Energy and Analytic Gradients for the Orbital-Optimized Coupled-Cluster Doubles Method with the Density-Fitting Approximation: An Efficient Implementation

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Abstract

Efficient implementations of the orbital-optimized coupled-cluster doubles [or simply "optimized CCD", OCCD, for short] method and its analytic energy gradients with the density-fitting (DF) approach, denoted by DF-OCCD, are presented. In addition to the DF approach, the Cholesky-decomposed variant (CD-OCCD) is also implemented for energy computations. The computational cost of the DF-OCCD method (available in a plugin version of the DFOCC module of Psi4) is compared with that of the conventional OCCD (from the Q-Chem package). The OCCD computations were performed with the Q-chem package, in which it is denoted by OD. In the conventional OCCD, one needs to perform four-index integrals transformations at each CCD iterations, which limits its applications to large chemical systems. Our results demonstrate that DF-OCCD provides dramatically lower computational costs compared to OCCD, there are almost 8-fold reductions in the computational time for the C_6H_{14} molecule with the cc-pVTZ basis set. For open-shell geometries, interaction energies, and hydrogen transfer reactions, DF-OCCD provides significant improvements upon DF-CCD. Further, the performance of the DF-OCCD method is substantially better for harmonic vibrational frequencies in the case of symmetry breaking problems. Moreover, several factors make DF-OCCD more attractive compared to CCSD: (1) for DF-OCCD there is no need for orbital relaxation contributions in analytic gradient computations (2) active spaces can readily be incorporated into DF-OCCD (3) DF-OCCD provides accurate vibrational frequencies when symmetry-breaking problems are observed (4) in its response function, DF-OCCD avoids artificial poles; hence, excited-state molecular properties can be computed via linear response theory (5) Symmetric and asymmetric triples corrections based on DF-OCCD [DF-OCCD(T)] has a significantly better performance in near degeneracy regions.

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I. INTRODUCTION

Orbital-optimized (OO) electron correlation methods have been of significant interest in contemporary quantum chemistry.[1–27] OO methods have been reported for various coupled-cluster (CC) and perturbation theory methods, such as coupled-cluster doubles (CCD),[1–3,5,13] coupled pair functionals,[28,29] the linearized coupled-cluster doubles (LCCD),[18,30] the density-cumulant functional theory (DCFT),[21] the second- and third-order perturbation theory (MP2 and MP3),[13,14,17,19,22,23,31,32] and the MP2.5 model.[24] Triples excitation corrections for the OO-CC methods have also been considered.[6,15,20,33,34] These studies showed that the OO methods are very helpful for computations of molecular properties of challenging molecular systems, free radicals,[10,17,18,23,35–37] such as symmetry-breaking problems,[2,13,14,17] transition states,[10,35–37] bond-breaking problems,[15,20,38] weak interactions in open-shell systems,[22,24,30,31,39] straightforward computation of ionization potentials[40] and electron affinities,[41] and evaluations of the chemical reactivity.[42]

One of the most common approximation for the tensor factorization of the electron repulsion integrals (ERIs) is the density fitting (DF) technique.[22,23,30–32,43–56] With the help of the DF technique, one can express the four-dimensional ERIs in terms of three-dimensional tensors. In addition to DF, the partial Cholesky decomposition (CD) of the ERI tensor is also commonly employed as a tensor decomposition approach.[22,31,51,57–60] The DF and CD approximations are quite beneficial to reduce the computational time due to the reduced I/O time. In context of the OO methods, the DF and CD approaches were utilized for the OO-MP2 (OMP2 for short) energy[10,22] and analytic gradients.[23] Further, the DF and CD techniques were applied to the orbital-optimized MP3, MP2.5, and LCCD methods.[30,31]

Analytic energy gradients for electronic structure methods, which employ the DF approach, have been reported for MP2 (DF-MP2),[52,61–64] the second-order coupled cluster (CC2) model,[65,66] second-order multireference perturbation theory (DF-CASPT2),[67] the DF-OMP2, DF-OMP2.5, and DF-OMP3 methods,[23,32] time-dependent local CC response theory (DF-TD-LCC2),[68] the CCD and coupled-cluster singles and doubles methods (DF-CCD and DF-CCSD),[54] and for the CCSD with perturbative triples, DF-CCSD(T).[55] However, analytic gradients with the CD approximation cannot be computed unless one employs a similar approach to that of Aquilante *et al.*[69] In a 2019 study, the CD-CCSD gradients were reported by Feng *et al.*[70]

In a 1998 study, Sherrill *et al.*[2] presented energy and analytic gradients of the OCCD method with the conventional 4-index integrals. In this research, energy and analytic gradients for the OCCD method[2,13,15] with the DF approach is presented, which is denoted by DF-OCCD. In addition to DF, the CD approximation is also considered for the energy computations, the resulting method is denoted by CD-OCCD. The equations reported have been implemented in a new computer code, written by present authors (U.B. and A.U.), and added to the Dfocc[22,23,30–32,52–55] module of the Psi4 package.[71] Our new implementation has both restricted and unrestricted Hartree-Fock (RHF and UHF) versions. Even though, in our previous studies analytic gradients of the DF-CCSD and DF-CCD methods were presented,[54] they include only the RHF reference. Hence, in the present study the UHF based DF-CCD method is implemented for the first time. The DF-OCCD method is applied to bond lengths, hydrogen transfer reactions, weak interactions, and symmetry breaking problems.

II. THEORETICAL APPROACH

A. Integral Tensor Decomposition Approaches

With the help of DF and CD approximations, the atomic-orbital (AO) basis ERIs can be expressed as follows:

$$(\mu\nu|\lambda\sigma)_{DF} = \sum_{Q}^{N_{aux}} b_{\mu\nu}^{Q} b_{\lambda\sigma}^{Q}, \tag{1}$$

In the CD approach, the CD vectors $b_{\mu\nu}^{Q}$ are obtained from the primary basis set integrals in the CD procedure, and Q is a Cholesky index. In the DF approximation, the DF factors $b_{\mu\nu}^{Q}$ may be defined as follows:

$$b_{\mu\nu}^{Q} = \sum_{P}^{N_{aux}} (\mu\nu|P)[\boldsymbol{J}^{-1/2}]_{PQ}, \tag{2}$$

where

$$(\mu\nu|P) = \int\int \chi_{\mu}(\boldsymbol{r}_1)\chi_{\nu}(\boldsymbol{r}_1)\frac{1}{r_{12}}\varphi_P(\boldsymbol{r}_2)\, d\boldsymbol{r}_1 d\boldsymbol{r}_2, \tag{3}$$

and

$$J_{PQ} = \int\int \varphi_P(\boldsymbol{r}_1) \frac{1}{r_{12}} \varphi_Q(\boldsymbol{r}_2)\, d\boldsymbol{r}_1 d\boldsymbol{r}_2, \tag{4}$$

where $\chi_\mu(\boldsymbol{r})$ and $\varphi_P(\boldsymbol{r})$ are the primary and auxiliary functions, respectively. Similar to the AO basis, the molecular-orbital (MO) basis ERIs can be written as follows:

$$(pq|rs)_{DF} = \sum_{Q}^{N_{aux}} b_{pq}^{Q} b_{rs}^{Q}. \tag{5}$$

where b_{pq}^{Q} is a MO basis CD/DF tensor.

B. DF-CCD Energy and Amplitude Equations

For the orbital indexing a common notation is used: i, j, k, l, m, n for occupied orbitals; a, b, c, d, e, f for virtual orbitals; and p, q, r, s, t, u, v, w for general spin orbitals. The correlation energy for the CCD method can be expressed as follows

$$\Delta E = \langle 0 | e^{-\hat{T}_2} \hat{H}_N e^{\hat{T}_2} | 0 \rangle, \tag{6}$$

where $\hat{H}_N$ is the normal-ordered Hamiltonian operator,[72,73] $|0\rangle$ is the reference determinant, and $\hat{T}_2$ is the cluster double excitation operator:

$$\hat{T}_2 = \frac{1}{4} \sum_{i,j}^{occ} \sum_{a,b}^{vir} t_{ij}^{ab}\ \hat{a}^{\dagger} \hat{b}^{\dagger} \hat{j} \hat{i}, \tag{7}$$

where $\hat{a}^{\dagger}$ and $\hat{i}$ are the creation and annihilation operators and t_{ij}^{ab} is a double excitation amplitude.

