# Spin-Component-Scaled Double-Hybrid Density Functionals with Nonlocal van der Waals Correlations for Noncovalent Interactions

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S *Supporting Information*

ABSTRACT: Nonlocal (NL) van der Waals correlation has been incorporated into the spin-component and spin-opposite scaled double-hybrid density functionals (DHDFs) for noncovalent interactions. The short-range attenuation parameters for the tested DHDFs with the NL correlations are optimized by minimizing the mean absolute deviations (MADs) against the S66 database. And consequently, the obtained DHDFs with the NL correlations are denoted as PWPB95-NL, DSD-BLYP-NL, DSD-PBEP86-NL, and DOD-PBEP86-NL. These four DHDFs with the NL correlations are further assessed with the S22B, NCCE31, and ADIM6 databases. On the basis of our benchmark computations, the cooperation of the NL correlation and the spin-component and spin-opposite scaled DHDFs is successful for noncovalent interactions. However, the performances of the four aforementioned DHDFs with the NL correlations on the charge transfer interactions are less than satisfactory.
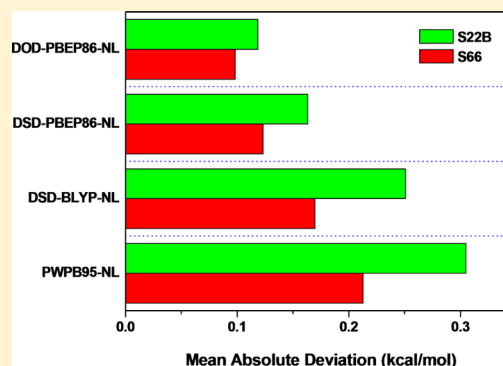
1. INTRODUCTION

Noncovalent interactions play important roles in the physical and life sciences, and therefore, extensive investigations have been performed to understand different types of noncovalent interactions.[1–6] Density functional theory (DFT) has become a promising methodology for studying noncovalent interactions.[7–18] Among various density functionals, double-hybrid density functionals (DHDFs) are much more powerful.[19–26] However, additional corrections for the standard density functionals and/or specially devised density functionals are needed for practical applications.[7–18,20–22]

Different revisions of dispersion corrections for various density functionals (DFT-D) are efficient and popular methods for noncovalent interactions.[27–33] The revision of Grimme's DFT-D3 is generally recommended to investigate various noncovalent interactions with different essences.[30,31] Note that there are two different versions of the Grimme's DFT-D3. The DFT-D3 version with zero damping is denoted as DFT-D3(0),[30] whereas the DFT-D3 version with Becke–Johnson damping[34–36] is dubbed as DFT-D3(BJ).[31] Moreover, the DFT-D3 refers to a generic notation for both the DFT-D3(0) and DFT-D3(BJ) in this paper. van der Waals density functional theory paves another way for studying noncovalent interactions.[37–44] In this method, a nonlocal (NL) correlation functional based on the electron density is utilized to describe the dispersion interaction. Simple NL van der Waals density functionals have been developed by Vydrov and Van Voorhis.[40–44] The advanced NL correlation part[44] has also been applied to different density functionals including the DHDFs, and thus, the density functionals with the NL correlations are generally denoted as DFT-NL.[45–47] According

to extensive benchmark computations, the DFT-NL method is accurate as the DFT-D3 method for both thermochemistry and noncovalent interactions.[46,47] Furthermore, noncovalent interactions can also be investigated with the exchange-hole dipole-moment model,[48–52] pseudopotentials,[53–59] and Buckingham–Hirshfeld method.[60] Additionally, the long-range van der Waals interactions are able to be well characterized even for complicated condensed matters.[61–67] A lot of specially devised density functionals can also be employed to study noncovalent interactions.[68–81] For example, we have optimized two DHDFs of B2NC-PLYP and mPW2NC-PLYP without any further correction for noncovalent interactions.[81] However, the limit of accuracy for some aforementioned methods has been presented by Mardirossian and Head-Gordon.[82]

Recently, dispersion corrected, spin-component and spin-opposite scaled DHDFs known as DSD-DFT and DOD-DFT methods have been developed by Martin and co-workers.[83–85] The spin-component and spin-opposite scaled MP2 approaches (SCS-MP2 and SOS-MP2)[86,87] were applied within the DSD-DFT framework, and moreover, Grimme's DFT-D models including DFT-D2[29] and DFT-D3(BJ)[31] were employed for dispersion corrections. The exchange-correlation energy E_{xc} for the general DSD-DFT method[83–85] was expressed as

$$E_{xc} = (1 - c_x)E_x^{DFT} + c_x E_x^{HF} + c_c E_c^{DFT} + c_o E_o^{MP2} + c_s E_s^{MP2} + E_D \tag{1}$$

Table 1. Exchange Functionals, Correlation Functionals, and Parameters for the DHDFs Tested in This Work[a]

DHDF	exchange	correlation	c_x	c_c	c_s	c_o	b	ref
PWPB95-NL	PW	B95	0.50	0.731	0	0.269	11.1	88,[b]90, 91,
DSD-BLYP-NL	B88	LYP, VWN3	0.69	0.54	0.37	0.46	12.0	83,[b]102−104
DSD-PBEP86-NL	PBE	P86, VWN5	0.69	0.44	0.22	0.52	14.2	84, 85,[b]104−106
DOD-PBEP86-NL	PBE	P86, VWN5	0.65	0.47	0	0.54	10.4	85,[b]104−106

[a] c_x, HF exchange parameter; c_c, DFT correlation parameter; c_s, same spin parameter for the MP2-like perturbative correlation; c_o, opposite spin parameter for the MP2-like perturbative correlation; and b, short-range attenuation parameter. The parameter b is optimized for each DHDF within the framework of the NL correlation,[44−46] and the long-range parameter C is kept as 0.0093 for all the tested DHDFs. [b] Key reference for the listed parameters except b, which is utilized in the NL correlation.

In this formula, the E_o^{MP2} and E_s^{MP2} were defined as the opposite spin and same spin MP2-like perturbative correlation energies, respectively. In addition, the E_D was the dispersion energy obtained with Grimme's DFT-D2[29] and DFT-D3(BJ) methods.[31] The DSD-DFT and DOD-DFT functionals performed very well on thermochemistry, thermochemical kinetics, noncovalent interaction, and so on.[83−85] Similarly, the PTPSS-D3(0) and PWPB95-D3(0) functionals were DHDFs fitted with the DFT-D3(0) correction[30] simultaneously by Goerigk and Grimme.[88] The SOS-MP2 procedure[87] was applied for the perturbative correlation. For the PTPSS-D3(0) functional, the first letter "P" denoted "perturbative," and the TPSS exchange and correlation[89] with revised parameters were utilized. As to the PWPB95-D3(0) functional, the second letter "P" implied "perturbative," and the reparameterized PW exchange[90] and B95 correlation[91] were employed.

