Efficient yet Accurate Dispersion-Corrected Semilocal Exchange-Correlation Functionals For Non-Covalent Interactions

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Due to several attractive features, the meta-generalized-gradient approximations (meta-GGAs) are considered to be the most advanced and potentially accurate semilocal exchange-correlation functionals in the rungs of the Jacob’s ladder of Density Functional Theory. So far, several meta-GGA are proposed by fitting to the test sets or and satisfying as many as known exact constraints. Although the density overlap is treated by modern meta-GGA functionals efficiently, for non-covalent interactions, a long-range dispersion correction is essential. In this work, we assess the benchmark performance of different variants of the Tao-Mo semilocal functional (i.e. TM of Phys. Rev. Lett. 117, 073001 (2016) and revTM of J. Phys. Chem. A 123, 6356 (2019)) with Grimme’s D3 correction for the several non-covalent interactions, including dispersion and hydrogen bonded systems. We consider the zero, Becke-Johnson(BJ), and optimized power (OP) damping functions within the D3 method, with both TM and revTM functionals. It is observed that the overall performance of the functionals gradually improved from zero to BJ and to OP damping. However, the constructed “OP” corrected (rev)TM+D3(OP) functionals perform considerably better compared to other well-known dispersion corrected functionals. Based on the accuracy of the proposed functionals, the future applicability of these methods is also discussed.

I. INTRODUCTION

Semilocal exchange-correlation (XC) density functionals are the most preferred choice of doing electronic structure calculations within the Kohn-Sham (KS) Density Functional Theory (DFT).\(^{12}\) Starting from the local density approximation (LDA)\(^{23,24}\) to the higher rungs of the Jacob’s ladder classification of XC functionals,\(^{2,25}\) the semilocal approximations are characterized as the generalized gradient approximations (GGAs)\(^{25-50}\) and meta-GGAs.\(^{51-57}\) Higher rungs than meta-GGA use non-local information from KS orbitals and eigenvalues, and are recognized from the point of view of their sophistication, as the so-called rung 3.5\(^{58,59}\), hybrids and hyper-GGA functionals\(^{60-62}\), double hybrids and DFT coupled-cluster based methods\(^{63-65}\), adiabatic-connection methods and generalizations of the random phase approximation (RPA).\(^{66-69}\)

Meta-GGA XC functionals improve the overall performance of GGAs, and the hybrid methods do the same over their bare semilocal counterparts. But none of these functionals able to incorporate the long-range correlation, which is essential for systems dominated by weak bonds. For the last couple of decades, the formulation of meta-GGA functionals has been made very physical insightful through the inclusion of short- and intermediate-range behavior of the weakly bonded systems.\(^{29,38}\) However, studies show that semilocal approximations do not incorporate short- and intermediate-range dispersion.\(^{107,108}\) Designing density functionals, irrespective of the short- and intermediate-range dispersion or van der Waals (vdW) interactions as well as to retain their accuracy for the density overlap region, a long-range vdW correction is always necessary to describe the functional performance correctly for the binding energies of weakly bonded systems.\(^{79,109,112}\)

The long-range vdW interaction can be captured via\(^{113}\)

\[
E_{vdW} = - \sum_{i<j} \sum_{n=6,8,10,\ldots} \frac{s_n}{r_{ij}^{n+3}} \sum_{m,n} C_{n,ij} f_{damp,n}(r_{ij}) ,
\]

where the dispersion coefficients, \(C_{n,ij}\) are determined either experimentally\(^{113}\) or theoretically\(^{113}\) and those may be chemically insensitive; \(s_n\) are density functional dependent global scaling parameters; and \(r_{ij}\) is the inter-nuclear distance between the \(i^{th}\) and \(j^{th}\) atoms. This simple term, when added to any semilocal or hybrid density functionals leads to the well known dispersion corrected density functional (DFT+D) method.\(^{114,115}\) To avoid the singularities at small \(r_{ij}\) a damping function \(f_{damp,n}(r_{ij})\) is used. The form of the damping function plays a dramatic role in the functional performance when applied to the dispersion bonded systems. However, the cutoff procedure of the vdW range through the damping function should be judiciously chosen with caution to avoid deterioration of the functional performance or over-binding problem in case of non-covalent interaction. This is crucial for the H-bonded systems for which the inclusion of the dispersion correction deteriorates the functional performance. We will discuss all these points in our results section.

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Note that by truncating Eq. (1) up to \( n = 6 \) and choosing the damping function as,

\[
f_{dmp,6}^{D3}(r_{ij}) = \frac{1}{1 + e^{-\alpha(r_{ij}/r_0,ij) - 1}}, \tag{2}
\]

one ends up with the Grimme’s DFT-D2 model\(^ {113} \), where \( r_{0,ij} \) is the sum of atomic vdW radii, and \( \alpha = 20 \) is chosen for better damping or steepness of this function\(^ {114,115} \). The scaling factor \( s_6 \) depends on the choice of the particular density functional, and the \( C_6 \) coefficients are obtained by fitting to the binding energies (\( \Delta E \)) and intermolecular distances of experimental or accurate theoretical values\(^ {115} \).

Grimme’s DFT-D3 dispersion correction\(^ {116} \) was proposed using both the \( C_{6,i} \), and \( C_{8,i} \) terms. However, the higher-order terms corresponding to \( n > 6 \) are more short-ranged and strongly influence the short-range part of the dispersion interaction\(^ {116} \). Several choices of the damping function are proposed, improving the functional performance in different prospects. Among the different choices of damping functions, the widely used ones are:

(i) D3(0): The zero damping function is having the following analytic form\(^ {116} \):

\[
f_{dmp,n}^{D3(0)}(r_{ij}) = [1 + 6\left(\frac{r_{ij}}{s_{r,n} r_{0,ij}}\right)^{-n}]^{-1}. \tag{3}
\]

The adjustable parameters of vdW energy terms and damping function are chosen as following: \( s_6 = 1 \), \( \alpha_6 = 14 \), \( \alpha_8 = 16 \). Also, \( s_{r,8} = 1 \) is chosen for most of the density functionals, leaving the parameters \( s_{r,6} \) and \( s_8 \), that depend on the density functional form.

(ii) D3(BJ): The Becke-Johnson (BJ) damping function is having the form\(^ {117-121} \):

\[
f_{dmp,n}^{D3(BJ)}(r_{ij}) = \frac{r_{ij}^n}{r_{ij}^n + (\alpha_1 r_{0,ij} + \alpha_2)^n}. \tag{4}
\]

The rationale behind the chosen damping function form of the BJ is due to the exchange-hole dipole-moment (XDM) correction of Becke and Johnson\(^ {117,118,120,122} \). The BJ damping approaches to a constant value at small inter-atomic separation (\( r_{ij} \to 0 \)), that differs from the D3(0). For most of the functionals, \( s_6 \) is generally fixed to unity.

