Accuracy and Efficiency of Coupled-Cluster Theory Using Density Fitting/Cholesky Decomposition, Frozen Natural Orbitals, and a t_1-Transformed Hamiltonian

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Ⓢ *Supporting Information*

ABSTRACT: We present an algorithm for coupled-cluster through perturbative triples [CCSD(T)] based on a t_1-dressed Hamiltonian and the use of density fitting (DF) or Cholesky decomposition (CD) approximations for the construction and contraction of all electron repulsion integrals (ERIs). An efficient implementation of this algorithm is then used to explore whether preoptimized density fitting basis sets [specifically, the (aug-)cc-pVXZ-RI series designed for DF-MP2 computations] are suitable for DF-CCSD(T) computations and how they compare to the CD representation of the integrals. The code is also used to systematically explore the accuracy and efficiency of DF/CD

$$(pq|rs) \approx B_{pq}^Q B_{rs}^Q$$

$$E_{CCSD(T)}^{MO} \approx E_{CCSD(T)}^{NO} + \Delta E_{MP2}$$

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combined with frozen natural orbitals (FNOs) to reduce computational costs. The mean absolute errors due to DF/CD in the CCSD(T)/aug-cc-pVDZ interaction energies of 11 van der Waals dimers are only 0.001 kcal mol^{-1} for the preoptimized RI basis set and only 0.002 and 0.001 kcal mol^{-1} for CD with cutoffs of 10^{-4} and 10^{-5}, respectively. The very similar performance of the aug-cc-pVDZ-RI auxiliary set is a bit surprising considering that the numbers of CD vectors using these thresholds are, on average, 28% and 73% larger than the dimension of the RI set. When FNOs are coupled with DF/CD, the DF/CD error is roughly an order of magnitude less than the FNO truncation error (at a conservative FNO occupation cutoff of 10^{-5}). Utilizing t_1-dressed three-index integrals, which remove the explicit dependence of the doubles residual equations on the t_1-amplitudes, results in a moderate performance acceleration for the CCSD portion of the algorithm. Moreover, the t_1-dressing results in a simpler code which will be more amenable to parallelization. Utilizing both CD and FNO techniques, we observe a speedup of four times for the evaluation of the three-body contribution to the interaction energy for the benzene trimer described by an aug-cc-pVDZ basis set; the error incurred by the CD and FNO approximations in the three-body contribution is only 0.002 kcal mol^{-1}.
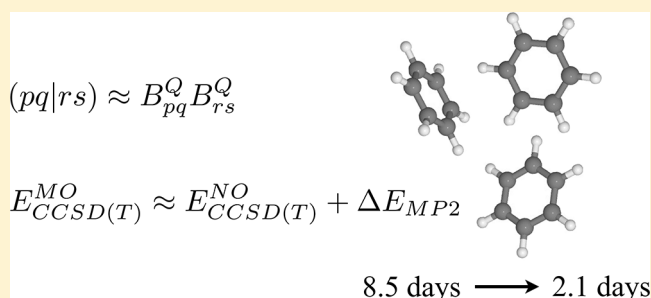
1. INTRODUCTION

Approximate tensor factorizations are becoming increasingly common in electronic structure theory as a means to both accelerate computations and eliminate the storage or generation of the four-index electron repulsion integral (ERI) tensor. The most well recognized of these integral approximations is known as density fitting (DF) or the resolution of the identity (RI).[1−8] The DF approach allows one to express the four-index ERI tensor as a contraction of three-index tensors. One first considers the ERI as an interaction between two generalized densities; these densities are then approximately represented by an auxiliary basis set that is optimized for a given level of theory [e.g., Hartree−Fock (HF)[6] or MP2[9,10]]. A similar approach involves the partial Cholesky decomposition (CD) of the ERI tensor.[11−14] Cholesky-decomposed integrals have the desirable property that the accuracy of the approximation can be controlled to arbitrary precision, and thus a method that uses CD integrals can be applied with some guarantee as to the accuracy of the final total energy. Additionally, recently introduced tensor hypercontraction (THC) density fitting[15−17] techniques express the ERI tensor as a contraction of five rank-2 tensors.

Density fitting techniques are popular and effective for self-consistent field approaches like Hartree−Fock and density functional theory (DFT),[4] second order perturbation theory (RI-MP2),[3] and symmetry adapted perturbation theory.[18−20] DF and related technologies are less common in coupled cluster (CC) theory,[22] although several examples have recently emerged.[5,22−25] Most studies have been limited to the CD approximation because, to date, no group has developed RI auxiliary basis sets specific to coupled-cluster methods. Boström et al.[25] used auxiliary basis sets derived from CD integrals within the CC with singles, doubles, and perturbative triples [CCSD-(T)][26] method to compute noncovalent interaction energies (IEs) for the 11 smallest members of the S22 set of van der Waals dimers.[27] CD decomposition thresholds of 10^{-4} were found to introduce errors in the IEs on the order of only a few thousandths of 1 kcal mol^{-1}. Their study provides some indication of the reliability of CD-CCSD(T), but the question remains as to the applicability of DF-CCSD(T) with existing DF

basis sets. To our knowledge, no studies have investigated the errors associated with the DF approximation in CCSD(T) for noncovalent interaction energies. The accuracy of the DF/CD approximation has been investigated for total energies at the HF/DFT/MP2 levels of theory[28] and for vertical excitation energies from complete active space self-consistent field (CASSCF) and peturbation theory (CASPT2) methods,[29] as well as in the context of equation-of-motion (EOM) CCSD.[30] We extend these works by assessing the quality of DF/CD CC methods for describing an expanded set of van der Waals dimers and for computing reaction energies.

Similar efforts to accelerate coupled cluster singles and doubles (CCSD)[31] computations decompose the CCSD (or related) amplitudes themselves. Kinoshita et al.[32] use singular value decomposition (SVD) of the amplitudes of third-order perturbation theory (MP3) to establish a compressed space in which subsequent coupled cluster computations can be performed. It has also been shown that, by using a "least-squares" (LS) THC density fitting in both the ERI tensor and the coupled cluster amplitudes, the CCSD method can be implemented on a computer with N^4 floating point operations,[17] where N represents the number of one electron basis functions in the primary basis set. Since this reduced-scaling method assumes the use of DF/CD techniques, it is at best an approximation to DF/CD-CCSD. We thus have an additional impetus to systematically assess the quality of this initial approximation.

In this paper, we present an algorithm for DF/CD-CCSD that uses t_1-dressed three-index integrals in the solution of the singles and doubles amplitude equations. The use of t_1-dressed Hamiltonians in coupled cluster theory is well-known,[33] but it is usually only of practical use in integral-direct CCSD algorithms. For CCSD algorithms that use precomputed ERIs, dressing the Hamiltonian necessitates a costly transformation of the four-index ERI tensor every iteration. By using three-index integrals, the N^5 transformation is replaced by a cheaper N^4 transformation. The algorithm presented herein only contains one term that depends on a tensor with more than two indices that are unoccupied (virtual) in the reference function. Further, the complexity of the resulting equations is comparable to that of the conventional coupled cluster doubles (CCD) equations. This simplicity will prove useful in future distributed parallel and GPU implementations DF/CD-CCSD(T).

