices first in the tensor contractions. The IS in the ISCI therefore also minimizes the number of times an integral will have to be calculated which is essential in very large basis sets where the integrals no longer can be stored in memory but have to be calculated on the fly. The energy in the IISCC, like the ISCI, can be more accurately approximated than other low scaling methods since the screening is directly built into the method and therefore does not need to introduce domains for a distance dependent interaction screening in order to obtain a low scaling. Unlike all other low scaling methods where the scaling locally in their domains are the same as in the regular CC method the IISCC will still show reduced scaling within these domains and is therefore not as sensitive to the number of basis functions included. Strong-field time-dependent calculations with the ISCI has shown that the ISCI method is capable of using very large basis sets even without any form of parallelization. It is therefore expected that the IISCC method will show similar qualities as the ISCI method since the IIS or IS, which is essential in the scaling reduction, is the same for both methods.
The main reason why CC and Møller-Plesset (MP) perturbation theory\textsuperscript{30} is central in the development of low scaling methods and not CI is due to the CC and MP methods being size-extensive.\textsuperscript{31,32} The central problem in transferring the IS from the ISCI to the IISCC is the non-linear nature of the CC equations which normally results in the construction of intermediates in the CC method. While the non-linear ansatz in CC does not resemble the linear ansatz in CI the difference between these from an implementation viewpoint are not significantly different since both methods can be reduced to a series of tensor contractions where the main difference is the contractions and collection of intermediates that occur in the CC method.

In the following the ISCI and the idea of IS behind this is briefly repeated since this can immediately be used in the IISCC to show that all contractions that are within the projection manifold can be handled in the exactly same manner as in the ISCI method. This will help to substantiate that the results shown for the ISCI\textsuperscript{28} is almost directly transferable to the IISCC. Thereafter will the CC equations briefly be presented along with the idea behind the IISCC method where also the great similarities between the ISCI and IISCC methods will be illustrated. In order to obtain not only IS but integral and intermediate screening (IIS), where a screening is performed every time an integral or intermediate is multiplied with an amplitude, a discussion about the best way of collecting intermediates for large systems in large basis sets is undertaken. This will be followed by a derivation of the IISCC working equations where three very different approaches to obtain a simple and rigorous IIS is discussed. Here it will be shown that a complete IIS is possible for nested commutators in several very different ways and that the scaling reduction seen in the ISCI also will be possible for the IISCC. The rewriting of the Hamiltonian, like in the ISCI, will also make the CC equations separable up to an overall sign and is what enables the IIS.

Despite the IISCC method not yet being implemented a pseudo code of how an implementation can be performed in two different ways is shown in order to show how IIS and reduced scaling of the IISCC method is possible without any need to introduce domains for a range dependent screening. The first way will be very similar to the usual way the CC equations are solved by using intermediates but where every tensor contraction is performed in a way similar to the ISCI. This
will give an IIS in all the usual terms in the CC equations and therefore reduce the scaling of these individually. If the rate limiting step is the loop over the integrals all excitations below doubles will have a cost similar to the ISCISD. If, however, triples or higher are included the construction of the intermediates will increase the cost of the limiting step. The second way will perform all contractions in the nested commutators in a single step and therefore not explicitly construct any intermediates. While this formally will give the wrong scaling the IIS can be used to reduce this since a higher screening threshold can be used for nested commutators. The second advantage of performing all contractions in a single step and not collecting intermediates is that the rate limiting step will not be affected by including higher excitations.

While the IISCC here is derived as a separate method this can be combined with both the fragmentation method and the local coupled-cluster methods to give local screening and enable the use of much larger orbital spaces in the correlation of the different domains. Exactly like in the ISCI will it also be possible in the IISCC to introduce a range dependent interaction screening in a simple way to reduce the loop over the integrals.

2 Theory

In order to derive the IISCC equations in a way where the similarities to the ISCI equations is evident the CI and ISCI\textsuperscript{28} methods will briefly be recapitulated. The CC method will follow where the usual approach to collecting intermediates will be revisited. Here it will be shown that a combined IIS in the nested commutators in the CC method can be realized in several different ways by using the separation techniques from the ISCI. For very large systems the size of the intermediates will become significant and therefore impossible to store in memory or on disc.\textsuperscript{33} Although the large size of the intermediates can be overcome by a stepwise construction of the intermediates alternatives where no intermediates are explicitly constructed but which still have a simple and rigorous IIS will be shown.

Throughout the indices p,q,r,s… are general indices running over both the occupied orbitals
(O) and the virtual orbitals (V) while a,b,c,d... will be used for the virtual orbitals and i,j,k,l... for the occupied orbitals. Both the ISCI and IISCC formulation are based on a single reference determinant. Excitation and de-excitation terms with respect to the reference determinant can be defined which means that any creation operator $\hat{a}^\dagger$ with indices a,b,c... is an excitation operator while the indices i,j,k... will give a de-excitation operator and the opposite is true for the annihilation operator $\hat{a}$. The de-excitation terms are found in both the Hamiltonian and the intermediates, if the latter are constructed, and that the de-excitation indices will have to be matched by excitation terms from the CC or CI excitation operator to give non-zero contributions.

### 2.1 Configuration Interaction (CI)

In CI the wavefunction $|C\rangle$ is constructed as a linear combination of Slater determinants which corresponds to a parameterization where an excitation operator $\hat{X}$ works on a reference determinant $|0\rangle$,

$$|C\rangle = \hat{C}|0\rangle = \sum_i c_i \hat{X}_i |0\rangle,$$

which generates all possible determinants. The expansion coefficients $c_i$ are found by a variational optimization of the expectation value of the electronic energy which is equivalent to an eigenvalue problem for the coefficients and energy

$$H|C\rangle = E|C\rangle.$$  \hfill (2)

The FCI in Eq. 1 is exact in a complete basis and the best approximation in an incomplete basis but only possible for systems with few electrons in modest basis sets due to an exponential scaling. A hierarchy

$$\hat{C} = \sum_{i=0}^N \hat{C}_i = c_0 + \sum_{a,i} V_O c_i^a \hat{a}_i^\dagger \hat{a}_i + \sum_{a>b, i>j} V_O c_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j + \ldots,$$

where the excitation operator is divided into excitation operators with particle rank (see Eq. 52 in Appendix A) spanning from zero to $N$ is therefore introduce, where $N$ is the number of particles.
The eigenvalue problem in Eq. 2 is solved iteratively by repeatedly applying the Hamiltonian to an approximate eigenvector \( \mathbf{v} \) to give the linearly transformed approximate eigenvector \( \sigma \)

\[
\mathbf{Hv} = \sigma,
\]

which is known as the \( \sigma \)-vector. An efficient solution to the \( \sigma \)-vector step is central in CI. Apart from the \( \sigma \)-vector step an optimization step where typically a Davidson\(^{34}\) or Lanczos\(^{35}\) algorithm is used to find the step for the new approximate eigenvector \( \mathbf{v} \).

### 2.2 The ISCI and integral screening

The CI Hamiltonian is typically very sparse where the first part comes from trivially zero matrix elements, the Slater-Condon rules, and the second part from many very small elements which can be considered numerically zero. The position of the trivially zero matrix elements are easy to find but the numerical zeros in the CI Hamiltonian are significantly harder to predict. In the usual low or linearly scaling methods the numerical zeros are found by transforming to local orbitals and introducing a distance dependent screening. The distant dependent screening can also be used in the IISCC but will not at the present stage. Another type of sparsity also exist, that is present also for large matrix elements, where the matrix element is a sum of one or many integrals since these matrix elements will contain many numerically zero integrals. Since these small integrals takes time to calculate but makes no contribution to any properties it is desirable to screen away all the small integrals, even those inside large matrix elements. The central idea in the ISCI is to minimize the number of times an integral have to be calculated and completely screen away all small integrals in a simple way.

Any matrix element in the Hamiltonian \( H_{pq} \) can be written as a sum of integrals \( I_r \)

\[
H_{pq} = \sum_r I_r.
\]
Matrix multiplication is distributive so the $\sigma$-vector step in Eq. 4 can be written as

$$\sum_{t} I_{all} H_t v = \sigma,$$

$$\begin{cases} 0, \\ I_t, \end{cases} (H_t)_{pq} =$$

where the sum is over all integrals $I_{all}$. Each matrix element in $H_t$ can now only take the values 0 or $I_t$ and $H_t$ is therefore extremely sparse. By introducing a predefined threshold parameter $\varepsilon$ for the IS the summation in Eq. 6 can be split into two sums

$$\sum_{t} I_{all} H_t = \sum_{l} I_{large} H_l + \sum_{s} I_{small} H_s,$$

$$|I_s| < \varepsilon \leq |I_l|.$$ (7)

From Eq. 7 introducing an IS which affects all matrix elements containing a given integral $(H_t)$ is very simple since this only requires knowing the value of $I_t$. The integral $I_t$ in principle only needs to be calculated once in order to screen away $I_t$ in all of $H$. In this way the number of times an integral have to be calculated is minimized and a complete IS, even of large matrix elements, is easily accomplished. This type of IS is ideal for very large basis sets where the integrals cannot be stored in memory but have to be calculated on the fly.