(iii) D3(CSO): The Becke-Johnson damping function became the most preferred method for the DFT+D functional as it outperforms the D3(0) in most cases. However, later on, Schröder et al.\(^ {123} \) simplified it by proposing the \( C_6 \)-Only (CSO) approach, where the eighth-order term is approximated within the sigmoidal interpolation function. The damping function of D3(CSO) is given by\(^ {123} \),

\[
f_{dmp,n}^{D3(CSO)}(r_{ij}) = \frac{r_{ij}^6}{r_{ij}^6 + (\alpha_3 r_{0,ij} + \alpha_4)^6}\left[\frac{1}{1 + \frac{\alpha_1}{s_6 [1 + \exp(r_{ij} - \alpha_2 r_{0,ij})]}}\right]. \tag{5}
\]

A closer look shows the similarities between Eqs. (4) and (5). For most density functionals, Schröder et al.\(^ {123} \) fixed \( \alpha_3 \approx 0 \), \( \alpha_4 \approx 6.25 \), and \( \alpha_2 \approx 2.5 \).

(iv) The more general form of BJ damping is proposed recently by Witte et al.\(^ {124} \). This is known as “optimize-power” damping with the following analytic form

\[
f_{dmp,n}^{D3(OP)}(r_{ij}) = \frac{r_{ij}^{\beta_n}}{r_{ij}^{\beta_n} + (\alpha_1 r_{0,ij} + \alpha_2)^\beta_n}. \tag{6}
\]

The similarities between D3(BJ) and D3(OP) are noticeable. Most importantly, the parameter \( \beta \) controls the rate of dispersion interaction. Here, \( \beta_8 = \beta_6 + 2 \), and the same dispersion coefficients and vdW radii are used in D3(OP) damping. Also, similar to the D3(BJ), the parameters \( \alpha_1 \) and \( \alpha_2 \) control the distance where the damping function corresponding to the dispersion correction will be switched on or off. It was also shown that the D3(OP) improves the descriptions of weakly bonded molecular systems when coupled with any density functionals\(^ {124} \).

These dispersion correction methods are important for our present study. There are several studies on the performance of the density functionals with dispersion corrections\(^ {78,79,109-111,125-130} \). Several recent, accurate meta-GGA density functionals suitable for quantum chemical calculations are also proposed and tested for a broad range of systems\(^ {112,131} \). However, these functionals are not benchmarked for a wide range of molecular properties. The motivation of the present study follows from the very accurate performance of the different variants of TM semilocal functionals (TM\(^ {22} \) and revTM\(^ {44} \)) for quantum chemistry. Here, we combine the D3(0), D3(BJ), and D3(OP) with the TM and revTM functionals to assess their performance for non-covalent interaction test sets and H bonded water systems. We observe that the combination of the TM and revTM with D3(OP) gives improvements over various other combinations proposed so far. Most importantly, the TM+D3(OP) and revTM+D3(OP) do not deteriorate much the H-bond energies compared to their base functional accuracy. To present the functionals performance, we arrange our paper as follows: In the beginning, we briefly review the TM and revTM meta-GGA functionals, and we construct their dispersion corrected terms. Next, we test the proposed functionals concerning different non-covalent interaction test sets. Lastly, we conclude and summarize our results based on insightful analysis.
state and molecular properties.\cite{133,138,139} Specially, the best performance of the TM functional is evident from the lattice constants of the ionic solids\cite{134,138} and hydrogen-bonded complexes.\cite{133,138,139} In ref\cite{134,136,138} it has been argued that the TM exchange enhancement factor shares slightly oscillatory behavior to some extent as it is shown in Voorhis-Scuseria (VSXC)\cite{28} and M06-L\cite{20} functionals. On the other-hand the revTM exchange enhancement factor behaves differently in the region $\alpha > 1$ and $s \approx 0$ which is important for the overlapping of the closed shells or weekly bonded systems. But none of the functionals (including TM and revTM) do not incorporate correct $1/r^6$ form or the long-range interaction or correct dispersion physics.\cite{139}

To further elaborate on this point, and distinguish the different behavior of the TM and revTM for weekly interacting systems, we also plot the binding energy curve of Ar$_2$ dimer for both the functionals (shown in the lower panel of Fig.\ [1]). From the figure, we observe that the bare revTM functional unbound the Ar$_2$ dimer because $\tilde{q}_b < \tilde{q}$ in the middle of the bonding region. The behavior of the $\alpha$ and $\tilde{q}_b$ can be found in Fig. 4 and Fig. 5 of the ref.\cite{20}. The difference in capturing the interaction by both the functionals are important for non-covalent bonded molecules. Note that bare TM functional is already quite good without including any vdW correction.

The behavior of the TM and revTM functionals can also be understood from the recent investigation of the functionals performance for the water clusters.\cite{140} In ref\cite{140} it is shown that both the TM and revTM predicts correctly the ordering stability of the water hexamers, whereas, the revTM is quite good for overall performance of water and ice structures.

(ii) Secondly, the other important difference is arising due to the correlation content of both the functionals. In revTM, the linear response parameter $\beta$ has been generalized to the form of the exact, density-dependent second-order gradient expansion (GE2) parameter proposed in the revTPSS meta-GGA\cite{21} correlation energy functional. We recall that TM correlation functional uses the high-density GE2 parameter (a.i. $\beta = 0.066725$). The revTM also keeps all the useful features of the TM correlation by making the correlation energy functional spin-independent in the low-density or strong-interaction limit\cite{20}. The change in correlation energy functional improves the jellium surface XC energies\cite{44}, which are relevant for the surface energies of simple metals. Note that the change in the correlation does not affect the non-covalent interaction systems.

\section*{B. Dispersion corrected TM and revTM functionals}

To construct the dispersion corrected functionals, we combine D3(0), D3(BJ), and D3(OP) dispersion corrections with the TM and revTM functionals. To determine the dispersion parameters associated with the functionals, one needs to fit the functional with appropriate non-
to use the S22 test set of Jurecka et. al. All the functionals, we consider the standard covalent interaction test set. The most preferred choice is the SCAN+D3(0) has been also proposed by considering the mean absolute error (MAE) of the S22 test set. Also, in the error statistics by incorporating the TM functional, we do not observe any improvement to the respective functionals are summarized in Table 1.