The DF-CCD correlation energy can be written explicitly as follows:

$$\Delta E = \frac{1}{4} \sum_{i,j}^{occ} \sum_{a,b}^{vir} t_{ij}^{ab} \sum_{Q}^{N_{aux}} \left(b_{ia}^{Q} b_{jb}^{Q} - b_{ib}^{Q} b_{ja}^{Q} \right), \tag{8}$$

The DF-CCD amplitude equation can be written as

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}_2} \hat{H}_N e^{\hat{T}_2} | 0 \rangle = 0, \tag{9}$$

where $\langle\Phi_{ij}^{ab}|$ is a doubly-excited Slater determinant. The explicit form of DF-CCD amplitude equation can be obtained from our equations for the density-fitted coupled-cluster singles and doubles (DF-CCSD) method. Hence, for details of our DF-CCD implementations, one may refer to our previous studies.[53–55]

C. DF-CCD-Λ Energy Functional (Lagrangian)

It is convenient[74,75] to define a Lagrangian ($\mathcal{L}$) for the DF-CCD method (DF-CCD-Λ functional) as follows:

$$\mathcal{L} = \langle 0|(1+\hat{\Lambda}_2)e^{-\hat{T}_2}\hat{H}e^{\hat{T}_2}|0\rangle, \tag{10}$$

where $\hat{H}$ is the Hamiltonian operator and $\hat{\Lambda}_2$ is the CC double de-excitation operator,

$$\hat{\Lambda}_2 = \frac{1}{4}\sum_{i,j}^{occ}\sum_{a,b}^{vir}\lambda_{ab}^{ij}\,\hat{i}^{\dagger}\hat{j}^{\dagger}\hat{b}\hat{a}, \tag{11}$$

where λ_{ab}^{ij} is a double de-excitation amplitude.

The CCD T_2-amplitude equations are obtained by minimizing $\mathcal{L}$ with respect to Λ_2-amplitudes, whereas the minimization with respect to T_2-amplitudes yields to the Λ_2-amplitude equations[76–80]

$$\langle 0|(1+\hat{\Lambda}_2)\left[e^{-\hat{T}_2}\hat{H}e^{\hat{T}_2} - E\right]|\Phi_{ij}^{ab}\rangle = 0, \tag{12}$$

where E is the CCD total energy. The explicit form of DF-CCD Λ_2 amplitude equations can be obtained from our equations for the DF-CCSD method in previous studies.[53–55]

D. The Parametrization of the DF-OCCD Wave Function

We follow our previous formulations[13–15,17–19,24,30,31,39,40] for the DF-OCCD wave function. The MO transformations may be achieved with the help of a unitary operator[81–84]

$$\tilde{\hat{p}}^{\dagger} = e^{\hat{K}} \hat{p}^{\dagger} e^{-\hat{K}}, \tag{13}$$

$$\tilde{\hat{p}} = e^{\hat{K}} \hat{p} e^{-\hat{K}}, \tag{14}$$

$$|\tilde{p}\rangle = e^{\hat{K}} |p\rangle, \tag{15}$$

where $e^{\hat{K}}$ is the MO rotation operator, $\tilde{\hat{p}}^{\dagger}$, $\tilde{\hat{p}}$, and $|\tilde{p}\rangle$ are the transformed creation, annihilation operators and a transformed spin-orbital, respectively, and $\hat{K}$ is:

$$\hat{K} = \sum_{p,q} K_{pq} \hat{p}^{\dagger} \hat{q} = \sum_{p>q} \kappa_{pq} (\hat{p}^{\dagger} \hat{q} - \hat{q}^{\dagger} \hat{p}), \tag{16}$$

hence,

$$\boldsymbol{K} = Skew(\boldsymbol{\kappa}), \tag{17}$$

where $\{\kappa_{pq}\}$ are the MO rotation parameters. The transformed MO coefficients matrix can be written as

$$\boldsymbol{C}(\boldsymbol{\kappa}) = \boldsymbol{C}^{(0)} e^{\boldsymbol{K}}, \tag{18}$$

where $\boldsymbol{C}^{(0)}$ and $\boldsymbol{C}(\boldsymbol{\kappa})$ are the old and new MO coefficient matrices, respectively.

For DF-OCCD, the following Lagrangian can be written,[13]

$$\mathcal{L}(\boldsymbol{\kappa}) = \langle 0 | (1 + \hat{\Lambda}_2) e^{-\hat{T}_2} \hat{H}^{\kappa} e^{\hat{T}_2} | 0 \rangle, \tag{19}$$

where,

$$\hat{H}^{\kappa} = e^{-\hat{K}} \hat{H} e^{\hat{K}}. \tag{20}$$

Derivatives of $\mathcal{L}(\boldsymbol{\kappa})$ with respect to $\boldsymbol{\kappa}$ can be expressed as follows,

$$w_{pq} = \left. \frac{\partial \mathcal{L}}{\partial \kappa_{pq}} \right|_{\boldsymbol{\kappa}=0}, \tag{21}$$

$$A_{pq,rs} = \left. \frac{\partial^2 \mathcal{L}}{\partial \kappa_{pq} \partial \kappa_{rs}} \right|_{\boldsymbol{\kappa}=0}. \tag{22}$$

Then, a second-order series expansion can be written for $\mathcal{L}(\boldsymbol{\kappa})$ as follows:

$$\mathcal{L}^{(2)}(\boldsymbol{\kappa}) = \mathcal{L}^{(0)} \; + \; \boldsymbol{\kappa}^{\dagger} \boldsymbol{w} \; + \; \frac{1}{2} \boldsymbol{\kappa}^{\dagger} \boldsymbol{A} \boldsymbol{\kappa}, \tag{23}$$

where $\boldsymbol{\kappa}$ is the MO rotation vector, $\boldsymbol{w}$ is the MO gradient vector, and $\boldsymbol{A}$ is the orbital Hessian matrix. Hence, one can obtain the following equation by minimizing $\mathcal{L}$ with respect to $\boldsymbol{\kappa}$,

$$\boldsymbol{\kappa} = -\boldsymbol{A}^{-1} \boldsymbol{w}. \tag{24}$$

E. Response Density Matrices

Particle density matrices (PDMs) are central for the evaluation of the energy derivatives. The CCD one-particle density matrix (OPDM) can be defined as follows:[13,15]

$$\gamma_{pq} = \frac{1}{2} P_{+}(pq) \langle 0 | (1 + \hat{\Lambda}_2) \; e^{-\hat{T}_2} \; \hat{p}^{\dagger} \hat{q} \; e^{\hat{T}_2} | 0 \rangle, \tag{25}$$

The OPDM can be partitioned into the reference and correlation parts as follows:

$$\gamma_{pq} = \gamma_{pq}^{ref} \; + \; \gamma_{pq}^{corr}, \tag{26}$$

where γ_{pq}^{ref} and γ_{pq}^{corr} are the reference and correlation parts of OPDM, respectively.

With the DF/CD approximation we can avoid the formation of four-index two-particle density matrix (TPDM), we may form a three-index TPDM, instead. The three-index TPDM is defined as follows:[22,23,52,54]

$$\Gamma_{pq}^{Q} = \frac{1}{2} \hat{P}_{+}(pq) \sum_{r,s} \langle 0 | (1 + \hat{\Lambda}_2) e^{-\hat{T}_2} \; \hat{p}^{\dagger} \hat{r}^{\dagger} \hat{s} \hat{q} \; e^{\hat{T}_2} | 0 \rangle \; b_{rs}^{Q}, \tag{27}$$

where $\hat{P}_+(pq)$ is the symmetrizer, which has the following effect on a tensor:

$$\hat{P}_+(pq)\ A_{pq} = A_{pq}\ +\ A_{qp}. \tag{28}$$

The three-index TPDM can be decomposed as in the case of OPDM as follows:[22]

$$\Gamma_{pq}^{Q} = \Gamma_{pq}^{Q(ref)}\ +\ \Gamma_{pq}^{Q(corr)}\ +\ \Gamma_{pq}^{Q(sep)}, \tag{29}$$

where $\Gamma_{pq}^{Q(ref)}$ and $\Gamma_{pq}^{Q(corr)}$ are the reference and correlation parts of TPDM, respectively, and $\Gamma_{pq}^{Q(sep)}$ is the separable part of TPDM. The explicit form of DF-CCD response PDMs can be obtained from our equations for the DF-CCSD method in previous studies.[54,55]

Then, the energy of the DF-CCD-Λ functional may be re-written in terms of PDMs as follows

$$\mathcal{L} = \sum_{p,q} \gamma_{pq} h_{pq}\ +\ \frac{1}{2}\sum_{Q}^{N_{aux}}\sum_{p,q} \Gamma_{pq}^{Q} b_{pq}^{Q} \tag{30}$$

where h_{pq} is the core-Hamiltonian matrix.