If $I_{small} \gg I_{large}$ and if there is a fast way of finding and multiplying the non-zero elements in $H_t$ with the elements in $v$ then solving the CI problem using Eq. 7 can give a significant reduction in the scaling.\textsuperscript{28} Using local orbitals $I_{small}$ will grow as $N^4$, in a Gaussian basis set, with system size while $I_{large}$ only will grow as $N$ if the system is sufficiently spatially extended since all integrals between orbitals sufficiently far apart will be below $\varepsilon$. The reduction in scaling will depend on the desired accuracy hence $\varepsilon$. The IS in the ISCI is unlike all the IS in all other methods which rely on a distance dependent screening for spatially extended systems in local orbitals.\textsuperscript{15–27,36}

Due to the focus on having a simple and rigorous IS the ISCI does not follow the usual strategy for CI algorithms where matrix elements are constructed from a sum of integrals. The ISCI is instead completely driven by the integrals, which will have to be in the outer loop in the $\sigma$-vector step, and no matrix elements will ever be constructed.
2.2.1 Hamiltonian

A time-independent non-relativistic one- and two-body Hamiltonian, where the one particle functions can be related by the spin-flip operator, is here used but the ISCI formalism is completely general so any other Hamiltonian could easily be inserted instead. In second quantization the Hamiltonian is a sum of one- and two-body operators,

\[
\hat{H} = \sum_{pq} h_{pq} (\hat{a}_{p\alpha}^\dagger \hat{a}_{q\alpha} + \hat{a}_{p\beta}^\dagger \hat{a}_{q\beta}) \\
+ \sum_{p>r, q>s} (g_{prqs} - g_{pqrs}) (\hat{a}_{p\alpha}^\dagger \hat{a}_{r\alpha}^\dagger \hat{a}_{q\alpha} \hat{a}_{s\alpha} + \hat{a}_{p\beta}^\dagger \hat{a}_{r\beta}^\dagger \hat{a}_{q\beta} \hat{a}_{s\beta}) \\
- \sum_{pqrs} g_{pqrs} \hat{a}_{p\alpha}^\dagger \hat{a}_{r\beta}^\dagger \hat{a}_{q\alpha} \hat{a}_{s\beta}.
\]  

(8)

where \( h_{pq} = \langle \phi_p | h | \phi_q \rangle \) and \( g_{pqrs} = \langle \phi_p \phi_r | g | \phi_s \phi_q \rangle \) are the integrals associated with the one- and two-body operators. The Hamiltonian in Eq. 8, is normal- and spin-ordered and index-restricted unlike the UGA Hamiltonian.\(^{37,38}\) The order chosen for the spin order and index restriction are arbitrary and any other order would not change the ISCI method since any sign change in the integrals in the Hamiltonian would be compensated by an overall sign change in Eq. 11.

By choosing a canonical orbital ordering, i.e., occupied before virtual orbitals, it can be shown\(^{28}\) that any term in the Hamiltonian in Eq. 8 can be written as

\[
\hat{H}_{\text{any}} = \hat{C}_{\alpha}^\text{ex} \hat{a}_{\alpha}^\dagger \hat{a}_{\alpha} + \hat{A}_{\beta}^\text{dx} \hat{a}_{\beta}^\dagger \hat{a}_{\beta}.
\]  

(9)

In Eq. 9 the operator is written in terms of strings of second quantized operators with indices ordered according to the order in the Hamiltonian in Eq. 8. Here \( \hat{C} \) and \( \hat{A} \) are strings of creation and annihilation operators, \( \alpha \) and \( \beta \) the spin and the \( \text{ex} \) and \( \text{dx} \) superscripts denotes if an operator is an excitation or a de-excitation operator, respectively. \( \hat{C}_{\alpha}^\text{ex} \) is therefore the excitation part of the creation operators with \( \alpha \) spin. The integrals have been omitted since these will be defined from the strings in a given operator.
2.2.2 The $\sigma$-vector step

Any part in the $\sigma$-vector step in Eq. 4 can be written like

$$\hat{\sigma}_{c\alpha} \hat{\sigma}_{c\beta} \hat{\sigma}_{a\alpha} \hat{\sigma}_{a\beta} = \hat{C}_{\alpha}^{ex} \hat{C}_{\beta}^{ex} \hat{A}_{\alpha}^{ex} \hat{A}_{\beta}^{ex} \hat{v}_{c\alpha} \hat{v}_{c\beta} \hat{v}_{a\alpha} \hat{v}_{a\beta}. \quad (10)$$

Rearranging Eq. 10 using the elementary anti-commutation rules for second quantized operators

$$\hat{\sigma}_{c\alpha} \hat{\sigma}_{c\beta} \hat{\sigma}_{a\alpha} \hat{\sigma}_{a\beta} = \hat{C}_{\alpha}^{ex} \hat{A}_{\alpha}^{ex} \hat{v}_{c\alpha} \hat{C}_{\beta}^{ex} \hat{A}_{\beta}^{ex} \hat{v}_{c\beta} \hat{C}_{\alpha}^{ex} \hat{A}_{\beta}^{ex} \hat{v}_{a\alpha} \hat{v}_{a\beta} (-1)^M, \quad (11)$$

where only transpositions which can give a sign change have been performed. $M$ is then the number of transpositions needed to rearrange the operators from Eq. 10 to Eq. 11. It is seen that Eq. 11 can be split into four parts:

$$\hat{\sigma}_{c\alpha} = \hat{C}_{\alpha}^{ex} \hat{A}_{\alpha}^{dx} \hat{v}_{c\alpha}, \quad (12)$$

$$\hat{\sigma}_{c\beta} = \hat{C}_{\beta}^{ex} \hat{A}_{\beta}^{dx} \hat{v}_{c\beta}, \quad (13)$$

$$\hat{\sigma}_{a\alpha} = \hat{C}_{\alpha}^{dx} \hat{A}_{\alpha}^{ex} \hat{v}_{a\alpha}, \quad (14)$$

$$\hat{\sigma}_{a\beta} = \hat{C}_{\beta}^{dx} \hat{A}_{\beta}^{ex} \hat{v}_{a\beta}, \quad (15)$$

which each have to be fulfilled for a non-zero contribution in the $\sigma$-vector calculation.

Equations 12-15 have been solved by applying a Hamiltonian term to $\hat{v}$, which in the operator form is identical to the excitation operator $\hat{x}$. Using elementary operations for second quantized operators, the different parts of the $\sigma$-vector can be found. For every non-zero operation the indices of the Hamiltonian, $\hat{v}$ and $\hat{\sigma}$ is tabulated and used in the $\sigma$-vector step since each of these indices will give a part of the integral multiplied with the coefficients in $\hat{v}$ to $\hat{\sigma}$.

By combining the solutions from Eqs. 12-15 the desired loop structure from Sec. 2.2 in the $\sigma$-vector step can be achieved. By looping over the indices for the integrals a simple and rigorous IS can be accomplished by a simple if-statement which can be seen from the pseudo code where
all integral below $\varepsilon$ are screened away in line 3.

1: loop { Integral indices }
2: Fetch or calculate integral $I$
3: if $|I| > \varepsilon$ then
4: loop { Matrix elements }
5: Multiply integral with element in $\hat{v}$ to element in $\hat{\sigma}$
6: end loop[ Matrix elements ]
7: end if
8: end loop[ Integral indices ]

The integral loop constitutes the minimum in the number of parameters that have to be looped over in any calculation if no assumption about a long range decay of the integrals is invoked. The IS will give a gradual scaling reduction, until linear, in the inner loop where the integral is multiplied with a CI coefficient for spatially extended systems expressed in local orbitals. The aim is to rewrite the CC equations in a similar way where the outer loop consist over the integral indices even for nested commutators since this also will give a simple and rigorous IS in CC.

2.3 The Coupled-Cluster Approach

We will now turn to the single-reference CC theory in order to show the different wave function ansatz in comparison to CI and to demonstrate the reason why intermediates are collected in the CC method. In CC theory the wave function is parameterized by the exponential of an excitation operator working on an $N$-particle reference function $|0\rangle$.

$$|CC\rangle = \exp(\hat{T})|0\rangle.$$  \hfill (16)

In the similarity-transformed formulation, the CC energy and amplitude equations become

$$\langle 0|\exp(-\hat{T})\hat{H}\exp(\hat{T})|0\rangle = E$$ \hfill (17)
and

\[ \langle \mu | \exp(-\hat{T})\hat{H} \exp(\hat{T}) | 0 \rangle = 0, \]  

(18)

respectively. It is seen that the Baker-Cambell-Hausdorff expansion

\[ \Omega_{\hat{T}} = \langle 0 | \hat{\tau}^\dagger_{\mu} (\hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!} [[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!} [[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}], \hat{T}]]) | 0 \rangle \]  

(19)

terminates after the fourth order for the similarity-transformed Hamiltonian since the Hamiltonian is a two-particle operator and \( \hat{T} \) a pure excitation operator.

Including all excitations into \( \hat{T} \) leads to the full coupled-cluster model (FCC) which solves the Schrödinger or Dirac equation in the defined one-electron basis. However, the operator \( \hat{T} \) is typically restricted like seen in CI in Eq. 3

\[ \hat{T} = \sum_{i=1}^{m} \hat{T}_i = \sum_{a,i} t_{i}^{a} a_{a}^{\dagger} a_{i} + \sum_{a>b,i>j} t_{ij}^{ab} a_{a}^{\dagger} a_{b}^{\dagger} a_{i} a_{j} + \ldots \]  

(20)

where a truncation at \( \hat{T}_2 \) or \( \hat{T}_3 \) will give the familiar CCSD or CCSDT models, respectively.

### 2.3.1 Contractions and collection of intermediates

In CC the focus is not only on capturing the direct interaction, like in CI, but also the indirect interaction where the latter appears as disconnected clusters or nested commutators in the BCH expansion in Eq. 19. Here in particular does the doubly nested commutator \( \frac{1}{2!}[[\hat{H}, \hat{T}_2], \hat{T}_2] \) play the essential role in the numerical success of CC. In the calculation of the nested commutators the usual procedure is to construct intermediates. The two main reasons for the construction of intermediates is to obtain the correct scaling by not having to perform multiple contractions between multiple tensors in a single step and to reduce the prefactor in the contractions by noting that there will be several tensors with the same rank that has to be contracted with the cluster operator and these tensors can be added prior to the contraction since the tensor product is distributive. This was realized very early on but finding the optimal way of contracting the tensors even for CCSD was
not easy.\textsuperscript{39,40} The optimal way is, however, very dependent on the size of the basis set and should in principle be optimized separately for every calculation with for example a genetic algorithm.\textsuperscript{41} The discussion about the scaling and collection of intermediates is not new and the vast majority of CC codes will collect the intermediates in some way for the reasons given here. The discussion is, however, relevant to repeat once the IS in the IISCC is introduced.

The contraction processes between two operators will be written as

\begin{equation}
\hat{O}^{P,H} \otimes \hat{T}(XY) \Rightarrow \hat{O}^{P',H'} \tag{21}
\end{equation}

where \( P \) is the number of particle indices still to be contracted in operator \( \hat{O} \), before this can be added to the projection manifold \( \Omega_{\hat{T}} \), \( X \) is the number of particle indices contracted and \( P' = P - X \) is the remaining particle indices to be contracted and likewise for the holes \( H' = H - Y \). In Eq. 21 it is assumed that the contraction is always done with \( \hat{T} \) and all contractions between the \( N\Delta M \) classes, as defined in Appendix A, are performed. Eq. 21 should therefore read as the tensor contraction between all operators in \( \hat{O}^{P,H} \) and \( \hat{T}(XY) \) added to \( \hat{O}^{P',H'} \) where \( X \) and \( Y \) defines the indices contracted. In this way it is easy to address which contraction is taking place and to have different contractions pointing to the same intermediate with given \( P,H,N,\Delta M,\mu_{\alpha\beta} \) indices or to see how contractions from different nested commutators can be combined to a single intermediate.

