

Size-intensive decomposition of orbital energy denominators

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We introduce an alternative to Almlöf and Häser's Laplace transform decomposition of orbital energy denominators used in obtaining reduced scaling algorithms in perturbation theory based methods. The new decomposition is based on the Cholesky decomposition of positive semidefinite matrices. We show that orbital denominators have a particular short and size-intensive Cholesky decomposition. The main advantage in using the Cholesky decomposition, besides the shorter expansion, is the systematic improvement of the results without the penalties encountered in the Laplace transform decomposition when changing the number of integration points in order to control the convergence. Applications will focus on the coupled-cluster singles and doubles model including connected triples corrections [CCSD(T)], and several numerical examples are discussed. © 2000 American Institute of Physics. [S0021-9606(00)30713-9]

I. INTRODUCTION

The aim of reducing the computational scaling of modern electronic structure models is of great importance in quantum chemistry. The unphysical N^7 scaling of the coupled-cluster singles and doubles model including connected triple excitations [CCSD(T)], where N is the number of orbitals, severely restricts the size of molecular systems that can be studied. Although we know that all models should eventually scale linearly with the size of the molecular system, our inappropriate formulation of the algebraic and computational expressions makes it difficult to exploit this inherent sparsity.

Important advances in linear scaling have already been made in several areas. For wave function-based methods like the second-order Møller–Plesset perturbation theory (MP2) one obstacle is the orbital denominator that connects products of two-electron integrals. In 1991 Almlöf and Häser^{1,2} suggested to use the Laplace transform to decompose orbital denominators, i.e.,

$$\frac{1}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} = \int_0^\infty \exp(-(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t) dt, \quad (1)$$

and recently this concept has been used in an implementation of linear scaling MP2.³ Häser and Almlöf also made another important observation in this connection. Once the orbital denominator is decomposed the algebraic expression for fourth-order Møller–Plesset perturbation theory (MP4) may be rearranged to obtain an N^6 algorithm. However, the N^6 computational step must be repeated for each integration point used in the numerical integration of the Laplace transformation.

The use of the Laplace transform decomposition is not without complications as the numerical integration must be performed at some point in the calculation and the number of integration points and accuracy will be very critical in determining the crossover point between the conventional and the

Laplace based approach. As we shall see in this article it may require more than 50 integration points in the Gauss–Legendre integration procedure in order to obtain machine precision in all elements of the orbital denominator. Instead we propose to use a Cholesky decomposition of the energy denominators entering the expressions in higher-order perturbation theory-based models. The Cholesky decomposition requires a much smaller number of vectors in order to give the same accuracy and as Wilkinson⁴ has shown, it is exceedingly numerically stable. In addition, as we show later in this article, the Cholesky decomposition also allows for the implementation of an N^6 algorithm for CCSD(T) and related models.

The idea of using the Cholesky decomposition to obtain reduced scaling in electronic structure calculations is by no means new. In 1977, Beebe and Linderberg⁵ introduced the Cholesky decomposition of the two-electron integral matrix in order to reduce the computational effort in the transformation of two-electron integrals from the atomic orbital (AO) basis to the molecular orbital (MO) basis. Due to the computational limitations at that time, the authors could not completely exploit the large reductions attainable. In this article we focus on orbital energy denominators, although some of the conclusions also apply to the two-electron integral matrix. We defer this analysis to a future publication.

This article has been organized as follows. In Sec. II we describe the second- and third-rank decompositions. In Sec. III we discuss the Cholesky CCSD(T) model, and numerical examples are presented in Sec. IV. Our final remarks are given in the last section.