![FIG. 2. The lower panel shows the behavior of damping functions with respect to inter-nuclear distance }r_{ij}\). The upper panel shows the contribution to the dispersion energy of Ne2 for three types of damping functions. For all the figures, we have used }r_{0,ij}=3.3\text{Å}, and for Ne2, }C_6=6.35. The inset of the upper panel is for D3(0), as the scale of energy is different.

\begin{table}[h]
\centering
\caption{Parameters used in the calculations.} \label{tab:parameters}
\begin{tabular}{llll}
\hline
Parameters & TM & D3(0) & D3(BJ) & D3(OP) \\
\hline
\hline
\text{D3(0)}(Zero damping) & & & & \\
\text{s}_6 & 1.00 & 1.00 & & \\
\text{s}_8 & 0.00 & 0.00 & & \\
\text{s}_{6,8} & 1.47 & 1.16 & & \\
\text{D3(BJ)}(Becke and Johnson damping) & & & & \\
\text{s}_6 & 1.00 & 1.00 & & \\
\text{s}_8 & 0.00 & 0.00 & & \\
\text{a}_1 & 0.825 & 0.23 & & \\
\text{a}_2 & 5.42 & 5.42 & & \\
\text{D3(OP)}(Optimized Power damping) & & & & \\
\text{s}_6 & 1.00 & 1.00 & & \\
\text{s}_8 & 0.00 & 0.00 & & \\
\text{a}_1 & 0.64 & 0.24 & & \\
\text{a}_2 & 5.42 & 5.42 & & \\
\beta & 14.00 & 14.00 & & \\
\hline
\end{tabular}
\end{table}

To understand the role played by and impact of different parameters on the damping function as well as energy component, in Fig. 2 we plot the damping function (lower panel) and }E_{vdW} of Eq. (1) (upper panel), in case of the Ne2 dimer for which the }C_6 coefficient is known. By construction, the DFT+D3(BJ) damping approach shows constant value at small inter-atomic separation, while the D3(OP) works within D3(0) and D3(BJ).

It is noteworthy to mention that in this work the 3-body term is used with all the D3 schemes, being.

\begin{equation}
E_{\text{D3}}^{3\text{-body}} = -\frac{1}{6} \sum_{A,B,C} C_{ABC}^{A} (1 + 3 \cos \phi_A \cos \phi_B \cos \phi_C) \times f_d^A(r_{ABC}),
\end{equation}

where the damping function }f_d^A is related to the D3 dispersion interaction coupled with the correlation part of the semilocal density functional. Here }\phi_A, }\phi_B and }\phi_C are the angles formed of the three atoms }A, }B and }C, and }r_{ABC} is the geometric mean distance. We recall that the 3-body term represents only a small fraction of the total dispersion interaction, being analyzed in several works.
TABLE III. Interaction energies (in kcal/mol) of S22 data set. The mean error (ME) and mean absolute error (MAE) are also reported. The best values are marked with bold style.

| S22 complex | CCSD(T) TM+D3(0) | TM+D3(BJ) | TM+D3(OP) | revTM+D3(0) | revTM+D3(BJ) | revTM+D3(OP) |
|-------------|------------------|-----------|-----------|-------------|-------------|-------------|
| Hydrogen bonded complexes |
| NH₃ dimer (C₂₃) | 3.133 | 3.397 | 3.403 | 3.352 | 3.257 | 3.303 | 3.150 |
| H₂O dimer (C₂) | 4.989 | 5.360 | 5.361 | 5.317 | 5.373 | 5.394 | 5.247 |
| Formic acid dimer (C₂₃) | 18.775 | 18.852 | 18.717 | 19.033 | 19.258 | 18.801 |
| Formamide dimer (C₂₅) | 16.966 | 15.782 | 15.658 | 15.968 | 16.139 | 15.791 |
| Uracil dimer (C₂₉) | 20.641 | 19.708 | 19.623 | 20.068 | 20.211 | 19.890 |
| 2-pyridone-2-aminopyridine (C₁₄) | 16.934 | 16.583 | 16.521 | 17.134 | 17.250 | 16.922 |
| Adenine-thymine WC (C₁) | 16.660 | 15.931 | 15.840 | 16.395 | 16.462 | 16.132 |
| ME | -0.23 | -0.22 | -0.30 | 0.00 | 0.12 | -0.17 |
| MAE | 0.42 | 0.44 | 0.46 | 0.27 | 0.30 | 0.26 |

Dispersion bonded complexes

| CH₄ dimer (D₃d) | 0.527 | 0.578 | 0.568 | 0.517 | 0.635 | 0.470 | 0.479 |
| C₂H₄ dimer (D₂d) | 1.472 | 1.633 | 1.691 | 1.599 | 1.418 | 1.453 | 1.269 |
| Benzene-Ch₄ (C₆) | 1.448 | 1.560 | 1.482 | 1.460 | 1.470 | 1.459 | 1.413 |
| Benzene dimer (C₂₅) | 2.654 | 2.670 | 2.663 | 2.531 | 2.772 | 2.908 | 3.267 |
| Pyrazine dimer (C₆) | 4.255 | 3.999 | 4.076 | 3.847 | 4.018 | 4.196 | 4.317 |
| Uralc dimer (C₂) | 9.805 | 10.028 | 10.028 | 9.730 | 9.756 | 9.704 | 9.700 |
| Indole-benzene (C₁) | 4.524 | 4.432 | 4.467 | 4.267 | 4.406 | 4.723 | 5.078 |
| Adenine-thymine (C₁) | 11.730 | 12.127 | 12.179 | 11.792 | 11.397 | 11.644 | 11.524 |
| ME | 0.07 | 0.09 | 0.08 | -0.06 | 0.01 | 0.07 |
| MAE | 0.16 | 0.15 | 0.13 | 0.12 | 0.09 | 0.22 |

