

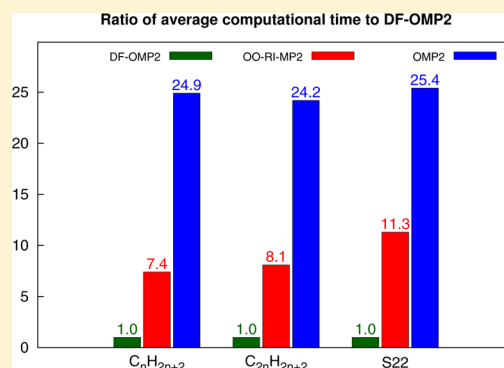
Orbital-Optimized Second-Order Perturbation Theory with Density-Fitting and Cholesky Decomposition Approximations: An Efficient Implementation

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S Supporting Information

ABSTRACT: An efficient implementation of the orbital-optimized second-order perturbation theory with the density-fitting (DF-OMP2) and Cholesky decomposition (CD-OMP2) approaches is presented. The DF-OMP2 method is applied to a set of alkanes, conjugated dienes, and noncovalent interaction complexes to compare the computational cost with the conventional orbital-optimized MP2 (OMP2) [Bozkaya, U.; Turney, J. M.; Yamaguchi, Y.; Schaefer, H. F.; Sherrill, C. D. *J. Chem. Phys.* **2011**, *135*, 104103] and the orbital-optimized MP2 with the resolution of the identity approach (OO-RI-MP2) [Neese, F.; Schwabe, T.; Kossmann, S.; Schirmer, B.; Grimme, S. *J. Chem. Theory Comput.* **2009**, *5*, 3060–3073]. Our results demonstrate that the DF-OMP2 method provides substantially lower computational costs than OMP2 and OO-RI-MP2. Further application results show that the orbital-optimized methods are very beneficial for the computation of open-shell noncovalent interactions. Considering both computational efficiency and the accuracy of the DF-OMP2 method, we conclude that DF-OMP2 is very promising for the study of weak interactions in open-shell molecular systems.



1. INTRODUCTION

Orbital-optimized methods have considerable importance in contemporary quantum chemistry.^{1–26} The orbital optimization techniques for the electron correlation methods have been reported for the coupled-cluster doubles (CCD),^{1,12,13} the coupled-electron pair approximation (CEPA),^{6,10} coupled pair functional theories,^{27,28} active space and excited state coupled-cluster (CC) methods,^{14,15} second-order Møller–Plesset perturbation theory (MP2)^{1,5} and its spin-component scaled variants,^{2,4,20,21} and third-order Møller–Plesset perturbation theory (MP3) and its spin-component scaled variants.^{2,4,7} Further, triples corrections based on orbital-optimized CC methods have been developed and applied to potential energy surfaces.^{3,16,24,29,30} These studies demonstrated that the orbital-optimized Møller–Plesset perturbation (MP) theory and CC methods are very helpful for molecular systems with challenging electronic structures, such as symmetry-breaking problems,^{1,2,5–7,13} transition states, free radicals,^{4,10,21} bond-breaking problems,^{3,24,31} and open-shell noncovalent interactions.

Approximate factorizations of the four-index two-electron integrals (TEIs) have been of great interest in modern computational chemistry. One of the popular approximations is the density fitting (DF), which is also known as the resolution of the identity (RI).^{32–40} The DF approximation enables one to express the four-index TEIs in terms of the three-index tensors. Another TEI approximation technique is the partial Cholesky decomposition (CD) of the TEI

tensor.^{41–44} The DF and CD approximations are quite successful to reduce the storage cost of TEIs as well as the computational time. In the DF approach, TEIs of the primary basis set are written in terms of a preconstructed auxiliary basis set, while in the CD approach one does not need a separate auxiliary basis, the three-index tensors are directly generated from the primary basis set, instead.

The DF approach was employed for orbital-optimized many-body perturbation theory, which is denoted as OO-RI-MP2.²¹ However, in the study of Neese et al.²¹ they used the DF approach only for the correlation energy but not for the reference contribution of the OMP2 energy. Hence, their method can be described as the conventional Hartree–Fock (HF) reference plus a density-fitted second-order energy correction (with optimized orbitals). Further, Neese et al.’s orbital optimization algorithm²¹ has a lack of the orbital Hessian (full or approximate). Therefore, their algorithm converges slowly compared to the algorithms presented in our previous studies.^{1,2,6} Moreover, the CD approach has not yet been applied to the OMP2 method.

In this research, the orbital-optimized MP2 method with the DF and CD approximations is presented, which are denoted as DF-OMP2 and CD-OMP2, respectively. The equations presented have been implemented in a new computer code, dfomp2, and added to the psi4 package.⁴⁵ Both restricted and

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unrestricted formalisms are implemented. The computational time of the DF-OMP2 method is compared with those of OMP2^{1,5} and OO-RI-MP2.²¹ The DF/CD-OMP2 methods are applied to open-shell noncovalent interactions where standard MP2 has difficulties.

2. THEORETICAL APPROACH

2.1. TEI Approximations. In the DF/CD approaches the atomic-orbital (AO) basis TEIs are approximated as

$$(\mu\nu|\lambda\sigma)_{\text{DF}} = \sum_Q^{N_{\text{aux}}} b_{\mu\nu}^Q b_{\lambda\sigma}^Q \quad (1)$$

In the CD approach, the factors $b_{\mu\nu}^Q$ are obtained directly from the Cholesky decomposition, and Q is a Cholesky vector. In the DF method, $b_{\mu\nu}^Q$ is defined as

$$b_{\mu\nu}^Q = \sum_P^{N_{\text{aux}}} (\mu\nu|P) [\mathbf{J}^{-1/2}]_{PQ} \quad (2)$$

where

$$(\mu\nu|P) = \int \int \chi_\mu(\mathbf{r}_1) \chi_\nu(\mathbf{r}_1) \frac{1}{r_{12}} \phi_P(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (3)$$

and

$$J_{PQ} = \int \int \phi_P(\mathbf{r}_1) \frac{1}{r_{12}} \phi_Q(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (4)$$

where $\{\chi_\mu(\mathbf{r})\}$ and $\{\phi_P(\mathbf{r})\}$ are members of the primary and auxiliary basis sets, respectively.