F. Orbital Gradient

The MO gradient is defined as follows:[13,14,18,24]

$$w_{pq} = 2(F_{pq} - F_{qp}), \tag{31}$$

where F_{pq} is the generalized-Fock matrix (GFM). Similar to the TPDM, the GFM can be partitioned into reference, correlation, and separable components as follows:[22,23,52]

$$F_{pq} = F_{pq}^{ref}\ +\ F_{pq}^{corr}\ +\ F_{pq}^{sep}. \tag{32}$$

For F_{pq}^{ref} and F_{pq}^{sep} the DF-REF basis integrals, while for F_{pq}^{corr} the DF-CC basis integrals are employed. The explicit form of the GFM is reported in our previous studies.[22,23,52]

G. The Orbital Optimization Procedure

The DF-OCCD wave function is described by the set of $\boldsymbol{\kappa}$, $\boldsymbol{t_2}$, and $\boldsymbol{\lambda_2}$ parameters. Similar to previous studies,[2,13,14,17–19] the $\boldsymbol{t_2}$, $\boldsymbol{\lambda_2}$, and $\boldsymbol{\kappa}$ parameters are simultaneously optimized. The parameters $\boldsymbol{\kappa}$ are obtained from Eq.(24) using the approximate Hessian introduced in our 2014 study.[22] The direct inversion in the iterative subspace (DIIS) method[85] is utilized to accelerate the convergence.[18]

H. DF-OCCD Analytic Gradients

The DF-OCCD energy is minimized with respect to the MO parameters. Hence, there is no need to consider orbital relaxation effects for analytic gradients. However, the DF-OCCD energy is not stationary with respect to CC amplitudes; hence, one need to consider their response in the gradient expression. Hence, we employ the Lagrangian of Eq.(10). The first derivative of the energy may be written as follows[74,75,84,86–91]

$$\left.\frac{\mathrm{d}E}{\mathrm{d}x}\right|_{x=x_0} = \left.\frac{\partial \mathcal{L}}{\partial x}\right|_{x=x_0}. \tag{33}$$

The first derivative equation can be cast into the following form:[23]

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \sum_{p,q} \gamma_{pq} h^x_{pq} \; - \; \sum_{p,q} F_{pq} S^x_{pq} \; + \; \sum_{Q}^{N_{aux}} \sum_{pq} \widetilde{\Gamma}^Q_{pq} (Q|pq)^x \; - \; \sum_{P,Q}^{N_{aux}} \Gamma_{PQ} \boldsymbol{J}^x_{PQ}, \tag{34}$$

where h^x_{pq}, S^x_{pq}, $(Q|pq)^x$, and $\boldsymbol{J}^x_{PQ}$ are the first derivatives of the core-Hamiltonian matrix, overlap matrix, 3-index integrals, and metric integrals, respectively.

Two- and three-index TPDMs are defined by[23,52]

$$\widetilde{\Gamma}^Q_{pq} = \sum_{P}^{N_{aux}} \Gamma^P_{pq} \; [\boldsymbol{J}^{-1/2}]_{PQ}, \tag{35}$$

$$\Gamma_{PQ} = \frac{1}{2} \sum_{p,q} c^P_{pq} \widetilde{\Gamma}^Q_{pq} \; = \; \frac{1}{2} \sum_{p,q} \widetilde{\Gamma}^P_{pq} c^Q_{pq}, \tag{36}$$

$$c^Q_{pq} = \sum_{P}^{N_{aux}} b^P_{pq} \; [\boldsymbol{J}^{-1/2}]_{PQ}. \tag{37}$$

Then, the PDMs and GFM are back-transformed into the AO basis.[92–94]

$$F_{\mu\nu} = \sum_{pq} C_{\mu p} C_{\nu q} F_{pq}, \tag{38}$$

$$\gamma_{\mu\nu} = \sum_{pq} C_{\mu p} C_{\nu q} \gamma_{pq}, \tag{39}$$

$$\Gamma^{Q}_{\mu\nu} = \sum_{pq} C_{\mu p} C_{\nu q} \widetilde{\Gamma}^{Q}_{pq}, \tag{40}$$

where $F_{\mu\nu}$, $\gamma_{\mu\nu}$, and $\Gamma^{Q}_{\mu\nu}$ are the AO basis GFM, OPDM, and three-index TPDM, respectively. The two-index TPDM may be expressed as follows:

$$\Gamma_{PQ} = \frac{1}{2} \sum_{p,q} c^{P}_{pq} \widetilde{\Gamma}^{Q}_{pq} \;=\; \frac{1}{2} \sum_{\mu\nu} c^{P}_{\mu\nu} \Gamma^{Q}_{\mu\nu}, \tag{41}$$

$$c^{Q}_{\mu\nu} = \sum_{P}^{N_{aux}} b^{P}_{\mu\nu} \, [\boldsymbol{J}^{-1/2}]_{PQ}, \tag{42}$$

Hence, the final analytic gradient expression in the AO basis can be written as follows[52]

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \sum_{\mu\nu} \gamma_{\mu\nu} h^{x}_{\mu\nu} \;-\; \sum_{\mu\nu} F_{\mu\nu} S^{x}_{\mu\nu} \;+\; \sum_{Q}^{N_{aux}} \sum_{\mu\nu} \Gamma^{Q}_{\mu\nu} (Q|\mu\nu)^{x} \;-\; \sum_{P,Q}^{N_{aux}} \Gamma_{PQ} \boldsymbol{J}^{x}_{PQ}. \tag{43}$$

III. RESULTS AND DISCUSSION

The efficiency of the OCCD[2,13] and DF-OLCCD methods were compared using a set of alkanes. For the alkanes set, Dunning's correlation-consistent polarized valence triple-ζ basis set (cc-pVTZ) was employed.[95,96] The cc-pVTZ-JKFIT[48] and cc-pVTZ-RI[97] auxiliary basis sets were employed for the reference and correlation energies, respectively, as the fitting basis sets for cc-pVTZ. Further, the MP2, DF-CCD, DF-OCCD, CCSD, and CCSD(T) methods were applied to a set of molecules[18] for comparison of equilibrium geometries. For geometries, Dunning's correlation-consistent polarized core and valence quadruple-ζ (cc-pCVQZ) basis set was used.[95,96] The cc-pVQZ-JKFIT[48] and cc-pVQZ-RI[97] auxiliary basis sets were used for reference and correlation energies, respectively, as fitting basis sets for cc-pCVQZ. Geometry optimizations were performed with analytic gradients for each method. Moreover, hydrogen transfer reaction energies (HTRE)[17,24,98] were regarded to investigate the performance of DF-OCCD. For the HTRE set, the cc-pVTZ primary basis set, and its canonical auxiliary basis sets (cc-pVTZ-JKFIT and cc-pVTZ-RI[97]) were employed. In the CD-OCCD computations, a CD threshold of 10^{-4} was employed. In all computations the DF approximation was applied to the reference and correlation energies.

Further, noncovalent interaction complexes (the A24 and O20 sets)[39,99] were considered to investigate the performance of DF-OCCD for open-shell noncovalent interactions. For weak interactions, single-point energies were obtained at optimized geometries, and the total energies were extrapolated to complete basis set (CBS) limits.[100,101] The two-point extrapolation approach of Halkier *et al.*[102] was used for this purpose.[103] In the two-point extrapolation procedure, for the A24 set the aug-cc-pVDZ and aug-cc-pVTZ basis sets were employed, while for the O20 set the aug-cc-pVTZ and aug-cc-pVQZ basis sets were used. For the noncovalent interaction complexes, the corresponding auxiliary basis sets, aug-cc-pVXZ-JKFIT[48] and aug-cc-pVXZ-RI,[97] were employed as fitting basis sets. For the He atom, the aug-cc-pVXZ-JKFIT basis set is not available; hence, we employed the def2-QZVPP-JKFIT auxiliary basis set. Similarly, for the Li atom, the def2-QZVPP-JKFIT and def2-QZVPP-RI basis sets were used. Counterpoise corrections are considered for all intermolecular interaction energies.[104] Finally, the O_4^+ molecule, where symmetry-breaking problems are observed, was considered to assess the performance of the DF-OCCD method.