Hydrogen + dispersion (mixed) bonded complexes

| C₂H₂-C₂H₂ (C₂) | 1.496 | 1.486 | 1.486 | 1.458 | 1.598 | 1.588 | 1.537 |
| Benzene-H₂O (C₆) | 3.275 | 3.886 | 3.863 | 3.754 | 3.874 | 3.781 | 3.646 |
| Benzene-NH₃ (C₂) | 2.312 | 2.600 | 2.543 | 2.480 | 2.564 | 2.498 | 2.427 |
| Benzene-HCN (C₆) | 4.541 | 4.657 | 4.685 | 4.597 | 4.420 | 4.741 | 4.531 |
| Benzene dimer (C₂₅) | 2.717 | 2.684 | 2.614 | 2.623 | 2.609 | 2.711 | 2.673 |
| Indole-benzene (C₆) | 5.627 | 5.626 | 5.566 | 5.552 | 5.595 | 5.661 | 5.521 |
| Phenol dimer (C₁) | 7.097 | 6.825 | 6.761 | 6.756 | 6.723 | 6.706 | 6.475 |
| ME | 0.09 | 0.06 | 0.06 | 0.02 | 0.04 | 0.08 | -0.03 |
| MAE | 0.19 | 0.21 | 0.17 | 0.22 | 0.20 | 0.18 |
| ME | -0.01 | -0.01 | -0.12 | -0.00 | 0.07 | -0.03 |
| MAE | 0.25 | 0.26 | 0.25 | 0.20 | 0.19 | 0.22 |

III. RESULTS

All the calculations are done with the developer version of Q-Chem simulation package. For XC integrals the 99 points radial grid and 590 points angular Lebedev grid are used. Note that the non-bonded systems binding energies are very sensitive on the choice of the grid. The present choice of the grid is adequate and highly recommended for the complete energy convergence of the nonbonded systems. The test sets used in our calculations and the corresponding basis sets are mentioned in Table III. All calculations are performed with def2-QZVP basis set except the AHB21, IL16, WATER27, DSCONF, and MG8 test sets, where the calculations are performed with the def2-QZVPD basis set. It is shown that the use of diffuse basis set drastically improves the results for those test set.

A. S22 test set

To start with, we consider the S22 test set. As mentioned before it contains important non-covalent interacting molecules, that are often used for the benchmark calculations. The details of the different functional performance for the individual molecules are presented in Table III. For reference values those obtained from CCSD(T)/CBS calculations by Sherrill et. al. are considered. Regarding the performance of individual dispersion corrected functionals, we observe that all functionals perform in a impressive way. Regarding the H-bonded molecules, which consist of different complexes having biological interests, the NH₃ and H₂O dimer energies are overestimated by the -D3(0) and -D3(BJ) dispersion corrections, while for -D3(OP) the overestimation tendency is less evident. For other H-bonded systems, we also observe same tendency as -D3(OP), indicating its balanced performance for H-bonded systems.

In case of the dispersion bonded systems, we observe a systematic slight underestimation of -D3(OP) functionals compared to the -D3(0) and -D3(BJ) ones. Overall both the -D3(OP) corrected functionals underestimate the interaction energies.

Next, for the mixed interaction, we observe underestimation or overestimation in the interaction energies from -D3(OP) functional based on the interaction strength.
TABLE IV. ME and MAE (in kcal/mol) of different functionals for the S22 data set. The best values are marked with bold style.

| Methods               | ME   | MAE   |
|-----------------------|------|-------|
| PBE\(^{a}\)          | -2.55| 2.55  |
| TPSS\(^{a}\)         | -3.44| 3.44  |
| SCAN\(^{a}\)         | -0.57| 0.91  |
| TM\(^{b}\)           | -0.53| 0.61  |
| revTM\(^{b}\)        | -1.80| 1.82  |
| M06-L\(^{L}\)        | -0.77| 0.81  |
| B3LYP\(^{a}\)        | -3.78| 3.78  |
| PBE0\(^{a}\)         | -2.33| 2.37  |
| TPSS0\(^{a}\)        | -3.06| 3.06  |
| \(\text{semi-local/hybrid}\) |       |       |
| PW66B-VV10\(^{e}\)   | 0.27 | 0.35  |
| rVV10\(^{e}\)        | 0.16 | 0.30  |
| SCAN+rVV10\(^{e}\)   | 0.22 | 0.43  |
| SCAN+D3\(^{a}\)      | 0.38 | 0.45  |
| SCAN+D3(BJ)\(^{a}\)  | 0.45 | 0.42  |
| TM+D3(0)\(^{b}\)     | -0.01| 0.25  |
| TM+D3(BJ)\(^{b}\)    | -0.01| 0.26  |
| TM+D3(OP)\(^{b}\)    | -0.12| 0.25  |
| M06-L+D3(0)\(^{a}\)  | 0.44 | 0.52  |
| MS2+D3(OP)\(^{e}\)   | -    | 0.43  |
| revTM+D3(0)\(^{b}\)  | -0.00| 0.20  |
| revTM+D3(BJ)\(^{b}\) | 0.07 | 0.19  |
| revTM+D3(OP)\(^{b}\) | -0.03| 0.22  |
| \(\text{(range-separated) hybrid/dispersion}\) |       |       |
| B3LYP+D3\(^{a}\)     | 0.18 | 0.37  |
| B3LYP+D3(BJ)\(^{a}\) | 0.29 | 0.31  |
| PBE0+D3\(^{a}\)      | 0.30 | 0.58  |
| PBE0+D3(BJ)\(^{a}\)  | 0.30 | 0.48  |
| revPBE0+D3(OP)\(^{a}\)| 0.30 | 0.39  |
| TPSS0+D3\(^{a}\)     | 0.22 | 0.46  |
| TPSS0+D3(BJ)\(^{a}\) | 0.19 | 0.38  |
| \(\omega\)B97X-D3\(^{a}\) | 0.07 | 0.21  |
| \(\omega\)B97X-V\(^{a}\) | -0.10| 0.22  |

Note that for this case the -D3(0P) balances more the interaction energies for individual molecules compared to the other two dispersion interactions.

To complete our analysis, in Table [IV] we compare the ME and MAE of several popular GGA, meta-GGA and hybrid density functionals (global and range-separated). The dispersion corrected functionals are consistently improving their performance compared to the corresponding bare functionals. Note that revTM+D3(BJ) achieves the best accuracy among the dispersion corrected semilocal functionals with MAE=0.19 kcal/mol, being significantly better than other dispersion corrected semilocal functionals. Within hybrid functionals, the \(\omega\)B97X-D3 is close to that of the revTM+D3(BJ).

