r²SCAN-D4: Dispersion corrected meta-generalized gradient approximation for general chemical applications

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We combine a regularized variant of the strongly constrained and appropriately normed semilocal density functional [J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. 115, 036402 (2015)] with the latest generation semi-classical London dispersion correction. The resulting density functional approximation r²SCAN-D4 has the speed of generalized gradient approximations while approaching the accuracy of hybrid functionals for general chemical applications. We demonstrate its numerical robustness in real-life settings and benchmark molecular geometries, general main group and organo-metallic thermochemistry, as well as non-covalent interactions in supramolecular complexes and molecular crystals. Main group and transition metal bond lengths have errors of just 0.8%, which is competitive with hybrid functionals for main group molecules and outperforms them for transition metal complexes. The weighted mean absolute deviation (WTMAD2) on the large GMTKN55 database of chemical properties is exceptionally small at 7.5 kcal/mol. This also holds for metal organic reactions with an MAD of 3.3 kcal/mol. The versatile applicability to organic and metal-organic systems transfers to condensed systems, where lattice energies of molecular crystals are within chemical accuracy (errors <1 kcal/mol).

I. INTRODUCTION

The quantum mechanical description of physical and chemical materials at electronic resolution is an increasingly important task for in silico simulations. Here, density functional theory (DFT) has emerged in the past decades as one of the most versatile methodological frameworks. This leading position in both materials and chemical applications is largely due to the excellent accuracy over computational cost ratio, as well as the broad applicability across system classes of today’s density functional approximations (DFAs)

The Jacob’s ladder hierarchy is commonly used to classify DFAs. In this hierarchy, DFAs are systematically improved by ascending rungs of different approximations: the local density approximation (LDA), generalized gradient approximations (GGAs), meta-GGAs, hybrid functionals (including a fraction of nonlocal exact exchange), and double-hybrid functionals (including nonlocal correlation). In terms of efficiency, meta-GGAs are in a favorable spot, as they have the same cubic scaling with system size as LDA. Yet, many of the meta-GGAs proposed so far cannot truly leverage the full potential of their rung. Some shortcomings of existing functionals are increased sensitivity to the numeric integration grid, as observed in the SCAN functional or several Minnesota type functionals, purely empirical parameters, as present in the B97M functional and sensitivity to the kinetic energy density. Recent developments of semi-local DFAs combine exact constraints with various degrees of parametrization to improve descriptions of short- to medium-range electron correlation.

The strongly constrained and appropriately normed (SCAN) functional is constructed to rigorously satisfy all known exact constraints for meta-GGAs. While the functional itself has shown excellent performance in previous studies, the severe numerical instabilities inherent to the functional impeded its adoption for many computational studies. With the recently proposed regularized SCAN (rSCAN) and the subsequent restoration of exact constraints in r²SCAN, the main drawback of the SCAN functional seems to be resolved.

Nevertheless, semilocal functionals cannot include long-range correlation effects like London dispersion interactions. To truly judge its applicability, we extensively tested r²SCAN combined with the state-of-the-art D4 dispersion correction, which shows unprecedented performance for a range of diverse chemical and physical properties. To investigate the development of the SCAN-type functionals we include both SCAN-D4 and rSCAN-D4 in the comparison to r²SCAN-D4, and can attribute improvements in non-covalent interactions mainly to the regularization and improvements for thermochemistry and barrier heights to the restoration of the exact constraints.

We give a concise methodological overview (Section I) on r²SCAN and D4 before testing the full method against established DFAs over a wide range of benchmarks (Section III), with particular focus on molecular geometries, thermochem-
chemistry, kinetics, and non-covalent interactions in small and large complexes.

II. METHODS

The rSCAN functional regularizes the severe numerical instability or inefficiency of the otherwise successful SCAN functional at the expense of breaking exact constraints SCAN was constructed to obey. This problem arises in many codes that employ localized basis sets, and is less problematic in many codes that employ plane-wave basis sets. While numerical challenges are indeed resolved, a rigorous adherence to exact constraints is core to the design of the SCAN functional and likely important for transferable accuracy across domains of applicability. This seems to be reflected in rSCAN’s relatively poor performance for molecular atomization energies compared to other tests. The r²SCAN functional combines the good accuracy of SCAN with the numerical efficiency of rSCAN by directly restoring exact constraint satisfaction to the rSCAN regularizations.