A. The Efficiency of DF-OCCD

A set of alkanes is considered to investigate the efficiency of the OCCD and DF-OCCD methods. The conventional OCCD computations were performed with the Q-CHEM 5.3 package.[105] The computational time for the OCCD and DF-OCCD methods are presented graphically in Figure 1. Timing computations were performed with a 10^{-7} energy convergence tolerance on a single node (1 core) Intel(R) Xeon(R) Gold 5218 CPU @ 2.30 GHz computer (memory $\sim$ 500 GB). RHF versions of the OCCD and DF-OCCD codes were used in timing computations. The DF-OCCD method dramatically reduces the computational cost compared to the conventional OCCD, there are 7.8-fold reductions in the computational time compared to OCCD for the largest member (C_6H_{14}) of the alkanes set. The dramatic difference between the computational cost of DF-OCCD and OCCD is mainly arising from the efficiency of DF integral transformation procedure due to reduced I/O time. The accuracy of the DF approximation is well assessed in previous studies,[22,30–32,54,55] it introduces quite negligible errors compared to the conventional methods: noncovalent energies exhibit mean absolute errors (MAEs) of 0.01–0.09 kcal mol^{-1}, equilibrium bond lengths has a MAE value of 10^{-4} Å, and vibrational frequencies yield a MAE of 0.5 cm^{-1}.[22,30–32,54,55]

B. Geometries

We start with a set of closed-shell as the first step of our investigation.[24] Table S1 of the supporting information reports bond lengths of molecules considered. Errors in bond lengths for the MP2, DF-CCD, DF-OCCD, CCSD, and CCSD(T) methods with respect to experiment are presented in Figure 2, while the MAE values are illustrated in Figure 3. The MAE values are 0.006 (MP2), 0.009 (DF-CCD), 0.007 (DF-OCCD), 0.007 (CCSD), and 0.002 [CCSD(T)] Å. The DF-CCD method yields the largest error compared to the experiment, while CCSD(T) yields the lowest error as expected. The DF-OCCD, OCCD, and CCSD methods yield the same MAE value. The DF-OCCD method remarkably enhances the MP2 and DF-CCD results, by 25% and 31%, respectively.

Next, we study a set of open-shell molecules.[106] Table S2 of the supporting information reports bond lengths of open-shell molecules considered. Errors in bond lengths for the MP2, DF-CCD, DF-OCCD, CCSD, and CCSD(T) methods with respect to experiment are presented in Figure 4, while the MAE values are illustrated in Figure 5. The MAE values are 0.014 (MP2), 0.015 (DF-CCD), 0.013 (DF-OCCD), 0.012 (CCSD), and 0.007 [CCSD(T)] Å. The DF-CCD method again yields the largest error compared with the experiment, while CCSD(T) yields the lowest error as expected. Further, the performances of DF-OCCD and CCSD are almost identical.

C. Hydrogen Transfer Reactions

It was demonstrated that the canonical methods, such as MP2, MP3, and LCCD, dramatically fail for the HTREs, which include free radicals.[17,18,24,98] It was reported that the OO methods, such as OMP2 and OLCCD, provide remarkably better performance than their canonical versions (MP2 and LCCD), providing 5- and 6-fold lower MAEs compared with MP2 and OO linearized CCD (OLCCD).[17,18,24] Hence, we consider the same test set[17] to assess the performance of DF-OCCD.

Table I reports the HTRE values (in kcal mol^{-1}) from the MP2, DF-CCD, DF-OCCD, CD-OCCD, CCSD, and CCSD(T) methods at the CBS limit. Errors with respect to CCSD(T) are presented in Figure 6, whereas the MAE values (Figure 7) are 14.6 (MP2), 8.2 (DF-CCD), 0.5 (DF-OCCD), 0.5 (CD-OCCD), and 0.5 (CCSD) kcal mol^{-1}. Hence, the results of DF-OCCD, CD-OCCD, and CCSD are identical and significantly better than those of MP2 and DF-CCD. Furthermore, our results indicate that there is a reduction in DF-CCD errors by more than a factor of 16 when optimized orbitals are used, and comparing to MP2 there is a more than 29-fold decrease in errors.

D. Noncovalent Interactions

In this section we consider weak interactions to investigate the performance of DF-OCCD, and we start with the A24 set.[99] For the A24 set, interaction energies from the MP2, DF-CCD, DF-OCCD, CD-OCCD, and CCSD methods at the CBS limit are reported in Table II. Errors and the mae values with respect to reference energies (Table II) are depicted in Figure 8 and Figure 9, respectively. The MAE values are 0.11 (MP2), 0.25 (DF-CCD), 0.25 (DF-OCCD), 0.26 (CD-OCCD), and 0.26 (CCSD)kcal mol^{-1}. Hence, the performance of DF-CCD, DF-OCCD, CD-OCCD, and CCSD are identical. It is well-known that the HF orbitals are reliably used in most of the closed-shell systems. It is unexpected that the DF-OCCD and CCSD methods yield a larger MAE value compared with MP2. But, it is consistent with a previous study.[107]

Finally, we consider the O20 set[22,39] to investigate the performance of DF-OCCD. Table III reports noncovalent interaction energies (in kcal mol^{-1}) for the O20 set from the MP2, DF-CCD, DF-OCCD, CCSD, and CCSD(T) methods at the CBS limit. Errors with respect to CCSD(T) are presented in Figure 10, whereas the MAE values are illustrated in Figure 11. The MAE values are 0.60 (MP2), 0.50 (DF-CCD), 0.36 (DF-OCCD), 0.38 (CD-OCCD), and 0.34 (CCSD) kcal mol^{-1}. Hence, there is a noticeable improvement upon DF-CCD when optimized orbitals are used. Further, the performance of DF-OCCD, CD-OCCD, and CCSD are virtually the same.

E. Symmetry Breaking in O_4^+

The O_4^+ molecule is an electronically challenging molecule, which suffers from the symmetry breaking problem.[2,13,14,30,108–110]. For the O_4^+ molecule ($^4B_{1g}$), total energies, bond lengths, and the harmonic vibrational frequency, where symmetry breaking occurs, are presented in Table IV. The CCSD(T) computations was performed with the Molpro package.[111] All consider methods yield to rectangular geometries. For bond lengths, DF-OCCD and DF-CCSD provides the lowest errors compared to CCSD(T) ($\Delta r = 0.011 - 0.012$ Å). For the ω (b_{3u}) mode, where symmetry breaking is observed, the absolute errors of the DF-MP2, DF-CCD, DF-OCCD, DF-CCSD, and CCSD(T) methods, with respect to the latest experimental value of 1323 cm^{-1},[112] are: 2130 (DF-MP2), 2612 (DF-CCD), 40 (DF-OCCD), 385 (DF-CCSD), and 1027 [CCSD(T)] cm^{-1}. Hence, the results of DF-MP2 and DF-CCD are in dramatic errors. Further, the DF-OCCD method provides the lowest error and performs significantly better than DF-CCSD and CCSD(T). This example demonstrates that the DF-OCCD method is very helpful for vibrational frequency computations of the molecules suffers from symmetry breaking problems, where the results of canonical methods are in dramatic errors.

IV. CONCLUSIONS

The density-fitted orbital-optimized CCD (DF-OCCD) and its analytic energy gradients have been presented. In addition to DF-OCCD, the Cholesky decomposed variant (CD-OCCD) is also presented for energy computations. Results from the DF-OCCD method have been obtained for closed- and open-shell molecular geometries, HTREs, and interaction energies of noncovalent complexes for comparison with those from the MP2, DF-CCD, CCSD, and CCSD(T) methods.

For the minimization of the MOs of the DF-OCCD wave function, a Lagrangian-based technique has been utilized as in the case of previous OO methods.[13,14,18,22,24,30,31] Both the OCCD and CCSD methods scale formally as $O(N^6)$, where N is the number of basis functions. However, the main drawback of the conventional OCCD is that one needs to perform four-index integral transformations at each CC iteration.[2,13] Even though, the MO transformation scales as $O(N^5)$, it can not be performed in the core memory, except for the very small molecular systems; hence, it is the most expensive part of CC iterations due to the slow I/O procedure. However, with the DF approach, the cost of MO transformations is reduced to $O(N^4)$, and memory requirements are significantly reduced, by a factor of N. Therefore, with the DF approach, it is possible to perform MO transformations in the core memory in many cases. Even if there is no enough memory for the DF algorithm, it is still significantly faster in out-of-core algorithm. Hence, the DF approximation dramatically reduces the cost of the conventional OCCD method.

For molecular geometries, HTREs, and interaction energies the DF-OCCD significantly improves upon MP2 and DF-CCD. For example, for hydrogen transfer reactions there are 16- and 29-fold reductions in errors when DF-OCCD is employed compared with DF-CCD and MP2, respectively. Furthermore, the DF-OCCD method provide remarkably better vibrational frequencies compared to the canonical methods in the case of symmetry breaking problems. Moreover, for some test systems the performance of DF-OCCD and CCSD are virtually the same. However, several factors make DF-OCCD more attractive compared to CCSD: (1) for DF-OCCD there is no need for orbital relaxation contributions in analytic gradient computations (2) active spaces[5] can readily be incorporated into OCCD (3) DF-OCCD provides accurate vibrational frequencies when symmetry-breaking problems[2,13] are observed (4) in its response function, DF-OCCD avoids artificial poles; hence, excited-state molecular properties can be computed via linear response theory[4,7,113] (5) Symmetric and asymmetric triples corrections based on DF-OCCD [OCCD(T)] has a significantly better performance in near degeneracy regions.[15]

V. SUPPLEMENTARY MATERIAL

Computed and experimental bond lengths for the closed- and open-shell molecules.

