Multilevel CC2 and CCSD in reduced orbital spaces: electronic excitations in large molecular systems

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Abstract

We present efficient implementations of the multilevel CC2 (MLCC2) and multilevel CCSD (MLCCSD) models. As the system size increases, MLCC2 and MLCCSD exhibit the scaling of the lower level coupled cluster model. In order to treat large systems, we combine MLCC2 and MLCCSD with a reduced orbital space approach where the multilevel coupled cluster calculation is performed in a significantly truncated molecular orbital basis. The truncation scheme is based on the selection of an active region of the molecular system and the subsequent construction of localized Hartree-Fock orbitals. These orbitals are used in the multilevel coupled cluster calculation. The electron repulsion integrals are Cholesky decomposed using a screening protocol that guarantees accuracy in the truncated molecular orbital basis. The Cholesky factors are constructed directly in the truncated basis, ensuring low storage requirements. Even larger systems can be treated by using a multilevel Hartree-Fock reference. With the
reduced space approach, we can handle systems with more than a thousand atoms.
This is demonstrated for paranitroaniline in aqueous solution.

Introduction

The scaling properties of the coupled cluster hierarchy of methods severely limits the systems for which it is applicable.\textsuperscript{11} The methods have polynomial computational scaling, $O(N^n)$, where $N$ is a measure of system size and $n$ increases with complexity of the method. Memory and disk space requirements also increase significantly as one moves up through the hierarchy.

The development of reduced cost and reduced scaling coupled cluster methods has been an active topic of research for decades. Arguably, the most popular approach has emerged from the work of Pulay and Sæbø.\textsuperscript{2,3} They demonstrated that dynamical electronic correlation could be described compactly using localized orbitals rather than canonical orbitals; specifically, they used localized occupied orbitals, such as Boys\textsuperscript{4} or Pipek-Mezey\textsuperscript{5} orbitals, and projected atomic orbitals\textsuperscript{2,3} (PAOs) to span the virtual space. This local correlation approach was later applied to coupled cluster theory by Hampel, Werner, and Schütz.\textsuperscript{6,7} Other local coupled cluster methods include the local pair natural orbital\textsuperscript{8,9} and the orbital-specific-virtual\textsuperscript{10} coupled cluster methods. Whereas the success of these local coupled cluster methods in the description of the ground state correlation energy is indisputable, their extension to excited states has turned out to be more complicated.\textsuperscript{11–16}

A very different approach originates from the multireference coupled cluster method of Piecuch, Olifant, and Adamowicz.\textsuperscript{17,18} While introduced to describe multireference character, the method is formulated in the framework of single reference coupled cluster theory. An active orbital space is used, and higher order excitation operators (e.g., triple or quadruple excitations) are included with some indices restricted to the active space. Köhn and Olsen\textsuperscript{19} recognized that the method could be used to reduce the cost for single reference systems, and this was further demonstrated by Kállay and Rolik.\textsuperscript{20} This approach is similar to multilevel...
coupled cluster (MLCC) introduced by Myhre et al.\textsuperscript{21}\textsuperscript{23}

In MLCC, the goal is to accurately describe excitation energies and other intensive properties, rather than extensive properties such as correlation energies. This is done by restricting the higher order excitation operators to excite within an active orbital space. For example, in the multilevel CCSD\textsuperscript{24} (MLCCSD) method, the double excitation operator is restricted to excite out of active occupied orbitals and into active virtual orbitals. In this work, we consider the MLCC2 and MLCCSD models introduced in Ref. \textsuperscript{24}. We demonstrate the available computational savings in our MLCC2 and MLCCSD implementations and show that, for sufficiently large inactive spaces, the cost is dominated by the lower level method. This has previously been demonstrated for multilevel CC3 (MLCC3) by Myhre et al.\textsuperscript{23}

The polynomial scaling of the lower level model can, however, not be avoided. Therefore, in order to use the methods for large systems, they must be combined with other multilevel or multiscale approaches. For instance, MLCC could be used within a QM/MM\textsuperscript{25}\textsuperscript{26} framework or with the polarizable continuum model\textsuperscript{27}\textsuperscript{28}. Here, we have chosen another approach: MLCC calculations are performed in a significantly truncated molecular orbital (MO) basis. The truncation of the MO basis in coupled cluster calculations is used routinely. For example, the frozen core approximation falls into this category. We use a truncation scheme for the MOs based on the construction of semi-localized Hartree-Fock orbitals (virtual and occupied), which can be used to calculate localized intensive properties in large molecular systems. When the region of interest is sufficiently small compared to the full system, the number of MOs in the coupled cluster calculation is much smaller than the total number of atomic orbitals (AOs). This \textit{MLCC-in-HF} approach bears similarities to the LCCSD(T)-in-HF approach suggested in Ref. \textsuperscript{29}. Lastly, to handle larger systems, we combine the reduced space MLCC approach with the use of a multilevel Hartree-Fock\textsuperscript{30}\textsuperscript{31} (MLHF) reference wave function.

The MLCC2 and MLCCSD implementations are based on Cholesky decomposed electron repulsion integrals.\textsuperscript{32}\textsuperscript{34} We present and implement an algorithm for direct construction of
the Cholesky vectors in the truncated MO basis. This reduces the memory requirement of the vectors from $O(N_{AO}^3)$ to $O(N_{AO})$, making it possible to efficiently perform reduced space calculations on systems with several thousands of basis functions. We also use an MO-screening in the Cholesky decomposition that leads to fewer Cholesky vectors, further reducing the memory requirement and computational cost.