In this work, we try to employ the NL correlation[44−46] to replace the DFT-D methods[29−31] in the PWPB95-D3(0),[88] DSD-BLYP-D2/D3(0),[83,88] DSD-PBEP86-D3(BJ),[84,85] and DOD-PBEP86-D3(BJ)[85] functionals for noncovalent interactions. The corresponding performances are assessed with the S22 (set 22),[92−95] S66 (set 66),[96,97] NCCE31 (noncovalent complexation energies),[9,98,99] and ADIM6 (interaction energy database for six n-alkane dimers) databases.[88,100,101] The S22 database contains 22 small model complexes for noncovalent interactions,[92] whereas the S66 database is much more comprehensive.[96] These two databases were designed by Hobza and co-workers for noncovalent interactions relevant to biochemistry.[92,96] The NCCE31 database is related to diverse nonbonded interactions,[98,99] and this database has been utilized to parametrize and assess density functionals by Truhlar's group.[7−9] Moreover, the ADIM6 database was designed to study the London-dispersion correction by Grimme et al.[30] In the field of theoretical and computational chemistry, more accurate methods are expected to study noncovalent interactions. And thus, the major aim of this work is to examine the cooperation of the DFT-NL method and the DHDFs using the SCS-MP2 and SOS-MP2 procedures for noncovalent interactions.

2. COMPUTATIONAL METHODS

The databases of S22,[92−95] S66,[96,97] NCCE31,[9,98,99] and ADIM6[88,100,101] were employed for our benchmark computations. Note that the interaction energies in ref 95 (denoted as S22B) and ref 97 for the S22 and S66 databases were utilized, respectively. The signed mean deviation (MD), mean absolute deviation (MAD), root-mean-square deviation (RMSD), and mean absolute percent deviation (MA%D) were used to assess the performances of the tested methods. The definitions of these four deviations were described in detail in ref 11. The

parameters for the PWPB95-NL, DSD-BLYP-NL, DSD-PBEP86-NL, and DOD-PBEP86-NL functionals are listed in Table 1, and the specific exchange and correlation functionals[89−91,102−106] were also presented. The Hartree−Fock (HF) exchange parameter (c_x), DFT correlation parameter (c_c), and same (c_s) and opposite (c_o) spin coefficients for the MP2-like correlation were taken from the related references.[83−85,88] With the framework of the DFT-NL method,[44−47] the short-range attenuation parameter b for each functional was optimized by minimizing the MAD with the S66 database. Meanwhile, the long-range parameter C was kept as 0.0093,[44,46] which had been proven to be reasonable for the DHDFs.[47] The NL correlation was added non-self-consistently, because the improvement of the self-consistent procedure was negligible.[46] Subsequently, these four obtained functionals with the NL correlations were further assessed with the S22B, NCCE31, and ADIM6 databases. As comparisons, the MP2 method[107] was also examined with the four databases mentioned above.

All the computations in this work were carried out with the ORCA program.[108] The quadruple-ζ def2-QZVP[109] basis set was utilized for single-point energy computations. On the basis of previous works,[88,101] this large basis set was competent for benchmark computations, and the basis set superposition errors for the tested methods could be ignored. The resolution of the identity (RI-JK[110,111] and RI[112]) methods were employed with the auxiliary basis sets of def2-QZVP/JK[113] and def2-QZVP/C[114] to accelerate the self-consistent-field (SCF) and perturbative correlation computations, respectively. The integration grid for the Kohn−Sham SCF computations was Grid6[115,116] in the ORCA program, whereas vdwGrid4 was used for the NL correlation computations. According to the original work,[83−85,88] the MP2-like computations for the DSD-PBEP86-NL and DOD-PBEP86-NL functionals were performed with the frozen core option, and those for the PWPB95-NL and DSD-BLYP-NL functionals were carried out with correlating all electrons. As to the total energies of molecules, the accuracy of our proposed functionals with the NL correlations was relatively low even for small molecules against the CCSD(T)[117−119] results (Table S1 in the Supporting Information). Note that the errors of the density functionals for computing the total energies are generally large, and the errors of the total energies are about 1 hartree for medium-sized molecules.[120] In addition, the MP2 computations were also performed with the frozen core option, and the relative costs for the MP2 method and our proposed functionals with the NL correlations were presented in the Supporting Information (Table S2).

3. RESULTS AND DISCUSSION

3.1. Assessment of the PWPB95-NL, DSD-BLYP-NL, DSD-PBEP86-NL, and DOD-PBEP86-NL Functionals with

the S66 and S22B Databases. The short-range attenuation parameters for the PWPB95-NL, DSD-BLYP-NL, DSD-PBEP86-NL, and DOD-PBEP86-NL functionals were determined by minimizing the corresponding MADs with the S66 database. The obtained short-range attenuation parameters have been listed in Table 1. The performances of these four functionals with NL correlations on the S66 and S22B databases are presented in Table 2. As shown in Table 2,

Table 2. Performances of the Tested Methods on the S66 and S22B Databases[a]

| method	MD	MAD	RMSD	MA%D
		S66 database		
PWPB95-NL	0.13	0.21	0.29	3.9
DSD-BLYP-NL	−0.03	0.17	0.21	4.0
DSD-PBEP86-NL	−0.03	0.12	0.15	3.1
DOD-PBEP86-NL	−0.01	0.10	0.12	2.3
MP2	−0.57	0.59	0.87	16.3
revPBE0-DH-NL[b]	−0.04	0.19		4.1
B2PLYP-NL[b]	−0.12	0.20		3.6
		S22B database		
PWPB95-NL	0.12	0.31	0.46	4.3
DSD-BLYP-NL	−0.19	0.25	0.32	6.2
DSD-PBEP86-NL	−0.13	0.16	0.20	4.2
DOD-PBEP86-NL	−0.04	0.12	0.15	3.0
MP2	−1.00	1.02	1.60	23.3

[a]The MD (kcal/mol), MAD (kcal/mol), RMSD (kcal/mol), and MA%D (%) are employed to evaluate the performances, and the def2-QZVP basis set is used for single-point energy computations. [b]Results taken from ref 47.

these four functionals with NL correlations perform well on both the S66 and S22B databases, because the training set selected in this work is the well designed S66 database. The performance trend of these four functionals with the NL correlations for the S22B database is same as that for the S66 database. Furthermore, the DOD-PBEP86-NL functional is the best performer for both the S66 and S22B databases. The MADs of the DOD-PBEP86-NL/def2-QZVP level against the S66 and S22B databases are only 0.10 and 0.12 kcal/mol, respectively.