II. RANK DECOMPOSITIONS

Consider an orbital denominator of the form

$$D_{pq} = \frac{1}{\omega_p + \omega_q}, \quad (2)$$

where we assume that $\{\omega_p|p=1,N\}$ are positive real numbers. In the following, indices p, q, r denote compound orbital indices. The \mathbf{D} matrix is positive semidefinite as is easily shown by analyzing the quadratic form

$$\sum_{pq} x_p \frac{1}{\omega_p + \omega_q} x_q = \int_0^\infty \left(\sum_p x_p \exp(-\omega_p t) \right)^2 dt \geq 0, \quad (3)$$

where \mathbf{x} is an arbitrary nonzero vector and we have used the Laplace transform to rewrite the quadratic form. The equal sign in the inequality in Eq. (3) occurs in the case of degenerate ω -values, otherwise the matrix is positive definite. The semidefiniteness gives no complications in practice as the Cholesky decomposition is terminated when all diagonal elements are smaller than a specified threshold $\delta > 0$. The remainder in a given step of the Cholesky decomposition is calculated recursively as

$$D_{pq}^n = D_{pq}^{n-1} - \frac{D_{pJ_n}^{n-1} D_{qJ_n}^{n-1}}{D_{J_n J_n}^{n-1}}, \quad (4)$$

where J_n denotes the particular row and column that is being removed in the n th step and $D_{ij}^0 = D_{ij}$. In order to proceed, we introduce the algebraic identity,

$$\begin{aligned} \frac{1}{\omega_p + \omega_q} - \frac{2\omega_J}{(\omega_p + \omega_J)(\omega_q + \omega_J)} \\ = \frac{1}{\omega_p + \omega_q} \left(\frac{\omega_p - \omega_J}{\omega_p + \omega_J} \right) \left(\frac{\omega_q - \omega_J}{\omega_q + \omega_J} \right), \end{aligned} \quad (5)$$

that will be used in deriving simple analytical expressions for the Cholesky vectors. The diagonal elements in the n th step are given by the expression

$$D_{pp}^n = \frac{1}{2\omega_p} \prod_{m=1}^{n-1} \left(\frac{\omega_p - \omega_{J_m}}{\omega_p + \omega_{J_m}} \right)^2. \quad (6)$$

Using this expression we may determine the order in which the Cholesky decomposition is performed without any ex-

PLICIT calculation of the associated Cholesky vectors. This follows from the fact that the largest element is located on the diagonal as the remainder is positive semidefinite. Given the order $\{J_n|n=1,N_\delta\}$ in which the Cholesky decomposition is to be performed, relevant parts of the Cholesky vectors may be calculated from the expression

$$M_p^n = \frac{\sqrt{2\omega_{J_n}}}{(\omega_p + \omega_{J_n})} \prod_{m=1}^{n-1} \left(\frac{\omega_p - \omega_{J_m}}{\omega_p + \omega_{J_m}} \right). \quad (7)$$

The decomposed matrix can now be written as

$$D_{pq} = \sum_{n=1}^{N_\delta} M_p^n M_q^n, \quad (8)$$

where N_δ denote the number of Cholesky vectors needed in order to make all diagonal elements of the residual matrix less than δ . Usually N_δ is referred to as the effective numerical rank of the matrix.⁵ From the expression for the diagonal in Eq. (6) we observe that the range of the ω -values rather than the number of values determines the number of Cholesky vectors needed in order to make all diagonal elements smaller than the threshold δ . The quadratic product dependence nicely explains the fast convergence of the decomposition, especially if the ω -values are close-lying. Furthermore, we also observe the size-intensive nature of the decomposition as an orbital denominator, for identical non-interacting subsystems can be decomposed with the same number of Cholesky vectors as required for one subsystem.

We now consider the third-rank orbital denominator

$$T_{pqr} = \frac{1}{\omega_p + \omega_q + \omega_r}, \quad (9)$$

and we readily observe that when fixing one index, the remaining two indices define a positive semidefinite matrix. To the best of our knowledge, the problem of decomposing higher-rank tensors in a Cholesky manner does not seem to have been solved in the mathematical literature. Based on the following algebraic identity,