The SCAN functional is constructed as an interpolation between single orbital and slowly-varying energy densities designed to maximize exact constraint satisfaction. The interpolation is controlled by an iso-orbital indicator

$$\alpha = \frac{\tau - \tau_W}{\tau_U},$$

where $\tau_W = \frac{\nabla \rho^2}{8\rho}$ and $\tau_U = 3(3\pi^2)^{2/3}\rho^{5/3}/10$ are the von-Weizsäcker and uniform electron gas kinetic energy densities respectively. In subsequent studies, $\alpha$ has been shown to contribute to numerical instability. To remove these effects, a regularized $\alpha'$ was used in rSCAN that removes single orbital divergences at the expense of breaking exact coordinate scaling conditions and the uniform density limit. These conditions are restored in r²SCAN by adopting a different regularization:

$$\tilde{\alpha} = \frac{\tau - \tau_W}{\tau_U + \eta \tau_W},$$

where $\eta = 10^{-3}$ is a regularization parameter.

The second regularization made in the rSCAN functional is to substitute the twisted piece-wise exponential interpolation of the original SCAN with a smooth polynomial function. This removes problematic oscillations in the exchange-correlation potential, but introduces spurious terms in the slowly-varying density gradient expansion that deviate from the exact expansion recovered by SCAN. A corrected gradient expansion term is used in r²SCAN that cancels these spurious terms so the functional recovers the slowly-varying density gradient expansion to second order. A recent modification of SCAN for improved band gap accuracy from Ascherebrock and Kümmel named “TASK” is able to enforce the fourth-order gradient expansion for the exchange energy without apparent numerical problems, although TASK uses an LSDA for correlation. The importance of the fourth-order exchange terms is not established however, and we are thus satisfied using one less exact constraint compared to SCAN.

Numerical instabilities are revealed by SCAN’s sensitivity to the choice of numerical integration grid, often requiring dense, computationally costly grids. This issue has been addressed with the rSCAN and r²SCAN functionals. Fig. 1 shows that the regularization indeed leads to two orders of magnitude error reduction when comparing r²SCAN with SCAN. This holds for both total energy and nuclear gradients for all chosen numerical settings. In practice, this allows for more computationally favorable settings. To give a rough estimate of the computational cost of r²SCAN compared to SCAN, we consider system 10 of the S30L with 158 atoms and 8250 atomic orbitals in a def2-QZVP basis set. A SCAN calculation using Turbomole’s grid 4 and radsize 50 would take approximately 10 hours, while an r²SCAN calculation with Turbomole grid m4 and radsize 6 takes only three and a half hours for the same numerical accuracy, resulting in a computational saving of a factor of three to five. We recommend using r²SCAN with 6 radial points and potentially increasing it to 10 for problematic geometry optimizations.

B. Training of damping functions

As London dispersion interactions arise from nonlocal electron correlations, they cannot be captured by any meta-GGA. In the past years, a range of schemes have been developed to capture these interactions in the DFT framework. Here, we combine r²SCAN with the semi-classical D4 dispersion...
correction. Its energy contribution is calculated by

\[
P_{\text{disp}}^{\text{D4}} = -\frac{1}{2} \sum_{n=6,8} \sum_{A,B} s_n^{AB} \frac{C_n^{AB}}{R_{AB}^n} f_{BJ}^{(n)}(R_{AB}) - \frac{1}{6} \sum_{A,B,C} s_{9}^{ABC} \frac{C_9^{ABC}}{R_{ABC}^3} f_{BJ}^{(9)}(R_{ABC}, \theta_{ABC}),
\]

where \( R_{AB} \) is the atomic distance, \( C_n^{AB} \) is the \( n \)th-order dispersion coefficient, and \( f_{BJ}^{(n)}(R_{AB}) \) is the Becke–Johnson damping function. \( R_{AB} \) and \( C_9^{ABC} \) denote the geometrically averaged distance and dispersion coefficient, respectively, and \( \theta_{ABC} \) is the angle dependent term of the triple-dipole contribution.