With the large def2-QZVP basis set, the MAD of the PWPB95-NL functional (0.21 kcal/mol) is close to those of the revPBE0-DH-NL (0.19 kcal/mol) and B2PLYP-NL (0.20 kcal/mol) functionals for the S66 database.[47] The revPBE,[121] a revised version of PBE, in the revPBE0-DH-NL functional was proposed by Zhang and Yang, which was different from the original PBE developed by Perdew and co-workers.[105] Moreover, the DSD-BLYP-NL functional (with an MAD of 0.17 kcal/mol) performs slightly better than the revPBE0-DH-NL and B2PLYP-NL functionals. However, the improvements of the DSD-PBEP86-NL and DOD-PBEP86-NL functionals are more significant. The MADs of the PWPB95-D3(0) and PWPB95-D3(BJ) functionals for the S66 database are 0.19 and 0.22 kcal/mol, respectively.[122] The MAD of the PWPB95-NL functional falls in between these two values. Similarly, the MADs of the DSD-BLYP-D3(0) and DSD-BLYP-D3(BJ) functionals against the S66 database are 0.21 and 0.23 kcal/mol, respectively.[122] The DSD-BLYP-NL functional performs slightly better than these two DFT-D3 methods.

There are three different subsets in the S66 and S22 databases. The concrete subsets are hydrogen-bonded (HB)

complexes, dispersion-dominated (DD) complexes, and complexes with mixed (MX) influence. The assignments of the complexes are determined on the basis of the original refs92 and 96. The MDs and MADs for the subsets of both the S66 and S22B databases are presented in Figure 1. Note that the
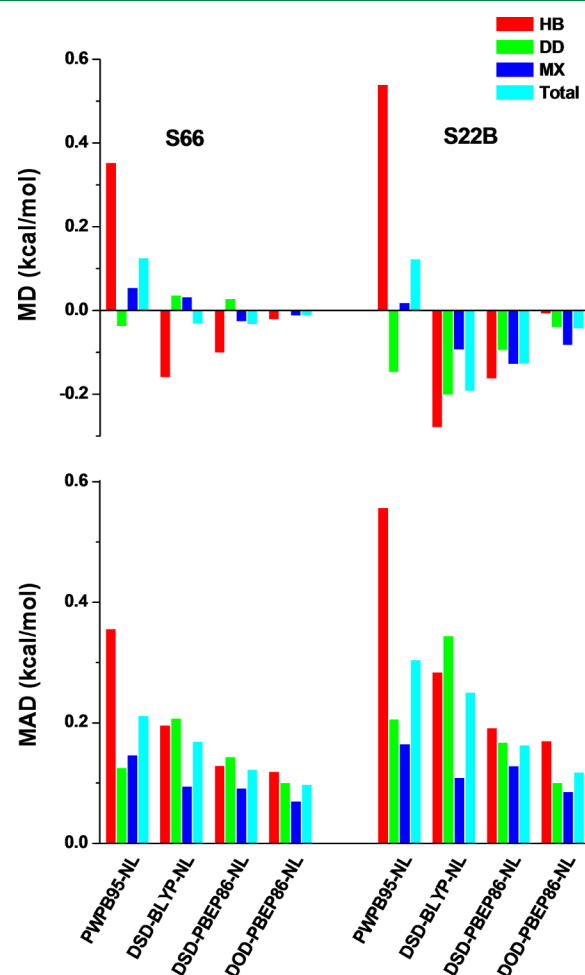
Figure 1. MDs (kcal/mol) and MADs (kcal/mol) for the subsets of both the S66 and S22B databases. The subsets are hydrogen-bonded (HB) complexes, dispersion-dominated (DD) complexes, and complexes with mixed (MX) influence.

reference interaction energies in the S66 and S22B databases are negative values. As illustrated in Figure 1, the DOD-PBEP86-NL functional is the best performer for all the subsets of both the S66 and S22B databases. Compared with the DD and MX subsets, the PWPB95-NL functional performs worse on the HB subsets, and this functional generally tends to overestimate the interaction energies, i.e., underestimate the binding energies for the HB subsets according to the positive MDs.

3.2. Performances of the Four Tested Functionals with the NL Correlations on the NCCE31 Database. In this section, the four tested functionals with the NL correlations are assessed with the NCCE31 database, which has been developed by Truhlar's group.[9,98,99] The detailed subsets for the NCCE31 database are six HB (HB6) complexes, seven charge transfer (CT7) complexes, six dipole interaction (DI6) complexes, seven weak interaction (WI7) complexes, and five π−π stacking (PPS5) complexes. The reference binding

energies are positive values, which are different from the S66 and S22B databases. As listed in Table 3, the range of the

Table 3. Assessment of the Tested Methods against the NCCE31 Database[a]

method	MD	MAD	RMSD	MA%D
PWPB95-NL	0.11	0.25	0.37	18.2
DSD-BLYP-NL	0.25	0.30	0.44	16.2
DSD-PBEP86-NL	0.23	0.25	0.39	12.5
DOD-PBEP86-NL	0.18	0.20	0.33	8.1
MP2	0.32	0.36	0.61	25.0
revPBE0-DH-NL[b]	0.15[c]	0.25		16.4
B2PLYP-NL[b]	0.35[c]	0.42		14.5

[a]The MD (kcal/mol), MAD (kcal/mol), RMSD (kcal/mol), and MA%D (%) are utilized to assess the performances, and these results are computed with the def2-QZVP basis set. [b]Results taken from ref 47. [c]The MDs have been converted with respect to the positive reference binding energies.

MADs for the tested functionals with the NL correlations is 0.20−0.30 kcal/mol, and the DOD-PBEP86-NL functional is also the best performer for the NCCE31 database. As comparisons, the MADs of the revPBE0-DH-NL and B2PLYP-NL functionals are 0.25 and 0.42 kcal/mol, respectively.[47]

As shown in Figure 2, the four tested functionals with the NL correlations perform worst on the CT7 subset of the NCCE31 database, and the MADs for the CT7 subset are within a range of 0.45−0.57 kcal/mol. For each functional with the NL correlation, the MAD for the CT7 subset is identical to the corresponding MD. With respect to the positive reference binding energies in the NCCE31 database, the meaning of the MD for this database is opposite that for the S66 or S22B databases. As a result, the four tested functionals with the NL correlations tend to overestimate the binding energies for the CT7 subset.

3.3. Assessment of the Four Tested Functionals with the NL Correlations against the ADIM6 Database. We now further examine the performances of the four tested functionals with the NL correlations on the ADIM6 database.[88,100,101] The reference energies in the ADIM6 database are binding energies as the NCCE31 database. The six *n*-alkane dimers in the ADIM6 database are remarkable complexes with dispersion effect, and thus, the performances of the DHDFs using the SCS-MP2 and SOS-MP2 procedures combined with the NL correlations on the dispersion effect will be presented much more clearly.