We assess the accuracy of DF/CD-CCSD(T) by computing IEs for the S22 set in an aug-cc-pVDZ basis set and its 11 smallest members (the S11 set) in an aug-cc-pVTZ basis set. We provide numerical evidence that the aug-cc-pVXZ-RI auxiliary sets (also known as aug-cc-pVXZ-MP2FIT)[10] optimized for RI-MP2 can be used in place of CD vectors for the computation of noncovalent IEs. The errors incurred by the use of RI auxiliary sets or CD vectors are on the order of thousandths of 1 kcal mol^{-1}, which is negligible compared to errors associated with other standard approximations, such as basis set errors, errors in CCSD(T) itself, or errors due to the truncation of the virtual space based on MP2 natural orbitals[34−38] or the optimized virtual orbital space.[39−43] We also present the first systematic study of the use of DF or CD integral representations in CCSD(T) computations of reaction energies. An examination of 47 reaction energies indicates that DF/CD-CCSD(T) works very well in this context, with mean absolute errors on the order of a few thousandths of 1 kcal mol^{-1}. Again, the preoptimized RI-MP2 auxiliary basis sets provide accuracy comparable to that observed when using CD vectors.

2. THEORY

In coupled cluster theory, the electronic wave function is parametrized by an exponential excitation operator

$$|\Psi\rangle = e^{\hat{T}}|\Psi_0\rangle \tag{1}$$

where $|\Psi_0\rangle$ represents a single closed-shell restricted Hartree–Fock reference configuration. For the CCSD method,[31] the operator, $\hat{T}$, is restricted to contain only single and double excitations out of this reference function:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \tag{2}$$

The electronic energy and CCSD excitation amplitudes are determined via the projection of the Schrödinger equation on the space of the reference configuration and all singly and doubly substituted configurations:

$$E = \langle\Psi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle \tag{3}$$

$$R_i^a = \langle\Psi_i^a|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle = 0 \tag{4}$$

$$R_{ij}^{ab} = \langle\Psi_{ij}^{ab}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle = 0 \tag{5}$$

Throughout, indices i, j, k, and l (a, b, c, and d) represent orbitals that are occupied (virtual) in the reference function. Indices p, q, r, and s will denote general orbitals.

In the DF/CD approaches, the electron repulsion integrals are approximated as

$$(pq|rs) \approx \sum_Q B_{pq}^Q B_{rs}^Q \tag{6}$$

In the CD method, the factors B_{pq}^Q are determined directly from the Cholesky decomposition, and Q represents a Cholesky vector. In the DF approach, using a symmetric factorization as we do here, the factors are defined by

$$B_{pq}^Q = \sum_P (pq|P)[\mathbf{J}^{-1/2}]_{PQ} \tag{7}$$

where

$$(pq|P) = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, \phi_p(\mathbf{r}_1)\, \phi_q(\mathbf{r}_1)\frac{1}{r_{12}}\phi_P(\mathbf{r}_2) \tag{8}$$

and

$$J_{PQ} = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, \phi_P(\mathbf{r}_1)\frac{1}{r_{12}}\phi_Q(\mathbf{r}_2) \tag{9}$$

In DF, indices P and Q represent functions in the auxiliary, density fitting basis set.

Using such decompositions of the electron repulsion integrals (whether CD or DF), the doubles residual, R_{ij}^{ab}, in a spin-free formalism is given by[33]

$$R_{ij}^{ab} = \sum_Q B_{ai}^Q B_{bj}^Q + A_{ij}^{ab} + B_{ij}^{ab} + P_{ij}^{ab}\left(\frac{1}{2}C_{ij}^{ab} + C_{ji}^{ab} + D_{ij}^{ab} + E_{ij}^{ab} + G_{ij}^{ab}\right) \tag{10}$$

$$A_{ij}^{ab} = \sum_{cd} t_{ij}^{cd}\left(\sum_Q B_{ac}^Q B_{bd}^Q\right) \tag{11}$$

$$B_{ij}^{ab} = \sum_{kl} t_{kl}^{ab}\left[\left(\sum_Q B_{ki}^Q B_{lj}^Q\right) + \left(\sum_{cd} t_{ij}^{cd}\left[\sum_Q B_{kc}^Q B_{ld}^Q\right]\right)\right] \tag{12}$$

$$C_{ij}^{ab} = -\sum_{kc} t_{kj}^{bc}\left[\left(\sum_Q B_{ki}^Q B_{ac}^Q\right) - \frac{1}{2}\left(\sum_{ld} t_{li}^{ad}\left[\sum_Q B_{kd}^Q B_{lc}^Q\right]\right)\right] \tag{13}$$

$$D_{ij}^{ab} = \frac{1}{2} \sum_{kc} u_{jk}^{bc} (L_{aikc} + \frac{1}{2} [\sum_{ld} u_{il}^{ad} L_{ldkc}]) \tag{14}$$

$$E_{ij}^{ab} = \sum_{c} t_{ij}^{ac} [F_{bc} - (\sum_{kld} u_{kl}^{bd} [\sum_{Q} B_{ld}^{Q} B_{kc}^{Q}])] \tag{15}$$

$$G_{ij}^{ab} = -\sum_{k} t_{ik}^{ab} [F_{kj} - (\sum_{lcd} u_{lj}^{cd} [\sum_{Q} B_{kd}^{Q} B_{lc}^{Q}])] \tag{16}$$

$$L_{pqrs} = 2 \sum_{Q} B_{pq}^{Q} B_{rs}^{Q} - \sum_{Q} B_{ps}^{Q} B_{rq}^{Q} \tag{17}$$

$$u_{rs}^{pq} = 2t_{rs}^{pq} - t_{rs}^{qp} \tag{18}$$

The operator, P_{ij}^{ab}, is a permutation operator: $P_{ij}^{ab} C_{ij}^{ab} = C_{ij}^{ab} + C_{ji}^{ba}$. The quantity B_{ij}^{Q} above is a t_1-transformed three-index integral obtained using either RI or CD methodologies (see below for discussion of the t_1-transformation). F_{pq} denotes a Fock matrix element. Brackets and parentheses denote the order of operations for the efficient construction of intermediates. The singles residual, R_i^a, is given by

$$R_i^a = F_{ai} + A_i^a + B_i^a + C_i^a \tag{19}$$

$$A_i^a = \sum_{dQ} (\sum_{kc} u_{ki}^{cd} B_{kc}^{Q}) B_{ad}^{Q} \tag{20}$$

$$B_i^a = -\sum_{klc} u_{kl}^{ac} (\sum_{Q} B_{ki}^{Q} B_{lc}^{Q}) \tag{21}$$

$$C_i^a = \sum_{kc} F_{kc} u_{ik}^{ac} \tag{22}$$

Once the singles and doubles residuals are formed, the amplitudes can be updated according to

$$t_i^a = t_i^a + R_i^a / (F_{ii} - F_{aa}) \tag{23}$$

$$t_{ij}^{ab} = t_{ij}^{ab} + R_{ij}^{ab} / (F_{ii} + F_{jj} - F_{aa} - F_{bb}) \tag{24}$$

In the expressions for the singles and doubles residuals given above, singles do not explicilty arise because their effects have been folded into the Hamiltonian. The Fock matrix and t_1-dressed integrals are defined by

$$F_{rs} = h_{rs} + \sum_{i} (2 \sum_{Q} B_{rs}^{Q} B_{ii}^{Q} - \sum_{Q} B_{ri}^{Q} B_{is}^{Q}) \tag{25}$$

$$h_{rs} = \sum_{\mu} X_{\mu r} (\sum_{\nu} Y_{\nu s} \tilde{h}_{\mu\nu}) \tag{26}$$

$$B_{rs}^{Q} = \sum_{\mu} X_{\mu r} (\sum_{\nu} Y_{\nu s} \tilde{B}_{\mu\nu}^{Q}) \tag{27}$$