The molecular-orbital (MO) basis integrals can be approximated as

$$(pq|rs)_{\text{DF}} = \sum_Q^{N_{\text{aux}}} b_{pq}^Q b_{rs}^Q \quad (5)$$

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

2.2. The DF-MP2- Λ Energy Functional and Amplitude Equations. For the orbital indexing, the conventional notation is used: i, j, k, l, m , and n for occupied orbitals; a, b, c, d, e , and f for virtual orbitals; and p, q, r, s, t , and u for general spin orbitals. The MP2 correlation energy can be written as follows

$$\Delta E_{\text{MP2}} = \langle 0 | (\hat{W}_N \hat{T}_2^{(1)})_c | 0 \rangle \quad (6)$$

where \hat{W}_N is the two-electron component of the normal ordered Hamiltonian operator,^{46,47} $|0\rangle$ is the reference determinant (Fermi-vacuum), $\hat{T}_2^{(1)}$ is the first-order cluster double excitation operator, and subscript c means only connected diagrams are included.

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

where $t_{ij}^{ab(1)}$ are the first-order double excitation amplitudes and \hat{a}^\dagger and \hat{a} are the creation and annihilation operators, respectively. We can write the MP2 energy more explicitly as follows

$$E_{\text{MP2}} = E_{\text{ref}} + \frac{1}{4} \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{vir}} t_{ij}^{ab(1)} \langle ij||ab \rangle_{\text{DF}} \quad (8)$$

where $\langle ij||ab \rangle_{\text{DF}}$ is the antisymmetrized TEI within the DF approximation and E_{MP2} and E_{ref} are the MP2 and reference energies, respectively. The amplitude equation can be written as

$$\langle \Phi_{ij}^{ab} | (\hat{f}_N^d \hat{T}_2^{(1)} + \hat{W}_N)_c | 0 \rangle = 0 \quad (9)$$

where \hat{f}_N^d is the diagonal part of the normal ordered Fock operator, $\langle \Phi_{ij}^{ab} |$ is a doubly excited Slater determinant. The MP2 amplitude equation can be written more explicitly as follows

$$t_{ij}^{ab(1)} D_{ij}^{ab} = \langle ij||ab \rangle_{\text{DF}} + \hat{P}_-(ab) \sum_{e \neq b}^{\text{vir}} t_{ij}^{ae(1)} f_{be} - \hat{P}_-(ij) \sum_{m \neq j}^{\text{occ}} t_{im}^{ab(1)} f_{mj} \quad (10)$$

where f_{pq} is the matrix element of the Fock operator, D_{ij}^{ab} and $\hat{P}_-(pq)$ are given by

$$D_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb} \quad (11)$$

$$\hat{P}_-(pq) = 1 - \hat{P}(pq) \quad (12)$$

where $\hat{P}(pq)$ is the permutation operator.

In order to obtain a variational energy functional (\tilde{E}_{MP2}), it is convenient^{48,49} to introduce a Lagrangian (DF-MP2- Λ functional) as follows

$$\Delta \tilde{E}^{(2)} = \langle 0 | (\hat{W}_N \hat{T}_2^{(1)})_c | 0 \rangle + \langle 0 | \{ \hat{\Lambda}_2^{(1)} (\hat{f}_N^d \hat{T}_2^{(1)} + \hat{W}_N)_c \} | 0 \rangle \quad (13)$$

where $\hat{\Lambda}_2^{(1)}$ is the first-order double de-excitation operator. One can readily verify that^{1,5}

$$\hat{\Lambda}_2^{(1)} = \hat{T}_2^{(1)} \quad (14)$$

The standard MP2 t_2 -amplitude equations are obtained by requiring that $\Delta \tilde{E}_{\text{MP2}}$ be stationary with respect to λ_2 amplitudes, while the stationary requirement with respect to t_2 amplitudes leads to the λ_2 -amplitude equation.

2.3. The Parametrization of the OMP2 Wave Function.

For the parametrization of the OMP2 wave function, we will follow our previous presentations.¹⁻¹⁰ The orbital variations may be expressed by means of an exponential unitary operator⁵⁰⁻⁵³

$$\tilde{\hat{p}}^\dagger = e^{\hat{K}} \hat{p}^\dagger e^{-\hat{K}} \quad (15)$$

$$\tilde{\hat{p}} = e^{\hat{K}} \hat{p} e^{-\hat{K}} \quad (16)$$

$$|\tilde{p}\rangle = e^{\hat{K}} |p\rangle \quad (17)$$

where $e^{\hat{K}}$ is the orbital 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. The operator \hat{K} can be written as

$$\hat{K} = \sum_{p,q} K_{pq} \hat{p}^\dagger \hat{q} = \sum_{p>q} \kappa_{pq} (\hat{p}^\dagger \hat{q} - \hat{q}^\dagger \hat{p}) \quad (18)$$

$$\mathbf{K} = \text{Skew}(\kappa) \quad (19)$$

where κ_{pq} are the orbital rotation parameters. The transformed molecular orbital (MO) coefficients may be written as

$$\mathbf{C}(\kappa) = \mathbf{C}^{(0)} e^{\mathbf{K}} \quad (20)$$

where $\mathbf{C}^{(0)}$ and $\mathbf{C}(\kappa)$ are the initial and transformed MO coefficient matrices, respectively.