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VI. DATA AVAILABILITY

The data that supports the findings of this study are available within the article [and its supplementary material].

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TABLE I. Reaction energies (in kcal/mol) of hydrogen transfer reactions from MP2, DF-CCD, DF-OCCD, CD-OCCD, CCSD and CCSD(T) at the CBS limit.

	Reaction	**MP2**[a]	**DF-CCD**	**DF-OCCD**	**CD-OCCD**	**CCSD**[a]	**CCSD(T)**[a]
1	$CH_3 + H_2 \rightarrow CH_4 + H$	−7.6	−2.6	−2.4	−2.4	−2.5	−3.5
2	$C_2H + H_2 \rightarrow C_2H_2 + H$	−50.9	−41.2	−31.4	−31.3	−31.4	−31.9
3	$C_2H_3 + H_2 \rightarrow C_2H_4 + H$	−20.0	−13.6	−8.7	−8.6	−8.7	−9.3
4	$C(CH_3)_3 + H_2 \rightarrow HC(CH_3)_3 + H$	−1.2	4.1	4.7	4.7	4.8	3.8
5	$C_6H_5 + H_2 \rightarrow C_6H_6 + H$	−44.7	−28.0	−10.7	−10.7	−10.6	−11.1
6	$C_2H + C_2H_4 \rightarrow C_2H_2 + C_2H_3$	−30.9	−27.7	−22.7	−22.7	−22.8	−22.6
7	$C(CH_3)_3 + C_2H_4 \rightarrow HC(CH_3)_3 + C_2H_3$	18.8	17.7	13.4	13.4	13.4	13.1
8	$C_6H_5 + C_2H_4 \rightarrow C_6H_6 + C_2H_3$	−24.6	−14.4	−2.0	−2.0	−2.0	−1.7
9	$C_2H + HC(CH_3)_3 \rightarrow C_2H_2 + C(CH_3)_3$	−49.7	−45.3	−36.1	−36.1	−36.2	−35.7
10	$C_6H_5 + HC(CH_3)_3 \rightarrow C_6H_6 + C(CH_3)_3$	−43.4	−32.1	−15.5	−15.4	−15.4	−14.9
11	$C_2H + C_6H_6 \rightarrow C_2H_2 + C_6H_5$	−6.2	−13.2	−20.7	−20.7	−20.8	−20.8
12	$C_2H + CH_4 \rightarrow C_2H_2 + CH_3$	−43.3	−38.7	−29.0	−28.9	−29.0	−28.4
13	$C_2H_3 + CH_4 \rightarrow C_2H_4 + CH_3$	−12.4	−11.0	−6.3	−6.3	−6.2	−5.8
14	$C(CH_3)_3 + CH_4 \rightarrow HC(CH_3)_3 + CH_3$	6.4	6.7	7.1	7.1	7.2	7.3
15	$C_6H_5 + CH_4 \rightarrow C_6H_6 + CH_3$	−37.1	−25.4	−8.3	−8.3	−8.2	−7.6
	MAE	**14.6**	**8.2**	**0.5**	**0.5**	**0.5**	
	Δ_{max}	**33.6**	**17.9**	**1.1**	**1.1**	**1.1**	

[a] Bozkaya and Sherrill.[24]

TABLE II. Closed-shell noncovalent interaction energies (in kcal mol^{-1}) from MP2, DF-CCD, DF-OCCD, CD-OCCD, and CCSD at the CBS limit, and the mean absolute errors (MAE) with respect to reference energies.

	Complex	**Interaction Type**	**MP2**	**DF-CCD**	**DF-OCCD**	**CD-OCCD**	**CCSD**	**Ref**[a]
1	water···ammonia (C_s)	H-bond	-6.53	-6.10	-6.14	-6.14	-6.14	-6.52
2	water dimer (C_s)	H-bond	-4.89	-4.67	-4.71	-4.70	-4.71	-5.01
3	HCN dimer ($C_{\infty v}$)	H-bond	-4.89	-4.62	-4.64	-4.63	-4.63	-4.75
4	HF dimer (C_s)	H-bond	-4.33	-4.27	-4.30	-4.30	-4.30	-4.57
5	ammonia dimer (C_{2h})	H-bond	-3.14	-2.87	-2.89	-2.89	-2.89	-3.16
6	methane···HF (C_{3v})	Mixed	-1.68	-1.48	-1.51	-1.51	-1.52	-1.68
7	ammonia···methane (C_{3v})	Mixed	-0.71	-0.63	-0.64	-0.64	-0.64	-0.78
8	methane···water (C_s)	Mixed	-0.62	-0.55	-0.56	-0.56	-0.56	-0.67
9	formaldehyde dimer (C_s)	Mixed	-4.46	-3.83	-4.00	-4.00	-4.01	-4.47
10	ethene···water (C_s)	Mixed	-2.78	-2.35	-2.31	-2.31	-2.30	-2.58
11	ethene···formaldehyde (C_s)	Mixed	-1.69	-1.37	-1.37	-1.37	-1.36	-1.63
12	ethyne dimer (C_{2v})	Mixed	-1.67	-1.41	-1.38	-1.38	-1.36	-1.54
13	ethene···ammonia (C_s)	Mixed	-1.52	-1.21	-1.17	-1.17	-1.17	-1.39
14	ethene dimer (C_{2v})	Mixed	-1.28	-0.84	-0.79	-0.78	-0.78	-1.11
15	methane···ethene (C_s)	Mixed	-0.56	-0.41	-0.38	-0.38	-0.37	-0.51
16	borane···methane (C_s)	DD[b]	-1.48	-1.13	-1.16	-1.15	-1.16	-1.52
17	methane···ethane (C_s)	DD	-0.81	-0.61	-0.61	-0.61	-0.62	-0.84
18	methane···ethane (C_3)	DD	-0.55	-0.44	-0.45	-0.45	-0.45	-0.62
19	methane dimer (D_{3d})	DD	-0.49	-0.39	-0.39	-0.39	-0.39	-0.54
20	methane···Ar (C_{3v})	DD	-0.41	-0.28	-0.28	-0.28	-0.28	-0.41
21	ethene···Ar (C_{2v})	DD	-0.43	-0.26	-0.23	-0.23	-0.23	-0.37
22	ethene···ethyne (C_{2v})	DD	0.47	1.13	1.22	1.22	1.23	0.78
23	ethene dimer (D_{2h})	DD	0.68	1.29	1.38	1.38	1.39	0.90
24	ethyne dimer (D_{2h})	DD	0.70	1.41	1.49	1.49	1.50	1.08
		MAE	**0.11**	**0.25**	**0.25**	**0.26**	**0.26**	
		Δ_{max}	**0.38**	**0.64**	**0.49**	**0.49**	**0.50**	

[a] At the CCSD(T)/CBS + ΔE_{cc} + ΔE_{rel} + ΔCCSDT(Q) level, where ΔE_{cc} and ΔE_{rel} are the core correlation and the relativity corrections, respectively.[99]

[b] Dispersion dominated.

TABLE III. Open-shell noncovalent interaction energies (in kcal mol^{-1}) from MP2, DF-CCD, DF-OCCD, CD-OCCD, CCSD, and CCSD(T) at the CBS limit, and the mean absolute errors (MAE) with respect to CCSD(T).