The \( s_8 \) parameter for the two-body dispersion and the \( a_1 \) and \( a_2 \) parameter entering the critical radius in the damping function are adjusted to match the local description of a specific DFA. Damping parameters are fitted using a Levenberg–Marquardt least-squares minimization to reference interaction energies as described in Ref. 19. Optimized parameters are given in Table I.

### C. Computational details

All ground state molecular DFT calculations were performed with a development version of Turbomole. The resolution of identity (RI) approximation was applied in all calculations for the electronic Coulomb energy contributions. For all functionals except SCAN, Turbomole’s modified grids of type m4 were used. For all SCAN calculations, grid 4 with increased radial integration size of 50 was used instead. Self-consistent field convergence criteria of 10\(^{-7}\) Hartree were applied. Ahrlichs’ type quadruple-zeta basis sets, def2-QZVP, were used throughout if not stated otherwise.

The periodic electronic structure calculations were conducted with VASP 6.1 with projector-augmented plane waves with an energy cutoff of 800 or 1000 eV (hard PAW). Tight self-consistent field settings and large integration (and fine FFT) grids are used. The Brillouin zone sampling has been increased to converge the interaction energy to 0.1 kcal/mol. The non-periodic directions use a vacuum spacing of 12 Å.

### III. RESULTS

#### A. Bond length and molecular geometries

![FIG. 2. Errors in bond length from \( r^2\text{SCAN-D4} \) and other DFAs separated into light main group bonds (LGMB35), heavy main group bonds (HMGB11), transition metal complexes (TMC32), and semi-experimental organic molecules (CCSe21, PBE0-D4, TPSS-D4 and PBE-D4 results for the first three sets are taken from Ref. 19). Optimized parameters are given in Table I.](image)

To evaluate the description of covalent bond distances, we compare experimental and calculated ground-state equilibrium distances \( R_e \) (in pm) for 35 light main group bonds (LGMB35), 11 heavy main group bonds (HMGB11), and 50 bonds in 32 3d transition metal complexes (TMC32). Additionally, we investigate the bond distances and angles for a set of simple organic molecules against accurate semi-experimental references. Extended statistics and optimized geometries are made freely available.

We include \( r^2\text{SCAN-D4} \), PBE0-D4, TPSS-D4, and PBE-D4 in the comparison shown in Fig. 2. For organic molecules, we find exceptional performance for all functionals, with errors smaller than 1 pm in the bond distances and half a degree in the bond angles. While all methods reproduce the reference values closely, we observe the best agreement from \( r^2\text{SCAN-D4} \) with a mean absolute deviation (MAD) of 0.4 pm and 0.3 degree for the bond distances and angles, respectively. For light main group elements, all methods give a mean absolute deviation of less than 1 pm as well, which was also observed in previous studies. In comparison with the other methods tested here, \( r^2\text{SCAN-D4} \) also yields the lowest MAD of only 0.7 pm. Finally, for transition metal complexes \( r^2\text{SCAN-D4} \) performs reasonably well with an MAD of 1.9 pm. Overall, the performance of \( r^2\text{SCAN} \) is similar to, and sometimes even better than, the hybrid PBE0-D4, which in turn is one of the best performing hybrid functionals for molecular geometries.
B. General main group thermochemistry and non-covalent interactions

To investigate the performance of \( r^2 \text{SCAN-D4} \) for general main group chemistry, we use the main group thermochemistry, kinetics and non-covalent interactions (GMTKN55) database. The GMTKN55 database is a compilation of 55 benchmark sets to assess the performance of DFAs and allows a comprehensive comparison of DFAs. It contains five categories, namely basic properties, barrier heights, isomerisations and reactions, intermolecular, and intramolecular non-covalent interactions (NCIs). With the exception of the semi-empirical B97M-V [11](and its B97M-D4 variant [67]), \( r^2 \text{SCAN-D4} \) is the best non-hybrid functional on the GMTKN55 so far with a weighted total MAD (WTMAD2) of 7.5 kcal/mol. For the isomerization and reactions category as well as for the intramolecular NCIs, \( r \text{SCAN-D4} \) can even compete with the performance of the hybrid PBE0-D4.