The tensor, $\tilde{B}_{\mu\nu}^{Q}$, represents the three-index integrals in the AO basis (the indices μ and ν correspond to AO basis functions), and the matrices **X** and **Y** are defined by modifying the AO/MO transformation matrix, **C**, by a matrix of current t_1 amplitudes:[33]

$$\mathbf{t}_1 = \begin{matrix} & \overset{o \quad v}{} \\ \begin{matrix} o \\ v \end{matrix} & \begin{pmatrix} 0 & 0 \\ t_i^a & 0 \end{pmatrix} \end{matrix} \tag{28}$$

$$\mathbf{X} = \mathbf{C}(1 - \mathbf{t}_1^{T}) \tag{29}$$

$$\mathbf{Y} = \mathbf{C}(1 + \mathbf{t}_1) \tag{30}$$

In the $\mathbf{t}_1$ matrix, only the lower-left block is nonzero, with ov elements. Here, o and v represent the number of orbitals that are occupied and virtual in the reference function, respectively. Note that by dressing the integrals with t_1, we have destroyed some permutational symmetry: $B_{rs}^{Q} \neq B_{sr}^{Q}$, $h_{rs} \neq h_{sr}$, and $F_{rs} \neq F_{sr}$.

In order to build the four-virtual-index integrals required by the term A_{ij}^{ab}, one must evaluate a contraction involving $v^4 N_{aux}$ floating point operations, where N_{aux} denotes the number of auxiliary basis functions in the DF approach or the number of Cholesky vectors in the CD approach. As N_{aux} is typically a large number (often 2−4 times the number of functions in the primary basis set) and v is often a large fraction of the number of primary basis functions (especially for larger basis sets), the cost of this term can contribute significantly to the total wall time for a DF/CD-CCSD computation. This floating point cost is unique to the DF/CD algorithm; in a conventional CCSD algorithm, the four-virtual-index integral tensor, $(ac|bd)$, may be stored on disk. By using DF/CD techniques, we are electing to introduce a large number of floating-point operations in order to eliminate the on-disk storage of the $(ac|bd)$ tensor and the associated I/O costs. The DF/CD approach is desirable because the extra work to construct the tensor on the fly is parallelizable, while the I/O associated with the conventional algorithm is inherently serial. Nonetheless, in designing a robust DF/CD-CCSD algorithm, we have considered several strategies to reduce the cost of evaluating A_{ij}^{ab}.

An efficient DF/CD-CCSD algorithm should utilize the packed symmetric and antisymmetric four-virtual-index tensors described in ref 44. Fortunately, the destruction of permutational symmetry incurred by dressing the three-index integrals with t_1 does not preclude the use of this algorithm:

$$A_{ij}^{ab} = {}^{(S)}A_{ij}^{ab} + {}^{(A)}A_{ij}^{ab} \tag{31}$$

$${}^{(+)}t_{i \leq j}^{a \leq b} = t_{ij}^{ab} + t_{ij}^{ba}(1 - \delta_{ab}) \tag{32}$$

$${}^{(-)}t_{i \leq j}^{a \leq b} = t_{ij}^{ab} - t_{ij}^{ba} \tag{33}$$

$$V_{cd}^{a \leq b} = \sum_{Q} B_{ac}^{Q} B_{bd}^{Q} \tag{34}$$

$${}^{(\pm)}V_{c \leq d}^{a \leq b} = V_{cd}^{a \leq b} \pm V_{dc}^{a \leq b} \tag{35}$$

$${}^{(S)}A_{ij}^{ab} = \sum_{c \leq d} {}^{(+)}V_{c \leq d}^{a \leq b} \, {}^{(+)}t_{i \leq j}^{c \leq d} \tag{36}$$

$${}^{(A)}A_{ij}^{ab} = \sum_{c \leq d} {}^{(-)}V_{c \leq d}^{a \leq b} \, {}^{(-)}t_{i \leq j}^{c \leq d} \tag{37}$$

The tensors ${}^{(S)}A_{ij}^{ab}$ and ${}^{(A)}A_{ij}^{ab}$ are symmetric and antisymetric with respect to exchange of indices i and j or a and b. This algorithm reduces the cost of the construction of the four virtual index ERI tensor [eq 34] by a factor of 2. The cost of the contraction with the CC amplitudes [eqs 36 and 37] is reduced by a factor of 4.

Truncation of the virtual space based on the frozen natural orbitals (FNOs) of second-order perturbation theory (MP2) reduces the cost of the construction of the term A_{ij}^{ab} by a factor of $(N_v^{NO}/N_v^{MO})^4$, where N_v^{MO} and N_v^{NO} represent the number of virtual orbitals in the full molecular orbital and truncated natural orbital spaces, respectively. The FNO procedure used in these studies is a slightly modified version of that found in

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ref 38. The virtual—virtual block of the unrelaxed MP2 one-particle density matrix (OPDM) is given by

$$\gamma_{ab} = 2 \sum_{ijc} \frac{[2(ia|jc) - (ic|ja)](ib|jc)}{(F_{ii} + F_{jj} - F_{aa} - F_{cc})(F_{ii} + F_{jj} - F_{bb} - F_{cc})} \tag{38}$$
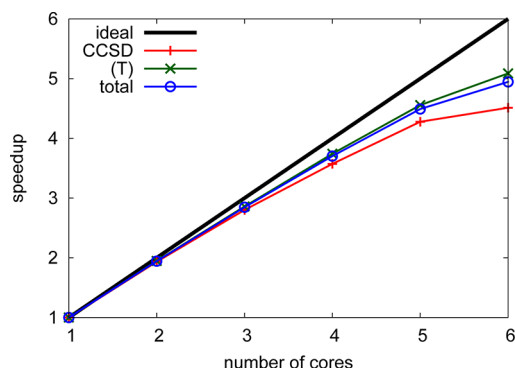
Figure 1. Scaling for DF-CCSD(T)/aug-cc-pVDZ computations of the adenine—thymine dimer. All computations use a single six-core Intel Core i7-3930K CPU (3.20 GHz) with access to 64 GB of memory.

where the four-index ERIs are defined by contractions of three-index integrals:

$$(ia|jb) = \sum_Q B_{ia}^Q B_{jb}^Q \tag{39}$$

This block of the OPDM is diagonalized to obtain natural virtual orbitals, and only those orbitals with occupations above a given threshold are retained. The DF/CD-CCSD(T) procedure is then performed using this truncated space of natural virtual orbitals. A second-order correction to the energy captures the correlation effects neglected by this truncation:

$$E_{CCSD(T)}^{MO} \approx E_{CCSD}^{NO} + E_{(T)}^{NO} + \Delta E_{MP2} \tag{40}$$