As illuminated in Table 4, the PWPB95-NL and DOD-PBEP86-NL functionals perform better than the DSD-BLYP-NL and DSD-PBEP86-NL functionals on the ADIM6 database. Compared with the performances of the PWPB95, PWPB95-D3(0), DSD-BLYP without any dispersion correction, and DSD-BLYP-D3(0) functionals, the improvement of the NL correlation is similar to that with Grimme's DFT-D3(0) correction.[88,123]

3.4. Comments on the Four Tested Functionals with the NL Correlations. On the basis of our benchmark computations, the MADs of the DOD-PBEP86-NL functional for the S66, S22B, and NCCE31 databases are 0.10, 0.12, and 0.20 kcal/mol, respectively. Therefore, this functional with the NL correlation is highly recommended to study noncovalent interactions. Moreover, the other three functionals with the NL
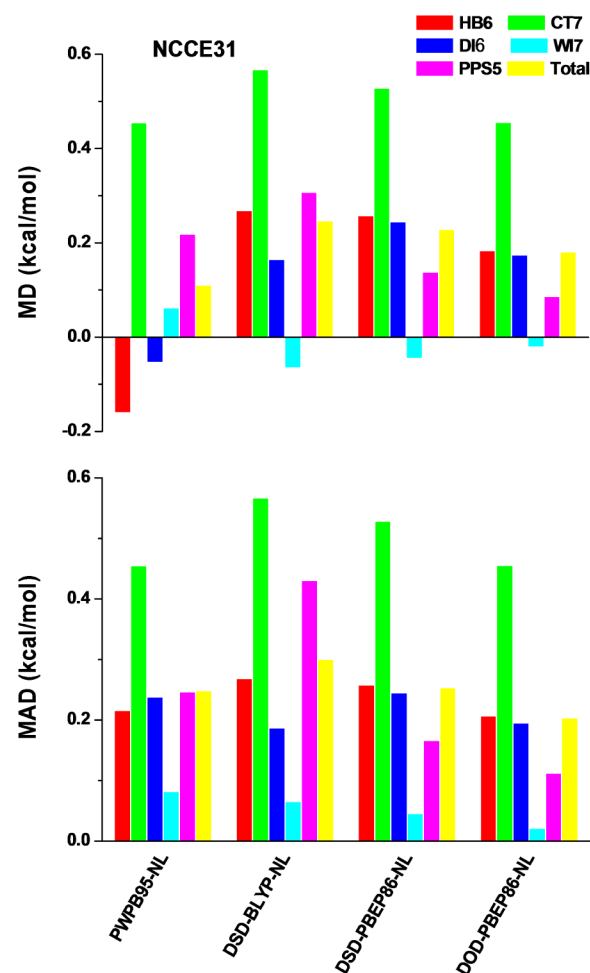
Figure 2. MDs (kcal/mol) and MADs (kcal/mol) for the subsets of the NCCE31 database. The subsets are six hydrogen-bonded (HB6) complexes, seven charge transfer (CT7) complexes, six dipole interaction (DI6) complexes, seven weak interaction (WI7) complexes, and five π−π stacking (PPS5) complexes.

Table 4. Performances of the Tested Methods on the ADIM6 Database[a]

method	MD	MAD	RMSD	MA%D
PWPB95-NL	0.08	0.13	0.14	4.0
DSD-BLYP-NL	−0.34	0.34	0.35	11.8
DSD-PBEP86-NL	−0.25	0.25	0.27	8.0
DOD-PBEP86-NL	−0.13	0.13	0.15	4.5
MP2	0.29	0.29	0.34	7.5
PWPB95[b]	−1.69	1.69	1.86	
PWPB95-D3(0)[b]	0.36	0.36	0.40	
DSD-BLYP[b,c]	−1.89	1.89	2.06	
DSD-BLYP-D3(0)[b]	−0.13	0.13	0.13	

[a]The MD (kcal/mol), MAD (kcal/mol), RMSD (kcal/mol), and MA%D (%) are utilized to evaluate the performances, and these results are obtained with the def2-QZVP basis set. [b]Results taken from ref 123. [c]Without any dispersion correction.

correlations tested in this work also perform well on noncovalent interactions. However, the performances of these four functionals with the NL correlations on the charge transfer interactions are unsatisfactory, and they tend to overestimate the binding energies of the charge transfer complexes. The reason may be that the NL correlation optimized with the S66

database generally overestimates the dispersion components of the charge transfer interactions. Therefore, further efforts should be made on this issue in the future. As far as we know, range-separated density functionals with additional dispersion corrections may be suitable for the charge transfer interactions.[70,78,79,124−130] With respect to the charge transfer effect, noncovalent interactions involving open-shell species[126,131] are suggested for the relevant databases under construction.

The fraction of Fock-exchange for the PWPB95 functional is only 50%.[88] As demonstrated by Goerigk and Grimme,[88] this fraction is reasonable for general chemistry. Moreover, this relatively low fraction of Fock exchange makes the PWPB95 functional much more stable for complicated electronic structures.[88] On the basis of the good performance of the PWPB95-D3(0) functional on the comprehensive GMTKN30 database,[88] the PWPB95-NL functional is expected to perform well on other chemical properties beyond noncovalent interactions, especially for the complicated electronic structures.

4. CONCLUSIONS

Four DHDFs with the NL correlations denoted as PWPB95-NL, DSD-BLYP-NL, DSD-PBEP86-NL, and DOD-PBEP86-NL have been proposed for investigating noncovalent interactions. Among them, the DOD-PBEP86-NL functional is highly recommended. More importantly, this functional with the NL correlation performs very well on the hydrogen-bonded, dispersion-dominated, and mixed influence complexes. However, based on the benchmark computations with the NCCE31 database, the performances of these four density functionals with the NL correlations on the charge transfer interactions are less than satisfactory compared with other types of noncovalent interactions. In practical applications, the DHDFs with the DFT-D3(0) and/or DFT-D3(BJ) corrections may be employed for cross validations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Total energies (hartree) of the selected molecules computed with CCSD(T) and our proposed methods (Table S1) and relative costs for MP2 and our proposed methods (Table S2). 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.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Müller-Dethlefs, K.; Hobza, P. Noncovalent Interactions: A Challenge for Experiment and Theory. *Chem. Rev.* **2000**, *100*, 143−167.

(2) Hobza, P.; Müller-Dethlefs, K. *Non-covalent Interactions: Theory and Experiment*; Royal Society of Chemistry: Cambridge, U. K., 2010; pp 1−69.