We additionally evaluated \( r \text{SCAN-D4} \) and \( \text{SCAN-D4} \) on the GMTKN55 set to monitor the development in the SCAN-family of functionals. The main difference between SCAN-D4 and \( r \text{SCAN-D4} \) is the general improvement in the description of non-covalent interactions, while both functionals perform similarly well in all other categories. Here \( r \text{SCAN-D4} \) improves for both NCI categories with a weighted MAD of 6.8 kcal/mol over SCAN-D4, which yields a weighted MAD of 7.6 kcal/mol. This improvement in \( r \text{SCAN-D4} \) is mainly responsible for the smaller WTMAD2 of 7.5 kcal/mol compared to the WTMAD of 8.6 kcal/mol for SCAN-D4. For \( r^2 \text{SCAN-D4} \), the improved description of NCI in \( r \text{SCAN-D4} \) is preserved (weighted MAD of 6.6 kcal/mol) but \( r^2 \text{SCAN-D4} \) bests its predecessor in all three remaining categories, resulting in its exceptional WTMAD2 of 7.5 kcal/mol. The mindless benchmark (MB16-43 subset of GMTKN55) is specifically useful for testing a methods robustness to deal with unusual chemistry in artificial molecules. Here, we see that enforcing exact constraints in non-empirical DFAs yields generally lower errors for artificial molecules than their empirical counterparts (see Table II).

To stress the importance of including a dispersion correction we test the plain dispersion-uncorrected \( r^2 \text{SCAN} \) which yields a significantly worse WTMAD2 of 8.8 kcal/mol, a difference similar in magnitude to the improvement from SCAN-D4 to \( r^2 \text{SCAN-D4} \). In summary, \( r^2 \text{SCAN-D4} \) shows a systematic improvement over its predecessor SCAN-D4 in all categories of GMTKN55 and can preserve improvements present in \( r \text{SCAN-D4} \). This makes \( r^2 \text{SCAN-D4} \) one of the best non-empirical meta-GGAs that have been broadly benchmarked so far.

### TABLE II. Comparison of a few non-empirical and empirical dispersion corrected DFAs for the MB16-43 subset (artificial molecules) of GMTKN55. The non-empirical DFAs yield generally lower MADs (in kcal/mol) indicating better transferability across diverse systems.

| Non-empirical DFA | MAD | Empirical DFA | MAD |
|-------------------|-----|---------------|-----|
| \( r^2 \text{SCAN-D4} \) | 14.6 | \( \text{MN15L} \) | 20.5 |
| \( \text{SCAN-D4} \) | 17.3 | \( \text{M06L} \) | 63.9 |
| TPSS-D4 | 25.8 | \( \text{M06L-D4} \) | 62.6 |
| PBE-D4 | 25.1 | \( \text{B97M-D4} \) | 37.5 |
| PBE0-D4 | 16.0 | \( \text{B3LYP-D4} \) | 28.4 |
C. Beyond main group chemistry

Metal organic chemistry is one of the major application areas of non-hybrid DFAs. Here, we use the MOR41 benchmark set that contains 41 closed-shell metal-organic reactions representing common chemical reactions relevant in transition-metal chemistry and catalysis. We compare the statistical deviations from high-level references of \( r^2 \)SCAN-D4 to PBE0-D4, TPSS-D4, and PBE-D4 in Tab. [II]. The \( r^2 \)SCAN-D4 functional is one of the best meta-GGAs tested so far on the MOR41 benchmark set, with an MAD of 3.3 kcal/mol. Compare this to B97M-D4, one of the best meta-GGAs tested on the GMKTN55 set, which yields a larger MAD of 3.8 kcal/mol.\(^\text{24}\)

![Graph showing MAD comparison for different functionals](image)

FIG. 4. Non-covalent interaction energies of host–guest systems, large systems and halogen-bonded systems from \( r^2 \)SCAN-D4 compared to high-level references as well as other DFAs.

| TABLE III. Reaction energies (kcal/mol) of 41 metal-organic reactions compared to high-level references| MD | MAD | SD | AMAX |
|---|---|---|---|---|
| \( r^2 \)SCAN | 2.1 | 4.4 | 5.6 | 17.3 |
| \( r^2 \)SCAN-D4 | -0.2 | 3.3 | 4.3 | 14.0 |
| TPSS-D4 | -1.5 | 3.5 | 4.4 | 22.6 |
| PBE0-D4 | -0.3 | 2.3 | 3.1 | 14.2 |
| PBE-D4 | -0.1 | 3.5 | 4.8 | 22.7 |

D. Non-covalent interactions in large complexes and molecular crystals

With the improved description of non-covalent interactions (NCIs), while retaining the computational efficiency of a meta-GGA, \( r^2 \)SCAN-D4 is a promising choice for interaction and association energies of large complexes. The results for the S30L, L7, and X40×10 benchmark set are shown in Fig. [1].