For OMP2, the following variational energy functionals (Lagrangians) can be written^{1,5}

$$\begin{aligned} \tilde{E}(\kappa) = & \langle 0 | \hat{H}^{\kappa} | 0 \rangle + \langle 0 | (\hat{W}_N^{\kappa} \hat{T}_2^{(1)})_c | 0 \rangle \\ & + \langle 0 | \{ \hat{\Lambda}_2^{(1)} (\hat{f}_N^{\kappa} \hat{T}_2^{(1)} + \hat{W}_N^{\kappa}) \}_c | 0 \rangle \end{aligned} \quad (21)$$

where \hat{H}^{κ} , \hat{f}_N^{κ} , \hat{W}_N^{κ} , and \hat{H}_N^{κ} are the transformed operators

$$\hat{H}^{\kappa} = e^{-\hat{K}} \hat{H} e^{\hat{K}} \quad (22)$$

$$\hat{f}_N^{\kappa} = e^{-\hat{K}} \hat{f}_N^d e^{\hat{K}} \quad (23)$$

$$\hat{W}_N^{\kappa} = e^{-\hat{K}} \hat{W}_N e^{\hat{K}} \quad (24)$$

$$\hat{H}_N^{\kappa} = e^{-\hat{K}} \hat{H}_N e^{\hat{K}} \quad (25)$$

where \hat{H} is the Hamiltonian operator.

The first and second derivatives of the Lagrangian with respect to κ (at $\kappa = 0$) can be written as

$$w_{pq} = \left. \frac{\partial \tilde{E}}{\partial \kappa_{pq}} \right|_{\kappa=0} \quad (26)$$

$$A_{pq,rs} = \left. \frac{\partial^2 \tilde{E}}{\partial \kappa_{pq} \partial \kappa_{rs}} \right|_{\kappa=0} \quad (27)$$

Then the Lagrangian can be expanded up to second-order as follows:

$$\tilde{E}^{(2)}(\kappa) = \tilde{E}^{(0)} + \kappa^\dagger \mathbf{w} + \frac{1}{2} \kappa^\dagger \mathbf{A} \kappa \quad (28)$$

where \mathbf{w} is the MO gradient vector, κ is the MO rotation vector, and \mathbf{A} is the MO Hessian matrix. Hence, minimizing the Lagrangian with respect to κ yields

$$\kappa = -\mathbf{A}^{-1} \mathbf{w} \quad (29)$$

This final equation is just the usual Newton–Raphson step. Hence, the orbitals are rotated until the convergence.

2.4. Response Density Matrices. Now, let us define the particle density matrices (PDMs). At first, the one-particle density matrix (OPDM) can be decomposed as follows

$$\gamma_{pq} = \gamma_{pq}^{\text{ref}} + \gamma_{pq}^{\text{corr}} \quad (30)$$

where γ_{pq}^{ref} and $\gamma_{pq}^{\text{corr}}$ are the reference and correlation contributions to OPDM. The reference OPDM is given by

$$\gamma_{ij}^{\text{ref}} = \delta_{ij} \quad (31)$$

where δ_{ij} denotes the Kronecker delta. The unique nonzero blocks of the correlation OPDM can be written as

$$\gamma_{ij}^{\text{corr}} = -\frac{1}{2} \sum_m^{\text{occ}} \sum_{e,f}^{\text{vir}} t_{im}^{ef(1)} \lambda_{ef}^{jm(1)} \quad (32)$$

$$\gamma_{ab}^{\text{corr}} = -\frac{1}{2} \sum_{m,n}^{\text{occ}} \sum_f^{\text{vir}} t_{mn}^{bf(1)} \lambda_{af}^{mn(1)} \quad (33)$$

where

$$\lambda_{ab}^{ij(1)} = t_{ij}^{ab(1)} \quad (34)$$

Similar to the OPDM case, the two-particle density matrix (TPDM) can be decomposed as follows

$$\Gamma_{pq}^Q = \Gamma_{pq}^{Q(\text{ref})} + \Gamma_{pq}^{Q(\text{corr})} + \Gamma_{pq}^{Q(\text{sep})} \quad (35)$$

where $\Gamma_{pq}^{Q(\text{ref})}$ and $\Gamma_{pq}^{Q(\text{corr})}$ are the reference and correlation contributions to TPDM, and $\Gamma_{pq}^{Q(\text{sep})}$ is the separable part of TPDM. The reference TPDM is given by

$$\Gamma_{ij}^{Q(\text{ref})} = \delta_{ij} J_Q - b_{ij}^Q \quad (36)$$

where b_{ij}^Q is evaluated using the reference auxiliary (DF-REF) basis, the JK-FIT basis set,³⁷ and J_Q is defined as

$$J_Q = \sum_m^{\text{occ}} b_{mm}^Q \quad (37)$$

The unique nonzero blocks of the separable TPDMs can be written as

$$\begin{aligned} \Gamma_{ij}^{Q(\text{sep})} = & \delta_{ij} (\gamma_Q + \tilde{\gamma}_Q) + \gamma_{ij}^{\text{corr}} J_Q - \sum_m^{\text{occ}} \gamma_{mj}^{\text{corr}} b_{mi}^Q \\ & - \sum_m^{\text{occ}} \gamma_{im}^{\text{corr}} b_{jm}^Q \end{aligned} \quad (38)$$

$$\Gamma_{ia}^{Q(\text{sep})} = - \sum_e^{\text{vir}} \gamma_{ea}^{\text{corr}} b_{ie}^Q \quad (39)$$

$$\Gamma_{ab}^{Q(\text{sep})} = \gamma_{ab}^{\text{corr}} J_Q \quad (40)$$

where b_{pq}^Q is again evaluated in the DF-REF basis, and intermediates are given by

$$\gamma_Q = \sum_{m,n}^{\text{occ}} \gamma_{mn}^{\text{corr}} b_{mn}^Q \quad (41)$$

$$\tilde{\gamma}_Q = \sum_{e,f}^{\text{vir}} \gamma_{ef}^{\text{corr}} b_{ef}^Q \quad (42)$$