Theory

In coupled cluster theory, the wave function is defined as

$$|\text{CC}\rangle = \exp(X)|\text{HF}\rangle, \quad X = \sum_{\mu} x_{\mu} \tau_{\mu}$$

(1)

where $|\text{HF}\rangle$ is the Hartree-Fock reference, $X$ is the cluster operator, $x_{\mu}$ are cluster amplitudes, and $\tau_{\mu}$ are excitation operators. The standard models within the coupled cluster hierarchy are defined by restricting $X$ to include the excitation operators up to a certain order. In the $\text{CC}_n$ models, such as CC2 and CC3, the $n$th order excitations are treated perturbatively.

In the following, we refer with indices $\alpha, \beta, \gamma, ...$ and $p, q, r, ...$ to atomic and molecular orbitals respectively, and with indices $i, j, k, ...$ and $a, b, c, ...$ to occupied and virtual orbitals.

**Multilevel CC2 and CCSD**

The MLCC2 cluster operator is given by

$$X^{\text{MLCC2}} = X_1 + S_2,$$

(2)

where the single excitation operator, $X_1$, is unrestricted, i.e. defined for all orbitals, whereas the double excitation operator, $S_2$, is restricted to excite within an active orbital space. As in standard CC2, $S_2$ is treated perturbatively. The MLCC2 ground state equations are given
by

\[ \Omega_{\mu_1} = \langle \mu_1 | \hat{H} + [\hat{H}, S_2] | \text{HF} \rangle = 0 \quad (3) \]
\[ \Omega_{\mu_2} = \langle \mu_2^S | \hat{H} + [F, S_2] | \text{HF} \rangle = 0, \quad (4) \]

where \( \hat{H} \) is the \( X_1 \)-transformed Hamiltonian. The doubles projection space, \( \{ \langle \mu_2^S | \} \) is associated with \( S_2 \). Except for the restriction of \( S_2 \) and the projection space, these equations are equivalent to the standard CC2 ground state equations. The MLCC2 equations are solved in a basis where the active-active blocks of the occupied-occupied and virtual-virtual Fock matrices are diagonal. In this semicanonical basis, eq (4) can be solved analytically for the \( S_2 \) amplitudes. The solution of eq (4) is then inserted into eq (3) which is solved iteratively for \( X_1 \). The MLCC2 excitation energies are determined as the eigenvalues of the Jacobian matrix,

\[ A_{\text{MLCC2}} = \begin{pmatrix} \langle \mu_1 | [\hat{H}, \tau_{\nu_1}] + [\hat{H}, [\tau_{\nu_1}, S_2]] | R \rangle & \langle \mu_1 | [\hat{H}, \tau_{\nu_2}^S] | R \rangle \\ \langle \mu_2^S | [\hat{H}, \tau_{\nu_1}] | R \rangle & \langle \mu_2^S | [F, \tau_{\nu_2}^S] | R \rangle \end{pmatrix}. \quad (5) \]

The excited state equations also assume the same form as in standard CC2, except for the restrictions of \( S_2 \), and the same strategies can therefore be used to solve the MLCC2 equations.

In MLCCSD, one defines two sets of active orbitals, where one is a subset of the other. The cluster operator has the form

\[ X_{\text{MLCCSD}} = X_1 + S_2 + T_2, \quad (6) \]

where \( X_1 \) is unrestricted, \( S_2 \) is restricted to the larger active orbital space, and \( T_2 \) is restricted to the smaller active orbital space. The \( S_2 \) operator is treated perturbatively (as in CC2 and MLCC2) and \( T_2 \) acts as a correction to \( S_2 \) in the smaller active space. This framework is flexible since it allows for both two-level calculations (CCS/CCSD and CC2/CCSD) and three-level calculations (CCS/CC2/CCSD). Previously, we have found that the cheaper and
significantly simpler CCS/CCSD method performs very well.\textsuperscript{24} In the CCS/CCSD method, the MLCCSD cluster operator reduces to

\[ X^{\text{MLCCSD}} = X_1 + T_2, \quad (7) \]

and only the active space for \( T_2 \) is needed. In this work, we only consider the CCS/CCSD method.

The MLCCSD (CCS/CCSD) ground state equations are

\[ \Omega_{\mu_1} = \langle \mu_1 | \hat{H} + [\hat{H}, T_2] | \text{HF} \rangle = 0 \quad (8) \]

\[ \Omega_{\mu_T} = \langle \mu_T^T | \hat{H} + [\hat{H}, T_2] + \frac{1}{2}[[\hat{H}, T_2], T_2] | \text{HF} \rangle = 0, \quad (9) \]

where the doubles projection space, \( \{ \langle \mu T^T \rangle \} \), is associated with \( T_2 \). Equations (8) and (9) are equivalent to the standard CCSD equations, except for the restriction of \( T_2 \) and the projection space. The excitation energies are obtained as the eigenvalues of the MLCCSD Jacobian,

\[
A^{\text{MLCCSD}} = \begin{pmatrix}
\langle \mu_1 | [\hat{H}, \tau_{\nu_1}] + [[\hat{H}, \tau_{\nu_1}], T_2] | R \rangle & \langle \mu_1 | [\hat{H}, \tau_{\nu_1}^T] | R \rangle \\
\langle \mu_2^T | [\hat{H}, \tau_{\nu_1}] + [[\hat{H}, \tau_{\nu_1}], T_2] | R \rangle & \langle \mu_2^T | [\hat{H}, \tau_{\nu_1}^T] + [[\hat{H}, \tau_{\nu_1}^T], T_2] | R \rangle
\end{pmatrix}. \quad (10)
\]

In standard CC2 and CCSD, the most expensive contractions involved in the ground and excited state equations scale as \( O(N^5) \) and \( O(N^6) \), respectively. In the following, we use \( N_o \) to denote the number of active occupied orbitals, \( N_v \) for number of active virtual orbitals, and \( N_O \) and \( N_V \) for the total number of occupied and virtual orbitals, respectively. The \( O(N^5) \) contractions in the MLCC2 ground and excited state equations scale as \( N_o^2 N_v^2 N_O \) and \( N_o^2 N_v^2 N_V \). For a fixed active space, these contractions scale linearly with system size, and as \( N_O < N_V \), the latter is the most expensive. In the MLCCSD (CCS/CCSD) ground and excited state equations, there are several iterative \( O(N^6) \) contractions. However, all indices
in these contractions are active, and for a fixed active space, the cost will be independent
of system size. In addition to the \( \mathcal{O}(N^6) \) terms, there are several \( \mathcal{O}(N^5) \) contractions in the
MLCCSD equations—including those that enter the MLCC2 equations. The MLCC2 and
MLCCSD (CCS/CCSD) equations can be found in the Supporting Information.