We choose the recently revised L7 benchmark set to assess the performance of \( r^2 \)SCAN-D4 against converged LNO-CCSD(T)/CBS interaction energies. Close agreement with an MAD of 0.9 kcal/mol is reached for \( r^2 \)SCAN-D4. This is a significant improvement over other meta-GGAs like SCAN-D4 and TPSS-D4 with MADs of 1.3 and 1.4 kcal/mol, respectively.

We also investigated the description of association energies for large supramolecular complexes using the S30L benchmark set. \( r^2 \)SCAN-D4 proved to be one of most accurate meta-GGAs in the previous benchmark,\(^\text{19}\) giving a remarkable MAD of 2.0 kcal/mol, close to the uncertainty of the provided reference interactions; \( r^2 \)SCAN-D4 further improves upon this.

In particular, the association energies of the halogen-bonded complexes (15 and 16) are improved with \( r^2 \)SCAN-D4. The same trend can be observed in the HAL59 benchmark set of the GMTKN55, which shows an MAD of 1.0 kcal/mol with SCAN-D4 and improves with \( r^2 \)SCAN-D4 to an MAD of 0.8 kcal/mol. To confirm this trend we additionally evaluated the X40×10 benchmark containing 40 halogen bond dissociation curves with SCAN-D4 and \( r^2 \)SCAN-D4. Again, \( r^2 \)SCAN-D4 gives the lowest MAD of 0.36 kcal/mol, showcasing overall improved description of this kind of NCIs.

To evaluate if the good performance for non-covalent interactions transfers from the gas phase to solids, molecular crystals and their polymorphic forms provide useful test cases.\(^\text{18,15}\) Here, we investigate the lattice energy benchmark DMC8 shown in Table [IV]. The DMC8 benchmark contains a subset of the X23,\(^\text{74,77–79}\) and ICE11\(^\text{80}\) benchmark sets with accurate structures and corresponding highly-accurate fixed node diffusion Monte Carlo (FN-DMC) results. Due to SCAN’s tendency to overbind hydrogen bonded systems, like ice polymorphs or hydrogen bonded molecular crystals, dispersion corrected SCAN was problematic for these systems. With the improved description of non-covalent interactions in \( r^2 \)SCAN-D4, this issue is mitigated and we find an overall improved MAD of 0.7 kcal/mol. This MAD is only half of the SCAN-D4 error of 1.5 kcal/mol for these systems and close to the very good performance of the hybrid PBE0-D4 of 0.5 kcal/mol.\(^\text{81}\) Only the ice polymorphs are systematically overbound by \( r^2 \)SCAN-D4, which is, however, a problem of many functionals,\(^\text{82,83}\) and may be a self-interaction error.\(^\text{84}\) In contrast, the relative stability of the ice polymorph is reproduced correctly. The energy difference of ice II and ice VIII with respect to ice Ih is 0.03 kcal/mol and 0.70 kcal/mol, respectively, agreeing well with the reference of 0.05 kcal/mol and 0.41 kcal/mol.