Finally, the unique nonzero blocks of the correlation TPDM can be expressed as

$$\Gamma_{ia}^{Q(\text{corr})} = \sum_m^{\text{occ}} \sum_e^{\text{vir}} t_{im}^{ae(1)} b_{me}^Q \quad (43)$$

where b_{me}^Q is evaluated using the correlation auxiliary (DF-MP2) basis, the RI basis set.⁵⁴

Then, the energy of the DF-MP2- Λ functional can be expressed in terms of PDMs as follows

$$\tilde{E}_{\text{MP2}} = \sum_{p,q} \gamma_{pq} h_{pq} + \frac{1}{2} \sum_Q^{\text{aux}} \sum_{p,q} \Gamma_{pq}^Q b_{pq}^Q \quad (44)$$

2.5. Generalized-Fock and Orbital Gradient. Now, let us turn our attention to the orbital gradient. The orbital gradient is expressed in terms of the generalized-Fock matrix (GFM) as^{1,2,5–7}

$$w_{pq} = 2(F_{pq} - F_{qp}) \quad (45)$$

Table 1. Open-Shell Noncovalent Interaction Energies (in kcal mol⁻¹) at the CBS MP2, DF-MP2, OMP2, OO-RI-MP2, DF-OMP2, CD-OMP2, CCSD, and CCSD(T) Levels, and the $\langle S^2 \rangle$ Values of the Complexes from the UHF and OMP2 Wave Functions

	complex	MP2	DF-MP2	OMP2	OO-RI-MP2	DF-OMP2	CD-OMP2	CCSD	CCSD(T)	$\langle S^2 \rangle_{\text{UHF}}$	$\langle S^2 \rangle_{\text{OMP2}}$
1	H ₂ O...NH ₃ ⁺	-17.40	-17.40	-18.80	-18.80	-18.77	-18.77	-17.68	-18.40	0.76	0.75
2	HOH...CH ₃	-1.67	-1.67	-1.81	-1.81	-1.81	-1.81	-1.49	-1.75	0.76	0.75
3	NH...NH ^a	-1.04	-1.04	-1.03	-1.03	-1.03	-1.03	-1.01	-1.02	6.03	6.01
4	Li...Li ^b	0.04	0.04	0.02	0.02	0.02	0.02	-0.94	-0.97	2.00	2.00
5	H ₂ O...HNH ₂ ⁺	-25.58	-25.58	-25.48	-25.48	-25.48	-25.48	-25.09	-25.42	0.76	0.75
6	H ₂ ...Li	-0.02	0.03	-0.01	-0.01	-0.08	-0.27	-0.02	-0.02	0.75	0.75
7	H ₂ O...F	-0.16	-0.16	-5.63	-5.62	-5.57	-5.65	-2.12	-3.71	0.76	0.75
8	FH...BH ₂	-4.11	-4.11	-4.28	-4.28	-4.28	-4.28	-3.95	-4.22	0.75	0.75
9	He...Li	0.00	-0.06	0.00	0.00	0.01	0.00	0.00	0.00	0.75	0.75
10	H ₂ O...HO ₂	-2.10	-2.10	-2.27	-2.27	-2.27	-2.27	-2.06	-2.23	0.76	0.75
11	H ₂ O...Al	-7.12	-7.38	-7.86	-8.15	-8.12	-8.15	-6.84	-7.75	0.79	0.76
12	Ar...NO	-0.33	-0.33	-0.47	-0.47	-0.31	-0.48	-0.24	-0.34	0.78	0.75
13	Ar...OH	-0.16	-0.16	-0.16	-0.16	-0.16	-0.16	-0.14	-0.16	0.76	0.75
14	FH...OH	-6.02	-6.06	-6.11	-6.11	-6.16	-6.19	-5.84	-6.10	0.76	0.75
15	He...OH	-0.02	0.34	-0.03	-0.02	0.27	0.22	-0.03	-0.05	0.76	0.75
16	H ₂ O...Be ⁺	-63.95	-63.92	-63.63	-63.65	-63.65	-63.65	-65.42	-65.22	0.75	0.75
17	HF...CO ⁺	-35.82	-35.82	-29.44	-29.43	-29.44	-29.44	-28.82	-30.37	0.86	0.76
18	H ₂ O...Cl	-2.95	-3.05	-4.29	-4.27	-4.28	-4.40	-2.66	-3.58	0.76	0.75
19	H ₂ O...Br	-3.11	-3.23	-4.05	-4.06	-4.15	-4.16	-2.64	-3.48	0.76	0.75
20	H ₂ O...Li	-11.64	-11.64	-12.05	-12.05	-12.05	-12.05	-12.46	-12.63	0.75	0.75
21	FH...NH ₂	-10.43	-10.43	-10.52	-10.52	-10.52	-10.52	-10.00	-10.33	0.76	0.75
22	NC...Ne	-0.06	-0.07	-0.08	-0.08	-0.02	-0.29	-0.06	-0.07	1.15	0.75
23	He...NH	-0.02	-0.06	-0.02	-0.02	-0.02	0.01	-0.03	-0.04	2.02	2.01
	$ \Delta _{\text{max}}$	5.45	5.45	1.92	1.91	1.85	1.93	1.59			

^aThe lowest quintet state of the dimer is considered, the lowest singlet and triplet states require multireference wave functions.⁶⁹ ^bThe lowest triplet state of the dimer is considered.

where F_{pq} is a generalized-Fock matrix element. As in case of PDMs, it is possible to separate GFM into reference, correlation, and separable parts:

$$F_{pq} = F_{pq}^{\text{ref}} + F_{pq}^{\text{corr}} + F_{pq}^{\text{sep}} \quad (46)$$