Our implementation of MLCC2 and MLCCSD uses Cholesky decomposed electron re-
pulsion integrals,

\[
g_{\alpha\beta\gamma\delta} = \sum_{J=1}^{N_J} L^{J}_{\alpha\beta} L^{J}_{\gamma\delta}, \tag{11}
\]

and the number of Cholesky vectors, \( N_J \), is proportional to \( N_{AO}^{39} \). The electron repulsion
integals are constructed when needed from the Cholesky vectors, which are stored in the
\( T_1 \)-transformed MO basis,

\[
\hat{g}_{pqrs} = \sum_{J=1}^{N_J} \hat{L}^{J}_{pq} \hat{L}^{J}_{rs}. \tag{12}
\]

Without index restrictions to the active space, this contraction scales as \( \mathcal{O}(N^5) \). All electron
repulsion integrals that enter the MLCC2 and MLCCSD equations, except those that also
enter at the CCS level of theory, have at least two indices restricted to the active space.
Depending on how many MO indices are restricted, the scaling with respect to the system
size for a fixed active space is \( \mathcal{O}(N) - \mathcal{O}(N^3) \) for these integrals. For the transformation by
the CCS Jacobian matrix, integral blocks with two virtual and two occupied indices (\( g_{VVOO} \)
and \( g_{VOOV} \)) must be calculated. These integrals also enter the transformation by \( A_{MLCC2} \)
and \( A_{MLCCSD} \). Since all indices are unrestricted, the computational cost to construct these
integrals is \( N_{\delta}^2 N_{V}^2 N_J \), that is, \( \mathcal{O}(N^5) \).
Partitioning the orbital space

Selecting the active orbital space for a multilevel coupled cluster calculation is not a trivial task. Generally, the canonical Hartree-Fock orbitals must be transformed (through occupied-occupied and virtual-virtual rotations) to a basis where an intuitive partitioning of the orbitals is possible. In order to determine the type of orbitals to use, both the property and the system must be considered. There are two main approaches to select the active spaces. If the property of interest is well described by a lower level coupled cluster method, then the information from that lower level method can be used to partition the orbitals. An example is the use of correlated natural transition orbitals. If the property of interest is spatially localized in the molecular system, then localized or semi-localized orbitals can be used. For instance, Cholesky orbitals have been used in multilevel coupled cluster calculations by Myhre et al.

The correlated natural transition orbitals are constructed using excitation vectors, $R$, from a lower level calculation. The matrices

\begin{align}
M_{ij} &= \sum_a R_{ai}R_{aj} + \frac{1}{2} \sum_{abk} (1 + \delta_{ai,bk}\delta_{ij}) R_{aibk}R_{ajbk} \\
N_{ab} &= \sum_i R_{ai}R_{bi} + \frac{1}{2} \sum_{ijc} (1 + \delta_{ai,cj}\delta_{ab}) R_{aicj}R_{bicj}
\end{align}

are constructed and diagonalized. The matrices that diagonalize $M$ and $N$ are the transformation matrices of the occupied and virtual orbitals, respectively. From eqs (13) and (14) it may seem that the lower level method must include double excitation amplitudes in its parametrization. However, CNTOs can be generated from CCS excitation vectors by constructing approximate double excitation vectors:

\begin{equation}
R_{aibj}^{\text{CCS}} = -\frac{1}{1 + \delta_{ai,bj} \epsilon_{ij}^{ab} - \omega^{\text{CCS}}} \tilde{g}_{aibj},
\end{equation}

Here, $\omega^{\text{CCS}}$ is the CCS excitation energy, and $\epsilon_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$, where the $\epsilon_q$ are orbital
energies. The integrals $\bar{g}_{abij}$ are defined as

$$
\bar{g}_{abij} = \mathcal{P}_{ij}^{ab} \left( \sum_{cJ} R_{ci} L^J_{bj} L^J_{ai} - \sum_{kJ} R_{bk} L^J_{kj} L^J_{ai} \right),
$$

where $g_{pqrs}$ are the electronic repulsion integrals in the molecular orbital basis and $\mathcal{P}_{ij}^{ab} I_{ai,bj} = I_{ai,bj} + I_{bj,ai}$. The approach given by eqs (15) and (16) was suggested by Baudin and Kristensen.\(^{44}\)

The active space is selected by considering the eigenvalues of $M$ and $N$: orbitals resulting from the eigenvectors corresponding to the largest eigenvalues are active. In this work, we select the number of active occupied orbitals, $N^a_o$, and let the number of active virtual orbitals be determined from the total fraction of virtual to occupied orbitals,

$$
N^a_v = \frac{N^a_v}{N^a_o} N^a_o.
$$

Alternatively, one can use the selection criterion given in Ref. 40. Several excited states can be considered simultaneously by summing $M$ and $N$ matrices generated from several excitation vectors (eqs (13) and (14)) before the diagonalization and subsequent transformation of the orbitals.\(^{24}\)

Cholesky orbitals\(^{41,42}\) are obtained by a limited partial Cholesky decomposition of the Hartree-Fock densities (occupied and virtual); the pivots of the decomposition procedure are restricted to correspond to AOs centered on a set of active atoms.