The benzene crystal has been frequently used for electronic benchmark purposes.\(^\text{85,87}\) Here, we evaluated the equation of state (EOS) to compare with experimental measurements and the Murnaghan EOS fit to the FN-DMC from Ref. [76]. The resulting EOS is shown in Fig. [5] and agrees excellently with the high-level method as well as the experimental estimate. A slight underestimation of the unit cell volume by 2.6% and
TABLE IV. Lattice energies (kcal/mol) of eight diverse molecular crystals compared to high-level references. Note the significant improvement from \( r^2 \text{SCAN} \) to \( r^2 \text{SCAN-D4} \) for the dispersion-bound solids.

| Crystal        | ref.       | TPSS-D4    | \( r^2 \text{SCAN} \) | \( r^2 \text{SCAN-D4} \) |
|---------------|------------|------------|------------------------|--------------------------|
| Ice Ih        | -14.2      | -15.6      | -14.6                  | -15.4                    |
| Ice II        | -14.1      | -14.6      | -14.3                  | -15.4                    |
| Ice VIII      | -13.7      | -12.5      | -13.4                  | -14.7                    |
| \( \text{CO}_2 \) | -6.7       | -5.5       | -4.7                   | -6.9                     |
| Ammonia       | -8.9       | -8.6       | -8.1                   | -9.5                     |
| Benzene       | -12.7      | -12.0      | -5.6                   | -12.3                    |
| Naphthalene   | -18.8      | -18.5      | -7.5                   | -18.6                    |
| Anthracene    | -25.2      | -24.8      | -9.9                   | -24.7                    |

| MD            | 0.3        | 4.6        | -0.4                   |
| MAD           | 0.8        | 5.7        | 0.7                    |
| SD            | 0.9        | 6.0        | 0.8                    |
| AMAX          | 1.4        | 15.4       | 1.3                    |

overestimation of the bulk modulus by 6.4% can be seen. To highlight once again the importance of London dispersion on properties beyond the mere energy, we report plain \( r^2 \text{SCAN} \) results as well. The \( r^2 \text{SCAN} \) EOS has a significant offset equilibrium volume that is overestimated by 5.4% and a bulk modulus underestimated by 34.0%.

IV. CONCLUSIONS

We have presented an accurate and robust combination of the non-empirical \( r^2 \text{SCAN} \) DFA with the state-of-the-art D4 dispersion correction. The resulting \( r^2 \text{SCAN-D4} \) electronic structure method shows exceptional performance across several diverse categories of chemical problems assessed by thousands of high-level data-points in a number of comprehensive benchmark sets. Included in the assessment were molecular thermochemistry for both main group and transition metal compounds, barrier heights, structure optimizations, lattice energies of molecular crystals, as well as both inter- and intramolecular non-covalent interactions of small to large systems, creating an extensive coverage of chemically relevant problems.

For the large GMTKN55 benchmark collection of about 1500 data points, \( r^2 \text{SCAN-D4} \) is one of the most accurate meta-GGAs tested so far. Unlike the best meta-GGA on this set, the dispersion corrected B97M functional, \( r^2 \text{SCAN-D4} \) can transfer this accuracy to chemically distinct systems like metalorganic reactions. We find significant improvements in NCIs, which were one of the weak-spots of SCAN based methods. More detailed analysis showed that improvements can mainly be found in the description of hydrogen and halogen bonded systems. The same trend is found for molecular crystals, where SCAN-D4’s tendency to overbind is mostly resolved in \( r^2 \text{SCAN-D4} \), giving close to hybrid DFT results for lattice energies.

We found \( r^2 \text{SCAN-D4} \) to be an accurate and (more importantly) consistent DFA for a large variety of problems and chemical systems. The already good performance of the original SCAN functional is kept and systematically improved in \( r^2 \text{SCAN} \), while the numeric stability is almost on par with established GGA functionals. We were able to gain some insight in the improvement from SCAN over rSCAN to \( r^2 \text{SCAN} \), where we can attribute the improved description of non-covalent interactions to the regularization in the step from SCAN to rSCAN, and the improved thermochemistry and barrier heights to the constraint restoration in the step from rSCAN to \( r^2 \text{SCAN} \). Like SCAN, \( r^2 \text{SCAN} \) is not fitted to molecules, so its accuracy in extensive molecular tests demonstrates the predictive power of its exact constraints and appropriate norms.

With \( r^2 \text{SCAN-D4} \), a meta-GGA method is finally available that truly leverages the advantages of its rung in Jacob’s ladder, while retaining favorable numerical properties and fulfilling important exact constraints. We anticipate \( r^2 \text{SCAN-D4} \) to be a valuable electronic structure method with broad applications in computational chemistry and material science.