More explicitly, we can write

$$F_{pq}^{\text{ref}} = \sum_r h_{pr} \gamma_{rq}^{\text{ref}} + \sum_Q^{N_{\text{aux}}} \sum_r \Gamma_{qr}^{Q(\text{ref})} b_{pr}^Q \quad (47)$$

$$F_{pq}^{\text{corr}} = \sum_r h_{pr} \gamma_{rq}^{\text{corr}} + \sum_Q^{N_{\text{aux}}} \sum_r \Gamma_{qr}^{Q(\text{corr})} b_{pr}^Q \quad (48)$$

$$F_{pq}^{\text{sep}} = \sum_Q^{N_{\text{aux}}} \sum_r \Gamma_{qr}^{Q(\text{sep})} b_{pr}^Q \quad (49)$$

For F_{pq}^{ref} and F_{pq}^{sep} one should use the DF-REF basis integrals, while for F_{pq}^{corr} the DF-MP2 basis integrals should be employed.

2.6. Orbital Hessian. The efficiency of the optimization algorithm is very sensitive to the employed orbital Hessian. For an efficient code, one should use an approximate Hessian, at least. Moreover, one only needs to consider orbital Hessian block(s) corresponding to nonredundant rotations. When all orbitals are correlated, only virtual-occupied rotations are nonredundant. However, in the presence of the frozen-core orbitals, rotations between frozen cores and active occupieds should be considered as well. For the DF/CD-OMP2 approach, the exact HF and an approximately diagonal MP2 MO-Hessian are implemented. In case of the HF MO-Hessian, eq 29 is equivalent to the MP2 orbital response equation, and eq 29 is

solved iteratively with the preconditioned conjugate gradient algorithm (PCG). For the PCG algorithm, the linear transformed HF MO-Hessian ("the σ vector") is defined as

$$\sigma_{ai} = \sum_{bj} A_{ai,bj} p_{bj} \quad (50)$$

where \mathbf{p} is a trial vector of orbital rotation parameters. More explicitly, we can write

$$\begin{aligned} \sigma_{ai} = & 2 \sum_b^{\text{vir}} f_{ab} p_{bi} - 2 \sum_j^{\text{occ}} f_{ij} p_{aj} + 4 \sum_Q^{N_{\text{aux}}} b_{ai}^Q p^Q \\ & - 2 \sum_Q^{N_{\text{aux}}} \sum_j b_{aj}^Q p_{ij}^Q - 2 \sum_Q^{N_{\text{aux}}} \sum_j b_{ij}^Q p_{aj}^Q \end{aligned} \quad (51)$$

and intermediates are defined as

$$p^Q = 2 \sum_{bj} b_{bj}^Q p_{bj} \quad (52)$$

$$p_{ij}^Q = \sum_b b_{bi}^Q p_{bj} \quad (53)$$

$$p_{aj}^Q = \sum_b b_{ba}^Q p_{bj} \quad (54)$$

The cost of the PCG algorithm scales formally as $O(N^4)$, where N is the number of basis functions.

The HF MO-Hessian is a good approximation to the MP2 MO-Hessian for closed-shell molecules. However, for the open-shell molecules suffering from spin or spatial symmetry breaking problems, the HF MO-Hessian is no more a good

approximation. For such problematic cases, an approximately diagonal MP2 MO-Hessian is implemented. The analytic expression for the exact MP2 MO-Hessian was given in our previous study.¹ Hence, we can obtain an analytic formula for the diagonal Hessian starting from the exact MO Hessian.¹ Further, it is not necessary to use the exact diagonal Hessian, we may obtain an approximately diagonal Hessian by keeping the leading terms of the exact diagonal MO Hessian. Hence, we suggest the following approximately diagonal Hessians for the virtual–occupied (VO) and occupied–occupied (OO) blocks

$$A_{ai,ai} = -2(F_{ii} + F_{aa}) + 2h_{aa}\gamma_{ii} + 2h_{ii}\gamma_{aa} + 2 \sum_Q^{N_{\text{aux}}} b_{aa}^Q \Gamma_{ii}^Q + 2 \sum_Q^{N_{\text{aux}}} b_{ii}^Q \Gamma_{aa}^Q + 2\gamma_{ii} \sum_m^{\text{occ}} (\text{malma})_{\text{DF}} \quad (55)$$

and

$$A_{ij,ij} = -2(F_{ii} + F_{jj}) + 2h_{ii}\gamma_{jj} - 4h_{ij}\gamma_{ij} + 2h_{jj}\gamma_{ii} + 2 \sum_Q^{N_{\text{aux}}} b_{ii}^Q \Gamma_{jj}^Q + 2 \sum_Q^{N_{\text{aux}}} b_{jj}^Q \Gamma_{ii}^Q - 4 \sum_Q^{N_{\text{aux}}} b_{ij}^Q \Gamma_{ij}^Q + 2 \sum_m^{\text{occ}} [(\text{milmi})_{\text{DF}} - (\text{mjlmj})_{\text{DF}}] \quad (56)$$

2.7. The Orbital Optimization Procedure. The DF-OMP2 wave function is defined by a set of orbital rotation parameters κ and first-order double excitation amplitudes t_2 . For computational efficiency, t_2 and κ are optimized simultaneously, as previous studies.^{1,2,5–7,13} Orbital rotation parameters are obtained from eq 29 using the approximate Hessians described in eqs 50–56. The direct inversion in the iterative subspace (DIIS) extrapolation technique⁵⁵ is implemented for orbital rotation parameters following our recent study.⁶

3. RESULTS AND DISCUSSION

Results from the OMP2, OO-RI-MP2, CD-OMP2, and DF-OMP2 methods were obtained for a set of alkanes, conjugated dienes, and the S22 database⁵⁶ for comparison of the computational cost. For energy computations of alkanes and conjugated dienes, Dunning's correlation-consistent polarized valence triple- ζ basis set (cc-pVTZ) was used, while for energy computations of the S22 database the aug-cc-pVDZ basis set was employed without the frozen core approximation.^{57,58} For the cc-pVTZ and aug-cc-pVDZ primary basis sets, cc-pVTZ-JKFIT³⁷ and cc-pVTZ-RI⁵⁴ and aug-cc-pVDZ-JKFIT³⁷ and aug-cc-pVDZ-RI⁵⁴ auxiliary basis set pairs were used for reference and correlation energies, respectively.