As an alternative to Cholesky orbitals for the virtual space, one can use projected atomic orbitals\(^{3}\) (PAOs). To construct the PAOs, the occupied orbitals are projected out of the
AOs, \( \{ \chi_\alpha \} \), centered on the active atoms:

\[
\chi_{\alpha}^{\text{PAO}} = \chi_\alpha - \sum_i \langle \phi_i | \chi_\alpha \rangle \phi_i \\
= \chi_\alpha - \sum_{i\beta\gamma} C_{\beta i} C_{\gamma i} \langle \chi_\beta | \chi_\alpha \rangle \chi_\gamma \\
= \chi_\alpha - \sum_\gamma \chi_\gamma [DS]_{\gamma\alpha}.
\]

Here, \( C \) is the orbital coefficient matrix, \( D \) is the idempotent Hartree-Fock density, and \( S \) is the AO overlap matrix. The orbital coefficient matrix for the active PAOs is therefore \( C^{\text{PAO}} = I - DS' \), where \( S' \) is rectangular and contains the columns of \( S \) which correspond to AOs on active atomic centers. The PAOs are non-orthogonal and linearly dependent. In order to remove linear dependence and orthonormalize the active virtual orbitals, we use the Löwdin canonical orthonormalization procedure. The inactive virtual orbitals are obtained in a similar way: the active virtual orbitals, as well as the occupied orbitals are projected out of the AOs and the resulting orbitals are finally orthonormalized.

After the orbitals are partitioned—regardless of which orbitals are used—we transform to the semicanonical MO basis that is used in MLCC2 and MLCCSD calculations. That is, we block diagonalize the virtual-virtual and occupied-occupied Fock matrices such that the active-active and inactive-inactive blocks become diagonal.

**Reduced space multilevel coupled cluster**

MLCC methods still exhibit the polynomial scaling of the lower level model. In our current implementation of MLCC2 and CCS/CCSD MLCCSD, integral construction is the limiting step. To extend the treatable system size, we perform reduced space calculations where only a subregion of the molecule is described at the coupled cluster level. The orbitals of this subregion is then divided into active and inactive sets for the MLCC calculation. The rationale behind this approach is that localized intensive properties can be described accurately.
by using accurate and expensive methods only for the region of interest. The interactions with the more distant environment is sufficiently well captured through contributions to the Fock matrix. A few numerical results indicate that excitation energies can be described accurately with this frozen Hartree-Fock approach. However, a comprehensive study has not been published.

To perform reduced space multilevel coupled cluster calculations, we must first choose the region of the molecular system to be treated with MLCC. After the Hartree-Fock calculation, localized occupied and virtual orbitals are constructed for the active region. We use Cholesky orbitals for the occupied space and PAOs for the virtual space. However, any localization procedure can be used. This set of orbitals is used in the multilevel coupled cluster calculation. The remaining occupied orbitals enter the equations through their contributions to the Fock matrix,

\[
F_{pq} = \delta_{pq} + \sum_{i=1}^{N_o} (2g_{piiq} - g_{pippi}) + \sum_{I=1}^{N^e_o} (2g_{pIIq} - g_{pIII}) + F_{pq}^e,
\]

where \(N^e_o\) is the number of frozen occupied orbitals and the index \(I\) denotes a frozen occupied orbital. The multilevel coupled cluster calculation now has \(N_{MO} \ll N_{AO}\), but the procedure is otherwise unchanged: the reduced set of MOs is partitioned into active and inactive sets and the MLCC equations are solved.

A multilevel Hartree-Fock (MLHF) reference can also be used. As in MLCC, one first determines the active orbitals: a set of active atoms is selected, and the active occupied orbitals are obtained through a partial limited Cholesky decomposition of the initial idempotent density; PAOs can be used to determine the active virtual orbitals. In the Roothan-Hall procedure, performed in the MO basis, only the active orbitals are optimized. The inactive orbitals enter the optimization through an effective Fock matrix that assumes the same form as in eq 19. The inactive two-electron contribution \((F^e)\) is only computed once at the
beginning of the calculation and is subsequently transformed to the updated MO basis in every iteration. For details, see Ref. [30].

Figure 1: The different levels of active atoms used in a reduced space MLCC calculations. Left panels show active atoms configurations of reduced space MLCC calculation with an HF reference. Right panels show active atom configurations of reduced space MLCC calculation with an MLHF reference. The two lower panels show the active atom configurations when Cholesky/PAOs are used to determine the active orbitals of the MLCC calculation.

The reduced space MLCC approach relies on the definition of levels of active regions of the system, see Figure 1. We must first select which atoms are active in the Hartree-Fock (HF) calculation. If all atoms are active, we have a standard HF reference. Secondly, we must determine which atoms enter the MLCC calculation. Lastly, if we use Cholesky/PAOs to partition the orbitals in the MLCC calculation, we must determine which atoms should be treated with the higher level coupled cluster method. This is not necessary when CNTOs are used. Note that the active atom sets for higher level methods are contained within the active atom sets of lower level methods (see Figure 1).

Since these methods rely on determining active regions of the molecular system, they
are especially well suited for solute/solvent systems. They may also be used for other large systems where the region of interest is known.

**Integral handling for reduced space calculations**

When \( N_{MO} \ll N_{AO} \), as is the case in the reduced space approaches outlined in the previous section, there are some new aspects of handling the electron repulsion integrals which must be considered. The Cholesky vectors, \( L^J \), in the AO basis have a storage requirement of \( O(N_{AO}^3) \). As demonstrated by Røeggen and Wisløff-Nilssen\(^{39} \) the number of Cholesky vectors, \( N_J \), is approximately \( MN_{AO} \), when a decomposition threshold of \( 10^{-M} \) is used in the decomposition procedure. For example, with a loose Cholesky decomposition threshold of \( 10^{-2} \), almost 28 TB is needed to store the Cholesky vectors of a molecular system with 12000 AOs (using double precision and assuming that there is no screening).