B. L7 test set

The L7 test set consists of large sized complexes having dispersion dominated non-covalent bonds. Due to the computational efficiency, dispersion corrected semilocal XC functionals are very promising in case of such large complexes. Now, to test the accuracy of the above discussed methods, we apply both bare semilocal, and D3 corrected semilocal functionals to the optimized structures (TPSS-D/TZVP) of the complexes present in the L7 test set\(^{148}\). This data set includes mixed hydrogen bonded complexes along with aliphatic, and strong aromatic dispersion bonded complexes. The binding energies of all the seven large complexes are shown in Table [V] considering all D3 corrected functionals and the CCSD(T) reference data\(^{123}\). Among all the six dispersion corrected methods, revTM+D3(0P) has the least error with more accurately description of aromatic dispersion interactions(C3A, C3GC, C2C2PD) and hydrogen bonds (PHE). However, all the methods underbind the stacked Watson-Crick H-bonded guanine-cytosine dimer (GCCG) significantly. Such underestimation by TM based functionals is also reported in literature\(^{132}\). We also show the errors excluding the GCCG base pair from L7 data set in the lower panel of Table [V]. A drastic drop of the MAE for all the cases can be seen and the revTM+D3(0P) is the best method with MAE=0.86 kcal/mol. Now, it is necessary to compare our methods with contemporary dispersion corrected methods to understand the hierarchy of development. So, we list the errors of L7 data set for above discussed methods along with errors of some available functionals in Table [VI]. The TPSS+D3 method is proved to be best having least MAE value of 1.1 kcal/mol. Note that the S30L benchmark set proposed in ref\(^{179}\) is more realistic than L7. We will consider these test cases in our future study.

C. Inter and intra-molecular non-covalent interactions

The inter-molecular binding energies of the dispersion bonded molecular complexes, arise from atoms of the two separate molecular systems. All the test sets and geometries are taken from the GMTKN55 database, where we do not include the WATER27, which is discussed separately within the hydrogen bonded complexes. Table [VII] reports MAE of all the constructed dispersion corrected functionals, along with the best dispersion corrected semilocal and the overall best method.

To start with, the RG18 test set contains the rare-gas dimers, trimers, tetramers, hexamers and complexes of rare gas with HF, ethyne, ethane and benzene. We obtain the best MAE from revTM+D3(OP) within the considered functionals with MAE=0.15 kcal/mol. In all cases, the -D3(0P) improves over -D3(0) and -D3(BJ) functionals. The ADIM6 test set consists of six alkane dimers binding energies. We observe revTM+D3(BJ) achieves the best accuracy among the semilocal D3 corrected functionals with MAE=0.06 kcal/mol, performing as the best semilocal-D3 result found from the OLYP-D3(BJ) functional. Therefore, for alkane dimers binding energies, revTM+D3(BJ) is quite a good candidate.
TABLE V. Interaction energies (in kcal/mol) of L7 data set. The CCSD(T) reference values are given in the first column. The best values are marked with bold style.

| L7 Complexes                      | CCSD(T) | TM+D3(0) | TM+D3(BJ) | TM+D3(OP) | revTM+D3(0) | revTM+D3(BJ) | revTM+D3(OP) |
|-----------------------------------|---------|----------|-----------|-----------|-------------|--------------|--------------|
| Octadecane dimer (CBH)            | -11.6   | -11.33   | -10.99    | -10.40    | -12.08      | -10.23       | -10.91       |
| Guanine trimer (GGG)              | -1.9    | -2.08    | -1.87     | -1.65     | -2.09       | -1.71        | -2.22        |
| Circumcoronene-Adenine dimer (C3A)| -17.0   | -14.20   | -13.86    | -14.14    | -14.71      | -14.74       | -15.81       |
| Circumcoronene-Guanine-cytosine dimer (C3GC) | -29.1 | -25.12   | -24.50    | -24.76    | -25.57      | -25.58       | -27.43       |
| Phenylalanine trimer (PHE)        | -21.2   | -16.70   | -16.73    | -17.02    | -17.73      | -18.66       | -21.05       |
| Guanine-cytosine dimer (GCGC)     | -12.8   | -3.73    | -3.15     | -2.97     | -2.95       | -2.00        | -3.14        |
| Errors for L6 (removing GCGC from L7) |       |          |           |           |             |              |              |
| ME                                | -2.64   | -3.15    | -2.98     | -2.93     | -2.77       | -1.69        |              |
| MAE                               | 3.24    | 3.52     | 3.48      | 3.07      | 3.13        | 2.12         |              |

TABLE VI. The ME and MAE (in kcal/mol) of different functionals for the L7 data set.

| Methods        | ME     | MAE   |
|----------------|--------|-------|
| M06-L           | -3.0   | 3.0   |
| M062X           | -3.2   | 3.3   |
| SCAN            | -7.9   | 7.9   |
| TM              | -8.0   | 8.0   |
| revTM           | -15.0  | 15.0  |
| PBE+D3         | -2.1   | 2.6   |
| BLYP+D3         | 2.1    | 2.1   |
| TPS+D3          | -0.9   | 1.1   |
| SCAN+D3        | -1.2   | 2.5   |
| M062X-D3       | -0.1   | 1.3   |
| TM+D3(0)       | -2.6   | 3.2   |
| TM+D3(BJ)      | -3.1   | 3.5   |
| TM+D3(OP)      | -2.9   | 3.4   |
| revTM+D3(0)    | -2.3   | 3.0   |
| revTM+D3(BJ)   | -2.7   | 3.1   |
| revTM+D3(OP)   | -1.6   | 2.1   |
| PBE0+D3        | 1.4    | 1.6   |
| B3LYP+D3       | 1.7    | 1.7   |

Considering the S22 test set, it was already discussed in the previous section. In this case, revTM+D3(BJ) achieves the best accuracy among the semilocal D3 theory, better than so far best BLYP-D3(BJ). Similar accuracy is also observed for the S66 test set with the revTM+D3(BJ) functional. However, in this case we observe revTM+D3(OP) bit better than revTM+D3(BJ). This is due to the better performance of revTM+D3(OP) for H-bonded systems. The HEAVY28 test set consists of non-covalent binding energies of 28 heavy-element-hydride dimers. In this case also, revTM+D3(OP) outperforms other dispersion corrected functionals with MAE=0.18 kcal/mol. The CARBH21 test set contains the interaction energies of 21 anionic and neutral dimers. The TM+D3(OP) and revTM+D3(OP) are performing better compared to the others functionals, because -D3(OP) performs in a more balanced way for H-bonded and dipole-interacting systems. The revTM+D3(OP) is also performing comprehensively for the six cationic−neutral dimers test set CHB6. Next for the IL16 test set which consists of 16 cation−anion non-covalently bonded model dimers, revTM+D3(OP) represents non-covalent binding energies of halogenated dimers, being constructed from the combination of XB51 and X40 test sets. In this case also the slight overestimation is observed from all the dispersion corrected functionals, and the lowest MAE of 1.10 kcal/mol is obtained from revTM+D3(0), while the best semilocal D3 corrected functional is the M06-L-D3(0) with MAE=0.49 kcal/mol. The AHB21 test set contains the interaction energies of 21 anionic and neutral dimers. The TM+D3(OP) and revTM+D3(OP) are performing better compared to the others functionals, because -D3(OP) performs in a more balanced way for H-bonded and dipole-interacting systems. The revTM+D3(OP) is also performing comprehensively for the six cationic−neutral dimers test set CHB6.
TABLE VII. Mean errors and mean absolute errors (in kcal/mol) for benchmark test sets, using the D3-corrected semilocal XC functionals. For a better evaluation, we also provide the best semilocal+D3 and overall results for each test, taken from ref. 79. The best values within TM and revTM based dispersion methods are marked with bold style.