Complex	**MP2**[a]	**DF-CCD**	**DF-OCCD**	**CD-OCCD**	**CCSD**[a]	**CCSD(T)**[a]
1 $H_2O\cdots NH_3^+$	-17.40	-16.94	-17.55	-17.55	-17.68	-18.40
2 $HOH\cdots CH_3$	-1.67	-1.43	-1.48	-1.48	-1.49	-1.75
3 $NH\cdots NH$[b]	-1.04	-1.02	-1.01	-1.01	-1.01	-1.02
4 $Li\cdots Li$[c]	0.04	-0.87	-0.93	-0.94	-0.94	-0.97
5 $H_2O\cdots HNH_2^+$	-25.58	-25.16	-25.11	-25.10	-25.09	-25.41
6 $H_2\cdots Li$	-0.02	-0.02	-0.02	0.04	-0.02	-0.02
7 $FH\cdots BH_2$	-4.11	-3.88	-3.94	-3.94	-3.95	-4.22
8 $He\cdots Li$	0.00	0.00	0.00	0.00	0.00	0.00
9 $H_2O\cdots Al$	-7.12	-6.37	-6.89	-6.96	-6.84	-7.75
10 $Ar\cdots OH$	-0.16	-0.14	-0.14	-0.14	-0.14	-0.16
11 $FH\cdots OH$	-6.02	-5.80	-5.83	-5.90	-5.84	-6.10
12 $He\cdots OH$	-0.02	-0.09	-0.11	0.46	-0.03	-0.05
13 $H_2O\cdots Be^+$	-63.95	-65.42	-65.45	-65.45	-65.42	-65.22
14 $HF\cdots CO^+$	-35.82	-32.40	-28.90	-28.89	-28.82	-30.37
15 $H_2O\cdots Cl$	-2.95	-2.10	-2.57	-2.57	-2.66	-3.58
16 $H_2O\cdots Br$	-3.11	-2.24	-2.57	-2.49	-2.64	-3.48
17 $H_2O\cdots Li$	-11.64	-12.10	-12.45	-12.46	-12.46	-12.63
18 $FH\cdots NH_2$	-10.43	-9.98	-10.00	-10.00	-10.00	-10.33
19 $NC\cdots Ne$	-0.06	-0.04	-0.06	-0.06	-0.06	-0.07
20 $He\cdots NH$[c]	-0.02	-0.03	-0.03	-0.03	-0.03	-0.04
MAE	**0.60**	**0.50**	**0.36**	**0.38**	**0.34**	
Δ_{max}	**5.45**	**2.03**	**1.48**	**1.48**	**1.55**	

[a] From Soydaş and Bozkaya.[39] All systems are in doublet states unless otherwise noted.

[b] The lowest quintet state of the dimer is considered, the lowest singlet and triplet states require multireference wave functions.[114]

[c] The lowest triplet state of the dimer is considered.

TABLE IV. Total energies (hartree), bond distances (Å), and the harmonic vibrational frequency (cm^{-1}), where symmetry-breaking occurs, for the O_4^+ ($^4B_{1g}$) molecule using the 6-311G(d) basis set.

Method	E_{tot}	R_{oo}	R_{cc}	ω (b_{3u})
DF-MP2	−299.729 379	1.2002	2.3984	3453
DF-CCD	−299.687 618	1.1479	2.4072	3935
DF-OCCD	−299.695 431	1.1505	2.4072	1283
DF-CCSD	−299.697 341	1.1515	2.4074	1708
CCSD(T)	−299.732 447	1.1626	2.4057	2350
Experiment[a]				1320
Experiment[b]				1323

[a] Jacox and Thompson[115]

[b] Ricks, Douberly, and Duncan[112]

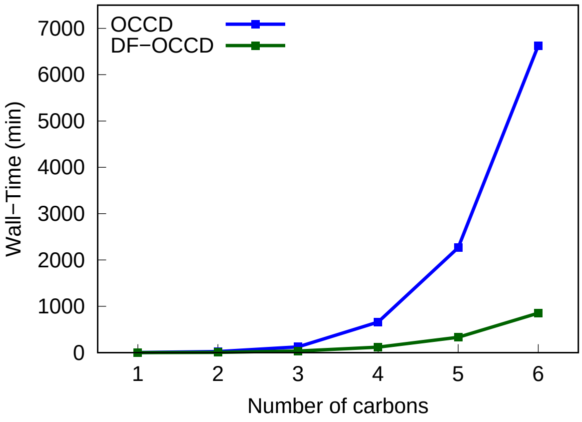

FIG. 1. Wall-time (in min) for computations of single-point energies for the C_nH_{2n+2} (n=1–5) set from the OCCD and DF-OCCD methods with the cc-pVTZ basis set. All computations were performed with a 10^{-7} energy convergence tolerance on a single node (1 core) Intel(R) Xeon(R) Gold 5218 CPU @ 2.30 GHz computer (memory $\sim$ 500 GB).

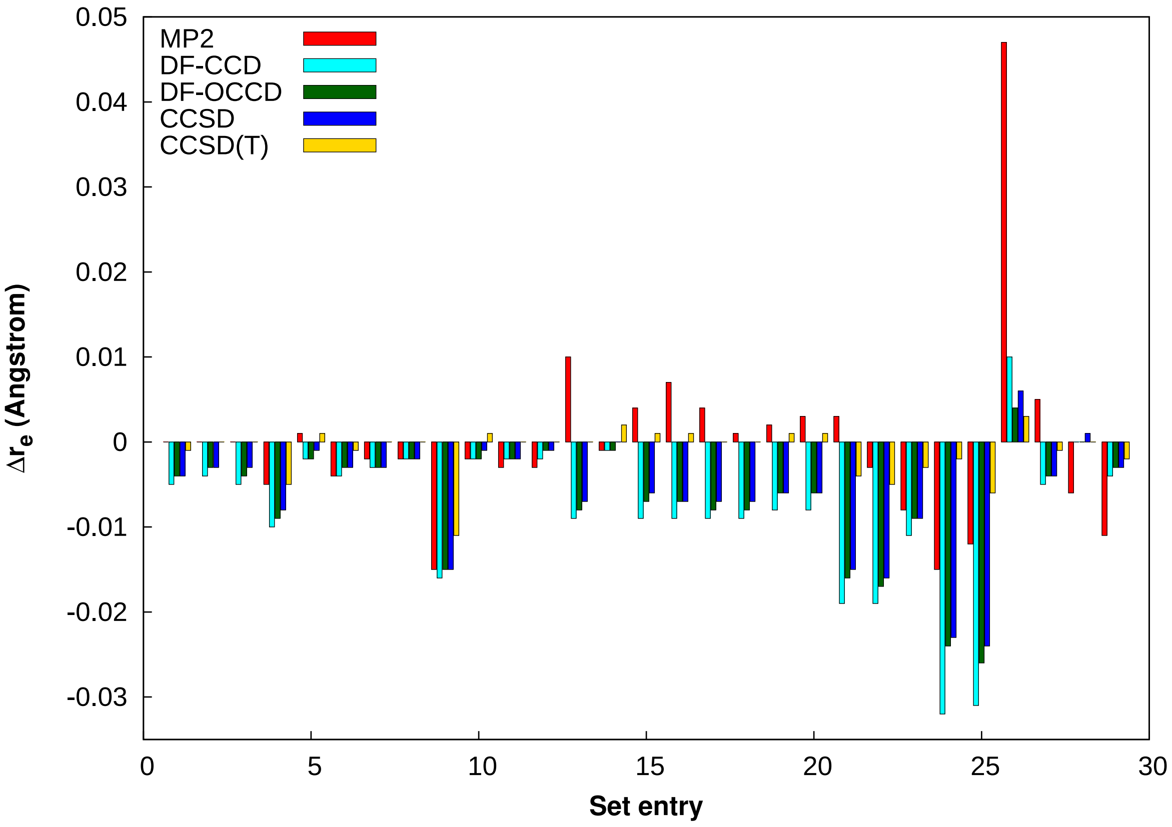

FIG. 2. Errors in bond lengths of closed-shell molecules for the MP2, DF-CCD, DF-OCCD, CCSD, and CCSD(T) methods with respect to experiment (the cc-pCVQZ basis set was employed).

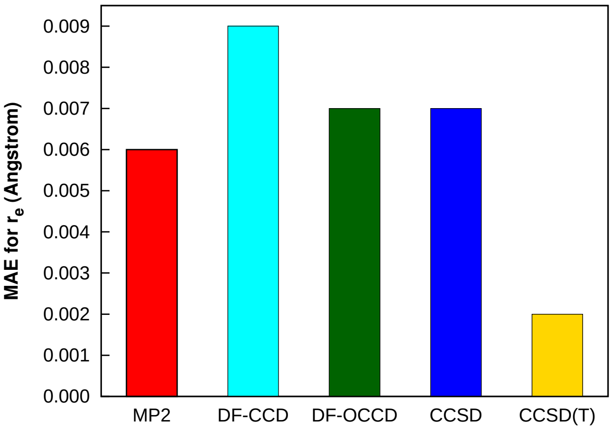

FIG. 3. Mean absolute errors in bond lengths of closed-shell molecules for the MP2, DF-CCD, DF-OCCD, CCSD, and CCSD(T) methods with respect to experiment (the cc-pCVQZ basis set was employed).