We have previously suggested a two-step Cholesky decomposition algorithm in which the Cholesky basis (the pivots of the decomposition procedure), \( B \), is determined in the first step. The Cholesky vectors are constructed in the second step through an RI-like expression,

\[
L^J_{\alpha\beta} = \sum_K (\alpha\beta|K)[Q^{-T}]_{KJ},
\]

where the matrix \( Q \) is the Cholesky factor of the matrix \( S_{KL} = (K|L) \) for \( K, L \in B \). This two-step algorithm makes it possible to directly construct the Cholesky vectors in the MO basis:

\[
L^J_{pq} = \sum_{\alpha\beta} C_{\alpha p} L^J_{\alpha\beta} C_{\beta q}
= \sum_{\alpha\beta K} C_{\alpha p} C_{\beta q} (\alpha\beta|K)[Q^{-T}]_{KJ}.
\]

We emphasize that this is not possible with Cholesky decomposition algorithms where the vectors are constructed during the decomposition procedure. Below we outline an algorithm
to construct and store the vectors directly in the MO basis (see Algorithm 1). This is done after the elements of the basis $K \in B$ have been determined, $S$ has been constructed and decomposed, and $Q$ has been inverted. When the Cholesky factor, $L$, is too large to store in memory, $L_{pq}^J$ is constructed for a maximum number of $p$ indices (resulting in several batches, $P_1, P_2, \ldots, P_n$). The direct construction of the Cholesky vectors in the MO basis reduces the storage requirement to $O(N_{AO}N_{MO}^2)$. Note that this is linear, rather than cubic, in $N_{AO}$.

Algorithm 1: Constructing MO Cholesky vectors from the RI expression

**Input:** $B$, $Q^{-T}$

Determine batches of $p$, $P_1, P_2, \ldots, P_n$

for $P_i$ do

Allocate $X_{pqK}$, $\forall p \in P_i$

for $K \in B$ do

Calculate $(\alpha\beta|K)$

$C_{\alpha p}C_{\alpha q}(\alpha\beta|K) \rightarrow X_{pqK}, \forall p \in P_i$

end

$X_{pqK}[Q^{-T}]_{KJ} \rightarrow L_{pq}^J, \forall p \in P_i$

Store $L_{pq}^J, \forall p \in P_i$

end

Boman et al.\textsuperscript{35} has demonstrated that a significant reduction in the number of Cholesky vectors can be achieved through method-specific screenings. We will use the active space screening given in Ref. 34. In a given iteration of the Cholesky decomposition procedure, the next element of the basis is determined by considering the updated diagonal of the integral matrix

$$D_{\alpha\beta} = g_{\alpha\beta\alpha\beta} - \sum_{J \in B} (L_{\alpha\beta}^J)^2. \quad (22)$$

Here, the sum is over the current elements of the basis. In the standard decomposition
algorithm, the next element of the basis is selected as the \( K = \alpha \beta \) corresponding to the largest element of \( D \). The decomposition procedure is terminated when

\[
\max_{\alpha \beta} D_{\alpha \beta} < \tau, \tag{23}
\]

where \( \tau \) is the decomposition threshold. By introducing a screening vector, e.g.,

\[
\nu_\alpha = \max_p (C^a_{\alpha p})^2, \tag{24}
\]

we can modify the procedure to determine the Cholesky basis. Here, \( C^a \) is the MO coefficient matrix of the reduced space multilevel coupled cluster calculation. The selection and termination criteria are changed, and we consider the screened diagonal,

\[
\tilde{D}_{\alpha \beta} = \nu_\alpha D_{\alpha \beta} \nu_\beta, \tag{25}
\]

instead of \( D \). Using the criteria in eq (25), we obtain a smaller Cholesky basis compared to the standard decomposition. The storage requirement of the Cholesky vectors is reduced to \( O(N_{\text{MO}}^3) \). However, no compromise is made in the accuracy of the MO integrals.

**Results and discussion**

The MLCC2 and MLCCSD codes have been implemented in a development version of the \( e^T \) program. Occupied Cholesky orbitals are constructed using a threshold of \( 10^{-2} \). Unless otherwise stated, the frozen core approximation is used. All geometries are available from Ref. 47.
Figure 2: Rifampicin on the left and adenosine on the right.

Table 1: MLCC2/aug-cc-pVDZ and CC2/aug-cc-pVDZ calculations for rifampicin. $N_o^a$ and $N_v^a$ are the number active occupied and virtual orbitals and $\omega$ is the lowest excitation energy. The wall times to solve the ground and excited state equations ($t_{gs}$ and $t_{es}$) and to construct the CNTOs ($t_{CNTO}$) are also given. The calculations were performed on two Intel Xeon E5-2699 v4 processors using 1.4 TB memory and 44 threads.

| Method  | $N_o^a$ | $N_v^a$ | $\omega$ [eV] | $t_{gs}$ [h] | $t_{es}$ [h] | $t_{CNTO}$ [h] |
|---------|---------|---------|---------------|--------------|--------------|----------------|
| 40 400  | 2.79    | 6.9     | 7.5           | 18.0         |
| 80 800  | 2.60    | 9.5     | 41.5          | 16.0         |
| CC2 161 | 1645    | 2.58    | 31.3          | 136.1        |

Table 2: MLCCSD/aug-cc-pVDZ and CCSD/aug-cc-pVDZ calculations on adenosine. $N_o^a$ and $N_v^a$ are the number active occupied and virtual orbitals and $\omega_i$ are excitation energies. The wall times to solve the ground and excited state equations ($t_{gs}$ and $t_{es}$) and to construct the CNTOs ($t_{CNTO}$) are also given. The calculations were performed on two Intel Xeon Gold 6138 processors using 40 threads and 360 GB memory.