$$\begin{aligned} \frac{1}{\omega_p + \omega_q + \omega_r} - \frac{(\omega_p + 2\omega_J)(\omega_q + 2\omega_J)(\omega_r + 2\omega_J)}{3\omega_J(\omega_p + \omega_q + \omega_J)(\omega_p + \omega_r + \omega_J)(\omega_q + \omega_r + \omega_J)} \\ + \frac{(\omega_p - \omega_J)(\omega_q - \omega_J)(\omega_r - \omega_J)}{3\omega_J(\omega_p + \omega_q + \omega_J)(\omega_p + \omega_r + \omega_J)(\omega_q + \omega_r + \omega_J)} \\ = - \frac{(\omega_p - \omega_J)(\omega_q - \omega_J)(\omega_r - \omega_J)}{(\omega_p + \omega_q + \omega_r)(\omega_p + \omega_q + \omega_J)(\omega_p + \omega_r + \omega_J)(\omega_q + \omega_r + \omega_J)}, \end{aligned} \quad (10)$$

we suggest the following third-rank decomposition:

$$T_{pqr} = \sum_{n=1}^{N_\delta} (-1)^{n-1} \{M_{pq}^n M_{pr}^n M_{qr}^n - N_{pq}^n N_{pr}^n N_{qr}^n\}, \quad (11)$$

where the \mathbf{M} and \mathbf{N} matrices are defined by successive application of Eq. (10). These matrices can, if needed, be further decomposed using the Cholesky decomposition. The numerical rank in Eq. (11) is much smaller than for the second-rank decomposition in Eq. (8) as the diagonal elements of the residual matrix now have a cubic product dependence. It is

evident that in order to obtain an N^6 scaling in the CCSD(T) model, two of the \mathbf{M} and \mathbf{N} matrices should be further decomposed. However, even though the smaller numerical rank of the decompositions, the total number of vectors may easily become larger than that of a second-rank decomposition. Nevertheless, we speculate that using the permutational symmetry of the ω -indices, an N^6 algorithm may be achieved by just decomposing one of the \mathbf{M} and \mathbf{N} matrices. The third-rank decomposition may also become useful in higher orders of perturbation theory or if the two-electron integrals are decomposed in the expression of the CCSD(T) energy. Any-

way, we shall see in the next section how to obtain an N^6 algorithm in CCSD(T) using the second-rank decomposition.

III. CHOLESKY CCSD(T)

The connected triple excitation amplitudes that enter the expression for the CCSD(T) energy is given by⁶

$$t_{ijk}^{abc} = -P_{ijk}^{abc} \left\{ \frac{\sum_d t_{ij}^{ad}(ck|bd)}{(\epsilon_a - \epsilon_i - \epsilon_j) + (\epsilon_c - \epsilon_k + \epsilon_b)} - \frac{\sum_l t_{il}^{ab}(ck|lj)}{(\epsilon_a - \epsilon_i + \epsilon_b) + (\epsilon_c - \epsilon_k - \epsilon_j)} \right\}, \quad (12)$$

where t_{ij}^{ab} denotes the coupled-cluster singles and doubles (CCSD) amplitudes and we have arranged the orbital energies to indicate the way we will decompose the denominators. The denominator is not symmetric as partitioned in Eq. (12) and thus we cannot use the second-rank decomposition directly. However, by defining the ω -values as elements of the vector

$$\omega_p = \begin{pmatrix} \epsilon_a & -\epsilon_i & -\epsilon_j \\ \epsilon_a & -\epsilon_i & +\epsilon_b \end{pmatrix}_p, \quad (13)$$

we may decompose the denominator as

$$\frac{1}{(\epsilon_a - \epsilon_i - \epsilon_j) + (\epsilon_c - \epsilon_k + \epsilon_b)} = \sum_{n=1}^{N_\delta} M_{aij}^n M_{ckb}^n, \quad (14)$$

where the Cholesky vectors should now be calculated from the decomposition determined by the ω -values defined in Eq. (13). Consequently, only the nondiagonal part of the decomposition is used and as the residual matrix is positive-semidefinite, the errors in the nondiagonal elements will be smaller than in diagonal elements. Inserting the expression for the decomposition in Eq. (14) into Eq. (12) we may write the triples amplitudes as

$$t_{ijk}^{abc} = -P_{ijk}^{abc} \sum_{n=1}^{N_\delta} \left\{ \sum_d V_{aijd}^n Z_{ckbd}^n - \sum_l W_{aibl}^n Y_{ckjl}^n \right\}, \quad (15)$$