$$\Delta E_{MP2} = E_{MP2}^{MO} - E_{MP2}^{NO} \tag{41}$$

In general, the set of three-index integrals, B_{rs}^Q, utilized in the DF/CD-CCSD(T) procedure is not necessarily identical to that used in the DF-SCF procedure. For example, one may wish to utilize a DF auxiliary set in the SCF procedure that was optimized for Hartree—Fock computations [e.g., aug-cc-pVDZ-JKFIT[6]] but may, for computational efficiency, want to use a
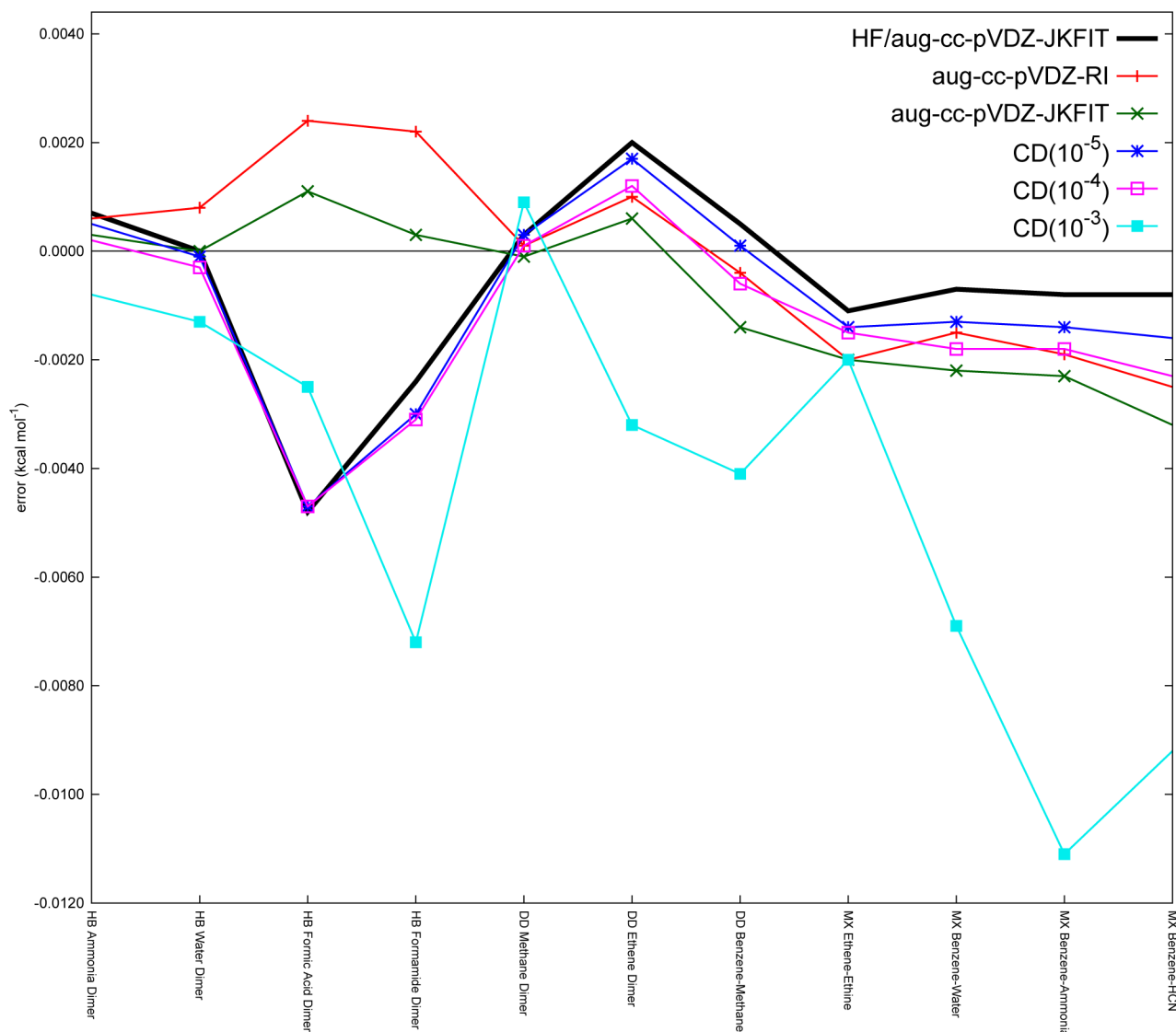
Figure 2. Errors in the total interaction energy (kcal mol^{-1}) for the DF/CD-CCSD(T) method relative to canonical CCSD(T) in the aug-cc-pVDZ basis set. Errors for DF-HF are also given, relative to canonical HF.
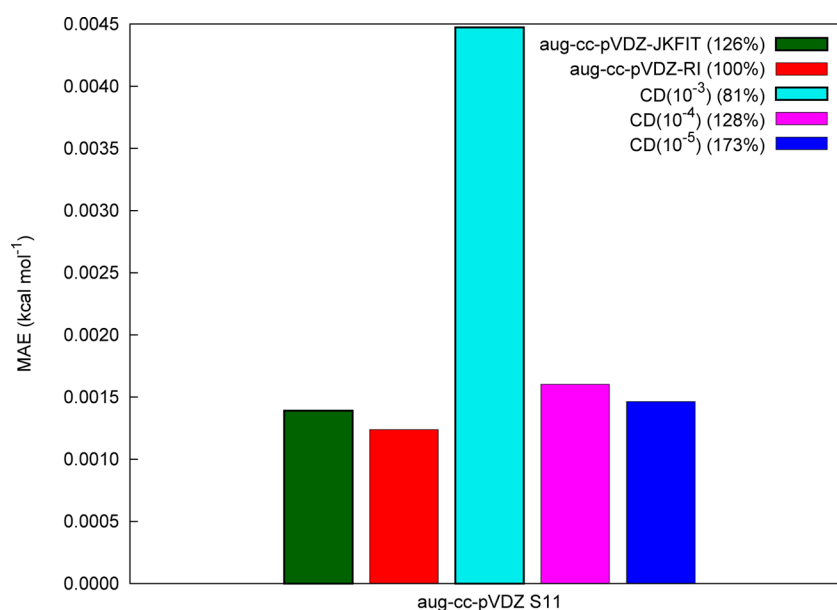
Figure 3. MAE (kcal mol^{-1}) for DF/CD-CCSD(T) S11/aug-cc-pVDZ interaction energies relative to canonical CCSD(T) values. The percentage in parentheses corresponds to the relative dimension of the auxiliary basis sets for DF and the number of retained Cholesky vectors for CD.

small set of CD vectors (obtained with a large error tolerance) for the correlated portion of the computation. Alternatively, the SCF procedure may have been performed without invoking DF or CD approximations. Regardless, if the integrals, B_{rs}^Q, do not correspond to those used in the SCF procedure, the Fock matrix constructed according to eq 25 is not strictly diagonal. Before the FNO procedure is executed as described here, we semicanonicalize the orbitals by separately diagonalizing the occupied–occupied and virtual–virtual blocks of the Fock matrix. The MP2 OPDM and energy are then evaluated in this semicanonical basis, and the effect of single excitations (due to the nonzero nature of the F_{ia} block of the Fock matrix) is ignored. We have verified that the magnitude of the MP2 singles amplitudes is quite small when using the DF sets and CD vectors outlined in this study.

3. COMPUTATIONAL DETAILS

The DF/CD-CCSD(T) algorithm described here has been implemented in the open-source PSI4 electronic structure package.[45] For all DF/CD-CCSD(T) computations, density fitting is utilized in the SCF procedure, and the auxiliary basis is the (aug-)cc-pVXZ-JKFIT basis. For the CCSD procedure, all intermediates (including all instances of the four-index ERI tensor) are constructed on the fly. The only quantities stored on disk throughout the computation are the three-index integrals in the atomic orbital basis, the doubles residual of the CCSD equations, and the old CC amplitudes and error vectors required by the CCSD direct inversion of the iterative subspace (DIIS) procedure.[46,47] These storage demands are significantly reduced compared to those of the reference conventional (MO-based) CCSD algorithm, which requires the disk storage of all classes of ERIs, including all $(vv|vv)$ and $(ov|vv)$ integrals. All computations reported here are performed within the frozen core approximation.