(3) Riley, K. E.; Pitoňák, M.; Jurečka, P.; Hobza, P. Stabilization and Structure Calculations for Noncovalent Interactions in Extended Molecular Systems Based on Wave Function and Density Functional Theories. *Chem. Rev.* **2010**, *110*, 5023−5063.

(4) Riley, K. E.; Hobza, P. Noncovalent Interactions in Biochemistry. *WIREs Comput. Mol. Sci.* **2011**, *1*, 3−17.

(5) Hobza, P. Calculations on Noncovalent Interactions and Databases of Benchmark Interaction Energies. *Acc. Chem. Res.* **2012**, *45*, 663−672.

(6) Riley, K. E.; Hobza, P. On the Importance and Origin of Aromatic Interactions in Chemistry and Biodisciplines. *Acc. Chem. Res.* **2013**, *46*, 927−936.

(7) Zhao, Y.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157−167.

(8) Zhao, Y.; Truhlar, D. G. Applications and Validations of the Minnesota Density Functionals. *Chem. Phys. Lett.* **2011**, *502*, 1−13.

(9) Peverati, R.; Truhlar, D. G. The Quest for a Universal Density Functional: The Accuracy of Density Functionals across a Broad Spectrum of Databases in Chemistry and Physics. *Philos. Trans. R. Soc. A* **2014**, *372*, 20120476.

(10) Johnson, E. R.; Mackie, I. D.; DiLabio, G. A. Dispersion Interactions in Density-Functional Theory. *J. Phys. Org. Chem.* **2009**, *22*, 1127−1135.

(11) Burns, L. A.; Vázquez-Mayagoitia, Á.; Sumpter, B. G.; Sherrill, C. D. Density-Functional Approaches to Noncovalent Interactions: A Comparison of Dispersion Corrections (DFT-D), Exchange-Hole Dipole Moment (XDM) Theory, and Specialized Functionals. *J. Chem. Phys.* **2011**, *134*, 084107.

(12) Grimme, S. Density Functional Theory with London Dispersion Corrections. *WIREs Comput. Mol. Sci.* **2011**, *1*, 211−228.

(13) Swart, M.; Solà, M.; Bickelhaupt, F. M. Inter- and Intra-molecular Dispersion Interactions. *J. Comput. Chem.* **2011**, *32*, 1117−1127.

(14) Podeszwa, R.; Szalewicz, K. Density Functional Theory Overcomes the Failure of Predicting Intermolecular Interaction Energies. *J. Chem. Phys.* **2012**, *136*, 161102.

(15) Klimeš, J.; Michaelides, A. Advances and Challenges in Treating van der Waals Dispersion Forces in Density Functional Theory. *J. Chem. Phys.* **2012**, *137*, 120901.

(16) Goerigk, L. How Do DFT-DCP, DFT-NL, and DFT-D3 Compare for the Description of London-Dispersion Effects in Conformers and General Thermochemistry? *J. Chem. Theory Comput.* **2014**, *10*, 968−980.

(17) Corminboeuf, C. Minimizing Density Functional Failures for Non-Covalent Interactions Beyond van der Waals Complexes. *Acc. Chem. Res.* **2014**, DOI: 10.1021/ar400303a.

(18) Kronik, L.; Tkatchenko, A. Understanding Molecular Crystals with Dispersion-Inclusive Density Functional Theory: Pairwise Corrections and Beyond. *Acc. Chem. Res.* **2014**, DOI: 10.1021/ar500144s.

(19) Grimme, S. Semiempirical Hybrid Density Functional with Perturbative Second-Order Correlation. *J. Chem. Phys.* **2006**, *124*, 034108.

(20) Zhang, I. Y.; Xu, X. Doubly Hybrid Density Functional for Accurate Description of Thermochemistry, Thermochemical Kinetics and Nonbonded Interactions. *Int. Rev. Phys. Chem.* **2011**, *30*, 115−160.

(21) Sancho-García, J. C.; Adamo, C. Double-Hybrid Density Functionals: Merging Wavefunction and Density Approaches to Get the Best of Both Worlds. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14581−14594.

(22) Goerigk, L.; Grimme, S. Double-Hybrid Density Functionals. *WIREs Comput. Mol. Sci.* **2014**, DOI: 10.1002/wcms.1193.

(23) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. Doubly Hybrid Meta DFT: New Multi-Coefficient Correlation and Density Functional Methods for Thermochemistry and Thermochemical Kinetics. *J. Phys. Chem. A* **2004**, *108*, 4786−4791.

(24) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. Multi-Coefficient Extrapolated Density Functional Theory for Thermochemistry and Thermochemical Kinetics. *Phys. Chem. Chem. Phys.* **2005**, *7*, 43−52.

(25) Zhao, Y.; Truhlar, D. G. Assessment of Model Chemistries for Noncovalent Interactions. *J. Chem. Theory Comput.* **2006**, *2*, 1009−1018.

(26) Zheng, J.; Zhao, Y.; Truhlar, D. G. The DBH24/08 Database and Its Use to Assess Electronic Structure Model Chemistries for Chemical Reaction Barrier Heights. *J. Chem. Theory Comput.* **2009**, *5*, 808−821.

(27) Wu, Q.; Yang, W. Empirical Correction to Density Functional Theory for van der Waals Interactions. *J. Chem. Phys.* **2002**, *116*, 515−524.

(28) Grimme, S. Accurate Description of van der Waals Complexes by Density Functional Theory Including Empirical Corrections. *J. Comput. Chem.* **2004**, *25*, 1463−1473.

(29) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787−1799.

(30) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate *Ab Initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(31) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456−1465.

(32) Steinmann, S. N.; Corminboeuf, C. Comprehensive Benchmarking of a Density-Dependent Dispersion Correction. *J. Chem. Theory Comput.* **2011**, *7*, 3567−3577.

(33) Marom, N.; Tkatchenko, A.; Rossi, M.; Gobre, V. V.; Hod, O.; Scheffer, M.; Kronik, L. Dispersion Interactions with Density-Functional Theory: Benchmarking Semiempirical and Interatomic Pairwise Corrected Density Functionals. *J. Chem. Theory Comput.* **2011**, *7*, 3944−3951.

(34) Becke, A. D.; Johnson, E. R. A Density-Functional Model of the Dispersion Interaction. *J. Chem. Phys.* **2005**, *123*, 154101.

(35) Johnson, E. R.; Becke, A. D. A Post-Hartree-Fock Model of Intermolecular Interactions. *J. Chem. Phys.* **2005**, *123*, 024101.