| Test sets | Errors | TM | TM | TM | TM | TM | TM | Best | Best |
|-----------|--------|----|----|----|----|----|----|------|------|
|           | +D3(0) | +D3(BJ) | +D3(OP) | +D3(0) | +D3(BJ) | +D3(OP) |  |  |  |
| Intermolecular non-covalent interactions (kcal/mol) | | | | | | | | | |
| RG18      | ME | 0.01 | 0.01 | -0.02 | -0.10 | -0.14 | -0.13 | 0.09 | 0.06 |
|           | MAE | 0.21 | 0.19 | 0.19 | 0.15 | 0.18 | 0.15 | (revPBE-D3(BJ)) | (revTPSSh-D3(BJ)) |
| ADIM6     | ME | 0.65 | 0.49 | 0.43 | 0.36 | -0.06 | -0.13 | 0.06 | 0.05 |
|           | MAE | 0.65 | 0.49 | 0.43 | 0.36 | 0.06 | 0.13 | (OLYP-D3(BJ)) | (BHLYP-D3(BJ)) |
| S22       | ME | -0.01 | -0.01 | -0.12 | -0.00 | 0.07 | -0.03 | 0.25 | 0.14 |
|           | MAE | 0.25 | 0.26 | 0.25 | 0.20 | 0.19 | 0.22 | (BLYP-D3(BJ)) | (B2GPPLYP-D3(BJ)) |
| S66       | ME | 0.26 | 0.16 | 0.09 | 0.16 | 1.10 | 0.01 | 0.17 | 0.12 |
|           | MAE | 0.32 | 0.24 | 0.21 | 0.22 | 0.16 | 0.15 | (BLYP-D3(BJ)) | (ωB97X-V) |
| HEAVY28   | ME | -0.07 | -0.05 | -0.08 | -0.19 | 0.15 | 0.08 | 0.23 | 0.12 |
|           | MAE | 0.25 | 0.24 | 0.25 | 0.32 | 0.22 | 0.18 | (OLYP-D3(BJ)) | (MPW2PLYP-D3(BJ)) |
| CARBHB12  | ME | 0.70 | 0.70 | 0.65 | 0.90 | 1.01 | 0.86 | 0.44 | 0.22 |
|           | MAE | 0.70 | 0.70 | 0.65 | 0.90 | 1.01 | 0.86 | (M06-L-D3(0)) | (DSD-PBEB95-D3(BJ)) |
| PNICO23   | ME | 1.01 | 1.06 | 0.99 | 0.85 | 1.31 | 1.02 | 0.25 | 0.14 |
|           | MAE | 1.05 | 1.09 | 1.03 | 0.94 | 1.32 | 1.02 | (MN12L-D3(BJ)) | (PWPB95-D3(BJ)) |
| HAL59     | ME | 1.06 | 1.08 | 1.05 | 0.87 | 1.29 | 1.00 | 0.49 | 0.29 |
|           | MAE | 1.14 | 1.16 | 1.14 | 1.10 | 1.36 | 1.12 | (M06-L-D3(0)) | (BHLYP-D3(BJ)) |
| AHB21     | ME | -1.50 | 0.03 | 0.08 | -1.52 | -0.10 | 0.12 | 0.47 | 0.29 |
|           | MAE | 1.50 | 0.68 | 0.66 | 1.52 | 0.73 | 0.66 | (revTPSS-D3(BJ)) | (DSD-PBEB95-D3(BJ)) |
| CHB6      | ME | -0.76 | -0.79 | -0.77 | 0.09 | -0.3 | -0.06 | 0.45 | 0.32 |
|           | MAE | 0.85 | 0.86 | 0.85 | 0.53 | 0.66 | 0.50 | (SCAN-D3(BJ)) | (MN15-D3(BJ)) |
| IL16      | ME | -1.66 | -0.36 | -0.25 | -1.35 | -0.28 | 0.18 | 0.31 | 0.23 |
|           | MAE | 1.66 | 0.50 | 0.46 | 1.35 | 0.42 | 0.38 | (rPW86PBE-D3(BJ)) | (DSD-PBEP86-D3(BJ)) |
| Intramolecular non-covalent interactions (kcal/mol) | | | | | | | | | |
| IDISP     | ME | 0.87 | 0.79 | 0.84 | 1.42 | 0.89 | 1.26 | 2.05 | 1.02 |
|           | MAE | 3.75 | 3.71 | 3.44 | 1.89 | 2.40 | 1.65 | (SCAN-D3(BJ)) | (DSD-BLYP-D3(BJ)) |
| ICONF     | ME | 0.01 | 0.01 | 0.01 | 0.07 | 0.05 | 0.01 | 0.19 | 0.14 |
|           | MAE | 0.33 | 0.33 | 0.34 | 0.30 | 0.29 | 0.26 | (TPSS-D3(BJ)) | (DSD-PBEP86-D3(BJ)) |
| ACONF     | ME | -0.22 | -0.22 | -0.16 | -0.00 | -0.10 | -0.03 | 0.04 | 0.03 |
|           | MAE | 0.22 | 0.22 | 0.16 | 0.02 | 0.10 | 0.04 | (OLYP-D3(BJ)) | (ωB97X-V) |
|           |       |       |       |       |       |       |       | (revTPSS-D3(BJ)) | (revTPSS-D3(BJ)) |
| Amino204x4| ME | 0.11 | 0.11 | 0.11 | 0.06 | 0.10 | 0.08 | 0.22 | 0.13 |
|           | MAE | 0.25 | 0.27 | 0.24 | 0.22 | 0.22 | 0.21 | (SCAN-D3(BJ)) | (B2GPPLYP-D3(BJ)) |
|           |       |       |       |       |       |       |       | (DSD-BLYP-D3(BJ)) | (DSD-BLYP-D3(BJ)) |
| PCONF21   | ME | -0.05 | -0.03 | -0.08 | -0.20 | -0.21 | -0.06 | 0.47 | 0.23 |
|           | MAE | 0.66 | 0.65 | 0.57 | 0.47 | 0.49 | 0.46 | (SCAN-D3(BJ)) | (DSD-BLYP-D3(BJ)) |
| MCONF     | ME | 0.43 | 0.38 | 0.37 | 0.25 | 0.18 | 0.14 | 0.33 | 0.10 |
|           | MAE | 0.56 | 0.53 | 0.52 | 0.49 | 0.45 | 0.40 | (XLYP-D3(BJ)) | (MPW2PLYP-D3(BJ)) |
| SCONF     | ME | 0.46 | 0.46 | 0.44 | 0.35 | 0.51 | 0.35 | 0.35 | 0.06 |
|           | MAE | 0.74 | 0.76 | 0.69 | 0.70 | 0.91 | 0.64 | (M11L-D3(0)) | (DSD-BLYP-D3(BJ)) |
| UPU23     | ME | -0.40 | -0.32 | -0.37 | -0.08 | -0.01 | -0.02 | 0.33 | 0.33 |
|           | MAE | 0.49 | 0.48 | 0.48 | 0.38 | 0.37 | 0.40 | (revTPSS-D3(BJ)) | (revTPSS-D3(BJ)) |
| BUT14DIOL| ME | -0.12 | -0.12 | -0.16 | -0.00 | 0.05 | 0.01 | 0.18 | 0.04 |
|           | MAE | 0.17 | 0.18 | 0.20 | 0.15 | 0.16 | 0.12 | (revTPSS-D3(BJ)) | (ωB97X-V) |