where the \mathbf{V} , \mathbf{Z} , \mathbf{W} , and \mathbf{Y} matrices are implicitly defined. Using this decomposed form of the triple excitation amplitudes in the expression for the CCSD(T) energy, we obtain an algorithm that scales as $N_\delta N^6$. We shall denote this method in brief as Cholesky CCSD(T) and the Laplace transform counterpart as Laplace CCSD(T). In principle, the basic idea² behind Cholesky CCSD(T) is to contract one Cholesky vector from the decomposition with the corresponding integral(s) before the summations over the d and l indices in Eq. (12) are carried out. The detailed discussion and implementation of this algorithm will be described elsewhere.

For iterative perturbation theory based connected triple excitation models, such as the CC3 model,⁶ similar reductions may also be obtained. Large scale applications of these models are virtually impossible due to the computational cost. However, if the scaling is reduced to the N^6 level, then the CC3 model might actually be used for more than just benchmark calculations.

TABLE I. Largest absolute error in the elements of the CCSD(T) orbital denominator using Cholesky and Laplace transform decompositions for different number of vectors (integration points).

Vectors	Ozone		Mg ₂	
	Cholesky ^a	Laplace ^b	Cholesky ^c	Laplace
5	6.5 × 10 ⁻⁴	1.0 × 10 ⁻²	1.3 × 10 ⁻³	2.5 × 10 ⁻²
10	9.1 × 10 ⁻⁷	1.7 × 10 ⁻³	6.1 × 10 ⁻⁶	2.7 × 10 ⁻³
15	1.5 × 10 ⁻⁹	5.2 × 10 ⁻⁵	3.9 × 10 ⁻⁸	1.1 × 10 ⁻³
20	1.1 × 10 ⁻¹²	2.2 × 10 ⁻⁶	2.2 × 10 ⁻¹¹	2.1 × 10 ⁻⁴
25		3.5 × 10 ⁻⁸	2.0 × 10 ⁻¹³	2.3 × 10 ⁻⁵
30		1.0 × 10 ⁻¹⁰		1.3 × 10 ⁻⁶
35		1.6 × 10 ⁻¹¹		3.9 × 10 ⁻⁸
40		5.3 × 10 ⁻¹³		6.3 × 10 ⁻¹⁰
45		7.6 × 10 ⁻¹⁴		4.7 × 10 ⁻¹¹
50				5.1 × 10 ⁻¹²

^aThe absolute errors for 25 vectors and beyond are less than machine precision.

^bThe absolute errors for 50 points and beyond are less than machine precision.

^cThe absolute errors for 30 vectors and beyond are less than machine precision.

IV. NUMERICAL EXAMPLES

In order to compare the Cholesky decomposition and the Laplace transform decomposition we make a simple variable substitution in the Laplace transform integral and write the denominator as

$$\frac{1}{\omega_p + \omega_q} = \int_0^1 \exp\left(-(\omega_p + \omega_q) \frac{s}{1-s}\right) \frac{1}{(1-s)^2} ds. \quad (16)$$

The numerical integration will be carried out using standard Gauss–Legendre quadrature integration.⁷ This integration procedure might not be the optimal. Indeed, Häser and Almlöf² have suggested a least-squares quadrature-type integration procedure in order to choose the best possible integration points for a given set of orbital energies. However, we have found standard Gauss–Legendre quadrature integration to be very accurate and thus we believe the comparisons are reasonable. In the following, we have decomposed all the possible denominators and not only the totally symmetric part.

In Table I we compare the Cholesky and the Laplace decompositions of the orbital energy denominator appearing in the CCSD(T) correction energy. We have chosen ozone as one of the test systems due the rather large triples contribution to the total energy. All calculations are carried out at the experimental geometry and we have used the cc-pVQZ basis set from Dunning's group.⁸ As large ranges of orbital energies are the most difficult cases for both methods, we have chosen to test both methods for a molecular system showing these characteristics. In particular, we have studied the residual errors in Mg₂ at the experimental geometry using an aug-cc-pCVTZ basis extended with a set of midbond functions.⁹ The core orbitals are frozen in the ozone calculations, but all electrons are included for Mg₂. We first observe that even for Mg₂ we have a maximum error of the order 10⁻³ using only five Cholesky vectors. Similarly, an accuracy to six decimal digits may be accomplished with about ten vectors. This should be compared to the 20 and 30 inte-