Moreover, the O23 database⁸ was considered to investigate the performance of DF-OMP2 and OO-RI-MP2 for open-shell noncovalent interactions. For the O23 database (Table 1), single-point energy computations were performed, and the total energies were extrapolated to complete basis set (CBS) limits.^{59–62} The two-point extrapolation technique of Halkier et al.⁶³ was employed as follows:

$$E_X^{\text{HF}} = E_{\text{CBS}}^{\text{HF}} + A e^{-\alpha X} \quad (57)$$

$$E_X^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} + B X^{-3} \quad (58)$$

where $E_{\text{CBS}}^{\text{HF}}$ and $E_{\text{CBS}}^{\text{corr}}$ are Hartree–Fock (HF) and correlation energies at the CBS limit, respectively, A and B are the fitting parameters, and X is the cardinal number of Dunning's augmented correlation-consistent polarized valence (aug-cc-pVXZ) basis set. The exponent α was chosen to be 1.63 as suggested.⁶³ For the two-point extrapolation procedure, the aug-cc-pVTZ and aug-cc-pVQZ basis sets^{57,58} were used without the frozen core approximation. The aug-cc-pVXZ-JKFIT³⁷ and aug-cc-pVXZ-RI⁵⁴ auxiliary basis sets were employed as fitting basis sets. For open-shell complexes, the unrestricted orbitals were employed, and no mixing of α and β spin orbitals was allowed. All noncovalent interaction energies are counterpoise corrected.⁶⁴ The MP2, DF-MP2, OMP2, DF-OMP2, coupled-cluster singles and doubles (CCSD),⁶⁵ and coupled-cluster singles and doubles with perturbative triples [CCSD(T)]^{66,67} computations were performed with the psi4 program package,⁴⁵ while the OO-RI-MP2 computations were carried out with the orca program.^{21,23,68}

3.1. The Efficiency of DF-OMP2. In order to assess the efficiency of the DF-OMP2 method, we first consider a set of alkanes. For the considered alkanes, total energies and the computational time (wall-time) from the OMP2, OO-RI-MP2, CD-OMP2, and DF-OMP2 methods are reported in Tables S1 and S2 of the Supporting Information. The computational time for the DF-OMP2, CD-OMP2, OO-RI-MP2, and OMP2 methods are presented graphically in Figure 1. The DF-OMP2 method substantially reduces the computa-

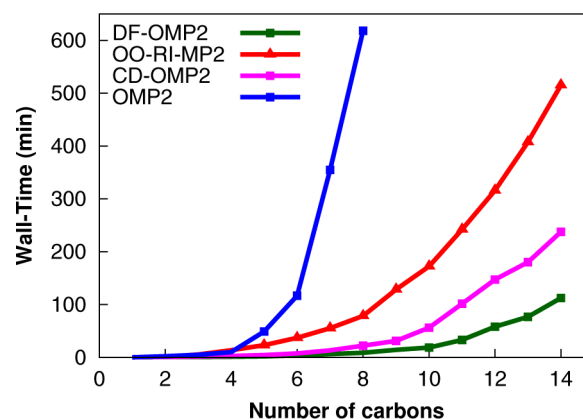


Figure 1. Wall-time (in min) for computations of single-point energies for the C_nH_{2n+2} ($n = 1–14$) set from the DF-OMP2, CD-OMP2 (CD threshold is 10^{-4}), OO-RI-MP2, and OMP2 methods with the cc-pvtz basis set. For the largest member, the number of basis functions is 840. All computation were performed with an 10^{-8} energy convergence tolerance on a single node (nproc=8) Intel Core i7–3930K CPU @ 3.20 GHz computer (memory ~64 GB).

tional cost compared to OMP2 and OO-RI-MP2; there are up to 70- and 12-fold reductions in the computational time compared to OMP2 and OO-RI-MP2, respectively. On average, the computational cost of DF-OMP2 is 24.9 and 7.4 times lower than those of OMP2 and OO-RI-MP2, respectively. Further, the cost of the DF-OMP2 method is also lower than that of CD-OMP2, by 2.2 times on average. The difference between the computational costs of DF-OMP2 and CD-OMP2 is mostly attributed to the difference between the number of Cholesky vectors and auxiliary basis functions. The number of Cholesky vectors is 1.7–1.8 times higher than that of auxiliary basis functions for the considered alkanes.

As the second step of the assessment for the efficiency of the DF-OMP2 method, we consider a set of conjugated dienes. For the considered conjugated dienes, total energies and the computational time from the OMP2, OO-RI-OMP2, CD-OMP2, and DF-OMP2 methods are reported in Tables S3 and S4 of the Supporting Information. The computational time for the DF-OMP2, CD-OMP2, OO-RI-MP2, and OMP2 methods are presented graphically in Figure 2. The DF-OMP2 method