| TME | 0.04 | 0.17 | 0.15 | 0.10 | 0.28 | 0.23 | 0.23 | 0.23 | 0.23 |
| TMAE | 0.79 | 0.68 | 0.64 | 0.61 | 0.59 | 0.48 | 0.48 | 0.48 | 0.48 |
TABLE VIII. Mean errors and mean absolute errors (in kcal/mol) for the WATER27 benchmark test set, using the studied semilocal functionals along with their dispersion corrected counterparts. The best semilocal+D3 and overall results are taken from ref. 79. TM and revTM results are from ref. 140.

| Errors | TM | revTM | TM+D3(0) | TM+D3(BJ) | TM+D3(OP) | M06-L-D3(0) | DSD-BLYP-D3(BJ) |
|--------|----|------|--------|----------|----------|--------------|-----------------|
| ME     | 1.32 | -1.24 | 2.71   | 2.38     | 1.94     | 3.21         | 2.88            |
| MAE    | 1.44 | 1.31  | 2.79   | 2.45     | 2.02     | 3.42         | 3.12            |

TABLE IX. Mean errors and mean absolute errors (in kcal/mol) for the in relative energies of the DSCONF Set of Conformers benchmark test set. L1, M1 and S1 are the energetically most stable conformers for Lactose, Maltose, and Sucrose. The relative energies are calculated with respect to those stable conformers. The errors are calculated considering total 30 conformers. Best semilocal and double hybrid functional results are also supplied from ref. 173.

| Errors | TM | TM+D3(0) | TM+D3(BJ) | TM+D3(OP) | revTM+D3(0) | revTM+D3(BJ) | revTM+D3(OP) | B-P86 |
|--------|----|---------|----------|----------|------------|------------|------------|-------|
| ME     | 0.15 | -0.24  | 0.23     | 0.23     | 0.20       | 0.12       | 0.19       | -0.02 |
| MAE    | 0.93 | 0.69   | 1.00     | 0.95     | 1.05       | 1.06       | 0.95       | 0.88  |

TABLE X. Mean absolute errors (in kcal/mol) for MG8 test set as calculated using different methods. The details of the test set and reference values are provided in ref. 174.

| Groups | description | TM | TM+D3(0) | TM+D3(BJ) | TM+D3(OP) | TM+D3(0) | TM+D3(BJ) | TM+D3(OP) |
|--------|-------------|----|---------|----------|----------|---------|----------|---------|
| NCED   | noncovalent interaction (easy, cluster) | 0.3 | 1.2     | 0.2      | 0.2      | 0.2     | 0.2      | 0.2     |
| NCEC   | noncovalent interaction (easy, dimer) | 3.5 | 15.1    | 3.0      | 1.3      | 0.1     | 4.4      | 2.3     |
| NCD    | noncovalent interaction (difficult)   | 2.9 | 2.6     | 2.9      | 2.9      | 2.9     | 2.9      | 3.1     |
| IE     | isomerization energy (easy)           | 0.4 | 0.4     | 0.4      | 0.4      | 0.4     | 0.4      | 0.4     |
| ID     | isomerization energy (difficult)      | 18.0 | 17.5    | 17.5     | 17.7     | 17.4    | 17.0     | 17.1    |
| TCE    | thermochemistry (easy)                | 6.9 | 6.1     | 6.9      | 6.8      | 6.9     | 5.9      | 6.0     |
| TCD    | thermochemistry (difficult)           | 14.3 | 14.1   | 14.4     | 14.4     | 14.4    | 14.1     | 14.8    |
| BH     | barrier height                        | 7.7 | 7.7     | 7.7      | 7.7      | 7.7     | 7.8      | 7.9     |

MGCDB82 2.3 2.7 2.2 2.2 2.2 2.1 2.1 2.1
performs quite well and very close to the most accurate semilocal D3 methods rPWS86PBE-D3(BJ).