| Method  | $N_o^a$ | $N_v^a$ | $\omega_1$ [eV] | $\omega_2$ [eV] | $\omega_3$ [eV] | $t_{gs}$ [h] | $t_{es}$ [h] | $t_{CNTO}$ [h] |
|---------|---------|---------|-----------------|-----------------|----------------|--------------|--------------|----------------|
| MLCCSD  | 25 150  | 5.25    | 5.34            | 5.36            | 0.8            | 7.2          | 1.1          |
| 35 210  | 5.24    | 5.34    | 5.39            | 2.2             | 8.8            | 1.5          |
| 45 270  | 5.24    | 5.34    | 5.41            | 3.5             | 14.1           | 1.8          |
| CCSD 70 | 484     | 5.25    | 5.34            | 5.41            | 6.6            | 87.6         | –            |
Table 3: MLCCSD/aug-cc-pVDZ calculations for rifampicin. \( N^a_o \) and \( N^a_v \) are the number active occupied and virtual orbitals and \( \omega \) is the lowest excitation energy. The wall times to solve the ground and excites state equations (\( t^{gs} \) and \( t^{es} \)) and to construct the CNTOs (\( t^{CNTO} \)) are also given. The calculations were performed on two Intel Xeon Gold 6138 processors using 40 threads and 360 GB memory.

| \( N^a_o \) | \( N^a_v \) | \( \omega \) [eV] | \( t^{gs} \) [h] | \( t^{es} \) [h] | \( t^{CNTO} \) [h] |
|---|---|---|---|---|---|
| 40 | 400 | 3.04 | 10.2 | 15.8 | 9.9 |
| 50 | 500 | 3.02 | 10.7 | 17.7 | 8.7 |
| 60 | 600 | 3.01 | 15.9 | 32.5 | 10.8 |

Performance and scaling of MLCC2 and MLCCSD

The MLCC2 and MLCCSD methods can be used to obtain excitation energies with CC2 and CCSD quality, at significantly reduced cost. This is illustrated for rifampicin and adenosine, see Figure 2. The lowest excitation energy of rifampicin was calculated at the MLCC2/aug-cc-pVDZ and CC2/aug-cc-pVDZ levels of theory. The three lowest excitation energies of adenosine were calculated at the MLCCSD/aug-cc-pVDZ and CCSD/aug-cc-pVDZ levels of theory. The CNTOs were used to partition the orbitals for both systems. The results are given in Tables 1 and 2, respectively. The error in the MLCCSD and MLCC2 excitation energies with respect to CC2 and CCSD is smaller than the expected error of CC2 and CCSD.\(^{48,49}\)

The lowest excitation energy of rifampicin was also calculated with MLCCSD/aug-cc-pVDZ, see Table 3. Since the system has 1806 MOs and a full CCSD calculation would be quite expensive, we do not present a reference CCSD calculation. However, the variation of the excitation energy is less than 0.05 eV for the different active spaces and can therefore be considered converged. In our experience, MLCCSD excitation energies converge smoothly to the CCSD values.\(^{24}\) Note that the MLCC2 and MLCCSD timings cannot be compared, as the calculations were performed on different processors. For instance, the theoretical cost to construct the CNTOs for rifampicin is the approximately same for all calculations in Tables 1 and 3.

Significant savings are available with MLCC even though the polynomial cost of the
Figure 3: PNA and water

Figure 4: Wall times for the transformation by $A_{\text{MLCC2}}$, $t_{\text{MLCC2}}$, and the contributions from CCS and CC2 terms. The calculations were performed on two Intel Xeon Gold 6152 processors using 1.4 TB memory and 44 threads.

Table 4: Fraction of time spent in the CCS calculation for the CNTOs construction, $t_{\text{CCS}}$, and to construct the CNTOs, $t_{\text{CNTO}}$, compared to the full calculation time, $t$, of the multilevel coupled cluster calculation. $N_w$ denotes the number of water molecules.

| $N_w$ | MLCC2 | MLCCSD |
|-------|-------|--------|
|       | $t_{\text{CCS}}/t$ | $t_{\text{CNTO}}/t$ | $t_{\text{CCS}}/t$ | $t_{\text{CNTO}}/t$ |
|  7   |  0.03 |  $< 10^{-2}$ |  0.04 |  $< 10^{-2}$ |
| 11   |  0.06 |       0.01  |  0.07 |  $< 10^{-2}$ |
| 19   |  0.21 |       0.03  |  0.21 |       0.01  |
| 24   |  0.30 |       0.03  |  0.26 |       0.05  |
| 34   |  0.31 |       0.04  |  0.28 |       0.01  |
Figure 5: Wall times for the transformation by $A_{\text{MLCCSD}}$, $t_{\text{MLCCSD}}$, and the contributions from CCS and CCSD terms. The calculations were performed on two Intel Xeon E5-2699 v4 processors using 1.4 TB memory and 44 threads.

lower level method (in this case CCS) cannot be avoided. We consider systems with paranitroaniline (PNA) and water molecules; water molecules are added to the system while the size of the active space is fixed ($N_a^o = 36$, $N_v^o = 248$), see Figure 3. In Figures 4 and 5, we show that, for sufficiently large inactive spaces, the MLCCSD and MLCC2 excited state calculations are dominated by terms arising from the transformation by the CCS Jacobian matrix. In these calculations, the frozen core approximation was not used. Note that the MLCC2 and MLCCSD timings cannot be compared as the calculations were performed on different processors.