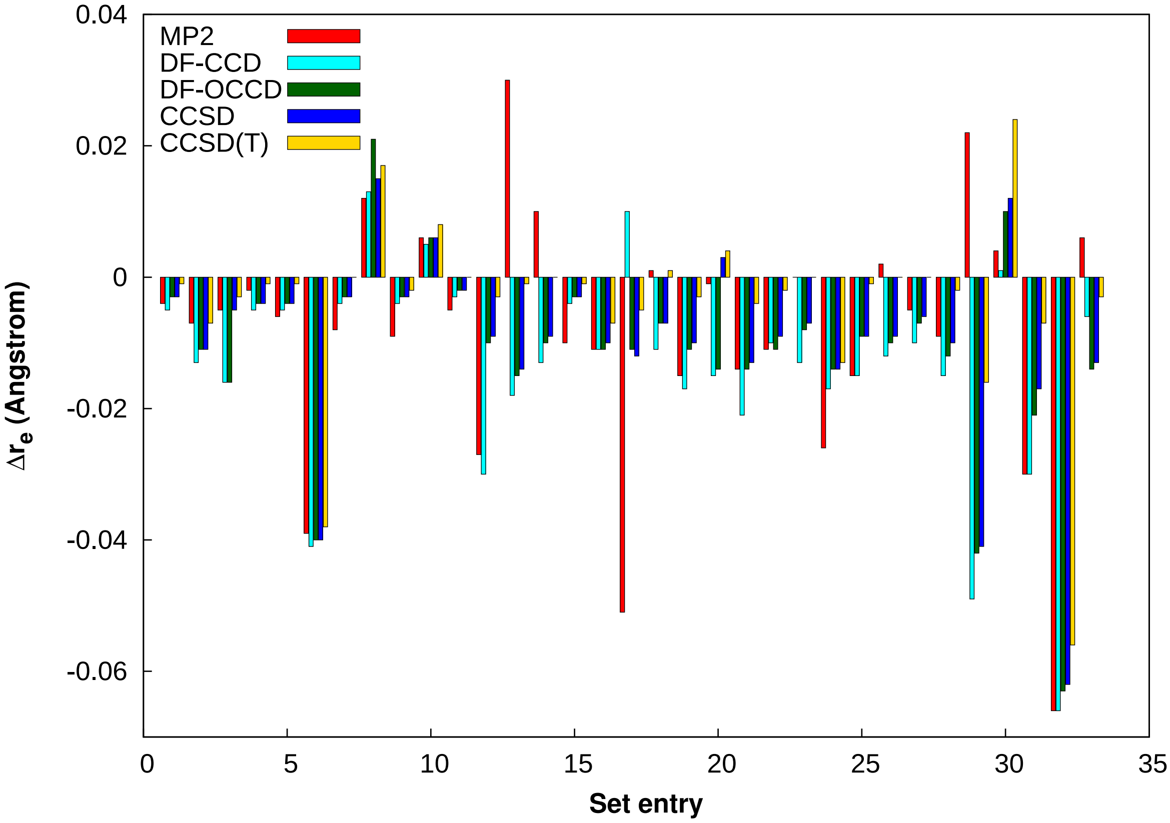

FIG. 4. Errors in bond lengths of open-shell molecules from Byrd *et al.*[106] for the MP2, DF-CCD, DF-OCCD, CCSD, and CCSD(T) methods with respect to experiment (the cc-pCVQZ basis set was employed).

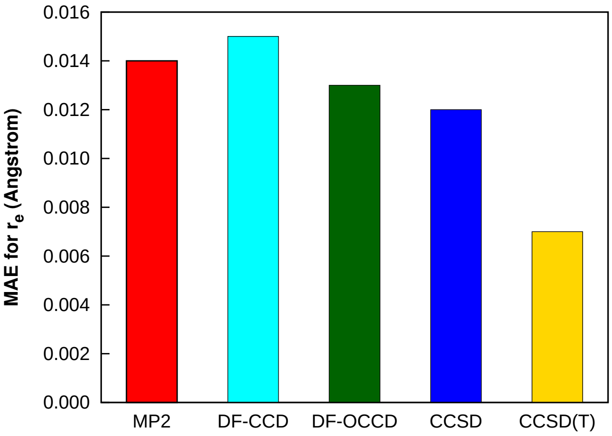

FIG. 5. Mean absolute errors in bond lengths of open-shell molecules from Byrd *et al.*[106] for the MP2, DF-CCD, DF-OCCD, CCSD, and CCSD(T) methods with respect to experiment (the cc-pCVQZ basis set was employed).

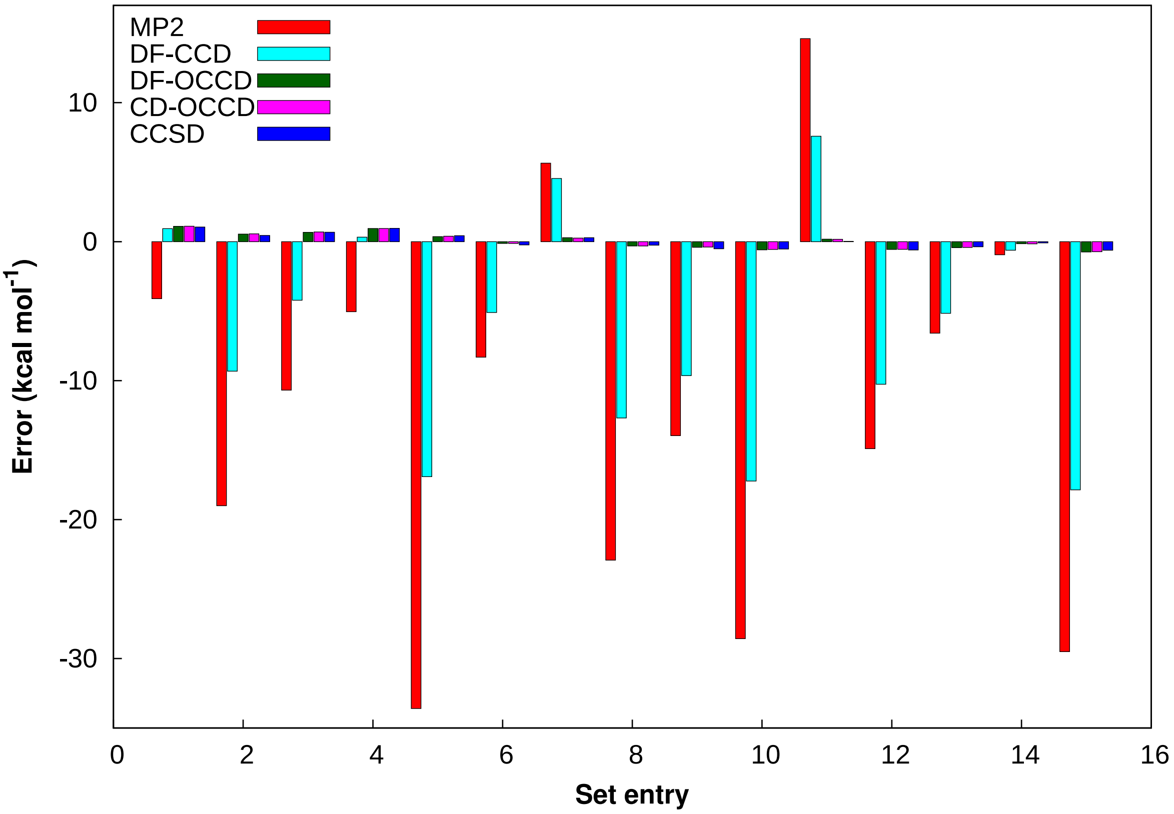

FIG. 6. Errors in hydrogen transfer reaction energies (Table I) for the MP2, DF-CCD, DF-OCCD, CD-OCCD, and CCSD methods with respect to CCSD(T), all in the CBS limit.

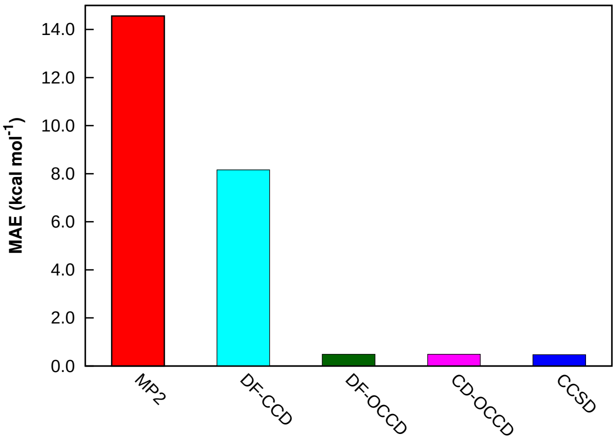

FIG. 7. Mean absolute errors in hydrogen transfer reaction energies (Table I) for the MP2, DF-CCD, DF-OCCD, CD-OCCD, OCCD, and CCSD methods with respect to CCSD(T), all in the CBS limit.