As has been noted previously,[5] the performance advantages of CD/DF techniques are less apparent in the (T) algorithm relative to the CCSD algorithm. The overhead of constructing the $(ov|vv)$ integrals on the fly outweighs any reduction in I/O for systems of the size studied herein. Accordingly, we simply construct the appropriate classes of four-index integrals [$(ov|vv)$, $(ov|ov)$, and $(oo|ov)$] from the (undressed) three-index integrals, write them to disk, and use our existing (T) module.[38] The working equations of this module are very similar to those found in ref 48. As noted above, the F_{ia} block of the Fock matrix used in DF/CD-CCSD(T) may be nonzero. These elements contribute to the (T) component of the energy at at fourth order,[49] and our algorithm accounts for their effects. It should be noted that the storage of the $(ov|vv)$ class of integrals on disk does not represent a serious bottleneck for the systems considered here, and the DF/CD-CCSD(T) algorithm completely avoids the storage of the largest $(vv|vv)$ class of integrals.

The DF/CD-CCSD(T) algorithm makes use of shared-memory parallelism through (i) threaded BLAS calls, (ii) OpenMP parallelization of all tensor manipulations, and (iii) explicit OpenMP threading of the (T) algorithm. Figure 1 illustrates the scaling for the DF-CCSD(T) algorithm for the adenine–thymine dimer described by an aug-cc-pVDZ basis set. The auxiliary basis set is the aug-cc-pVDZ-RI basis optimized for MP2. The algorithm scales quite well to six cores.

4. RESULTS AND DISCUSSION

The accuracy of the DF approximation in CCSD(T) is determined by the quality of the auxiliary basis set used to expand the three-index integrals. Because no work has been done to optimize RI auxiliary sets specific to CC methods, the conventional wisdom is that Cholesky decomposition of the ERI tensor should yield higher fidelity results than would be obtained with an "inappropriate" RI set, which may have been optimized for MP2 or Hartree–Fock methods. The quality of two RI auxiliary basis sets is assessed for computing interaction energies for the S11 set of van der Waals dimers, with an aug-cc-pVDZ primary basis set. Basis set superposition errors are corrected by the counterpoise method.[50] Results are compared to CD with various tolerance values. Figure 2 illustrates the error in the total DF/CD-CCSD(T) interaction energies relative to canonical CCSD(T) values for these systems. The error in the Hartree–Fock component of the interaction energy stemming from the use of DF techniques in the SCF procedure
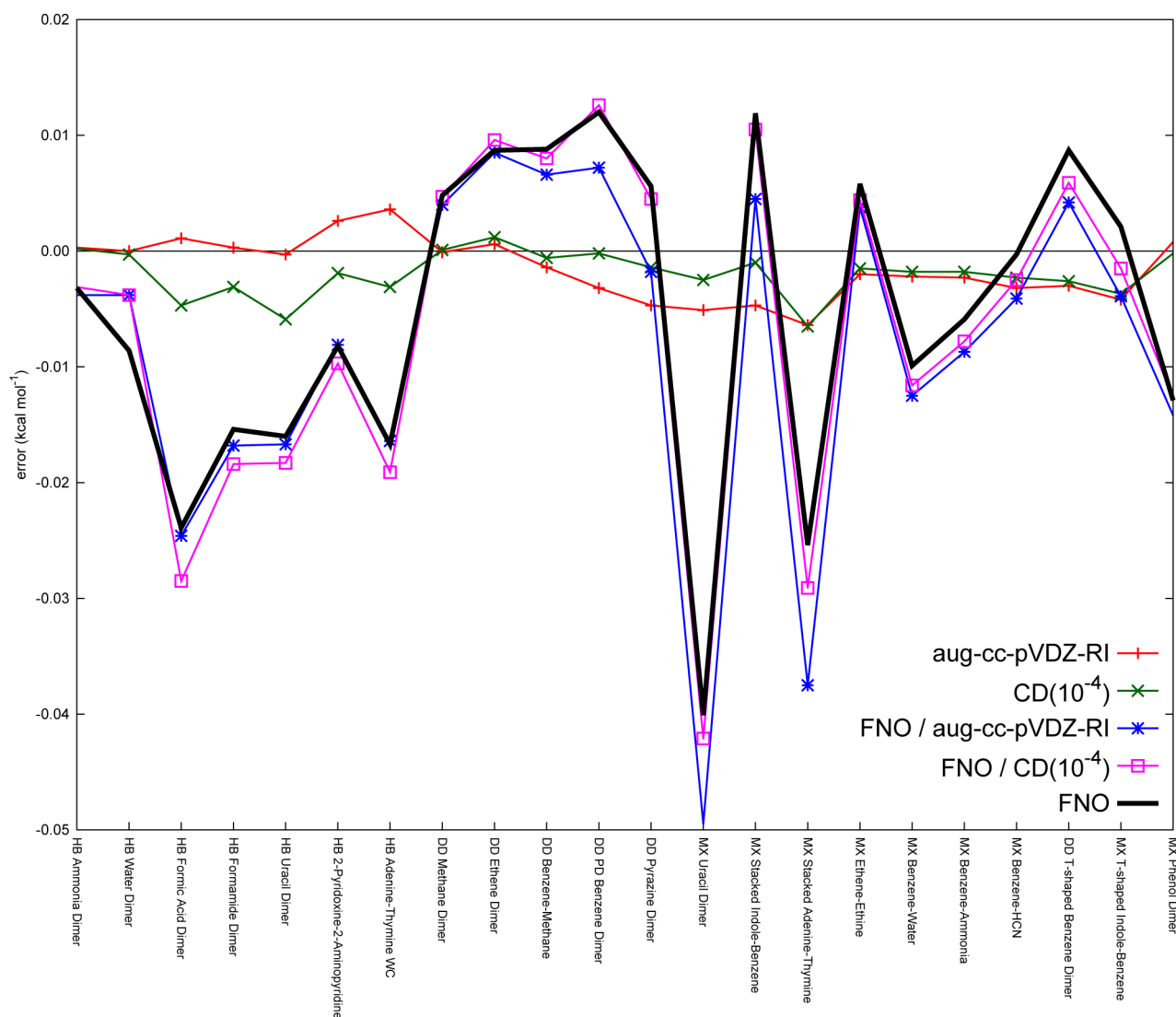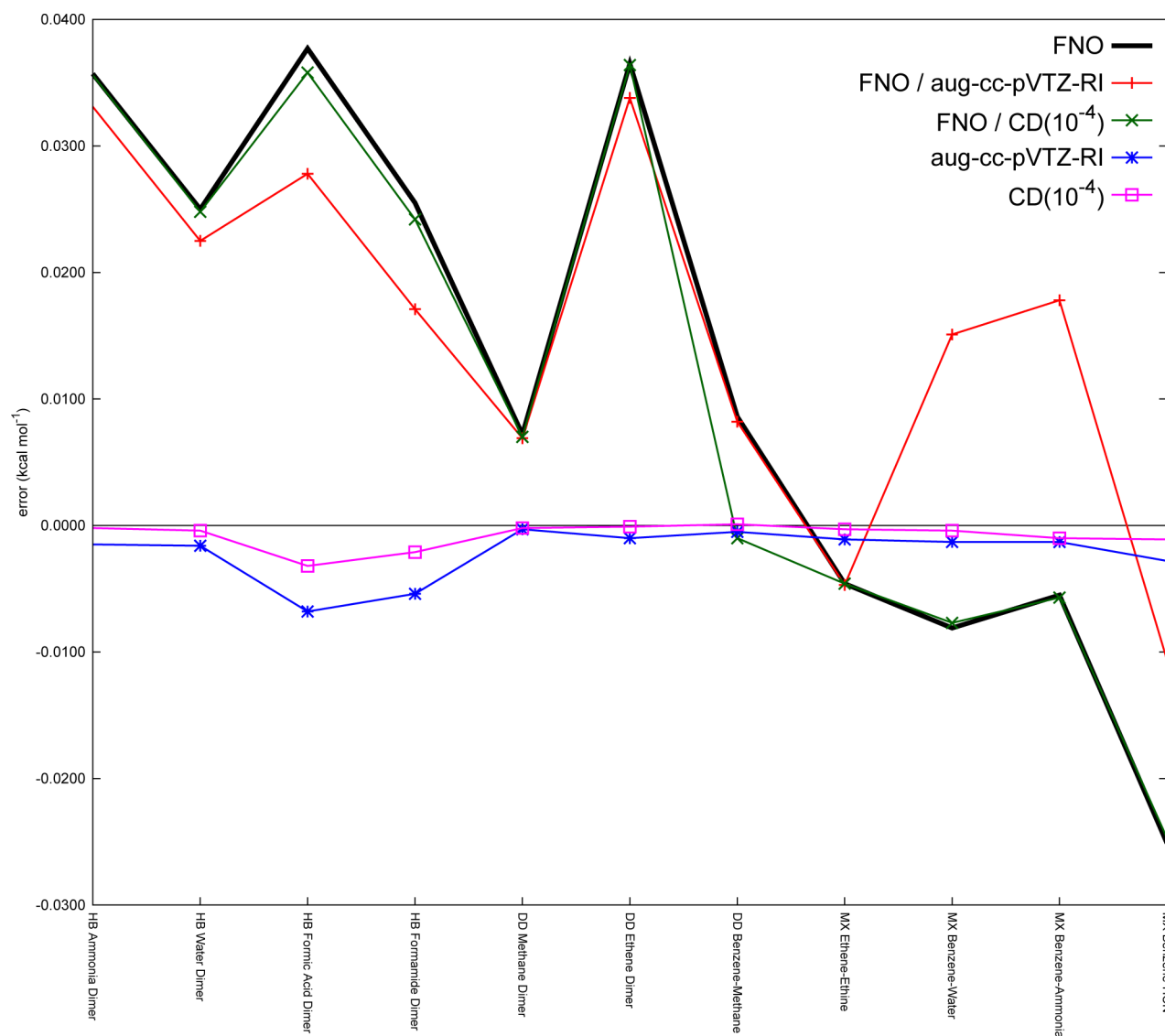
Figure 4. Errors in the total interaction energy (kcal mol^{-1}) for the FNO DF/CD-CCSD(T) method relative to canonical CCSD(T) for the S22 test set described by the aug-cc-pVDZ basis set.