(36) Johnson, E. R.; Becke, A. D. A Post-Hartree-Fock Model of Intermolecular Interactions: Inclusion of Higher-Order Corrections. *J. Chem. Phys.* **2006**, *124*, 174104.

(37) Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. Van der Waals Density Functional for General Geometries. *Phys. Rev. Lett.* **2004**, *92*, 246401.

(38) Thonhauser, T.; Cooper, V. R.; Li, S.; Puzder, A.; Hyldgaard, P.; Langreth, D. C. Van der Waals Density Functional: Self-Consistent Potential and the Nature of the van der Waals Bond. *Phys. Rev. B* **2007**, *76*, 125112.

(39) Lee, K.; Murray, É. D.; Kong, L.; Lundqvist, B. I.; Langreth, D. C. Higher-Accuracy van der Waals Density Functional. *Phys. Rev. B* **2010**, *82*, 081101.

(40) Vydrov, O. A.; Van Voorhis, T. Nonlocal van der Waals Density Functional Made Simple. *Phys. Rev. Lett.* **2009**, *103*, 063004.

(41) Vydrov, O. A.; Van Voorhis, T. Improving the Accuracy of the Nonlocal van der Waals Density Functional with Minimal Empiricism. *J. Chem. Phys.* **2009**, *130*, 104105.

(42) Vydrov, O. A.; Van Voorhis, T. Dispersion Interactions from a Local Polarizability Model. *Phys. Rev. A* **2010**, *81*, 062708.

(43) Vydrov, O. A.; Van Voorhis, T. Implementation and Assessment of a Simple Nonlocal van der Waals Density Functional. *J. Chem. Phys.* **2010**, *132*, 164113.

(44) Vydrov, O. A.; Van Voorhis, T. Nonlocal van der Waals Density Functional: The Simpler the Better. *J. Chem. Phys.* **2010**, *133*, 244103.

(45) Hujo, W.; Grimme, S. Comparison of the Performance of Dispersion-Corrected Density Functional Theory for Weak Hydrogen Bonds. *Phys. Chem. Chem. Phys.* **2011**, *13*, 13942−13950.

(46) Hujo, W.; Grimme, S. Performance of the van der Waals Density Functional VV10 and (hybrid)GGA Variants for Thermochemistry and Noncovalent Interactions. *J. Chem. Theory Comput.* **2011**, *7*, 3866−3871.

(47) Aragó, J.; Ortí, E.; Sancho-García, J. C. Nonlocal van der Waals Approach Merged with Double-Hybrid Density Functionals: Toward the Accurate Treatment of Noncovalent Interactions. *J. Chem. Theory Comput.* **2013**, *9*, 3437−3443.

(48) Becke, A. D.; Johnson, E. R. Exchange-Hole Dipole Moment and the Dispersion Interaction. *J. Chem. Phys.* **2005**, *122*, 154104.

(49) Becke, A. D.; Johnson, E. R. Exchange-Hole Dipole Moment and the Dispersion Interaction: High-Order Dispersion Coefficients. *J. Chem. Phys.* **2006**, *124*, 014104.

(50) Ángyán, J. G. On the Exchange-Hole Model of London Dispersion Forces. *J. Chem. Phys.* **2007**, *127*, 024108.

(51) Becke, A. D.; Johnson, E. R. Exchange-hole dipole moment and the dispersion interaction revisited. *J. Chem. Phys.* **2007**, *127*, 154108.

(52) Heßelmann, A. Derivation of the Dispersion Energy as an Explicit Density- and Exchange-Hole Functional. *J. Chem. Phys.* **2009**, *130*, 084104.

(53) von Lilienfeld, O. A.; Tavernelli, I.; Rothlisberger, U.; Sebastiani, D. Optimization of Effective Atom Centered Potentials for London Dispersion Forces in Density Functional Theory. *Phys. Rev. Lett.* **2004**, *93*, 153004.

(54) von Lilienfeld, O. A.; Tavernelli, I.; Rothlisberger, U.; Sebastiani, D. Performance of Optimized Atom-Centered Potentials for Weakly Bonded Systems Using Density Functional Theory. *Phys. Rev. B* **2005**, *71*, 195119.

(55) Lin, I.-C.; Coutinho-Neto, M. D.; Felsenheimer, C.; von Lilienfeld, O. A.; Tavernelli, I.; Rothlisberger, U. Library of Dispersion-Corrected Atom-Centered Potentials for Generalized Gradient Approximation Functionals: Elements H, C, N, O, He, Ne, Ar, and Kr. *Phys. Rev. B* **2007**, *75*, 205131.

(56) DiLabio, G. A. Accurate Treatment of van der Waals Interactions Using Standard Density Functional Theory with Effective Core-Type Potentials: Application to Carbon-Containing Dimers. *Chem. Phys. Lett.* **2008**, *455*, 348−353.

(57) Mackie, I. D.; DiLabio, G. A. Accurate Dispersion Interactions from Standard Density-Functional Theory Methods with Small Basis Sets. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6092−6098.

(58) Torres, E.; DiLabio, G. A. A (Nearly) Universally Applicable Method for Modeling Noncovalent Interactions Using B3LYP. *J. Phys. Chem. Lett.* **2012**, *3*, 1738−1744.

(59) Karalti, O.; Su, X.; Al-Saidi, W. A.; Jordan, K. D. Correcting Density Functionals for Dispersion Interactions Using Pseudopotentials. *Chem. Phys. Lett.* **2014**, *591*, 133−136.

(60) Krishtal, A.; Van Alsenoy, C.; Geerlings, P. Evaluating Interaction Energies of Weakly Bonded Systems Using the Buckingham-Hirshfeld Method. *J. Chem. Phys.* **2014**, *140*, 184105.

(61) Tkatchenko, A.; Scheffler, M. Accurate Molecular van der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett.* **2009**, *102*, 073005.

(62) Tkatchenko, A.; DiStasio, R. A., Jr.; Car, R.; Scheffler, M. Accurate and Efficient Method for Many-Body van der Waals Interactions. *Phys. Rev. Lett.* **2012**, *108*, 236402.

(63) Ruzsinszky, A.; Perdew, J. P.; Tao, J.; Csonka, G. I.; Pitarke, J. M. Van der Waals Coefficients for Nanostructures: Fullerenes Defy Conventional Wisdom. *Phys. Rev. Lett.* **2012**, *109*, 233203.

(64) Tao, J.; Perdew, J. P.; Ruzsinszky, A. Long-Range van der Waals Attraction and Alkali-Metal Lattice Constants. *Phys. Rev. B* **2010**, *81*, 233102.

(65) Tao, J.; Perdew, J. P.; Ruzsinszky, A. Accurate van der Waals Coefficients from Density Functional Theory. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 18−21.