TABLE II. The maximum diagonal element in the residual matrix for the Cholesky decomposition of the CCSD(T) orbital denominator.^a

n	H ₂ O	(H ₂ O) ₅	(H ₂ O) ₁₀	(H ₂ O) ₁₅	C ₆ H ₆ -Ar
1	4.5×10 ⁻²	2.0×10 ⁻¹	2.6×10 ⁻¹	5.9×10 ⁻¹	1.1×10 ⁻¹
2	8.8×10 ⁻³	3.9×10 ⁻²	5.1×10 ⁻²	1.1×10 ⁻¹	2.2×10 ⁻²
3	2.7×10 ⁻³	1.2×10 ⁻²	1.5×10 ⁻²	2.2×10 ⁻²	6.7×10 ⁻³
4	7.1×10 ⁻⁴	7.1×10 ⁻³	9.2×10 ⁻³	2.0×10 ⁻²	4.0×10 ⁻³
5	1.4×10 ⁻⁴	1.1×10 ⁻³	1.5×10 ⁻³	4.0×10 ⁻³	7.9×10 ⁻⁴
6	1.5×10 ⁻⁵	3.7×10 ⁻⁴	8.9×10 ⁻⁴	2.4×10 ⁻³	6.2×10 ⁻⁴
7	1.3×10 ⁻⁶	1.1×10 ⁻⁴	2.0×10 ⁻⁴	6.1×10 ⁻⁴	1.2×10 ⁻⁴
8	7.9×10 ⁻⁷	9.0×10 ⁻⁵	5.4×10 ⁻⁵	1.4×10 ⁻⁴	4.2×10 ⁻⁵
9	2.3×10 ⁻⁸	5.0×10 ⁻⁶	3.4×10 ⁻⁶	2.4×10 ⁻⁵	2.7×10 ⁻⁵
10	5.7×10 ⁻⁹	1.4×10 ⁻⁶	2.2×10 ⁻⁶	3.6×10 ⁻⁶	3.8×10 ⁻⁶
11	2.1×10 ⁻⁹	4.5×10 ⁻⁷	9.5×10 ⁻⁷	1.6×10 ⁻⁶	9.9×10 ⁻⁷
12	9.3×10 ⁻¹¹	7.4×10 ⁻⁸	4.0×10 ⁻⁷	1.6×10 ⁻⁶	3.2×10 ⁻⁷
13		1.8×10 ⁻⁸	7.7×10 ⁻⁸	1.9×10 ⁻⁷	1.2×10 ⁻⁷
14		7.4×10 ⁻⁹	1.1×10 ⁻⁸	5.1×10 ⁻⁸	4.3×10 ⁻⁸
15		2.7×10 ⁻⁹	2.6×10 ⁻⁹	1.5×10 ⁻⁸	7.9×10 ⁻⁹
16		6.1×10 ⁻¹¹	5.7×10 ⁻¹⁰	1.7×10 ⁻⁹	4.9×10 ⁻⁹
17			2.4×10 ⁻¹¹	1.1×10 ⁻⁹	2.9×10 ⁻⁹
18				6.5×10 ⁻¹¹	2.0×10 ⁻¹⁰
19					1.6×10 ⁻¹⁰
20					1.2×10 ⁻¹¹

^aAll-electron calculations.

gration points required by the Laplace transform for ozone and Mg₂, respectively. The most important feature to be stressed is the slow convergence of the Laplace transform decomposition compared to the Cholesky. As a consequence, more than 50 integration points are required in order to obtain machine precision for Mg₂.