(with the aug-cc-pVDZ-JKFIT auxiliary set) is also presented. For CD-CCSD(T), errors in the CCSD(T) interaction energy decrease with the increasing accuracy in the Cholesky decomposition, as expected. The mean absolute errors (MAEs) for decomposition thresholds of 10^{-3}, 10^{-4}, and 10^{-5} [denoted CD(10^{-5}), etc.] are 0.004, 0.002, and 0.001 kcal mol^{-1}, respectively. Note that the MAE for the DF−Hartree−Fock (DF-HF) interaction energy is 0.002 kcal mol^{-1}. The error in the total CD-CCSD(T) interaction energy when using CD(10^{-5}) is dominated by this DF-HF error. The MAEs for the DF-CCSD(T) method when using predefined aug-cc-pVDZ-JKFIT and aug-cc-pVDZ-RI auxiliary basis sets are 0.002 and 0.001 kcal mol^{-1}, respectively, with the error for aug-cc-pVDZ-RI being, surprisingly, slightly *smaller* than that observed for CD(10^{-5}), despite the fact that the number of retained CD vectors is, on average, 1.73 times larger than the number of auxiliary functions in the aug-cc-pVDZ-RI basis set. The MAE for each DF/CD-CCSD(T) method is illustrated in Figure 3. The percentages in the legend denote the relative dimension of the auxiliary basis sets and number of retained Cholesky vectors for DF- and CD-CCSD(T), respectively.

The errors observed for DF/aug-cc-pVDZ-RI or CD(10^{-4}) are acceptable for most benchmarking studies. We chose these approaches for further consideration and examined the full S22

test set, again in the aug-cc-pVDZ basis. We have chosen CD(10^{-4}) as the representative form of CD in coupled-cluster theory because, as can be seen in Figure 3, CD(10^{-4}) provides significantly more accuracy than CD(10^{-3}), while CD(10^{-5}) results in only a modest improvement over CD(10^{-4}) at the expense of retaining on average 35% more Cholesky vectors. Figure 4 illustrates the errors stemming from the DF approximation as well as those incurred by employing frozen natural orbital techniques, with a somewhat conservative FNO occupation tolerance of 10^{-5}. The MAEs in the DF/CD-CCSD(T) interaction energies are only 0.002 kcal mol^{-1} when using either the aug-cc-pVDZ-RI auxiliary set or CD(10^{-4}) vectors. The errors in the FNO approximation are roughly an order of magnitude larger than these values and are relatively independent of the choice of auxiliary basis. The MAEs for the FNO-DF/CD-CCSD(T) interaction energies versus canonical CCSD(T) values are 0.012 kcal mol^{-1} for both the aug-cc-pVDZ-RI set and CD(10^{-4}) vectors, which are unchanged from the FNO-CCSD(T) errors when using conventional, four-index ERIs. As was observed for the S11 set, the choice of auxiliary set seems to be irrelevant, and the errors here are dominated by the FNO approximation.

The accuracy of the DF and DF/FNO approximations were next assessed for the S11 test set represented by the larger

Figure 5. Errors in the total interaction energy (kcal mol^{-1}) for the FNO DF-CCSD(T) method relative to canonical CCSD(T) for the S11 test set described by the aug-cc-pVTZ basis set.

aug-cc-pVTZ basis set. Figure 5 illustrates the error relative to canonical CCSD(T) using CD(10^{-4}) vectors and the aug-cc-pVTZ-RI auxiliary basis set. The SCF procedure made use of the DF approximation with the aug-cc-pVTZ-JKFIT basis set. Errors are also presented for FNO-CCSD(T) utilizing conventional four-index ERIs within the SCF and CCSD(T) procedures. The errors incurred by the DF approximation alone, as measured by the MAEs, are only 0.002 and 0.001 kcal mol^{-1} for the aug-cc-pVTZ-RI set and CD(10^{-4}) vectors, respectively. The CD(10^{-4}) set here provides somewhat higher accuracy, at the expense of a larger auxiliary set; for benzene−ammonia, the number of CD(10^{-4}) vectors is about 60% larger than the dimension of the aug-cc-pVTZ-RI set. FNO errors are again roughly an order of magnitude larger than the DF errors. The MAE for FNO-CCSD(T) using conventional four-index ERIs in the SCF and CCSD(T) procedures is 0.020 kcal mol^{-1}. FNO-DF-CCSD(T) using the aug-cc-pVTZ-RI and CD(10^{-4}) sets leads to MAEs of 0.018 and 0.019 kcal mol^{-1}, respectively.