(66) Bučko, T.; Lebègue, S.; Hafner, J.; Ángyán, J. G. Tkatchenko-Scheffler van der Waals Correction Method with and without Self-Consistent Screening Applied to Solids. *Phys. Rev. B* **2013**, *87*, 064110.

(67) Ambrosetti, A.; Reilly, A. M.; DiStasio, R. A., Jr.; Tkatchenko, A. Long-Range Correlation Energy Calculated from Coupled Atomic Response Functions. *J. Chem. Phys.* **2014**, *140*, 18A508.

(68) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. Design of Density Functionals by Combining the Method of Constraint Satisfaction with Parametrization for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2006**, *2*, 364−382.

(69) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Non-covalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215−241.

(70) Chai, J.-D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom-Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615−6620.

(71) Chai, J.-D.; Head-Gordon, M. Systematic Optimization of Long-Range Corrected Hybrid Density Functionals. *J. Chem. Phys.* **2008**, *128*, 084106.

(72) Benighaus, T.; DiStasio, R. A., Jr.; Lochan, R. C.; Chai, J.-D.; Head-Gordon, M. Semiempirical Double-Hybrid Density Functional with Improved Description of Long-Range Correlation. *J. Phys. Chem. A* **2008**, *112*, 2702−2712.

(73) Chai, J.-D.; Head-Gordon, M. Long-Range Corrected Double-Hybrid Density Functionals. *J. Chem. Phys.* **2009**, *131*, 174105.

(74) Sancho-García, J. C.; Pérez-Jiménez, A. J. Assessment of Double-Hybrid Energy Functionals for π-Conjugated Systems. *J. Chem. Phys.* **2009**, *131*, 084108.

(75) Zhang, Y.; Xu, X.; Goddard, W. A., III. Doubly Hybrid Density Functional for Accurate Descriptions of Nonbond Interactions, Thermochemistry, and Thermochemical Kinetics. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 4963−4968.

(76) Zhang, I. Y.; Xu, X.; Jung, Y.; Goddard, W. A., III. A Fast Doubly Hybrid Density Functional Method Close to Chemical Accuracy Using a Local Opposite Spin Ansatz. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 19896−19900.

(77) Zhang, I. Y.; Xu, X. XYG3 and XYGJ-OS Performances for Noncovalent Binding Energies Relevant to Biomolecular Structures. *Phys. Chem. Chem. Phys.* **2012**, *14*, 12554−12570.

(78) Lin, Y.-S.; Li, G.-D.; Mao, S.-P.; Chai, J.-D. Long-Range Corrected Hybrid Density Functionals with Improved Dispersion Corrections. *J. Chem. Theory Comput.* **2013**, *9*, 263−272.

(79) Mardirossian, N.; Head-Gordon, M. ωB97X-V: A 10-Parameter, Range-Separated Hybrid, Generalized Gradient Approximation Density Functional with Nonlocal Correlation, Designed by a Survival-of-the-Fittest Strategy. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9904−9924.

(80) Yu, F. Intermolecular Interactions of Formic Acid with Benzene: Energy Decomposition Analyses with *Ab Initio* MP2 and Double-Hybrid Density Functional Computations. *Int. J. Quantum Chem.* **2013**, *113*, 2355−2360.

(81) Yu, F. Double-Hybrid Density Functionals Free of Dispersion and Counterpoise Corrections for Non-Covalent Interactions. *J. Phys. Chem. A* **2014**, *118*, 3175−3182.

(82) Mardirossian, N.; Head-Gordon, M. Exploring the Limit of Accuracy for Density Functionals Based on the Generalized Gradient Approximation: Local, Global Hybrid, and Range-Separated Hybrid Functionals with and without Dispersion Corrections. *J. Chem. Phys.* **2014**, *140*, 18A527.

(83) Kozuch, S.; Gruzman, D.; Martin, J. M. L. DSD-BLYP: A General Purpose Double Hybrid Density Functional Including Spin Component Scaling and Dispersion Correction. *J. Phys. Chem. C* **2010**, *114*, 20801−20808.

(84) Kozuch, S.; Martin, J. M. L. DSD-PBEP86: In Search of the Best Double-Hybrid DFT with Spin-Component Scaled MP2 and Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20104−20107.

(85) Kozuch, S.; Martin, J. M. L. Spin-Component-Scaled Double Hybrids: An Extensive Search for the Best Fifth-Rung Functionals Blending DFT and Perturbation Theory. *J. Comput. Chem.* **2013**, *34*, 2327−2344.

(86) Grimme, S. Improved Second-Order Møller−Plesset Perturbation Theory by Separate Scaling of Parallel- and Antiparallel-Spin Pair Correlation Energies. *J. Chem. Phys.* **2003**, *118*, 9095−9102.

(87) Jung, Y.; Lochan, R. C.; Dutoi, A. D.; Head-Gordon, M. Scaled Opposite-Spin Second Order Møller−Plesset Correlation Energy: An Economical Electronic Structure Method. *J. Chem. Phys.* **2004**, *121*, 9793−9802.

(88) Goerigk, L.; Grimme, S. Efficient and Accurate Double-Hybrid-Meta-GGA Density Functionals—Evaluation with the Extended GMTKN30 Database for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2011**, *7*, 291−309.

(89) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(90) Perdew, J. P. Unified Theory of Exchange and Correlation Beyond the Local Density Approximation. In *Electronic Structure of Solids '91*; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991; pp 11−20.

(91) Becke, A. D. Density-Functional Thermochemistry. IV. A New Dynamical Correlation Functional and Implications for Exact-Exchange Mixing. *J. Chem. Phys.* **1996**, *104*, 1040−1046.

(92) Jurečka, P.; Šponer, J.; Černý, J.; Hobza, P. Benchmark Database of Accurate (MP2 and CCSD(T) Complete Basis Set Limit) Interaction Energies of Small Model Complexes, DNA Base Pairs, and Amino Acid Pairs. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985−1993.

(93) Takatani, T.; Hohenstein, E. G.; Malagoli, M.; Marshall, M. S.; Sherrill, C. D. Basis Set Consistent Revision of the S22 Test Set of Noncovalent Interaction Energies. *J. Chem. Phys.* **2010**, *132*, 144104.

(94) Podeszwa, R.; Patkowski, K.; Szalewicz, K. Improved Interaction Energy Benchmarks for Dimers of Biological Relevance. *Phys. Chem. Chem. Phys.* **2010**, *12*, 5974−5979.

(95) Marshall, M. S.; Burns, L. A.; Sherrill, C. D. Basis Set Convergence of the Coupled-Cluster Correction, $\delta_{MP2}^{CCSD(T)}$: Best Practices for Benchmarking Non-Covalent Interactions and the Attendant Revision of the S22, NBC10, HBC6, and HSG Databases. *J. Chem. Phys.* **2011**, *135*, 194102.