From scaling considerations, collection and size of intermediates a priority for the order the contractions can be made or optimized on an individual basis with a genetic algorithm.\textsuperscript{41} Here the following contraction order is chosen

\begin{equation}
P,H : 2,2; 2,1; 2,2; 0,1; 1,1; 0,2; 0,2,0,1. \tag{22}
\end{equation}

where the contraction performed first will be the leftmost possible contraction. This kind of contraction order can be introduced since the order in which the contractions in the nested commutators are performed only matter from a scaling perspective and hence all permutations of contraction orders can therefore be collected in one order. Hence for the doubly nested commutator for \( \hat{H}^{1,1} \) the
particle index is contracted before the hole index since 1, 0 is before 0, 1 in the contraction order in Eq. 22. We have chosen to contract as many indices as possible and contract particles before holes except for the 1, 0 and 0, 2 contractions. For the 1, 0 and 0, 2 contraction we have chosen the large basis set limit where $V > O^2$. The choice for the large basis set limit was not only chosen, since the long term aim is to use very large basis sets, but was also motivated by the way the intermediates was collected since the largest of the intermediates $\hat{M}^{2,0}$ will not have to be constructed. An example of this comes from the important double commutator $\frac{1}{2!}[[\hat{H}, \hat{T}_2], \hat{T}_2]$ where only

$$\hat{H}^{2,2} \otimes \hat{T}(20) \Rightarrow \hat{M}^{0,2} \otimes \hat{T}(02) \Rightarrow \Omega$$

(23)

and not

$$\hat{H}^{2,2} \otimes \hat{T}(02) \Rightarrow \hat{M}^{2,0} \otimes \hat{T}(20) \Rightarrow \Omega$$

(24)

will be calculated since the result of the contractions are the same and Eq. 23 will give a more favorable scaling of the contractions ($V^2O^4$) in comparison to Eq. 24 ($V^4O^2$) and the intermediate $\hat{M}^{0,2}$ is significantly smaller than $\hat{M}^{2,0}$ even for reasonably sized basis sets.

For the nested commutator in Eq. 23 the scaling of the contractions are ($V^2O^4$) if the intermediate $\hat{M}^{0,2}$ is constructed. If, however, the problem becomes so large that the intermediate no longer can be stored this will either have to be constructed piecewise or the contractions will have to be performed in a single step as

$$\hat{H}^{2,2} \otimes \hat{T}(20) \otimes \hat{T}(02) \Rightarrow \Omega.$$

(25)

Performing the contractions in a single step as shown in Eq. 25 will give a scaling of $O^4V^4$ and therefore seem less favorable. When the contractions are performed in a single step the contraction order will, however, not matter so the opposite order

$$\hat{H}^{2,2} \otimes \hat{T}(02) \otimes \hat{T}(20) \Rightarrow \Omega.$$

(26)
will give exactly the same scaling as in Eq. 25.

The second reason for the collection of intermediates is to reduce the prefactor of the contractions by not having repeated contractions of same rank tensors. Continuing the example of contractions with $\hat{H}^{2,2}$ from Eq. 23 it is seen that $\hat{H}^{0,2}$ can be added to the intermediate so the second contraction in Eq. 23 and the direct $\hat{H}^{0,2}$ contraction

$$\hat{H}^{0,2} \otimes \hat{T}(02) \Rightarrow \Omega_f$$

(27)

can be combined to

$$\hat{H}^{2,2} \otimes \hat{T}(02) \Rightarrow (\hat{M}^{0,2} \oplus \hat{H}^{0,2}) \otimes \hat{T}(02) \Rightarrow \Omega_f.$$

(28)

Eq. 28 simply combines the two contractions into one and thereby halving the prefactor since the same type of contractions are not repeated. With the contraction order in Eq. 22 a contraction from $\hat{H}^{1,2}$ would also be added to the $\hat{M}^{0,2}$ intermediate

$$\hat{H}^{1,2} \otimes \hat{T}(10) \Rightarrow \hat{M}^{0,2}.$$  

(29)

In this way will a given tensor contraction only be performed once.

### 2.4 The IISCC

The aim in the formulation of the IISCC is to obtain a similar IS to that of the ISCI in Sec. 2.2. Once the IS has been introduced the problem of collecting intermediates will be revisited where, depending on the correlation level, it will be shown that it may be advantageous to divert from the two reasons for the collection of intermediates discussed in Sec. 2.3.1 since an IIS with the same accuracy but higher screening threshold for the nested commutators can be obtained if intermediates are not explicitly collected. After discussing the the different strategies for screening and contractions the de-excitation terms will be separated in the Hamiltonian and a set of separable CC equations similar to those for CI in Eqs. 12-15 presented.
By rewriting the nested commutator expression in Eq. 19 in terms of tensor contractions

$$\sum_{n=0}^{4} \frac{1}{n!} \hat{H} \otimes \hat{T}^{\otimes n} \Rightarrow \Omega_f$$

(30)

where the similarity to CI, as seen in Eq. 4, for $n$ up to one is seen. The IS in CC will therefore be introduced in the same way as in the ISCI in Eqs. 5-7 for the Hamiltonian. By introducing the IS in the tensor contractions of Eq. 30

$$\sum_{I=1}^{I_{ll}} \sum_{n=0}^{4} \frac{1}{n!} \hat{H}_I \otimes \hat{T}^{\otimes n} \Rightarrow \Omega_f$$

(31)

an expression, where there is a loop over the integral, for which the integrals can be screened is obtained exactly like in Eq. 7. The problem with the nested commutators or multiple tensor contractions is that the single integral from the Hamiltonian can be used in many contractions from the initial contraction with the cluster operator to an intermediate which means that the intermediate can have many different non-zero contributions and that the number of these non-zero contributions will grow with every contraction.

### 2.4.1 Contractions and collection of intermediates in the IISCC

The problem with the growth in the number of terms with every contraction for integrals larger than $\epsilon$ in principle suggests at least three different ways to perform the contraction where also an intermediate screening can be obtained. The first way would be similar to that normally used in CC theory where the intermediates are explicitly constructed or at least piecewise constructed and this would lead not only to an IS but also an IIS. In the second a partial intermediates would be constructed from the elements of the previous contraction where in each step the intermediate is screened in the contractions. In the third way all contractions are performed in a single step as shown in Eq. 25 and both integrals and intermediates are screened. Pseudo algorithms for the separable CC equation and with IIS will be shown in Sec. 3.
Collecting all intermediates: The main problem when the intermediates are explicitly constructed or at least piecewise constructed is the fact that these will have to be stored in some way. The equations will, however, be very similar to the usual CC methods. The intermediates can then be constructed as shown in Eqs. 28-29 where in the contraction of the intermediate $\hat{M}_0^0$ with the cluster operator also can be screened in the exact same manner as $\hat{H}_0^0$ can. The main problems with adding the intermediates in the traditional way, even if this is piecewise, is that the intermediates will have to be stored and several contractions will point to the same intermediate and the structure of the equations will therefore be more complicated. While at the doubles level none of the intermediates will be larger than the integral block and the looping over the intermediates will therefore not increase the outer loop in the contractions. However, once triples or higher is included not only will the size of the intermediates increase but the outer loop in the contractions will also increase in scaling and since this should be the limiting step in the IISCC this will be a problem.

Collecting intermediates from single integral: In the second way there will be an IS in the outer loop where once an integral is above the IS threshold $\varepsilon$ it will be multiplied with the CC amplitudes to an intermediate

$$\hat{H}_t^{2,2} \otimes \hat{T}(20) \Rightarrow \hat{M}_t^0$$

and screened. In the double commutator the storage of the intermediate will not be a problem but while formally only the prefactor will increase, since the intermediates is not collected from different contractions and integrals, the number of multiplication will be close to when all contractions
are performed in a single step as shown in Eq. 25 and below. If the number of small integrals and amplitudes is large in comparison to the large ones then the prefactor increase will not matter since the IIS will reduce this significantly. Furthermore for higher nested commutators a larger $\varepsilon$ can be used in the first contractions without compromising the accuracy since these will be multiplied with multiple amplitudes. Storage problems can, however, still occur for higher nested commutators. The order of contractions will here affect both the size of the intermediates and the scaling in the usual manner as described in Sec. 2.3.1.

**All contractions in a single step:** In the third way all contractions are performed simultaneously

$$\hat{H}_{t}^{2,2} \otimes \hat{T}(20) \otimes \hat{T}(02) \Rightarrow \Omega_{T}. \quad (34)$$

The main difference of this approach in comparison to the second approach is the fact that there is no need for storing the intermediates and the order of contraction does not matter with respect to the scaling. The simultaneous performance of contractions is usually not carried out since this complicates the algorithm and gives an incorrect scaling since terms are not collected after each contraction as shown in Eq. 25. The advantages are that the contraction order in principle does not matter, the efficiency of the loop structure can be optimized if some knowledge of the size and dimension of the different parts of $\hat{T}$ is used, a higher screening threshold for nested commutators can be used without any loss of accuracy and an IIS will ensure that only very few contributions from the nested commutators will be calculated.

### 2.4.2 The IISCC Hamiltonian and intermediates

Unlike in the CI not all de-excitation indices are contracted in a single step in CC. For the IISCC we will therefore assume that the Hamiltonian will at most contain two particle operators which means that the down rank will at most be two. In higher order CC the particle rank of the intermediates can be larger than two but the down rank will, however, always be lower than two since any contraction between the Hamiltonian and the cluster operator will reduce the down rank. A general mixed
operator $\hat{O}$ which covers both the Hamiltonian and the intermediates can be written as

$$\hat{O}_{\text{any}} = \hat{C}_\alpha^{\text{ex}} \hat{C}_\alpha^{d\alpha 1} \hat{C}_\beta^{d\alpha 2} \hat{C}_\beta^{d\alpha 1} \hat{C}_\alpha^{\text{ex}} \hat{A}_\alpha \hat{A}_\beta \hat{A}_\alpha \hat{A}_\beta$$  \hspace{1cm} (35)$$

where any integral or intermediate will be defined from the operator strings. In the general operator expression in Eq. 35 the particle rank can be any order but the down rank can maximally be two since the de-excitation terms are now explicitly written as indicated by the 1 and 2 in the $d \alpha$ superscript. $\hat{O}_{\text{any}}$ can therefore be used for any two-particle Hamiltonian and intermediate. For the Hamiltonian part the index restricted and normal- and spin-ordered Hamiltonian, exactly like in the ISCI in Eq. 8, is used and the intermediates are arranged likewise. Any term in the mixed operator in Eq. 35 will therefore consist of a sum of the integrals from the Hamiltonian and the coefficient from the intermediate.