The MLCC2 and MLCCSD calculations on the PNA-water systems were performed using CNTOs. The cost of constructing the CNTOs is given by the full CCS excited state calculation and the $O(N^5)$ operations to construct the approximate double excitation vectors, the contractions in eq (16), and the construction of $M$ and $N$, see eqs (13) and (14). As the size of the inactive orbital space is increased, the cost to construct the CNTOs will at some point become comparable to solving the MLCC2/MLCCSD ground and excited state equations. The fractions of wall times for the full CCS calculation ($t_{\text{CCS}}$), and the construction of the
CNTOs ($t_{CNTO}$), compared to the full MLCC2 and MLCCSD calculation times, are given in Table 4. For the larger inactive spaces, we find that the CNTO construction is approximately one third of the MLCC2 and MLCCSD calculation times. As an alternative to CNTOs, one can use Cholesky/PAOs to partition the orbital space. Construction of these orbitals scale as $O(N^3)$ instead of $O(N^5)$.

**Reduced space MLCC calculations**

We now consider a larger PNA-water system. The geometry is extracted from a single snapshot of a molecular dynamics simulation, see Refs. [50] and [47]. The PNA-water system is restricted to a sphere centered on PNA with a 15 Å radius and includes 499 water molecules, see Figure 6.

![Figure 6: PNA with 499 water molecules.](image)

To evaluate the MO-screening procedure of eqs (24) and (25), we consider the lowest MLCCSD-in-HF excitation energy of the system—a charge transfer process in PNA. We compare the MO-screened Cholesky decomposition and the standard Cholesky decomposition. Note that we use the partitioned Cholesky decomposition (PCD) algorithm described
Table 5: The lowest MLCCSD-in-HF excitation energy of the PNA-in-water system. Cholesky decomposition with and without the MO-screening. The PCD algorithm is used. The threshold, $\tau$, the number of Cholesky vectors, $N_J$, and the largest error in the approximated matrix in the AO basis, $\epsilon$, are given. There are 3971 basis functions.

| $\tau$ | $N_J$ | $\frac{N_J}{N_{AO}}$ | $\epsilon$ | $\omega$ | $\frac{N_J}{N_{MO}}$ | $\epsilon$ | $\omega$ |
|-------|-------|----------------------|---------|--------|----------------------|---------|--------|
| $10^{-2}$ | 8434  | 2.1                  | $1.1 \cdot 10^{-2}$ | 4.0501  | 606                  | 0.9     | 4.77   | No convergence |
| $10^{-3}$ | 12297 | 3.1                  | $1.1 \cdot 10^{-3}$ | 4.0771  | 1440                 | 2.2     | 4.77   | 4.0555        |
| $10^{-4}$ | 15474 | 3.9                  | $1.7 \cdot 10^{-4}$ | 4.0761  | 2445                 | 3.7     | 4.77   | 4.0785        |
| $10^{-6}$ | 24826 | 6.3                  | $1.6 \cdot 10^{-6}$ | 4.0753  | 5378                 | 8.2     | 4.76   | 4.0754        |

In Ref. [3], in these MLCCSD calculations, the atoms within a sphere of 5 Å are included in the MLCC region ($r_{CCS} = 5$ Å) and the atoms within a sphere of radius 3.5 Å are defined as active at the CCSD level of theory ($r_{CCSD} = 3.5$ Å). The orbitals are partitioned with the Cholesky/PAO approach. We use aug-cc-pVDZ on the CCSD atoms, cc-pVDZ basis on the remaining atoms treated with coupled cluster theory, and the STO-3G basis on the atoms which are only included in the Hartree-Fock calculation. The total number of basis functions is 3971, and in the MLCCSD-in-HF calculations we have $N_{o}^{CCSD} = 90$, $N_{v}^{CCSD} = 287$, $N_{o}^{CCS} = 57$, and $N_{v}^{CCS} = 219$, that is, $N_{MO} = 653$. The results are given in Table 5.

The MO-screening yields significantly fewer Cholesky vectors without introducing large errors in the excitation energies. The largest error in the approximated AO integral matrix, $\epsilon$, is also given in Table 5. For standard PCD, the errors are comparable to the decomposition threshold. With MO-screening, $\epsilon$ is large because AO integrals that do not contribute to the MO integrals are not described by the Cholesky vectors. Without MO-screening, a Cholesky decomposition threshold of $10^{-2}$ or $10^{-3}$ is typically sufficient. For MLCC2 or MLCCSD in a reduced space calculation, the MO-screening can be used and a threshold of $10^{-4}$ seems suitable. In the calculation with MO-screening and a $10^{-2}$ threshold of , the MLCCSD calculation did not converge. We have also calculated the fractions $N_J/N_{AO}$ and $N_J/N_{MO}$ for the standard and MO-screened decomposition, respectively. For this system, the proportionality between the number of AOs ($N_{AO}$) and the number of Cholesky vectors ($N_J$)
is as mentioned previously. With MO-screening, however, $N_f$ shows similar proportionality to the number of MOs ($N_{\text{MO}}$) for the thresholds used. The memory requirement to hold the Cholesky vectors obtained from the MO-screened decomposition is, for these calculations, proportional to $N_{\text{MO}}^3$.