(96) Řezáč, J.; Riley, K. E.; Hobza, P. S66: A Well-balanced Database of Benchmark Interaction Energies Relevant to Biomolecular Structures. *J. Chem. Theory Comput.* **2011**, *7*, 2427−2438.

(97) Řezáč, J.; Riley, K. E.; Hobza, P. Extensions of the S66 Data Set: More Accurate Interaction Energies and Angular-Displaced Non-equilibrium Geometries. *J. Chem. Theory Comput.* **2011**, *7*, 3466−3470.

(98) Zhao, Y.; Truhlar, D. G. Design of Density Functionals That Are Broadly Accurate for Thermochemistry, Thermochemical Kinetics, and Nonbonded Interactions. *J. Phys. Chem. A* **2005**, *109*, 5656−5667.

(99) Zhao, Y.; Truhlar, D. G. Benchmark Databases for Nonbonded Interactions and Their Use to Test Density Functional Theory. *J. Chem. Theory Comput.* **2005**, *1*, 415−432.

(100) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M. Estimated MP2 and CCSD(T) Interaction Energies of n-Alkane Dimers at the Basis Set Limit: Comparison of the Methods of Helgaker *et al.* and Feller. *J. Chem. Phys.* **2006**, *124*, 114304.

(101) Goerigk, L.; Grimme, S. A Thorough Benchmark of Density Functional Methods for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670−6688.

(102) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(103) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785−789.

(104) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin Density Calculations: A Critical Analysis. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(105) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(106) Perdew, J. P. Density-Functional Approximation for the Correlation Energy of the Inhomogeneous Electron Gas. *Phys. Rev. B* **1986**, *33*, 8822−8824.

(107) Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618−622.

(108) Neese, F. The ORCA Program System. *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78.

(109) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(110) Weigend, F.; Kattanneck, M.; Ahlrich, R. Approximated Electron Repulsion Integrals: Cholesky Decomposition versus Resolution of the Identity Methods. *J. Chem. Phys.* **2009**, *130*, 164106.

(111) Kossmann, S.; Neese, F. Comparison of Two Efficient Approximate Hartree-Fock Approaches. *Chem. Phys. Lett.* **2009**, *481*, 240–243.

(112) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. RI-MP2: Optimized Auxiliary Basis Sets and Demonstration of Efficiency. *Chem. Phys. Lett.* **1998**, *294*, 143–152.

(113) Weigend, F. Hartree–Fock Exchange Fitting Basis Sets for H to Rn. *J. Comput. Chem.* **2008**, *29*, 167–175.

(114) Hättig, C. Optimization of Auxiliary Basis Sets for RI-MP2 and RI-CC2 Calculations: Core–Valence and Quintuple-ζ Basis Sets for H to Ar and QZVPP Basis Sets for Li to Kr. *Phys. Chem. Chem. Phys.* **2005**, *7*, 59–66.

(115) Krack, M.; Köster, A. M. An Adaptive Numerical Integrator for Molecular Integrals. *J. Chem. Phys.* **1998**, *108*, 3226–3234.

(116) Lebedev, V. I.; Laikov, D. N. A Quadrature Formula for the Sphere of the 131st Algebraic Order of Accuracy. *Dokl. Math.* **1999**, *59*, 477–481.

(117) Wennmohs, F.; Neese, F. A Comparative Study of Single Reference Correlation Methods of the Coupled-Pair Type. *Chem. Phys.* **2008**, *343*, 217–230.

(118) Neese, F.; Hansen, A.; Wennmohs, F.; Grimme, S. Accurate Theoretical Chemistry with Coupled Electron Pair Models. *Acc. Chem. Res.* **2009**, *42*, 641–648.

(119) Kollmar, C.; Neese, F. The Coupled Electron Pair Approximation: Variational Formulation and Spin Adaptation. *Mol. Phys.* **2010**, *108*, 2449–2458.

(120) Hoffmann, R.; Schleyer, P. v. R.; Schaefer, H. F., III. Predicting Molecules—More Realism, Please! *Angew. Chem., Int. Ed.* **2008**, *47*, 7164–7167.

(121) Zhang, Y.; Yang, W. Comment on "Generalized Gradient Approximation Made Simple". *Phys. Rev. Lett.* **1998**, *80*, 890–890.

(122) Goerigk, L.; Kruse, H.; Grimme, S. Benchmarking Density Functional Methods against the S66 and S66 × 8 Datasets for Non-Covalent Interactions. *ChemPhysChem* **2011**, *12*, 3421–3433.

(123) http://www.thch.uni-bonn.de/tc/downloads/GMTKN/GMTKN30/ADIM6.html (accessed July 2014).

(124) Kamiya, M.; Tsuneda, T.; Hirao, K. A Density Functional Study of van der Waals Interactions. *J. Chem. Phys.* **2002**, *117*, 6010–6015.

(125) Steinmann, S. N.; Piemontesi, C.; Delachat, A.; Corminboeuf, C. Why are the Interaction Energies of Charge-Transfer Complexes Challenging for DFT? *J. Chem. Theory Comput.* **2012**, *8*, 1629–1640.

(126) Johnson, E. R.; Salamone, M.; Bietti, M.; DiLabio, G. A. Modeling Noncovalent Radical–Molecule Interactions Using Conventional Density-Functional Theory: Beware Erroneous Charge Transfer. *J. Phys. Chem. A* **2013**, *117*, 947–952.

(127) Modrzejewski, M.; Chałasiński, G.; Szczęśniak, M. M. Range-Separated, Meta-GGA Functional Designed for Noncovalent Interactions. *J. Chem. Theory Comput.* **2014**, DOI: 10.1021/ct500707w.

(128) Sato, T.; Nakai, H. Density Functional Method Including Weak Interactions: Dispersion Coefficients Based on the Local Response Approximation. *J. Chem. Phys.* **2009**, *131*, 224104.

(129) Sato, T.; Nakai, H. Local Response Dispersion Method. II. Generalized Multicenter Interactions. *J. Chem. Phys.* **2010**, *133*, 194101.

(130) Ikabata, Y.; Nakai, H. Local Response Dispersion Method: A Density-Dependent Dispersion Correction for Density Functional Theory. *Int. J. Quantum Chem.* **2014**, DOI: 10.1002/qua.24786.

(131) Soydaş, E.; Bozkaya, U. Accurate Open-Shell Noncovalent Interaction Energies from the Orbital-Optimized Møller–Plesset Perturbation Theory: Achieving CCSD Quality at the MP2 Level by Orbital Optimization. *J. Chem. Theory Comput.* **2013**, *9*, 4679–4683.

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