### 2.4.3 Rigorous integral and intermediate screening of nested commutators

By combining the general tensor contractions from the nested commutators in Eq. 30 with the general operator from Eq. 35 a general contraction scheme similar to that in CI in Eq. 10 can be written for any contraction in the nested commutators

$$\hat{C}_\alpha^{d\alpha 1} \hat{C}_\alpha^{d\alpha 2} \hat{C}_\beta^{d\alpha 1} \hat{C}_\beta^{d\alpha 2} \hat{C}_\alpha^{\text{ex}} \hat{A}_\alpha \hat{A}_\beta \hat{A}_\alpha \hat{A}_\beta (\hat{t}_c \hat{t}_a)^n = \hat{\Omega}_c \hat{\Omega}_a \hat{\Omega}_n.$$  \hspace{1cm} (36)$$

Exactly like in CI can Eq. 36 be reordered

$$\hat{C}_\alpha^{\text{ex}} \hat{A}_\alpha \hat{A}_\alpha \hat{t}_c \hat{t}_a \hat{C}_\beta \hat{C}_\beta \hat{A}_\beta \hat{A}_\beta (\hat{t}_c \hat{t}_a)^n = \hat{\Omega}_c \hat{\Omega}_a \hat{\Omega}_n \hat{\Omega}_n.$$  \hspace{1cm} (37)$$

for any nested commutator. Just like in CI in Eq. 37 are the CC equations separable up to an overall sign exactly like in Eqs. 12-15

$$\hat{C}_\alpha^{\text{ex}} \hat{t}_c \hat{t}_a = \hat{\Omega}_c.$$  \hspace{1cm} (38)
For $n$ equal to zero or one the contractions between the Hamiltonian and the cluster operator can be performed in the exact same way as in CI while for two, three and fourfold nested commutators special care have to be taken.

Since the Hamiltonian is a number conserving two-particle operator it is sufficient to show how the contractions can be performed for a doubly nested commutator where two indices of an operator with same spin and type is contracted after each other. For a doubly nested commutator for $\hat{H}_{202}^0$, where the following contraction are identical this can from Eq. 40 be written as

$$\hat{C}_\alpha \hat{C}_\alpha \hat{A}_\alpha \hat{A}_\alpha \hat{t}_{aa} \hat{t}_{aa} = \hat{C}_\alpha \hat{C}_\alpha \hat{A}_\alpha \hat{A}_\alpha \hat{t}_{aa} \hat{t}_{aa} (1) \hat{t}_{aa} = \hat{C}_\alpha \hat{C}_\alpha \hat{A}_\alpha \hat{A}_\alpha \hat{t}_{aa} \hat{t}_{aa} (1) \hat{t}_{aa} (2) (1)^M$$

(42)

since for doubly nested commutators where the two indices are contracted separately, unlike in CI, there can be no internal contractions. The number $x$ in $\hat{t}_{aa}^{(x)}$ only shows the order of appearance in the nested commutators. The contractions with the cluster operator can then be resolved as

$$\hat{A}_\alpha \hat{C}_\alpha \hat{C}_\alpha \hat{C}_\alpha \hat{A}_\alpha \hat{A}_\alpha \hat{t}_{aa} \hat{t}_{aa} = \hat{A}_\alpha \hat{C}_\alpha \hat{C}_\alpha \hat{C}_\alpha \hat{A}_\alpha \hat{A}_\alpha \hat{t}_{aa} \hat{t}_{aa} + \hat{A}_\alpha \hat{C}_\alpha \hat{C}_\alpha \hat{C}_\alpha \hat{A}_\alpha \hat{A}_\alpha \hat{t}_{aa} \hat{t}_{aa}$$

(43)

where the two contractions gives the same result

$$\hat{A}_\alpha \hat{C}_\alpha \hat{C}_\alpha \hat{C}_\alpha \hat{A}_\alpha \hat{A}_\alpha \hat{t}_{aa} \hat{t}_{aa} = 2 \hat{A}_\alpha \hat{C}_\alpha \hat{C}_\alpha \hat{C}_\alpha \hat{A}_\alpha \hat{A}_\alpha \hat{t}_{aa} \hat{t}_{aa}$$

(44)

The doubly nested contraction shown in Eq. 44 will appear for

$$\frac{1}{2!}[[\hat{H}_{202}^0, \hat{T}], \hat{T}] \Rightarrow \Omega_{\tilde{T}}$$

(45)
where it is seen that the prefactor $\frac{1}{n!}$ exactly cancels with the two in Eq. 44. The contractions in Eq. 42 can therefore be performed separately as shown in Eq. 44. The exact same can be seen for a four-fold nested commutator for Eq. 41 where, if the large basis set limit as shown in Eq. 22 is taken, the contraction will be in the outer commutator, here $t^{(3)}_{a\bar{a}}$ and $t^{(4)}_{a\bar{a}}$, which can be rearranged to

$$\hat{C}_{d\bar{a}} \hat{C}_{d\bar{a}} t^{(3)}_{a\bar{a}} = \hat{C}_{d\bar{a}} \hat{C}_{d\bar{a}} t^{(4)}_{a\bar{a}}$$

where again the contractions can be contracted separately as shown in Eq. 44. $\hat{A}^{e\alpha}_{\bar{a}}$ is not present in Eq. 46 since a four-fold nested commutator must have four de-excitation terms and only the Hamiltonian contain four de-excitation terms.

Since the Hamiltonian is index restricted the contractions for unequal following contractions is slightly different than for equal ones. The operator $\hat{H}^{1,2}_{202}$ can be taken as an example for this. For $\hat{H}^{1,2}_{202}$ the first contraction is 1,1 and the second 0,1 if the contraction order in Eq. 22 is taken. If now the contraction in Eq. 40 is performed as in Eq. 44 many contraction would be missed so here the contraction must be performed as shown in Eq. 43. The particle contraction from Eq. 38 will then have to be performed with $t^{(1)}_{a\bar{a}}$ in this example

$$\hat{A}^{d\bar{a}}_{\bar{a}} t^{(1)}_{a\bar{a}} \hat{C}_{d\bar{a}} t^{(2)}_{a\bar{a}}$$

The prefactor of $\frac{1}{n!}$ due to permutational symmetry can be therefore be completely removed by introducing a contraction order and fixing the contractions as shown in Eqs. 44 and 43 since this eliminates all prefactors. This was also used in an earlier implementation of a GASCC code\textsuperscript{33} although in that code for practical reason the fixing of the contraction order in Eq. 44 was not used and therefore these contractions came with a factor of $\frac{1}{n!}$. 

21
3 Algorithm

Despite the three ways to perform the calculation of the nested commutators presented in Sec. 2.4.1 appear different the algorithm for these will all be very reminiscent of the ISCI algorithm since the IS and IIS is obtained in the same way. The similarities in performance between between collecting the intermediates from a single integral and performing all contraction in a single step when an IIS is introduced is very small so only the latter is shown. The difference between the algorithms for collecting intermediates and performing all contractions in a single step will here be shown and analyzed.

3.1 Collecting intermediates

By collecting all intermediates an algorithm very similar to that presented for the GASCC\textsuperscript{33} combined with the ISCI can be constructed.\textsuperscript{28} The contraction pattern between the different PHNΔM-classes can then be set up exactly like in the GASCC\textsuperscript{33} if the very large basis set limit as shown in Eq. 22 is taken. Here it is also possible to construct the intermediates piecewise by using the GAS and in this way these can be made almost arbitrarily small without any increase in the prefactor or scaling. The number of times an integral will have to be fetched or calculated will, however, increase.

As mentioned in Sec. 2.4.3 that for \(n\) equal to zero and one in Eqs. 38-41 the contractions are exactly like for the ISCI with a slight modification. In fact the ISCI solution can be used for all contraction directly pointing to \(\Omega_T\) since in these contractions all indices are contracted. The ISCI solution can, however, not be used directly when only one of two de-excitation operators of the same kind has to be contracted, as shown in Eqs. 43 and 44, or when no contraction of a de-excitation operator is performed. This happens for doubly and higher nested commutators since not all indices in Eqs. 38-41 are contracted in a single step like in the ISCI. The differences between the algorithm for these cases are minor as will be shown below.