We further assess the accuracy of the DF/CD approximation for a set of 47 reaction energies. The reaction set is similar to that used to optimize the parameters in the spin-component-scaled

(SCS) MP2[51] and SCS-CCSD[52] methods. All geometries and CCSD(T) energies were obtained from the Supporting Information of ref 52. Table 1 provides the reaction energies and errors for DF/CD-CCSD(T) with and without FNO approximations. The FNO occupation tolerance was again 10^{-5}, and the auxiliary basis sets chosen were the preoptimized cc-pVQZ-RI set and CD(10^{-4}) vectors. All DF/CD-CCSD(T) computations use the DF approximation in the SCF procedure with the cc-pVQZ-JKFIT auxiliary basis set. The data in Table 1 suggest that DF/CD techniques introduce very little error for reaction energies. The MAEs for DF/CD-CCSD(T) are insignificant at only 0.004 and 0.003 kcal mol^{-1}, respectively. The smaller cc-pVQZ-RI basis set achieves comparable accuracy to the CD vectors over the entire set, further illustrating that energy differences are indifferent to the choice of auxiliary basis. FNOs introduce about an order of magnitude more error, with MAEs of 0.064 and 0.069 kcal mol^{-1} using the cc-pVQZ-RI auxiliary set and CD(10^{-4}) vectors, respectively. These errors are to be compared to reaction energies in the range of 0.410 to −426.122 (average −84.288) kcal mol^{-1}. Given the magnitude of the reaction

Table 1. Conventional Canonical CCSD(T) Reaction Energies Computed in the cc-pVQZ Basis Set and the Errors Resulting from the Use of the DF and FNO Approximations[a]

reaction	CCSD(T)	CD[g]	RI[h]	FNO[f] CD[g]	FNO[f] RI[h]
$F_2 + H_2 \rightarrow 2HF$	−134.101	−0.005	0.002	0.048	0.060
$F_2O + H_2 \rightarrow F_2 + H_2O$	−68.388	−0.007	−0.003	−0.043	−0.033
$O_3 + 3H_2 \rightarrow 3H_2O$	−223.363	−0.007	−0.005	−0.045	−0.031
$H_2O_2 + H_2 \rightarrow 2H_2O$	−86.321	−0.001	0.003	−0.038	−0.029
$CO + H_2 \rightarrow CH_2O$	−4.556	−0.004	−0.003	−0.030	−0.025
$CO + 3H_2 \rightarrow CH_4 + H_2O$	−63.639	−0.006	0.001	−0.017	−0.008
$N_2 + 3H_2 \rightarrow 2NH_3$	−37.968	−0.004	0.003	−0.032	−0.020
$^1CH_2 + H_2 \rightarrow CH_4$	−128.755	0.001	0.007	−0.105	−0.105
$N_2O + H_2 \rightarrow N_2 + H_2O$	−80.738	0.001	0.003	−0.046	−0.036
$HNO_2 + 3H_2 \rightarrow 2H_2O + NH_3$	−121.645	−0.007	−0.000	−0.068	−0.052
$C_2H_2 + H_2 \rightarrow C_2H_4$	−49.394	0.000	0.005	−0.144	−0.129
$CH_2=C=O + 2H_2 \rightarrow CH_2O + CH_4$	−43.068	−0.000	0.004	−0.038	−0.029
$BH_3 + 3HF \rightarrow BF_3 + 3H_2$	−94.302	0.012	−0.005	0.014	−0.018
$HCOOH \rightarrow CO_2 + H_2$	2.047	0.000	0.001	0.013	0.008
$CO + H_2O \rightarrow CO_2 + H_2$	−6.733	0.001	−0.003	0.059	0.046
$C_2H_2 + HF \rightarrow C_2H_3F$	−27.256	0.003	0.002	−0.102	−0.096
$HCN + H_2O \rightarrow CO + NH_3$	−12.574	0.005	0.007	−0.066	−0.060
$HCN + H_2O \rightarrow HCONH_2$	−21.763	0.003	0.002	−0.031	−0.029
$HCONH_2 + H_2O \rightarrow HCOOH + NH_3$	0.410	0.003	0.001	0.011	0.007
$HCN + NH_3 \rightarrow N_2 + CH_4$	−38.245	0.003	0.005	−0.051	−0.048
$CO + CH_4 \rightarrow CH_3CHO$	3.431	0.000	−0.004	−0.027	−0.029
$O_3 + CH_4 \rightarrow 2H_2O + CO$	−159.723	−0.001	−0.006	−0.028	−0.023
$N_2 + F_2 \rightarrow N_2F_2$	17.313	0.004	0.002	0.054	0.050
$BH_3 + 2F_2 \rightarrow BF + 3HF$	−248.089	−0.003	0.009	0.153	0.164
$2BH_3 \rightarrow B_2H_6$	−43.263	0.004	0.016	−0.095	−0.088
$2^1CH_2 \rightarrow C_2H_4$	−199.430	0.001	0.007	−0.282	−0.282
$CH_3ONO \rightarrow CH_3NO_2$	−3.205	0.002	0.005	0.003	0.004
$CH_2=C \rightarrow C_2H_2$	−44.836	−0.001	−0.002	0.076	0.070
allene → propyne	−1.341	−0.000	−0.004	0.088	0.076
cyclopropene → propyne	−23.449	−0.001	−0.004	0.080	0.071
oxirane → CH_3CHO	−26.508	0.004	0.006	0.015	0.015
vinylalcohol → CH_3CHO	−10.938	0.003	0.003	0.015	0.012
cyclobutene →1,3-butadiene	−11.270	−0.001	−0.002	−0.001	0.001
$C_2H_4 + {}^1CH_2 \rightarrow C_3H_6$	−115.117	0.002	0.005	−0.084	−0.089
$C_2H_2 + C_2H_4 \rightarrow$ cyclobutene	−32.543	0.004	0.003	−0.084	−0.082
$3C_2H_2 \rightarrow$ benzene	−153.347	0.004	−0.005	−0.320	−0.307
$HCN \rightarrow CNH(TS)$[b]	47.716	0.002	0.004	−0.036	−0.033
cyclobutene →1,3-butadiene(TS)[b]	34.966	−0.001	0.000	−0.021	−0.019
$HF + H^+ \rightarrow H_2F^+$	−122.911	0.000	0.006	−0.055	−0.047
$H_2O + H^+ \rightarrow H_3O^+$	−172.983	0.001	0.009	−0.047	−0.038
$NH_3 + H^+ \rightarrow H_4N^+$	−212.918	0.000	0.005	−0.136	−0.126
$F^- + H^+ \rightarrow HF$	−390.417	0.009	0.016	−0.127	−0.107
$OH^- + H^+ \rightarrow H_2O$	−412.533	0.000	0.006	−0.176	−0.156
$NH_2^- + H^+ \rightarrow NH_3$	−426.122	−0.003	−0.006	−0.154	−0.149
$2NH_3 \rightarrow (NH_3)_2$	−3.439	0.001	−0.000	0.042	0.036
$2H_2O \rightarrow (H_2O)_2$	−5.391	0.003	0.002	0.040	0.037
$2HF \rightarrow (HF)_2$	−4.854	0.001	0.001	−0.007	−0.005
MAE[c]		0.003	0.004	0.069	0.064
RMS[d]		0.004	0.005	0.095	0.090
MAX[e]		0.012	0.016	0.320	0.307

[a]All energies and errors are given in kcal mol^{-1}. [b]Transition states. [c]Mean absolute error. [d]Root mean squared error. [e]Maximum absolute error. [f]Using FNO occupation threshold of 10^{-5}. [g]CD auxiliary basis set with an accuracy of 10^{-4}. [h]Predefined cc-pVQZ-RI auxiliary basis set.

energies, the FNO approaches are probably acceptable for all but the most demanding benchmarking studies.