We analyze the behavior of Cholesky CCSD(T) with respect to molecular size and report the results for different systems in Table II. The linear water cluster calculations are carried out using a 3-21G basis set¹⁰ and constructed by repeating a basic unit consisting of a single water molecule at the experimental geometry with a 2 a.u. separation between adjacent oxygen atoms. For the benzene-argon complex we use an aug-cc-pVTZ basis set extended with midbond functions.⁹ The first point to note is that beyond a certain size the number of Cholesky vectors required to get a predefined accuracy is essentially constant. For the cluster of five molecules (with 975 single excitation energies) 10⁻³ accuracy may be accomplished with six vectors, the same number required in the ten molecules case (with dimension 3850). Only one additional vector is needed for (H₂O)₁₅ with 8550 single excitation energies. The largest considered system is the benzene-argon complex (dimension 14 130) and requires five vectors to get a maximum difference in the diagonal elements of 7.9×10⁻⁴. We recall as discussed above, a larger accuracy is obtained in the nondiagonal elements of the decomposed matrix. Similarly, the number of vectors needed for a 10⁻⁶ precision varies from 11 [benzene-argon and (H₂O)₅] to 13 in the case of (H₂O)₁₀.

The effect of increasing the basis set size in the connected triples correction to the CCSD energy is examined in Table III. We present in this table the triples correction for a single water molecule using correlation-consistent basis sets. We start by mentioning that the convergence of energy is much faster than of the individual elements of the denomi-

TABLE III. The CCSD(T) triples correction (E_h) in H₂O for different number of Cholesky vectors and correlation consistent basis sets.^a

Cholesky vectors	cc-pVTZ	cc-pVQZ	cc-pV5Z
1	-0.004 936 09	-0.005 661 02	-0.005 782 95
2	-0.007 847 95	-0.009 270 56	-0.009 811 94
3	-0.007 867 99	-0.009 373 03	-0.009 993 90
4	-0.007 863 54	-0.009 377 86	-0.010 002 24
5	-0.007 864 73	-0.009 380 35	-0.010 006 73
6	-0.007 865 54	-0.009 381 61	-0.010 008 39
7	-0.007 865 61	-0.009 381 68	-0.010 008 50
8	-0.007 865 63	-0.009 381 70	-0.010 008 54
9	-0.007 865 63	-0.009 381 70	-0.010 008 57
10	-0.007 865 63	-0.009 381 70	-0.010 008 58
Exact	-0.007 865 63	-0.009 381 70	-0.010 008 58

^aAll-electron calculations.

nator matrix. In fact, millihartree accuracy can be obtained with only two vectors in the three cases considered and six vectors are enough for microhartree accuracy. In addition, the obtained accuracy with a given number of vectors is approximately the same, independently of the considered basis. We should recall that in most of the studied cases we approach to the exact CCSD(T) correction from above. Nevertheless, in the cc-pVTZ basis set calculation the CCSD(T) correction is overestimated with three vectors and the usual trend is recovered only when the fifth vector is included.

Unlike the iterative triples corrected models, in CCSD(T) the accuracy of the orbital energy denominators may be disregarded, as long as the final energy correction is accurate enough. Therefore, in Table IV we present a comparison of the convergence of Cholesky and Laplace CCSD(T) correction energy for ozone. As stated before we usually approach the exact CCSD(T) correction from above and this is also the case for the two Cholesky CCSD(T) calculations presented here. Unfortunately, the convergence is not uniformly decreasing (cf. the correction for cc-pVQZ basis when four vectors have been included) and this makes it difficult to establish an extrapolation procedure. Anyway, millihartree accuracy is obtained with only three vectors and microhartree accuracy requires no more than six vectors. On the other hand, it seems that this system is a difficult case for the Laplace transform decomposition. Actually, even with

TABLE IV. The CCSD(T) triples correction (E_h) in ozone using Cholesky and Laplace decompositions and correlation consistent basis sets.