Table 6: The lowest excitation energy of the PNA-in-water system, calculated with MLCC2-in-HF and MLCC2-in-MLHF using the frozen core approximation. The aug-cc-pVDZ basis is used on the atoms that are included in the MLCC calculation and cc-pVDZ is used on the remaining atoms. The memory requirement to hold the Cholesky vectors obtained from the MO-screened decomposition is, for these calculations, proportional to $N_{\text{MO}}^3$.

| Ref. | $r_{\text{HF}}$ [Å] | $N_{\text{MO}}$ | $N_{\text{AO}}$ | $r$ [Å] | $N_o$ | $N_v$ | $r$ [Å] | $N_o$ | $N_v$ | $\omega$ [eV] |
|------|-----------------|--------------|-------------|--------|------|------|--------|------|------|---------|
| HF   | 15.0            | 1498         | 12669       | 6.0    | 186  | 938  | 3.5    | 88   | 286  | 3.821   |
| HF   | 15.0            | 1844         | 12795       | 6.5    | 243  | 1228 | 3.5    | 88   | 285  | 3.827   |
| HF   | 15.0            | 1498         | 12669       | 6.0    | 162  | 855  | 4.0    | 112  | 369  | 3.802   |
| HF   | 15.0            | 1498         | 12669       | 6.0    | 129  | 704  | 4.5    | 145  | 520  | 3.788   |
| MLHF | 10.0            | 1498         | 12669       | 6.0    | 184  | 941  | 3.5    | 88   | 285  | 3.832   |

Table 7: The lowest excitation energy ($\omega$) of the PNA-in-water system, calculated with MLCC2-in-HF, MLCC2-in-MLHF, MLCCSD-in-HF, and MLCCSD-in-MLHF using the frozen core approximation. The atoms within a radius of 6 Å are included in the MLCC calculation and the atoms within a radius of 3.5 Å are treated with the higher level coupled cluster method (CC2 or CCSD). In the MLHF reference calculation, the atoms within a radius of 10 Å are active. The aug-cc-pVDZ basis is used on the atoms that are included in the MLCC calculation, and cc-pVDZ is used on the remaining atoms. There are 12669 AOs and 1498 MOs. The wall times for the reference calculation ($t_{\text{Ref}}$) and the MLCC calculation ($t_{\text{MLCC}}$) are also given. The calculations were performed on two Intel Xeon Gold 6152 processors using 1.4 TB memory and 44 threads.

| Reference | $t_{\text{Ref}}$ [h] | $\omega$ [eV] | $t_{\text{MLCC}}$ [h] | $\omega$ [eV] | $t_{\text{MLCC}}$ [h] |
|-----------|-----------------|--------------|-----------------|--------------|-----------------|
| HF        | 41.9            | 3.821        | 18.9            | 4.075        | 27.4            |
| MLHF      | 36.5            | 3.832        | 18.6            | 4.083        | 27.1            |

We have also performed MLCC calculations on the PNA-water system in Figure 6 with larger basis sets and different active spaces. The MO-screening is used in the Cholesky
decomposition of the electron repulsion integrals and the decomposition threshold is $10^{-4}$. The aug-cc-pVDZ basis is used on the atoms that are included in the MLCC calculation and cc-pVDZ is used on the remaining atoms. Cholesky/PAOs are used to partition the orbital space, and active regions of the molecule are defined by placing a sphere around the PNA and selecting all atoms within that sphere as active. The lowest MLCC2-in-HF/MLHF excitation energy of the PNA-water system, for different active spaces, is given in Table 6. The excitation energy does not change significantly ($\sim 0.01\text{ eV}$) if we use the MLHF reference ($r_{\text{HF}} = 10\text{ Å}$) rather than the HF reference. It is also not sensitive to an increase in the CCS radius from 6.0 Å to 6.5 Å. Although this change entails a significant increase in the number of MOs treated at the MLCC level, the excitation energy increases by less than 0.01 eV. The excitation energy is more sensitive to an increase in $r_{\text{CC}2}$. The excitation energy decreases by about 0.03 eV as $r_{\text{CC}2}$ increases from 3.5 Å to 4.5 Å. However, the full CC2-in-HF calculation with $r_{\text{CC}2} = 6\text{ Å}$, the excitation energy is 3.732 eV and therefore all the MLCC2-in-HF calculations are within 0.1 eV of the CC2-in-HF calculation with a coupled cluster region determined by a sphere with a 6 Å radius, centered on PNA.

In Table 7, we present timings for MLCC2-in-HF/MLHF and MLCCSD-in-HF/MLHF calculations with $r_{\text{CC}S} = 6.0\text{ Å}$ and $r_{\text{CC}2/\text{CCSD}} = 3.5\text{ Å}$. Comparing Tables 5 and 7 we see that the MLCCSD-in-HF excitation energies do not change significantly with a larger basis and an increased $r_{\text{CC}S}$. For the calculations presented in Table 7 the reference calculations are more expensive than the MLCC calculations. Since the active region of the MLHF calculation is large (10.0 Å), we do not obtain large savings using an MLHF reference. However, this can be achieved by reducing $r_{\text{HF}}$. Furthermore, MLHF is applicable for systems where standard Hartree-Fock is not computationally feasible.

Solvation effects can be estimated by performing calculations on a series of snapshots from a molecular mechanics simulation, for instance using the QM/MM approach for the individual snapshots. The calculations in this paper demonstrate that the MLCC-in-HF framework can be used to determine such solvation effects with a fully quantum mechanical
approach.

Concluding remarks

In this paper, we have demonstrated the computational savings that can be obtained with MLCC2 and CCS/CCSD MLCCSD. These multilevel methods can be used for systems that are too large to describe at the CC2 and CCSD level. However, the methods are limited by the underlying scaling of the lower level coupled cluster method (CCS). We have therefore presented a framework of reduced space MLCC that can be used for systems with several thousand AOs. In this framework, MLCC is only applied to a restricted region of the molecular system; the environment is optimized with Hartree-Fock, or multilevel Hartree-Fock, and only contributes to the MLCC calculation through the Fock matrix. Efficient implementation of this framework requires careful handling of the electron repulsion integrals. We have implemented a direct construction of MO Cholesky vectors that reduces the storage requirement to $O(N_{AO}N_{MO}^2)$. With an additional screening during the Cholesky decomposition algorithm, we further reduce this requirement to $O(N_{MO}^3)$. Exploiting the Cholesky factorization in this manner, we can handle systems with several thousand basis functions using existing MLCC implementations. The MLCC-in-HF framework is therefore suited to accurately model solvation effects on intensive properties on the solute. It can also be used for chromophores in biomolecules.

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