Finally, we present timings for our canonical CCSD(T) algorithm relative to two different CD-CCSD(T) algorithms utilizing the set of CD(10^{-4}) vectors. We also present timings

for one of the CD algorithms within the FNO approximation. The timings correspond to the evaluation of one-, two-, and three-body contributions to the counterpoise-corrected interaction energy for a benzene trimer at the CCSD(T)/aug-cc-pVDZ level of theory. Because the magnitude of the three-body

Table 2. Timings (In Minutes) for CCSD(T) (Algorithm I) and CD-CCSD(T)^a (Algorithms II and III, See Text) Computations of Counterpoise-Corrected Three-Body Interaction Energies for a Benzene Trimer Described by the aug-cc-pVDZ Basis^b

	trimer				dimers^c				monomers^d			
module	I	II	III	III+FNO^e	I	II	III	III+FNO^e	I	II	III	III+FNO^e
four-index AO/MO transformation	221				247				266			
three-index integral generation		10	10	11		10	10	11		10	10	11
CC integral sort	187				228				221			
CCSD	920	815	682	547	691	517	455	87	345	365	348	8
(T)	2281	2351	2384	1760	760	788	799	139	117	123	126	2
total	3609	3176	3076	2318	1926	1315	1264	237	949	498	484	21

^{a}With CD threshold of 10^{-4}. ^{b}All computations use a single six-core Intel Core i7-3930K CPU (3.2 GHz, overclocked to 4.0 GHz) with access to 64 GB of memory. ^{c}Average timings for the three dimers are presented. ^{d}Average timings for the three monomers are presented. ^{e}With a very conservative 10^{-6} cutoff.

interaction in benzene trimer is small relative to two-body interaction, we have chosen a very conservative FNO occupation threshold of 10^{-6}. Table 2 illustrates the wall time required for each of the post-Hartree–Fock modules associated with the CCSD(T) method. Algorithm I represents our canonical CCSD(T) algorithm utilized in ref 38. Algorithm II represents a version of algorithm I which exploits CD techniques, and several diagrams arising in the CCSD portion of the algorithm can be refactored to yield lower computational scaling. This refactorization and a significant reduction in the I/O required by the CCSD algorithm result in a modest speedup of 13% for the trimer computation. Finally, algorithm III represents the CD-CCSD(T) algorithm outlined above that makes use of t_1-transformed three-index integrals in the CCSD module. For the trimer computation, the simplifications afforded by the use of t_1-dressed three-index integrals result in an additional 20% performance boost relative to algorithm II and a 35% improvement over algorithm I for the trimer computation. The CCSD portion of algorithm III is 52% faster than algorithm I for the dimer computations but 1% *slower* for the monomer computations. Because the monomer computations have small occupied spaces and very large virtual spaces, the cost of evaluating the A_{ij}^{ab} contribution to the doubles residual overwhelmingly dominates the CD-CCSD wall time and negates any performance advantages associated with the reduced I/O requirements. The total wall time for the post-Hartree–Fock contributions to the interaction energy were 12 238, 8618, 8322, 3093 min for algorithms I, II, III, and III (with FNOs), respectively. The three-body contributions to the IE determined by each of these algorithms were 0.0598, 0.0595, 0.0595, and 0.0582 kcal mol^{-1}. The total wall time is significantly reduced by the use of the FNO approximation, even with the very conservative 10^{-6} occupation tolerance. Algorithm III (with FNOs) allows us to evaluate the post-Hartree–Fock contributions to the counterpoise-corrected IE for the benzene trimer 4 times faster than with the conventional algorithm with canonical orbitals, while introducing an error of only 0.0016 kcal mol^{-1} into the three-body contribution to the IE relative to conventional CCSD(T).

5. CONCLUSIONS

We have presented an implementation of the CCSD(T) method that makes use of density-fitting or Cholesky decomposition techniques in the construction of all electron repulsion integrals. We have investigated the quality of preoptimized DF auxiliary basis sets relative to CD vectors in the context of DF/CD-CCSD(T) computations of noncovalent interactions and reaction energies. For noncovalent interactions, DF errors are on the order of only thousandths of

1 kcal mol^{-1}, regardless of the nature of the auxiliary basis sets, and CD provides comparable accuracy at a slightly increased cost. When DF/CD and FNO technologies are coupled, the error in the interaction energies is clearly dominated by the FNO approximation. For reaction energies, errors stemming from the DF/CD approximation again are on the order of thousandths of 1 kcal mol^{-1} for both DF basis sets and CD vectors. Errors incurred by FNO techniques are larger than for noncovalent interactions, but still insignificant when compared to the magnitude of the reaction energies. On the basis of these results, DF/CD techniques can safely be applied to both noncovalent interaction energies and reaction energies. While one might expect CD to provide greater accuracy, we have found that standard RI sets optimized for MP2 theory provide quite similar accuracy.

The use of t_1-dressed three-index integrals removes the dependence on the t_1 amplitudes from the doubles residual equations, and the cost of the resulting required transformation of the three-index integrals is negligible compared to the evaluation of the remaining CC diagrams. The CD-CCSD algorithm was found to be 35% faster than the original, conventional CCSD implementation for the benzene trimer in the aug-cc-pVDZ basis set. For this system, the evaluation of the $O(o^2v^4)$ A_{ij}^{ab} term constitutes a large portion of the walltime in the CD-CCSD algorithm. The FNO approximation thus becomes particularly effective because it reduces the cost of this term by a factor of $(N_v^{NO}/N_v^{MO})^4$. With a very conservative FNO cutoff of 10^{-6}, the CD-CCSD(T) interaction energy was computed 4 times faster than with the original algorithm.

The speedups achieved by CD-CCSD for the benzene dimer and trimer computations (especially when coupled with the FNO approximation), the trend toward machines with larger numbers of cores, and the lack of a local disk on many high-performance computing clusters all convince us that minimizing I/O as in the present algorithm is clearly beneficial. By using t_1-dressed four-index integrals, one can devise an algorithm that requires only two terms involving four-index tensors with more than two virtual indices. Furthermore, with density-fitting or Cholesky decomposition, we can eliminate the tensor with three virtual indices, so the only four-index tensor involving more than two virtual indices is found in the $O(o^2v^4)$ A_{ij}^{ab} term. This simplification will be important in future parallel and GPU implementations of the DF/CD-CCSD(T) method.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Absolute energies (au) for molecules involved in the 47 reactions presented in Table 1, absolute energies (au) and

interaction energies (kcal mol^{-1}) for the 11 smallest van der Waals dimers in the S22 set in the aug-cc-pVTZ and aug-cc-pVDZ basis sets, and absolute energies (au) and interaction energies (kcal mol^{-1}) for the S22 set in the aug-ccpVDZ basis set. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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