Vectors	Cholesky cc-pVTZ	Laplace cc-pVTZ	Cholesky cc-pVQZ	Laplace cc-pVQZ
1	-0.024 088 79	-0.009 903 40	-0.025 521 67	-0.010 181 77
2	-0.045 415 72	-0.036 888 62	-0.048 908 70	-0.038 336 39
3	-0.047 067 59	-0.045 485 94	-0.051 079 89	-0.047 377 95
4	-0.047 095 00	-0.046 983 16	-0.051 106 11	-0.050 128 31
5	-0.047 101 33	-0.047 121 01	-0.051 093 53	-0.050 919 30
6	-0.047 116 89	-0.047 118 49	-0.051 107 46	-0.051 062 50
7	-0.047 116 96	-0.047 115 97	-0.051 107 56	-0.051 092 03
8	-0.047 116 98	-0.047 116 96	-0.051 107 58	-0.051 102 61
9	-0.047 117 00	-0.047 117 14	-0.051 107 67	-0.051 106 21
10	-0.047 117 00	-0.047 117 00	-0.051 107 69	-0.051 107 20
Exact	-0.047 117 00	-0.047 117 00	-0.051 107 69	-0.051 107 69

TABLE V. The CCSD(T) triples correction (E_h) for Mg_2 using Cholesky and Laplace decompositions and an aug-cc-pCVTZ basis set extended with midbond functions.

Vectors	Cholesky	Laplace
1	-0.002 543 67	-0.001 649 68
2	-0.005 452 62	-0.003 234 80
3	-0.007 857 15	-0.005 167 52
4	-0.007 922 71	-0.006 423 92
5	-0.008 381 41	-0.007 275 92
6	-0.008 384 81	-0.007 789 78
7	-0.008 387 48	-0.008 064 18
8	-0.008 388 36	-0.008 206 39
9	-0.008 388 36	-0.008 283 05
10	-0.008 388 77	-0.008 326 79
Exact	-0.008 388 77	-0.008 388 77

ten integration points only a precision of 4.9×10^{-7} is achieved, while four and five vectors are needed for millihartree accuracy for the triple and quadruple-zeta basis sets, respectively. Moreover, the exact triples contribution to energy is overestimated for the cc-pVTZ basis with five or six points in the Gauss–Legendre quadrature integration.

To complete the study initiated in Table I, we have also studied the convergence of the approximated triples contribution to the exact contribution in Mg_2 . Surely, CCSD(T) is not well suited for Mg_2 , but we must remember that we are really interested in the ability of the approximate method to give the exact result, irrespective of the quality of the exact value. The results are presented in Table V and show that this is indeed an extremely difficult case. Actually, the full 10^{-8} accuracy can only be obtained by Cholesky CCSD(T) using ten vectors in the expansion of the orbital energy denominators, even though millihartree accuracy was reached with only three vectors. This last number should be compared to the six integration points required in Laplace CCSD(T), which furthermore cannot reach microhartree accuracy with ten integration points. On the other hand, both methods show a satisfactory uniform convergence behavior.

We have finally studied the dissociation energy in Ar_2 as this property is very sensitive to the errors in the computed total energies. In fact, the exact counterpoise corrected CCSD(T) value is only 99.75 cm^{-1} in this aug-pVTZ basis extended with midbond functions.⁹ In Table VI the Cholesky CCSD(T) results are reported and the corresponding ones for Laplace CCSD(T) are given in Table VII. As the dissociation energy is calculated as the difference between the total energy of the van der Waals complex at equilibrium distance and the counterpoise corrected total energy of the atom, a uniform behavior of the calculated dissociation energies should not be expected. This is confirmed by inspection of the results in the tables. The complications arising from the extreme high accuracy required clearly emerge, taking into account the number of vectors or integration points necessary to achieve the exact result. Indeed, at least seven Cholesky vectors should enter the expansion to recover the exact CCSD(T) dissociation energy. One could argue that the Laplace CCSD(T) behaves better than the Cholesky approach in this case, since with only four integration points,

TABLE VI. Cholesky CCSD(T) counterpoise corrected dissociation energy of Ar_2 and triples corrections to total energies.