For contractions pointing to \(\Omega_T\) the ISCI algorithm, where intermediate strings are constructed,\textsuperscript{28}
only needs very minor modification. Instead of contraction with the Hamiltonian, like in CI, the contraction is performed with an operator of general particle rank but with a maximum down rank of two as described in Eq. 35. In the case where only one of two de-excitation indices is contracted it is seen from Eq. 44 it is sufficient to demand that only the last index \((dx2)\) is contracted if the following contraction is identical while for non-identical Eq. 43 must be used. If no indices is contracted a copy of the string of indices suffices.

```
1: loop { Strings \( \hat{A}_{\alpha}^{dx} \) }
2:   loop { Strings \( \hat{r}_{c\alpha} \) }
3:     if All indices contracted then
4:       Contract \( \hat{A}_{\alpha}^{dx} \) with \( \hat{r}_{c\alpha} \) to intermediate strings \( \hat{I} \) with intermediate phase
5:     else if One of two indices contracted then
6:       if The second contraction is identical then
7:         Contract \( \hat{A}_{\alpha}^{dx2} \) with \( \hat{r}_{c\alpha} \) to intermediate strings \( \hat{I} \) with intermediate phase
8:       else if The second contraction is not identical then
9:         Contract \( \hat{A}_{\alpha}^{dx1} \) or \( \hat{A}_{\alpha}^{dx2} \) with \( \hat{r}_{c\alpha} \) to intermediate strings \( \hat{I} \) with intermediate phase
10:     end if Identi cal and non-identical contractions
11:   else if No indices contracted then
12:     Copy \( \hat{r}_{c\alpha} \) to intermediate strings \( \hat{I} \) with intermediate phase
13:   end if Number of indices contracted
14: end loop[ Strings \( \hat{r}_{c\alpha} \) ]
15: if Any contraction between \( \hat{A}_{\alpha}^{dx} \) and \( \hat{r}_{c\alpha} \) is possible i.e., number of \( \hat{I} \geq 1 \) then
16:   loop { Strings \( \hat{C}_{\alpha}^{ex} \) }
17:     loop { Strings \( \hat{I} \) }
18:       Add \( \hat{C}_{\alpha}^{ex} \) to intermediate string \( \hat{I} \) for final string \( \hat{O}_{c\alpha} \) and phase
19:     if Addition of \( \hat{C}_{\alpha}^{ex} \) and \( \hat{I} \) to \( \hat{O}_{c\alpha} \) is possible then
20:       Calculate a relative offset for \( \hat{O}_{c\alpha} \) string
21:     Store relative offset from strings \( \hat{r}_{c\alpha} \) and \( \hat{O}_{c\alpha} \)
```
22: Store Hamiltonian indices from strings $\hat{A}^{dx}_{\alpha}$ and $\hat{C}^{ex}_{\alpha}$
23: Store total phase for contraction and addition
24: \textbf{end if} Addition of $\hat{C}^{ex}_{\alpha}$ and $\hat{I}$ to $\hat{O}_{c\alpha}$ is possible
25: \textbf{end loop} [ Strings $\hat{I}$ ]
26: \textbf{end loop} [ Strings $\hat{C}^{ex}_{\alpha}$ ]
27: \textbf{end if} Any contraction between $\hat{A}^{dx}_{\alpha}$ and $\hat{i}_{c\alpha}$ is possible
28: \textbf{end loop} [ Strings $\hat{A}^{dx}_{\alpha}$ ]

The loop structure is very similar to the ISCI where first the indices in a given $\hat{A}^{dx}_{\alpha}$ annihilation string are contracted with the $\hat{T}$ creation string $\hat{i}_{c\alpha}$ to a set of intermediate creation strings $\hat{I}$. Here a simple if-statement is inserted to separate if all, one of two or no indices is contracted from the de-excitation operator. Since the Hamiltonian and the intermediate is index restricted there needs to be a separation between identical and non-identical following contractions as discussed in Sec. 2.4.3. Identical following contractions means that the same number of particle and hole indices are contracted after each other as shown in Eq. 45 while non-identical happens for contractions like

$$\hat{H}^{2,1} \otimes \hat{T}(11) \Rightarrow \hat{M}^{1,0} \otimes \hat{T}(10) \Rightarrow \Omega_{\hat{T}}$$ (48)

where the particle index contraction is split in two. After the contraction the creation strings $\hat{C}^{ex}_{\alpha}$ are then added to the intermediate creation strings $\hat{I}$. The relative offsets from the creation strings of $\hat{i}_{c\alpha}$ and $\hat{O}_{c\alpha}$, the operator indices in $\hat{A}^{dx}_{\alpha}$ and $\hat{C}^{ex}_{\alpha}$ along with a total phase for the contraction and addition of the strings are stored. The operator $\hat{O}_{c\alpha}$ can here either be an intermediate $\hat{M}_{c\alpha}$ or the projection manifold $\hat{\Omega}_{c\alpha}$ depending on where the contraction is pointing. Just like for the ISCI is the first loop over the operator indices crucial for a rigorous IIS. The major difference in comparison to the ISCI is that not all indices in $\hat{A}^{dx}_{\alpha}$ always will be contracted. For Eq. 39 the $\alpha$ spins in Eq. 38 are substituted with $\beta$ spins and the same algorithm can then be used. The loop structure for Eq. 40 is:

1: \textbf{loop} [ Strings $\hat{A}^{ex}_{\alpha}$ ]
2: \textbf{loop} \{ Strings \( \hat{t}_{a\alpha} \) \}
3: \hspace{1em} Add \( \hat{A}^e_{\alpha} \) to \( \hat{t}_{a\alpha} \) for intermediate strings \( \hat{I} \) with intermediate phase
4: \textbf{end loop} \{ Strings \( \hat{t}_{a\alpha} \) \}
5: \textbf{if} Addition of \( \hat{A}^e_{\alpha} \) and \( \hat{t}_{a\alpha} \) is possible i.e., number of \( \hat{I} \geq 1 \) \textbf{then}
6: \hspace{1em} \textbf{loop} \{ Strings \( \hat{C}^{dx}_{\alpha} \) \}
7: \hspace{2em} \textbf{loop} \{ Strings \( \hat{I} \) \}
8: \hspace{3em} \textbf{if} All indices contracted \textbf{then}
9: \hspace{4em} Contract \( \hat{C}^{dx}_{\alpha} \) with \( \hat{I} \) to final string \( \hat{O}_{a\alpha} \) and phase
10: \hspace{3em} \textbf{else if} One of two indices contracted \textbf{then}
11: \hspace{4em} \textbf{if} The second contraction is identical \textbf{then}
12: \hspace{5em} Contract \( \hat{C}^{dx2}_{\alpha} \) with \( \hat{I} \) to final string \( \hat{O}_{a\alpha} \) and phase
13: \hspace{4em} \textbf{else if} The second contraction is not identical \textbf{then}
14: \hspace{5em} Contract \( \hat{C}^{dx1}_{\alpha} \) or \( \hat{C}^{dx2}_{\alpha} \) with \( \hat{I} \) to final string \( \hat{O}_{a\alpha} \) and phase
15: \hspace{3em} \textbf{end if} Identical and non-identical contractions
16: \hspace{3em} \textbf{else if} No indices contracted \textbf{then}
17: \hspace{4em} Copy \( \hat{I} \) to final string \( \hat{O}_{a\alpha} \) and phase
18: \hspace{3em} \textbf{end if} Number of indices contracted
19: \hspace{3em} \textbf{if} Contraction of \( \hat{C}^{dx}_{\alpha} \) and \( \hat{I} \) to \( \hat{O}_{a\alpha} \) is possible i.e., number of \( \hat{O} \geq 1 \) \textbf{then}
20: \hspace{4em} Calculate a relative offset for \( \hat{O}_{a\alpha} \) string
21: \hspace{4em} Store relative offset from strings \( \hat{t}_{a\alpha} \) and \( \hat{O}_{a\alpha} \)
22: \hspace{4em} Store Hamiltonian indices from string \( \hat{A}^e_{\alpha} \) and \( \hat{C}^{dx}_{\alpha} \)
23: \hspace{4em} Store total phase for contraction and addition
24: \hspace{3em} \textbf{end if} Contraction of \( \hat{C}^{dx}_{\alpha} \) and \( \hat{I} \) to \( \hat{O}_{a\alpha} \) is possible
25: \hspace{3em} \textbf{end loop} \{ Strings \( \hat{I} \) \}
26: \hspace{2em} \textbf{end loop} \{ Strings \( \hat{C}^{dx}_{\alpha} \) \}
27: \textbf{end if} Addition of \( \hat{A}^e_{\alpha} \) and \( \hat{t}_{a\alpha} \) to intermediate string is possible
28: \textbf{end loop} \{ Strings \( \hat{A}^e_{\alpha} \) \}
where the only difference to the loop structure for Eq. 38 is the order in which the addition and contraction is performed. For Eq. 41 we again can substitute \( \alpha \) for \( \beta \). The strings in the contraction step are symbolically manipulated so the creation and annihilation operator that should be contracted stand next to each other, a sign for the number of transpositions is calculated and the contracted indices are removed for the resulting \( \hat{O}_{ax} \) string.

With the algorithms above Eqs. 38-41 can be solved for \( n \) equal to zero or one which is all that is necessary when intermediates are constructed. The aim here is to solve the tensor contractions in a way similar to the ISCI where there can be an IIS as shown in the algorithm below:

1: \textbf{loop} \{ Indices for } \hat{O} \textbf{ \} }
2: Fetch or calculate integral \( I \) and add to intermediate \( M \)
3: \textbf{if } |I + M| > \varepsilon \textbf{ then }
4: \hspace{1em} \textbf{loop} \{ Matrix elements \}
5: \hspace{2em} Multiply integral with element in \( \hat{v} \) to element in \( \hat{O}_f \)
6: \hspace{1em} \textbf{end loop}[ Matrix elements ]
7: \hspace{1em} \textbf{end if}
8: \textbf{end loop}[ Integral indices ]

Here the operator \( \hat{O}_f \) is either a new intermediate \( \hat{M} \) or the projection manifold \( \hat{\Omega} \). Once the solution to Eqs. 38-41 is known then a general loop structure where an integral and or intermediate only will be fetched once and then immediately multiplied with the amplitudes to a generic operator \( \hat{O} \) in a way very similar to the ISCI can be constructed.

1: \textbf{loop} \{ \( \hat{C}^{dx}_\beta \hat{A}^{ex}_\beta \) \}
2: Get indices from \( \hat{C}^{dx}_\beta \) and \( \hat{A}^{ex}_\beta \) if needed
3: Get number of \( \hat{t}_{a\beta} \) strings and offset
4: \textbf{loop} \{ \( \hat{C}^{dx}_\alpha \hat{A}^{ex}_\alpha \) \}
5: Get indices from \( \hat{C}^{dx}_\alpha \) and \( \hat{A}^{ex}_\alpha \) if needed
6: Get number of \( \hat{t}_{a\alpha} \) strings and offset