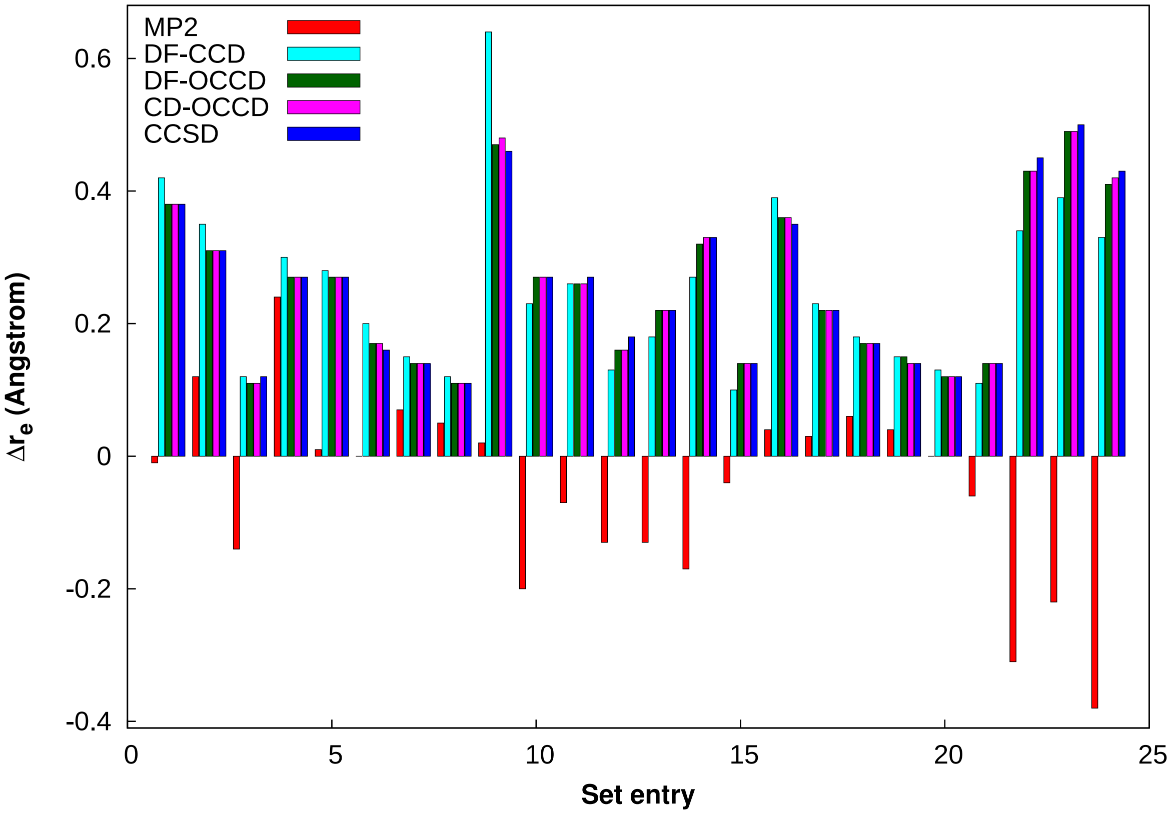

FIG. 8. Errors in closed-shell noncovalent interaction energies (Table II) for the MP2, DF-CCD, DF-OCCD, CD-OCCD, and CCSD methods (all in the CBS limit) with respect to reference energies.[99]

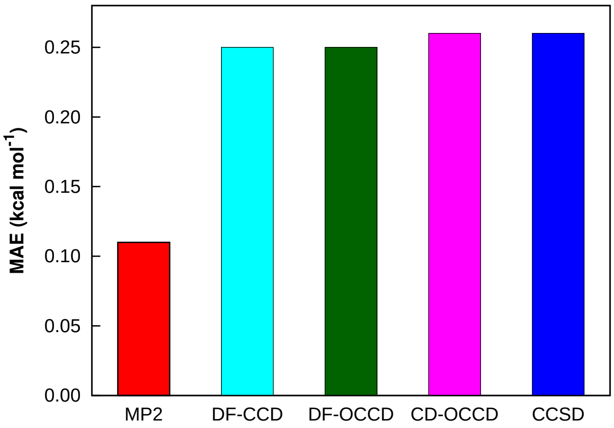

FIG. 9. Mean absolute errors in closed-shell noncovalent interaction energies (Table II) for the MP2, DF-CCD, DF-OCCD, CD-OCCD, and CCSD methods (all in the CBS limit) with respect to reference energies.[99]

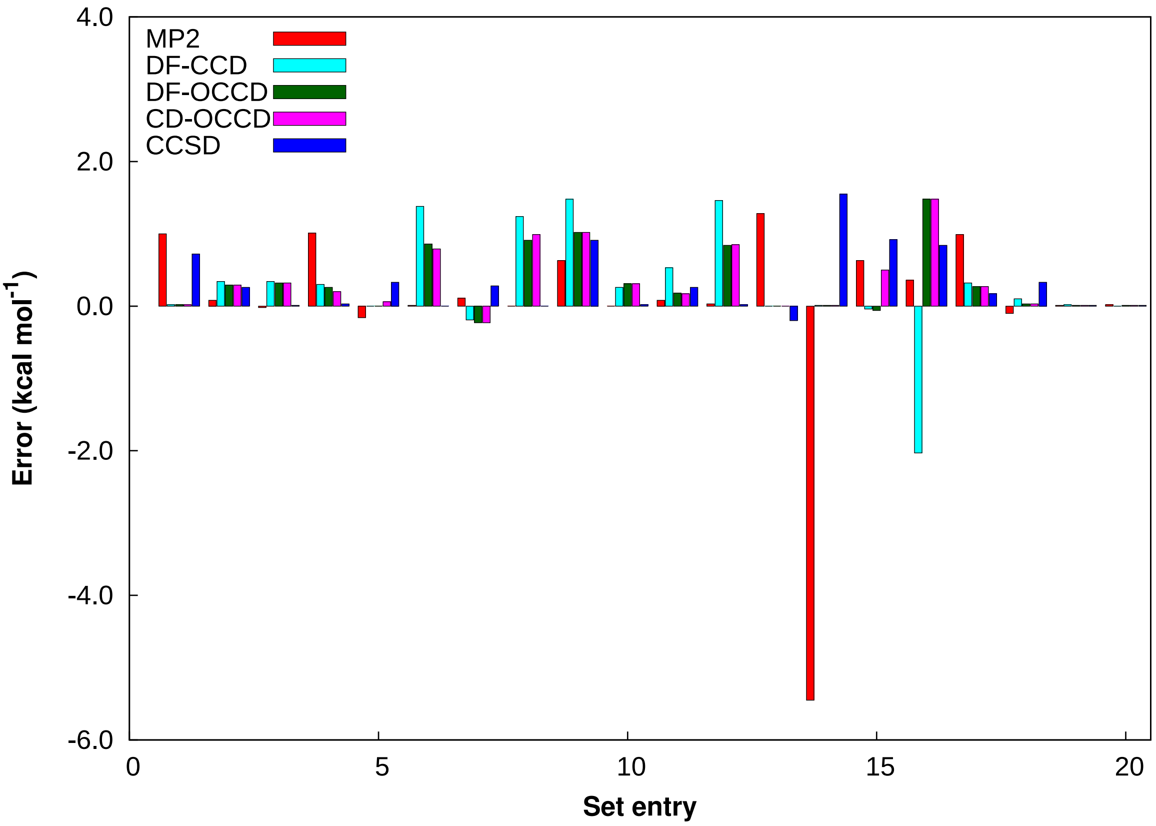

FIG. 10. Errors in open-shell noncovalent interaction energies (Table II) for the MP2, DF-CCD, DF-OCCD, CD-OCCD, and CCSD methods (all in the CBS limit) with respect to reference energies.[99]

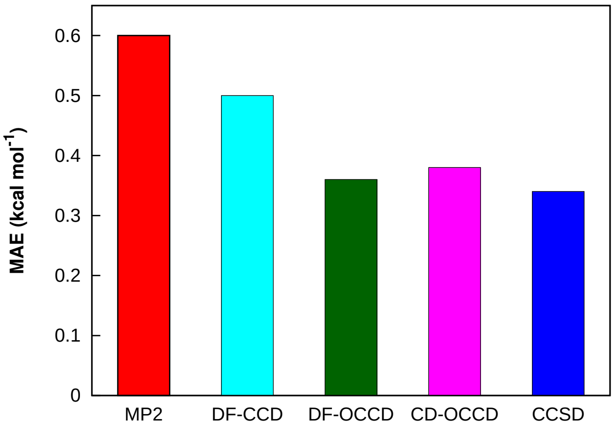

FIG. 11. Mean absolute errors in open-shell noncovalent interaction energies (Table II) for the MP2, DF-CCD, DF-OCCD, CD-OCCD, and CCSD methods (all in the CBS limit) with respect to reference energies.[99]