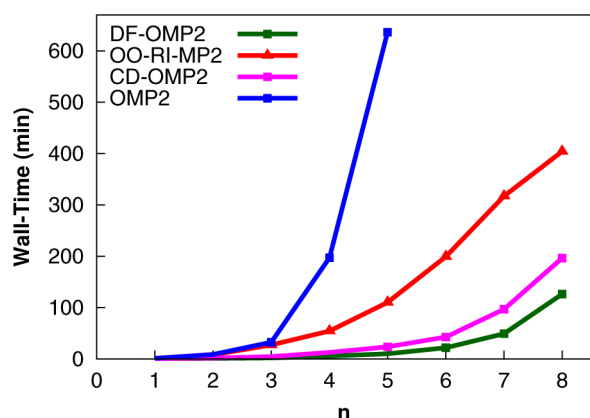


Figure 2. Wall-time (in min) for computations of single-point energies for the conjugated dienes ($C_{2n}H_{2n+2}$) from the DF-OMP2, CD-OMP2 (CD threshold is 10^{-4}), OO-RI-MP2, and OMP2 methods with the cc-pvtz basis set. For the largest member, the number of basis functions is 732. All computations were performed with a 10^{-8} energy convergence tolerance on a single node (nproc=8) Intel Core i7–3930K CPU @ 3.20 GHz computer (memory ~64 GB).

significantly decrease the computational cost compared to OMP2 and OO-RI-MP2; there are up to 62- and 13-fold reductions in the computational time compared to OMP2 and

OO-RI-MP2, respectively. On average, the computational cost of DF-OMP2 is 24.2 and 8.1 times lower than those of OMP2 and OO-RI-MP2, respectively. Further, the cost of the DF-OMP2 method is also lower than that of CD-OMP2, by 1.9 times on average. The difference between the computational cost of DF-OMP2 and CD-OMP2 is mostly attributed to the difference between the numbers of Cholesky vectors and auxiliary basis functions. The number of Cholesky vectors is 1.7 times higher than that of auxiliary basis functions for the considered conjugated dienes.

Finally, we turn our attention to noncovalent interaction and consider dimers of the S22 database.⁵⁶ For dimers of the S22 database, total energies and the computational time from the OMP2, OO-RI-OMP2, CD-OMP2, and DF-OMP2 methods are reported in Tables S5 and S6 of the Supporting Information. The computational time for the DF-OMP2, CD-OMP2, and OO-RI-MP2 methods are presented graphically in Figure 3. The DF-OMP2 method again substantially reduces the computational cost compared to OMP2 and OO-RI-MP2; there are up to 93- and 42-fold reductions in the cost (for the stacked indole...benzene complex) compared to OMP2 and OO-RI-MP2, respectively. On average, the computational cost of DF-OMP2 is 25.4 and 11.3 times lower than those of OMP2 and OO-RI-MP2, respectively. Further, the cost of the DF-OMP2 method is again lower than that of CD-OMP2, by 1.5 times on average. The difference between the computational cost of DF-OMP2 and CD-OMP2 is again attributed to the difference between the numbers of Cholesky vectors and auxiliary basis functions. The number of Cholesky vectors is 1.2 times higher than that of auxiliary basis functions for the S22 database.

For all considered test sets, the DF-OMP2 substantially accelerates the OMP2 method due to the reduced I/O time, as expected. Further, the decrease in the computational time of

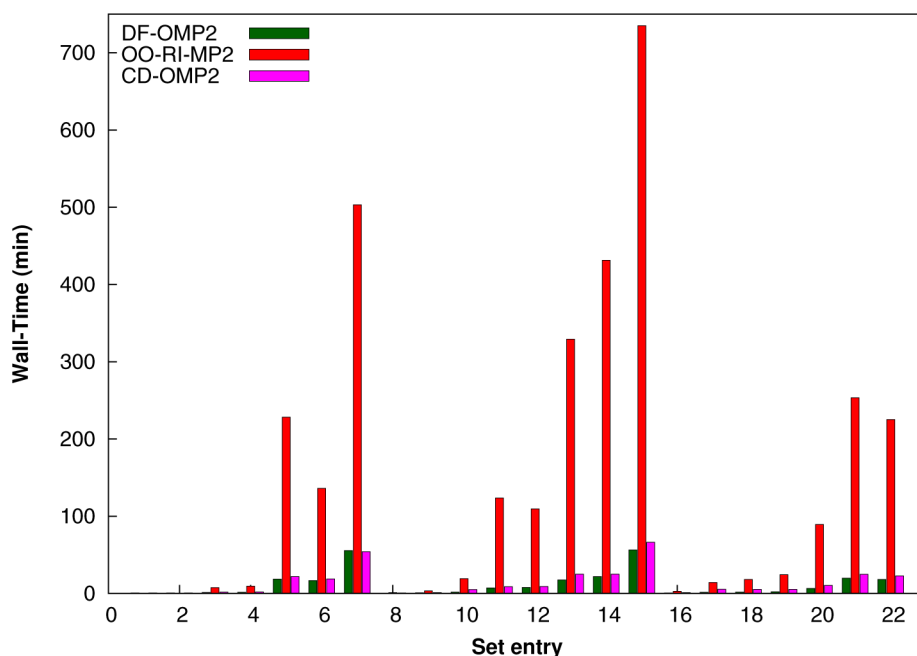


Figure 3. Wall-time (in min) for computations of single-point energies for dimers of the S22 database from the DF-OMP2, CD-OMP2 (CD threshold is 10^{-4}), and OO-RI-MP2 methods with the aug-cc-pVDZ basis set. For the largest member, the number of basis functions is 536. All computations were performed with a 10^{-8} energy convergence tolerance on a single node (nproc=8) Intel Core i7–3930K CPU @ 3.20 GHz computer (memory ~64 GB).