7: \textbf{loop} \{ \hat{C}^\text{ex}_\beta \hat{A}^{dx}_\beta \} \\
8: \quad \text{Get indices from } \hat{C}^\text{ex}_\beta \text{ and } \hat{A}^{dx}_\beta \text{ if needed} \\
9: \quad \text{Get number of } \hat{t}_{c\beta} \text{ strings and offset} \\
10: \textbf{loop} \{ \hat{C}^\text{ex}_\alpha \hat{A}^{dx}_\alpha \} \\
11: \quad \text{Get indices from } \hat{C}^\text{ex}_\alpha \text{ and } \hat{A}^{dx}_\alpha \text{ if needed} \\
12: \quad \text{Get number of } \hat{t}_{c\alpha} \text{ strings and offset} \\
13: \quad \text{Fetch or calculate integral } I \text{ and add intermediate } M \\
14: \quad \textbf{if } |I + M| > \varepsilon \textbf{ then} \\
15: \quad \quad \textbf{loop} \{ \hat{t}_{a\beta} \} \\
16: \quad \quad \quad \text{Get relative offsets and phase for } \hat{O}_{a\beta} \text{ and } \hat{t}_{a\beta} \\
17: \quad \quad \textbf{loop} \{ \hat{t}_{a\alpha} \} \\
18: \quad \quad \quad \text{Get relative offsets and phase for } \hat{O}_{a\alpha} \text{ and } \hat{t}_{a\alpha} \\
19: \quad \quad \quad \quad \textbf{loop} \{ \hat{t}_{c\beta} \} \\
20: \quad \quad \quad \quad \quad \text{Get relative offsets and phase for } \hat{O}_{c\beta} \text{ and } \hat{t}_{c\beta} \\
21: \quad \quad \quad \quad \textbf{loop} \{ \hat{t}_{c\alpha} \} \\
22: \quad \quad \quad \quad \quad \text{Get relative offsets and phase for } \hat{O}_{c\alpha} \text{ and } \hat{t}_{c\alpha} \\
23: \quad \quad \quad \quad \quad \text{Calculate total offset from relative offsets for } \hat{O} \text{ and } \hat{T} \\
24: \quad \quad \quad \quad \quad \text{Calculate total phase from relative phases and the overall phase} \\
25: \quad \quad \quad \quad \quad \text{Multiply integral with element in } \hat{T} \text{ and overall phase to element in } \hat{O} \\
26: \quad \quad \quad \quad \textbf{end loop}[ \hat{t}_{c\alpha} ] \\
27: \quad \quad \textbf{end loop}[ \hat{t}_{c\beta} ] \\
28: \quad \textbf{end loop}[ \hat{t}_{a\alpha} ] \\
29: \quad \textbf{end loop}[ \hat{t}_{a\beta} ] \\
30: \quad \textbf{end if} \\
31: \quad \textbf{end loop}[ \hat{C}^\text{ex}_\alpha \hat{A}^{dx}_\alpha ] \\
32: \textbf{end loop}[ \hat{C}^\text{ex}_\beta \hat{A}^{dx}_\beta ] \\
33: \textbf{end loop}[ \hat{C}^{dx}_\alpha \hat{A}^{ex}_\alpha ]
If the contraction is to the projection manifold $\hat{\Omega}$ then the ISCI algorithm can be used directly just by including the addition of the intermediate. If, however, the contraction is to an intermediate $\hat{M}$ the relative offset for $\hat{O}$ in the inner loops also needs to be modified since the uncontracted de-excitation operator is included in the outer loops.

In the ISCI the general algorithm can be broken into 42 different matrix-vector products. These products would all also be present in the IISCC along with 61 additional products, where an operator is contracted to an intermediate, if the large basis set limit for the contractions in Eq. 22 is taken.

By constructing intermediates and introducing a contraction order the IISCC will scale correctly and the prefactors can be minimized by the collection of intermediates as discussed in Sec. 2.3.1. The reduction in scaling is therefore assumed to be very close to that seen for the ISCI once an IIS threshold is set. The problem of storing the intermediates can be solved by introducing many GAS since this reduces each block that needs to be stored at the expense of a slightly more complicated algorithm. The main problem for this approach occurs once more than doubles is included since this increases the dimension of the outer loops over the integrals and intermediates which are the rate determining step in the IISCC for large systems. For very large systems it is, however, doubtful that all full iterative triples or higher excitations can be included due to the sheer number amplitudes. Introducing a range dependent IIS will, just like in the ISCI, reduce the size of the outer loop but can also help to significantly reduce the number of amplitudes and thereby making higher than double excitations possible.

### 3.2 All contractions in a single step

Taking the completely opposite approach where no intermediates are collected and all contractions are performed in a single step the IIS is still possible for every multiplication in the nested commutators. The algorithm will in many aspects be similar to the algorithm for collecting intermediates in Sec. 3.1. Here the contraction order will in principle not matter but the arrangement of the loop
structure will. While the scaling of the nested commutators is not correct this need not be a problem since the IIS will be performed for the integrals and every time a multiplication is performed in the nested commutators.

Exactly like in the algorithm which collects intermediates presented in Sec. 3.1 Eqs. 38-41 for \( n \) equal to zero or one can be solved using the ISCI algorithm. For the nested commutators the ISCI algorithm needs to be modified. Since the cluster operator is a pure excitation operator it easy to reorder this as shown in Eq. 46. The contraction can therefore be performed first and then added to the rest of the operators. To ensure that the correct part of the Hamiltonian is contracted with the cluster operator a contraction order must be set. For the particle contractions in the algorithms below the large basis set limit in Eq. 22 is taken.

```plaintext
1: loop { Strings \( \hat{A}^{dx}_\alpha \) }
2: Reorder \( \hat{t}^{a}_{c\alpha} \) so contractions are first with an overall phase, listed a,b,c,d
3: if Number of hole contractions is one then
4: loop { Strings \( \hat{t}^{a}_{c\alpha} \) }
5: Contract \( \hat{A}^{dx}_\alpha \) with \( \hat{t}^{a}_{c\alpha} \) to intermediate strings \( \hat{J} \) with intermediate phase
6: end loop[ Strings \( \hat{t}^{a}_{c\alpha} \) ]
7: else if Number of hole contractions is two then
8: if The second contraction is identical then
9: loop { Strings \( \hat{t}^{a}_{c\alpha} \) }
10: Contract \( \hat{A}^{dx2}_\alpha \) with \( \hat{t}^{a}_{c\alpha} \) to intermediate strings \( \hat{I} \) with intermediate phase
11: loop { Strings \( \hat{t}^{b}_{c\alpha} \) }
12: Contract \( \hat{A}^{dx1}_\alpha \) with \( \hat{t}^{b}_{c\alpha} \) and add \( \hat{I} \) to intermediate strings \( \hat{J} \) with intermediate phase
13: end loop[ Strings \( \hat{t}^{b}_{c\alpha} \) ]
14: end loop[ Strings \( \hat{t}^{a}_{c\alpha} \) ]
15: else if The second contraction is not identical then
16: loop { Strings \( \hat{t}^{a}_{c\alpha} \) }
17: Contract \( \hat{A}^{dx1}_\alpha \) or \( \hat{A}^{dx2}_\alpha \) with \( \hat{t}^{a}_{c\alpha} \) to intermediate strings \( \hat{I} \) with intermediate phase
```
In order to perform the contractions first the \( \hat{t}_{c\alpha}^n \) operators are reordered in line 2 to match the contraction order in Eq. 22. As shown in Eq. 46 this only introduces an overall phase. Since the particles are contracted before the holes in Eq. 22 the reorder is only applicable when the
de-excitation indices have different spins. After the contraction of the de-excitation part, where all indices are contracted, the excitation part is added and the remaining cluster operator for which the contraction is in Eqs. 39-41. Even though the algorithm above stores all possible contractions the storage requirement for this can be dramatically reduced by introducing many GAS’s exactly like in the ISCI.

For the hole contractions the reorder in line 2 will be happen more often since these contractions are usually performed last.

1: **loop** { Strings $\hat{A}_{\alpha}^{{ex}}$ }  
2: Reorder $\hat{I}_{a\alpha}'$ so contractions are first with an overall phase, listed a,b,c,d  
3: **if** Single contraction with $\hat{I}_{a\alpha}$ then  
4: **loop** { Strings $\hat{t}_{a\alpha}^{(a)}$ }  
5: Add $\hat{A}_{\alpha}^{{ex}}$ to $\hat{I}_{a\alpha}$ for intermediate strings $\hat{I}$ with intermediate phase  
6: **end loop**{ Strings $\hat{t}_{a\alpha}^{(a)}$ }  
7: **else if** Double contraction with $\hat{I}_{a\alpha}$ then  
8: **loop** { Strings $\hat{t}_{a\alpha}^{(a)}$ }  
9: Add $\hat{A}_{\alpha}^{{ex}}$ to $\hat{t}_{a\alpha}^{(a)}$ for intermediate strings $\hat{I}$ with intermediate phase  
10: **loop** { Strings $\hat{t}_{a\alpha}^{(b)}$ }  
11: Add $\hat{t}_{a\alpha}^{(b)}$ to $\hat{I}$ for intermediate strings $\hat{I}$ with intermediate phase  
12: **end loop**{ Strings $\hat{t}_{a\alpha}^{(b)}$ }  
13: **end loop**{ Strings $\hat{t}_{a\alpha}^{(a)}$ }  
14: **end if**  
15: **if** Addition of $\hat{A}_{\alpha}^{{ex}}$ and $\hat{I}_{a\alpha}$ is possible i.e., number of $\hat{I} \geq 1$ then  
16: **loop** { Strings $\hat{C}_{\alpha}^{dx}$ }  
17: **loop** { Strings $\hat{I}$ }  
18: **if** Single contraction with $\hat{I}_{a\alpha}$ then  
19: Contract $\hat{C}_{\alpha}^{dx}$ with $\hat{I}$ to intermediate strings $\hat{K}$ and phase  
20: **else if** Double contraction with $\hat{I}_{a\alpha}$ then
if The second contraction is identical then
  Contract $\hat{C}_\alpha^{dx}$ with $\hat{t}_{a\alpha}^{(a)}$ part in $\hat{I}$ to intermediate strings $\hat{L}$ and phase
  Contract $\hat{C}_\alpha^{dx}$ with $\hat{t}_{a\alpha}^{(b)}$ part in $\hat{L}$ to intermediate strings $\hat{K}$ and phase
else if The second contraction is not identical then
  Contract $\hat{C}_\alpha^{dx}$ or $\hat{C}_\alpha^{dx}$ with with $\hat{t}_{a\alpha}^{(a)}$ part in $\hat{I}$ to intermediate string $\hat{L}$ and phase
  Contract $\hat{C}_\alpha^{dx}$ or $\hat{C}_\alpha^{dx}$ with with $\hat{t}_{a\alpha}^{(b)}$ part in $\hat{L}$ to intermediate string $\hat{K}$ and phase
end if

end if

Identical and non-identical contractions

Number of indices contracted

loop { M-fold loop over remaining $\hat{t}_{a\alpha}^x$ }
  Add $\hat{t}_{a\alpha}^x$ to intermediate string $\hat{K}$ for final string $\hat{O}_{a\alpha}$ and phase
  if Contraction of $\hat{C}_\alpha^{dx}$ and $\hat{I}$ to $\hat{O}_{a\alpha}$ is possible i.e., number of $\hat{O}_{a\alpha} \geq 1$ then
    Calculate a relative offset for $\hat{O}_{a\alpha}$ string
    Store relative offset from strings $\hat{t}_{a\alpha}^x$ and $\hat{O}_{a\alpha}$
    Store Hamiltonian indices from string $\hat{A}_{\alpha}^{ex}$ and $\hat{C}_\alpha^{dx}$
    Store total phase for contraction and addition
  end if
  end loop[ Remaining commutators ]

end loop[ Strings $\hat{I}$ ]

end loop[ Strings $\hat{C}_\alpha^{dx}$ ]

end if

Addition of $\hat{A}_{\alpha}^{ex}$ and $\hat{t}_{a\alpha}$ to intermediate string is possible

end loop[ Strings $\hat{A}_{\alpha}^{ex}$ ]