Next, we perform the assessment of the dispersion corrected functionals for the intra-molecular binding energies of the GMTKN55 database. It consists of dispersion interactions within the same molecular complex. To start with, we consider the IDISP12 test set having interactions of large hydrocarbon molecules. The revTM+D3(OP) achieves the best accuracy in this case with MAE=1.65 kcal/mol and its accuracy is better than so far the best semilocal D3 method SCAN-D3(BJ). Similar accuracy of revTM+D3(OP) is also observed for the ICONF test set that consists of non-covalent interactions of inorganic molecules. The accuracy of the revTM+D3(OP) is also very prominent for the ACONF test set which contains relative energies of 15 n-butane, n-pentane and n-hexane conformers. It also gives the very similar accuracy as that of the so far best dispersion corrected semilocal method OLYP-D3(BJ). The revTM+D3(OP) is also very accurate for AMINO20×4 complexes having amino acids as a base pair. The peptide bonds within the amino acid are crucial for bio-molecular systems, as DNA and RNA pairs. The extended PCONF21 test set consists of relative energies of eleven phenylalanyl-glycyl-glycine tripeptide and ten tetrapeptide conformers respectively. Also in this case, revTM+D3(OP) is surprisingly the most accurate method within various semilocal+D3 approximations with MAE=0.46 kcal/mol. The accuracy of the revTM+D3(OP) is more evident (with MAE 0.40 kcal/mol) from MCONF test set which consists of relative binding energies of 52 melatonin having quadrupole–dipole, aromatic–amide, and hydrogen bond interactions important for biomolecules. The SCONF test set consists of 14 and 3 relative energies of 3,6-anhydro-4-O-methyl-D-galactitol and b-D-glucopyranose conformers, respectively. In this case also, revTM+D3(OP) performs better than the dispersion corrected functionals, while the best semilocal+D3 method is the M11L-D3(0). For UPU23 test set, all dispersion corrected revTM perform with almost same accuracy. Same is true for the TM based dispersion corrected methods. This test set consists of nucleic acids and biomolecules which are the main constituents of RNA. Finally, for the BUT14DIOL test set, which consists of strong intra-molecular hydrogen bonds, the revTM+D3(OP) is the best within the semilocal+D3 methods.

To make our comparison of the accuracy of different popular functionals in a more competitive manner, in Fig. 3 we plot the MAE of the inter-molecular non-covalent interactions versus the MAE of intra-molecular non-covalent interactions. It is noticed that, at the semilocal level, revTM+D3(OP) achieves the best accuracy. Moreover, the revTM+D3(OP) functional is even better than the ωB97X-V and ωB97X-D for the intramolecular non-covalent interactions, where both functionals are the range-separated hybrids and quite expensive for large molecular systems. Note also that revTM+D3(OP) is better than well known hybrid+D3 functionals like PBE0+D3(BJ) in both cases.

D. Water clusters

The remarkable accuracy of the -D3(OP) based semilocal functionals is also clearly evident from Table VIII where we assess the dispersion corrected semilocal functionals for various water clusters. This test set includes H-bonded water clusters which are either neutral or positively, and negatively charged. This test set is extracted from the GMTKN55 database as mentioned before, in order to emphasize the performance of the functionals for H-bond within water molecules. It is seemingly quite interesting that the -D3(OP) does not deteriorate the performance of TM and revTM functionals, unlike other -D3 methods. The bare TM and revTM give the MAE of about 1.44 kcal/mol and 1.31 kcal/mol, respectively, which are only slightly better than 2.02 kcal/mol and 1.47 kcal/mol obtained upon addition of the -D3(OP) correction. These results motivate us to further study the -D3(OP) corrected TM and revTM functionals for water properties. Note that very recently the revTM functional is assessed for different water properties and found to be very accurate for different water properties. In this case M06-L-D3(0) is the best dispersion corrected semilocal functional with MAE=1.11 kcal/mol and overall DSD-BLYP-D3(BJ) is the best functional with MAE=0.94 kcal/mol.

E. Conformers for lactose, maltose, and sucrose

Energetic of the bio-molecular conformers are important in various applications of chemical and biological systems. Being very large structures, the semilocal XC and functionals like PBE0+D3(BJ) in both cases.
F. Small representative MG8 thermochemical test set

Lastly, we assess the constructed functionals performance for the small representative MG8 thermochemical test set. The MG8 test set is proposed recently\textsuperscript{174} and it represents statistically accurate depiction of the MGCDB84 test set\textsuperscript{180}. This test set contains 64 data points instead of the large 5000 data points of the MGCDB82 test set. Like MGCDB84 on which it is based, MG8 divides the data into different types of properties like noncovalent interactions, isomerization energies, thermochemical properties, and barrier heights. The details of the test set and its benchmark values can be found in ref.\textsuperscript{174}. The MAEs of the each test set as obtained form different functionals are listed in Table \textsuperscript{X}. The MAEs for MGCDB82 are also calculated in Table \textsuperscript{X} using the formula suggested in Eq.(1) of ref.\textsuperscript{174}. It is obvious that the isomerization energy and thermochemistry of difficult cases are particularly challenging, though that is generally true for most functionals; for example, even B97M-V has an MAE over 10 kcal/mol for isomerization energy\textsuperscript{174}. In this respect, the dispersion corrected semi-local functionals show improvement in a systematic way than its bare functionals. Interestingly, the performance of the -OP corrected functionals is quite promising.

IV. CONCLUSIONS

We have assessed the benchmark calculations of the D3-corrected TM and revTM meta-GGA XC functionals, for a large palette of molecular complexes, characterized by various non-covalent interactions, such as inter- and intra-molecular dispersion, hydrogen, halogen, diphenyl, dipole-dipole and mixed bonded systems. We have constructed several forms of the D3-functionals, using the zero, rational damping, and optimized parameter damping functions. A total of six variants of dispersion corrected functionals are tested for a wide range of interesting systems. Our primary focus has been to measure the accuracy and applicability of the proposed methods for different kinds of dispersion interactions. It turns out that within the vdW-corrected semi-local approximations, the revTM+D3(OP) gives an outstanding performance, outclassing many popular functionals, and competing with the expensive dispersion corrected range-separated hybrids \(\omega B97X\)-D and \(\omega B97X\)-V.

For the energetic of the non-covalent binding energies, the performance of revTM+D3(OP) is obtained to be very good for S22, L7, various inter- and intra-molecular non-covalent interaction test sets of the well-known GMTKN55 database, and the H-bond interaction of charged moieties with neutral small molecules. For comparison purposes, we discuss separately the binding energy of the neutral and charged water clusters, where the inclusion of the -D3 within semi-local functional usually over-binds the energies. Interestingly, we observe that TM+D3(OP) and revTM+D3(OP) do not deteriorate much the accuracy of the bare functionals. The impressive performance of (rev)TM and (rev)TM+D3(OP) is also more evident from the relative conformer energies is OH-O hydrogen bond of the lactose, maltose, and sucrose. Overall, for the small representative MG8 thermochemical test set also the “OP” corrected functionals performance in an impressive manner.

Overall, revTM-D3 XC functional delivers awe-inspiring performance and acquire excellent accuracy close to the computationally costly range-separated hybrids and double-hybrid functionals. Importantly, it performs well for different interaction ranges of the non-covalent systems and can be considered as an important dispersion corrected functional within the dispersion corrected density functional theory zoo. As a concluding remark it is also important to note that recently the -D4 dispersion correction of Grimme shows its productive power over -D3, which we will consider in our future assessment.

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VI. DATA AVAILABLE ON REQUEST FROM THE AUTHORS

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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