DF-OMP2 compared to those of OO-RI-MP2 is noteworthy. One of the reason why the DF-OMP2 method provides significantly lower costs than OO-RI-MP2 is that the orbital optimization algorithm presented here is noticeably more efficient than that employed for the OO-RI-MP2 method.²¹ Hence, our method (DF-OMP2) generally converges in much fewer iterations (1.5–5.0 times) than OO-RI-MP2. Another reason is that in the OO-RI-MP2 method, the DF approximation was applied only to the correlation energy, while in DF-OMP2 we employ the DF approach to reference energy as well. Even though the reference energy has a lower cost than the correlation energy, one still needs to consider the four-index TEI tensors, which are generally handled by out of core algorithms, to build the Fock matrix in the case of OO-RI-MP2. Because in the DF-OMP2 method the DF approach is used for both reference and correlation energies, the storage of four-index TEIs is avoided; three-index TEI tensors are employed instead. Hence, the I/O bottleneck of an energy computation is significantly overcome in many cases.

3.2. Open-Shell Noncovalent Interactions. For closed-shell complexes of the S22 database, the performances of all considered methods are essentially the same; mean absolute errors (MAEs) are 0.97–0.98 kcal mol⁻¹. However, for open-shell complexes there are dramatic differences in performances of standard and orbital-optimized methods. For the considered test set (the O23 database),⁸ noncovalent interaction energies (in kcal mol⁻¹) from the MP2, DF-MP2, OMP2, OO-RI-MP2, DF-OMP2, CD-OMP2 (with a Cholesky decomposition threshold of 10⁻⁴), CCSD, and CCSD(T) methods at the CBS limit are reported in Table 1. The corresponding mean absolute errors with respect to CCSD(T)/CBS are presented graphically in Figure 4.

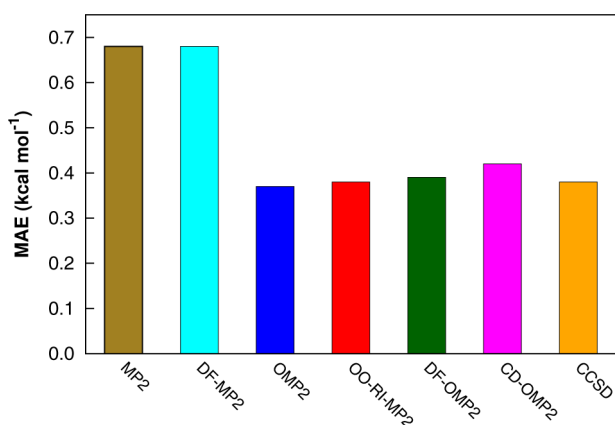


Figure 4. Mean absolute errors (in kcal mol⁻¹) in noncovalent interaction energies for the open-shell complexes (the O23 database) from the MP2, DF-MP2, OMP2, OO-RI-MP2, DF-OMP2, CD-OMP2 (CD threshold is 10⁻⁴), and CCSD methods with respect to CCSD(T)/CBS.

The MAE values are 0.68 (MP2), 0.68 (DF-MP2), 0.37 (OMP2), 0.38 (OO-RI-MP2), 0.39 (DF-OMP2), 0.42 (CD-OMP2), and 0.38 (CCSD) kcal mol⁻¹. Hence, performances of the OMP2, OO-RI-MP2, DF-OMP2, and CCSD methods are considerably better than those of MP2 and DF-MP2. The DF approximation introduces negligible errors compared to conventional methods, while it substantially reduces the computational cost. The MAE of OO-RI-MP2 is 0.01 kcal mol⁻¹ higher than that of OMP2, while there is a 0.02 kcal

mol⁻¹ difference between OMP2/DF-OMP2. This result is quite reasonable since in the OO-RI-MP2 method, the DF approximation is employed only for the correlation energy, whereas in DF-OMP2 the DF approach is applied in both reference and correlation energies. Further, the performance of the CD-OMP2 is slightly worse than that of DF-OMP2, which is also not surprising. Since the JKFIT/RI basis sets are optimized to minimize the energy difference between the conventional methods and corresponding density-fitted methods, these basis sets are the optimal choice for the density-fitted methods. On the other hand, in the CD approach the “auxiliary basis set” is directly constructed from the primary basis set, hence it is not the optimal choice for the approximate method.

Moreover, performances of the orbital-optimized MP2 methods are essentially equivalent to that of CCSD. However, there is a dramatic difference between the computational cost of OMP2/DF-OMP2 and CCSD [scaling formally as $O(N^6)$ for CCSD compared to $O(N^5)$ for OMP2/DF-OMP2]. Hence, it appears that one may achieve CCSD quality at the MP2 level by orbital optimization for open-shell noncovalent interactions. Therefore, one may prefer DF-OMP2 over CCSD for investigation of open-shell noncovalent interactions in the large molecular systems, where CCSD and CCSD(T) are too computationally costly.

4. CONCLUSIONS

An efficient implementation of the orbital-optimized MP2 method with the DF and CD approximations has been presented, which are denoted as DF-OMP2 and CD-OMP2, respectively. The computational time of the DF-OMP2 method has been compared with those of OMP2^{1,5} and OO-RI-MP2.²¹ Our results demonstrate that the DF-OMP2 method provides significantly lower computational costs than OMP2 and OO-RI-MP2 methods. On average, the computational cost of DF-OMP2 is 24–25 and 7–11 times lower than those of OMP2 and OO-RI-MP2, respectively.

Moreover, the DF/CD-OMP2 methods have been applied to open-shell noncovalent interactions where standard MP2 has difficulties. Our results show that the orbital relaxation effects are quite important for the computation of open-shell noncovalent interactions. The DF and CD approaches introduce negligible errors compared to the OMP2 method, by 0.01 and 0.05 kcal mol⁻¹, respectively. Further, the present results indicate that one may approach the quality of high level electron correlation methods, such as CCSD, employing lower cost orbital-optimized methods, such as DF-OMP2. Hence, considering both computational efficiency and the accuracy of the DF-OMP2 method, we conclude that the DF-OMP2 method emerges as a very useful tool for computational quantum chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Total energies and the computational time for all single point energy computations, and optimized geometries of all considered structures, except for the S22 database, are reported. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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