For the hole contractions in lines 3 and 7 an intermediate is built from either one or two cluster operators which are later contracted by $\hat{C}_\alpha^{dx}$. For the contraction it is again necessary to distinguish between how following contractions are performed and the each de-excitation term here is contracted with a specific part of the intermediate string. Since the information of the original strings of $\hat{t}_{a\alpha}^{(a)}$ and $\hat{t}_{a\alpha}^{(b)}$ is readily available finding the contraction in a part of the intermediate can be done
just by comparing $\hat{C}_\alpha^{dx}$ with $\hat{t}_a^{(a)}$ and $\hat{t}_a^{(b)}$. After the contraction the remaining cluster operators $\hat{t}_a^{\alpha}$ are looped over in line 29 in order to find the final operator $\hat{O}_{a\alpha}$ whereafter the information from the additions and contractions are stored.

Once the solution to Eqs. 38-41 is tabulated a general loop for up to four fold nested commutators can be constructed:

1: \textbf{loop} \{ $\hat{C}_\beta^{dx} \hat{A}_\beta^{ex}$ \}
2: \quad Get indices from $\hat{C}_\beta^{dx}$ and $\hat{A}_\beta^{ex}$ if needed
3: \quad Get number of $\hat{t}_a^{\beta}$ strings and offset
4: \quad \textbf{loop} \{ $\hat{C}_\alpha^{dx} \hat{A}_\alpha^{ex}$ \}
5: \quad \quad Get indices from $\hat{C}_\alpha^{dx}$ and $\hat{A}_\alpha^{ex}$ if needed
6: \quad \quad Get number of $\hat{t}_a^{\alpha\alpha}$ strings and offset
7: \quad \quad \textbf{loop} \{ $\hat{C}_\alpha^{ex} \hat{A}_\alpha^{dx}$ \}
8: \quad \quad \quad Get indices from $\hat{C}_\alpha^{ex}$ and $\hat{A}_\alpha^{dx}$ if needed
9: \quad \quad \quad Get number of $\hat{t}_c^{\beta\alpha}$ strings and offset
10: \quad \textbf{loop} \{ $\hat{C}_\alpha^{ex} \hat{A}_\alpha^{dx}$ \}
11: \quad \quad Get indices from $\hat{C}_\alpha^{ex}$ and $\hat{A}_\alpha^{dx}$ if needed
12: \quad \quad Get number of $\hat{t}_c^{\beta\alpha}$ strings and offset
13: \quad Fetch or calculate integral $I$
14: \quad \textbf{if} \ $|I| > \varepsilon_1$ \textbf{then}
15: \quad \quad \textbf{loop} \{ $\hat{t}_a^{(1)}$ \}
16: \quad \quad \quad Get relative offsets for $\hat{t}_a^{(1)}$
17: \quad \quad \quad \textbf{loop} \{ $\hat{t}_a^{(1)}$ \}
18: \quad \quad \quad \quad Get relative offsets for $\hat{t}_a^{(1)}$
19: \quad \quad \quad \quad \textbf{loop} \{ $\hat{t}_c^{(1)}$ \}
20: \quad \quad \quad \quad \quad Get relative offsets for $\hat{t}_c^{(1)}$
21: \quad \quad \quad \quad \quad \textbf{loop} \{ $\hat{t}_c^{(1)}$ \}
22: \quad \quad \quad \quad \quad \quad Get relative offsets for $\hat{t}_c^{(1)}$
33
Calculate total offset from relative offsets for $\hat{T}^{(1)}$

Multiply integral with element in $\hat{t}^{(1)}$ to element $J$

\[ \text{if } |J| > \varepsilon_2 \text{ then} \]

\[ \text{loop } \{ \hat{t}_{a\beta}^{(2)} \} \]

Get relative offsets for $\hat{t}_{a\beta}^{(2)}$

\[ \text{loop } \{ \hat{t}_{a\alpha}^{(2)} \} \]

Get relative offsets for $\hat{t}_{a\alpha}^{(2)}$

\[ \text{loop } \{ \hat{t}_{c\beta}^{(2)} \} \]

Get relative offsets for $\hat{t}_{c\beta}^{(2)}$

\[ \text{loop } \{ \hat{t}_{c\alpha}^{(2)} \} \]

Intermediate $J$ with element in $\hat{r}^{(2)}$ to element $K$

\[ \text{if } |K| > \varepsilon_3 \text{ then} \]

\[ \text{loop } \{ \hat{t}_{a\beta}^{(3)} \} \]

Get relative offsets for $\hat{t}_{a\beta}^{(3)}$

\[ \text{loop } \{ \hat{t}_{a\alpha}^{(3)} \} \]

Get relative offsets for $\hat{t}_{a\alpha}^{(3)}$

\[ \text{loop } \{ \hat{t}_{c\beta}^{(3)} \} \]

Get relative offsets for $\hat{t}_{c\beta}^{(3)}$

\[ \text{loop } \{ \hat{t}_{c\alpha}^{(3)} \} \]

Calculate total offset from relative offsets for $\hat{T}^{(3)}$

Intermediate $K$ with element in $\hat{r}^{(3)}$ to element $L$

\[ \text{if } |L| > \varepsilon_4 \text{ then} \]
Get relative offsets and phase for $\hat{O}_{a\beta}$ and $\hat{t}_{a\beta}^{(4)}$

Get relative offsets and phase for $\hat{O}_{a\alpha}$ and $\hat{t}_{a\alpha}^{(4)}$

Get relative offsets and phase for $\hat{O}_{c\beta}$ and $\hat{t}_{c\beta}^{(4)}$

Get relative offsets and phase for $\hat{O}_{c\alpha}$ and $\hat{t}_{c\alpha}^{(4)}$

Calculate total offset from relative offsets for $\hat{O}$ and $\hat{T}^{(4)}$

Calculate total phase from relative phases and the overall phase

Intermediate $L$ with element in $\hat{t}^{(4)}$ and overall phase to element in $\hat{O}$
Exactly like for the ISCI and when collecting intermediates in the IISCC the outer loops from lines 1-10 are over the indices in the Hamiltonian. An integral is fetched or calculated and screened in line 14. After the IS is a series of loops over the nested commutators with one cluster operator at a time follows. After the first loops over a cluster operator the integral is multiplied with an amplitude and screened as shown in line 25. A similar multiplication is performed after every cluster operator and in this way is not only the integrals screened but also the intermediates. While the loop structure in the general algorithm gives the wrong scaling the IIS in lines 14, 25, 36 and 47 will reduce the scaling for spatially extended systems. Since the numerical value of the amplitudes should be below one it is possible to obtain the same accuracy even while using a declining screening threshold so the outer IIS threshold is higher than the inner IIS

\[ |\epsilon_1| \geq |\epsilon_2| \geq |\epsilon_3| \geq |\epsilon_4|. \]  

(49)
A declining IIS threshold will give a further speed up without destroying the numerical accuracy.

From the general loop structure for a four-fold nested commutator it is easy to construct three- and two-fold nested commutators. For the remaining terms the algorithm is exactly like the ISCI algorithm. Since the IIS should reduce the scaling of the nested commutators it is expected that these will not significantly increase the scaling of the IISCC and that the performance will be similar to that shown for the ISCI. The advantage of not collecting the intermediates is that the outer loop will not depend on the excitation level included in the CC expansion which will be beneficial when triples or higher excitations are included.

4 Summary and prospects

We have here presented the derivation of the integral- and intermediate-screened coupled-cluster method (IISCC) in which an *a priori* combined integral and intermediate screening (IIS) of the integrals and intermediates is expected to significantly reduce the scaling in comparison to the regular CC method as seen in the integral-screened configuration-interaction method (ISCI). The simple and rigorous IIS ensures a good error control and will allow for the convergence of the energy to a very high accuracy while still retaining a very low scaling. The IIS only relies on numerical screening and does not contain any distance dependent screening so the IISCC is equally suited for both neutral and charged systems since both the short and long range of the wave function is equally well described. Due to the great similarities with the ISCI it is expected that the IISCC will exhibit the same low scaling properties for spatially extended systems but unlike the ISCI be size extensive and therefore also useful for many electron systems.

Currently the Hamiltonian is written in terms of index restricted and normal- and spin-ordered operators since this was shown to give a simple and rigorous IS in the ISCI. Following the derivation of the ISCI and expressing the Hamiltonian in strings of second quantized operators all contractions of all orders of nested commutators are separable up to a sign. This separability allows for a general loop structure where in the tensor contractions the outer loops are over the indices.
of the integrals in the Hamiltonian. Having the outer loops over the integrals allows for a very simple, efficient and rigorous \textit{a priori} IIS where only integrals and intermediates above a predefined threshold are computed. As shown for the ISCI such a procedure will automatically give a reduction in the scaling for spatially extended systems in local basis sets where linear scaling in the multiplication of integrals and coefficients step is gradually approached.