Cholesky vectors	D_e/cm^{-1}	E_{Ar_2}/E_h	E_{Ar}^c/E_h
1	201.81	-0.011 286 40	-0.005 350 25
2	103.38	-0.016 198 54	-0.008 030 56
3	97.97	-0.016 386 70	-0.008 136 96
4	99.61	-0.016 378 01	-0.008 128 89
5	99.63	-0.016 378 54	-0.008 129 10
6	99.44	-0.016 377 69	-0.008 129 10
7	99.75	-0.016 377 69	-0.008 128 40
8	99.75	-0.016 377 68	-0.008 128 40
9	99.75	-0.016 377 69	-0.008 128 39
10	99.75	-0.016 377 68	-0.008 128 39
Exact	99.75	-0.016 377 68	-0.008 128 39

the error of the approximated dissociation energy is no more than 0.03 cm^{-1} . As a matter of fact, it is also clear by inspection of the last two columns in Table VII that this extremely good result is obtained due to a favorable cancellation of errors. Actually, to reach an accuracy of 1 cm^{-1} requires roughly microhartree accuracy in the absolute energies, an accuracy that Laplace CCSD(T) cannot deliver with ten integration points. On the other hand, Cholesky CCSD(T) gives microhartree accuracy in both terms with seven vectors. To conclude, we would like to mention that for this particular case the Gauss–Legendre quadrature integration may give better results than the least-squares fitting procedure proposed by Häser and Almlöf. In fact, we treat the complex and the counterpoise corrected atom on an equal footing, as neither the selected abscissas, nor the weights depend on the actual values of orbital energies. This would not be the case if different least-squares fittings were used.

V. SUMMARY AND CONCLUSION

We have convincingly shown that the orbital energy denominators entering the expressions for perturbation theory based triple excitation methods can be efficiently Cholesky decomposed. The simple analytical expression in Eq. (7) for the Cholesky vectors makes it possible to evaluate the relevant parts of the vectors whenever needed in a computational implementation. Thus no precalculation and storage of

TABLE VII. Laplace transform CCSD(T) counterpoise corrected dissociation energy of Ar_2 and triples corrections to total energies.

Integration points	D_e/cm^{-1}	E_{Ar_2}/E_h	E_{Ar}^c/E_h
1	79.66	-0.017 645 40	-0.008 676 08
2	100.36	-0.013 705 62	-0.006 791 03
3	99.35	-0.015 596 01	-0.007 738 47
4	99.78	-0.016 046 81	-0.007 962 90
5	99.75	-0.016 270 00	-0.008 074 55
6	99.76	-0.016 344 61	-0.008 111 85
7	99.76	-0.016 365 42	-0.008 122 25
8	99.75	-0.016 371 15	-0.008 125 12
9	99.75	-0.016 373 41	-0.008 126 26
10	99.75	-0.016 374 79	-0.008 126 94
Exact	99.75	-0.016 377 68	-0.008 128 39

vectors are needed and the order in which the decomposition should take place is easily determined using the expression for the diagonal elements in Eq. (6).

The large variety of applications presented demonstrates the robustness of the approach with respect to numerical stability and convergence. The Cholesky decomposition is significantly shorter than the Laplace transform decomposition and offers a systematic approach to increase the accuracy of the results without additional cost.

Having established this numerical tool, we are convinced that Cholesky CCSD(T) is worth implementing and will certainly make integral-direct CCSD(T) much more attractive to computational chemists. The potential for making additional reductions in the computational scaling of Cholesky CCSD(T) is clearly possible using an integral prescreening approach.

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- ¹J. Almlöf, *Chem. Phys. Lett.* **181**, 319 (1991).
- ²M. Häser and J. Almlöf, *J. Chem. Phys.* **96**, 489 (1992).
- ³P. Y. Ayala and G. Scuseria, *J. Chem. Phys.* **110**, 3660 (1999).
- ⁴J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Clarendon, Oxford, 1965).
- ⁵N. F. S. Beebe and J. Linderberg, *Int. J. Quantum Chem.* **12**, 683 (1977).
- ⁶H. Koch, O. Christiansen, P. Jørgensen, A. Sanchez de Meras, and T. Helgaker, *J. Chem. Phys.* **106**, 1808 (1997).
- ⁷*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1965).
- ⁸T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- ⁹H. Koch, B. Fernández, and J. Makarewicz, *J. Chem. Phys.* **111**, 198 (1999).
- ¹⁰J. S. Binkley, J. A. Pople, and W. Hehre, *J. Am. Chem. Soc.* **102**, 939 (1980).