Three different approaches, where the algorithm is shown for two of them, which all have a simple and rigorous IIS is presented. In the first example, where intermediates are collected exactly like in the standard CC method, a simple and rigorous IIS can be obtained simply by first looping over the combined indices for the Hamiltonian and the intermediate. The algorithm in the very large basis set limit is therefore very close to a combination of the algorithm presented for the generalized-active space coupled-cluster method (GASCC)\cite{33} and the ISCI.\cite{28} The formal scaling and the prefactors will be like that of the regular CC method but these are expected to be reduced significantly by the IIS like seen for the ISCI. While the size of the intermediates grows significantly with system size and excitation level a piecewise construction of these can reasonably easy be obtained by introducing many GAS’s and storing these should therefore not be a problem. In the ISCI the most expensive step quickly becomes the loop over the integrals in the Hamiltonian and this is also expected to be the most expensive step for the IISCC. When only doubles is included then the addition of the intermediates to the integrals will not increase the cost of the outer loops, however, once triples or higher is included then this loop will increase significantly since intermediates with a particle rank of three will appear. Since the nested contractions are separable up to a sign a completely alternative route where all contractions in the nested commutators are contracted in a single step is presented. In this the intermediates are not explicitly constructed and the outer loops will therefore not be more expensive when higher than doubles excitations are included. The scaling of this approach for the nested commutators is higher than when intermediates is collected. The higher scaling is not expected to pose a problem since a gradual IIS in the nested commutators can be used which means even more integrals can in the outer step be safely discarded without any loss of accuracy. The scaling of the nested commutators will therefore decrease even faster than
the direct contractions. For both approaches much of the machinery developed for the ISCI appear to be directly applicable to the IISCC method. If the intermediates are collected an additional 61 tensor contractions will have to be implemented while for the single step contraction the double, triple and quadruple nested commutators should be implemented. When the CC hierarchy is truncated at the doubles level it will clearly be advantages to collect the intermediates while if more than doubles is included it will be advantages to perform all contractions in a single step as long as no distant dependent truncation of the interaction is introduced.

While the main aim of the ISCI method was the accurate simulations of physical processes where one or more electrons move in the continuum for atoms and molecules in strong laser fields the aim of the IISCC extends beyond this due to the size-extensive nature of the CC equations. The IISCC would therefore also be very interesting with in electronic structure theory for large system with many electrons either as a stand alone low scaling method or in combination with the fragment based linear scaling approach or the distance screening approach. The central advantage of the IISCC is the ability to use extremely large basis sets, as shown for the ISCI, which is a central problem in the current methods used to obtain linear scaling. Due to the rigorous IIS and error control the IISCC is expected to significantly reduce the errors for linearly scaling methods.

A Excitation-class Formalism

In this section we recapitulate the excitation class formalism for a non-relativistic Hamiltonian, as used in the ISCI,\textsuperscript{28} and originally presented in the relativistic framework for GASCC implementations.\textsuperscript{33,43} The excitation class formalism maps a normal-ordered operator, consisting of a string of second quantized operators, onto a set of classes helpful in characterizing different parts of an operator and in aiding the algorithm due to their simple algebra. We will assume that the orbitals have been optimized in some restricted way so that the orbitals can be related by the spin-flip operator.\textsuperscript{33}

The $PHN\Delta M$-classes introduces a set of auxiliary quantum numbers which depends only on
the number of alpha and beta creation and annihilation operators, \( N^c_\alpha, N^c_\beta, N^a_\alpha \) and \( N^a_\beta \), respectively, and hence have four indices where each preceding index represent a further division of the classes. Since we here are concerned with number conserving operators

\[ N^{c\alpha} + N^{c\beta} = N^{a\alpha} + N^{a\beta}, \]  

(50)

this leaves three additional indices which are chosen as the particle rank \( N \), spin flip \( \Delta M_s \) and the difference between the number of \( \alpha \) and \( \beta \) operators \( M_{\alpha\beta} \). The operator classes from a general operator like the Hamiltonian \( \hat{H} \), the excitation operator \( \hat{X} \), intermediate \( \hat{M} \) or any other number-conserving normal-ordered second quantized operators can all be divided in the \( PHN\Delta M \)-classes in the same way

\[ \hat{O} = \sum_{P,H,N,\Delta,M} \hat{O}^{PH}_{N,\Delta,M}. \]  

(51)

Here \( P \) and \( H \) denote the de-excitation part, \( P \) gives the number of annihilation de-excitation terms and \( H \) the number of creation de-excitation terms \( N \) is the particle rank

\[ N = \frac{1}{2}(N^{c\alpha} + N^{c\beta} + N^{a\alpha} + N^{a\beta}) \]
\[ = N^{c\alpha} + N^{c\beta} \Rightarrow N^{c\alpha} + N^{c\beta} = N^{a\alpha} + N^{a\beta}, \]  

(52)

\( \Delta \) is the spin flip of the spin orbitals\(^{33,44}\)

\[ \Delta M_s = \frac{1}{2}(N^{c\alpha} - N^{c\beta} + N^{a\alpha} - N^{a\beta}) \]
\[ = N^{c\alpha} - N^{a\alpha} \Rightarrow N^{c\alpha} + N^{c\beta} = N^{a\alpha} + N^{a\beta}, \]  

(53)

and \( M_{\alpha\beta} \) is the difference in the number of operators with alpha and beta spins

\[ M_{\alpha\beta} = \frac{1}{2}(N^{c\alpha} - N^{c\beta} + N^{a\alpha} - N^{a\beta}) \]
\[ = N^{c\alpha} - N^{a\beta} \Rightarrow N^{c\alpha} + N^{c\beta} = N^{a\alpha} + N^{a\beta}. \]  

(54)
While the Hamiltonian and the intermediate will have classes with non-zero $P$ and $H$ the excitation operator $\hat{X}$ will not, since $\hat{X}$ does not contain any de-excitation terms according to the definition of excitation and de-excitation operators in Section 2.

References

(1) Coester, F. Nuc. Phys. 1958, 7, 421.

(2) Coester, F.; Kümmel, H. Nuc. Phys. 1960, 17, 477.

(3) Čížek, J. J. Chem. Phys. 1966, 45, 4256.

(4) Paldus, J.; Čížek, J.; Shavitt, I. Phys. Rev. A 1972, 5, 50.

(5) Kellner, G. W. Z. Phys. 1927, 44, 91.

(6) Kellner, G. W. Z. Phys. 1927, 44, 110.

(7) Hylleraas, E. A. Z. Phys. 1928, 48, 469.

(8) Ragavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. Chem. Phys. Lett. 1989, 157, 479.

(9) Janowski, T.; Ford, A. R.; Pulay, P. J. Chem. Theo. Comp. 2007, 3, 1368.

(10) Janowski, T.; Pulay, P. J. Chem. Theo. Comp. 2008, 4, 1585.

(11) Harding, M. E.; Metzroth, T.; Gauss, J. J. Chem. Theo. Comp. 2008, 4, 64.

(12) Valiev, M.; Bylaska, E.; Govind, N.; Kowalski, T.; Straatsma, T.; Dam, H. V.; D. Wang; Nieplocha, J.; E. Apra; Windus, T.; deJong, W. A. Comp. Phys. Commun. 2010, 181, 1477.

(13) Asadchev, A.; Gordon, M. S. J. Chem. Theo. Comp. 2013, 9, 3385.

(14) Anisimov, V. M.; Bauer, G. H.; Chadalavada, K.; Olson, R. M.; Glenski, J. W.; Kramer, W. T. C.; Aprá, E.; Kowalski, K. J. Chem. Theo. Comp. 2014, 10, 4307.
(15) Hampel, C.; Werner, H. J. *J. Chem. Phys.* **1996**, *104*, 6286.

(16) Schütz, M.; Werner, H. J. *J. Chem. Phys.* **2001**, *114*, 661.

(17) Flocke, N.; Bartlett, R. J. *J. Chem. Phys.* **2004**, *121*, 10935.

(18) Ziolkowski, M.; Jansik, B.; Kjærgaard, T.; Jørgensen, P. *J. Chem. Phys.* **2010**, *133*, 014107.

(19) Ettenhuber, P.; Baudin, P.; Kjærgaard, T.; Jørgensen, P.; Kristensen, K. *J. Chem. Phys.* **2010**, *133*, 014107.

(20) Riplinger, C.; Pinski, P.; Becker, U.; Valeev, E. F.; Neese, F. *J. Chem. Phys.* **2016**, *144*, 024109.

(21) Friedrich, J.; Hanrath, M.; Dolg, M. Z. *Phys. Chem. Phys.* **2010**, *224*, 513.

(22) Stoll, H. *Chem. Phys. Lett.* **1992**, *191*, 548.

(23) Li, W.; Piecuch, P.; Gour, J. R.; Li, S. *J. Chem. Phys.* **2009**, *131*, 114109.

(24) Li, W.; Piecuch, P.; Gour, J. R.; Li, S. *J. Phys. Chem. A* **2010**, *114*, 8644.

(25) Kobayashi, M.; Nakai, H. *J. Chem. Phys.* **2009**, *131*, 114108.

(26) Pulay, P. *Chem. Phys. Lett.* **1983**, *100*, 151.

(27) Sæbø, S.; Pulay, P. *Chem. Phys. Lett.* **1985**, *113*, 13.

(28) Ørørensen, L. K.; Bauch, S.; Madsen, L. B. arXiv:1609.07757

(29) Larsson, H. R.; Bauch, S.; Ørørensen, L. K.; Bonitz, M. *Phys. Rev. A* **2016**, *93*, 013426.

(30) Møller, C.; Plessset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(31) Bartlett, R. J.; Purvis III, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561.

(32) Bartlett, R. J.; Purvis III, G. D. *Phys. Scr.* **1980**, *21*, 255.
(33) Sørensen, L. K.; Olsen, J. *Mol. Phys.* **2016**, DOI: 10.1080/00268976.2016.1195926.

(34) Davidson, E. R. *J. Comput. Phys.* **1975**, *17*, 87.

(35) Lanczos, C. *J. Res. Natl. Bur. Stand.* **1950**, *45*, 225.

(36) Chwee, T. S.; Szilva, A. B.; Lindh, R.; Carter, E. A. *J. Chem. Phys.* **2008**, *128*, 224106.

(37) Paldus, J. *J. Chem. Phys.* **1974**, *61*, 5321.

(38) Shavitt, I. *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1977**, *11*, 131.

(39) Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer III, H. F. *J. Chem. Phys.* **1986**, *86*, 2881.

(40) Scuseria, G. E.; Janssen, C. L.; Schaefer III, H. F. *J. Chem. Phys.* **1988**, *89*, 7382.

(41) Engels-Putzka, A.; Hanrath, M. *J. Chem. Phys.* **2011**, *134*, 124106.

(42) Sørensen, L. K. 2016; unpublished.

(43) Sørensen, L. K.; Olsen, J.; Fleig, T. *J. Chem. Phys.* **2011**, *134*, 214102.

(44) Jensen, H. J. Aa.; Dyall, K. G.; Saue, T.; Fægri, K. *J. Chem. Phys.* **1996**, *104*, 4083.