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1^R. G. Parr and W. Yang, 
Density-Functional Theory of Atoms and Molecules (Oxford University Press, Oxford, 1989).

2^W. Kohn, "Electronic structure of matter — wave functions and density functionals," Rev. Mod. Phys. 71, 1253–1266 (1998).

3^K. Burke, "Perspective on density functional theory," J. Chem. Phys. 136, 150901 (2012).

4^A. D. Becke, "Perspective: Fifty years of density-functional theory in chemical physics," J. Chem. Phys. 140, 18A301 (2014).

5^R. J. Maurer, C. Freysoldt, A. M. Reilly, J. G. Brandenburg, O. T. Hofmann, T. Bjoerkmann, S. Lebègue, and A. Tkatchenko, "Advances in density-functional calculations for materials modeling," Annu. Rev. Mater. Res. 49, 3:1–3:30 (2019).

6^J. P. Perdew and K. Schmidt, "Jacobi's ladder of density functional approximations for the exchange-correlation energy," AIP Conference Proceedings

7^J. Sun, A. Ruzsinszky, and J. P. Perdew, "Strongly constrained and appropriately normed semilocal density functional," Phys. Rev. Lett. 115, 036402 (2015).

8^Y. Zhao and D. G. Truhlar, "A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions," J. Chem. Phys. 125, 194101 (2006).

9^R. Peverati and D. G. Truhlar, "M11-L: A Local Density Functional That Provides Improved Accuracy for Electronic Structure Calculations in Chemistry and Physics," J. Phys. Chem. Lett. 3, 117–124 (2012).

10^N. Mardirossian and M. Head-Gordon, "Characterizing and understanding the remarkably slow basis set convergence of several Minnesota density functionals for intermolecular interaction energies," J. Chem. Theory Comput. 9, 4453–4461 (2013).

11^N. Mardirossian and M. Head-Gordon, "Mapping the genome of meta-generalized gradient approximation density functionals: The search for B97M-V," J. Phys. Chem. 112, 074111 (2015).

12^L. Goerigk, "Treating London-dispersion effects with the latest Minnesota density functionals: problems and possible solutions," J. Phys. Chem. Lett. 6, 3891–3896 (2015).

13^E. R. Johnson, A. D. Becke, C. D. Sherrill, and G. A. DiLabio, "Oscillations in meta-generalized-gradient approximation potential energy surfaces for dispersion-bound complexes," J. Chem. Phys. 131, 034111 (2009).

14^N. Mardirossian and M. Head-Gordon, "wB97X-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. 16, 9904–9924 (2014).

15^Y. Wang, X. Jin, H. S. Yu, D. G. Truhlar, and X. He, "Revised M06-L functional for improved accuracy on chemical reaction barrier heights, noncovalent interactions, and solid-state physics," Proc. Natl. Acad. Sci. 114, 8487–8492 (2017).

16^A. P. Bartók and J. R. Yates, "Regularized SCAN functional," J. Chem. Phys. 150, 161101 (2019).

17^J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, "Accurate and numerically efficient rS SCAN meta-generalized gradient approximation for van der Waals interactions in molecules and materials: Concepts, theory, and applications," Chem. Rev. 117, 4714–4758 (2017).

18^S. Grimme, A. Hansen, J. G. Brandenburg, and C. Bannwarth, "Dispersion-corrected mean-field electronic structure methods," Chem. Rev. 116, 5105–5154 (2016).

19^E. Caldeywerther, S. Ehler, A. Hansen, H. Neugebauer, S. Spichler, C. Bannwarth, and S. Grimme, "A generally applicable atomic-charge dependent London dispersion correction," J. Chem. Phys. 150, 154122 (2019).

20^J. W. Furness and J. Sun, "Enhancing the efficiency of density functionals with an improved iso-orbital indicator," Phys. Rev. B 99, 041119 (2019).

21^M. Levy and J. P. Perdew, "Helmholtz-Feynman, virial, and scaling requirements for the exact universal density functionals. Shape of the correlation potential and diamagnetic susceptibility for atoms," Phys. Rev. A 32, 2010–2021 (1985).

22^A. Görlich and M. Levy, "Correlation-energy functional and its high-density limit obtained from a coupling-constant perturbation expansion," Phys. Rev. B 47, 13105–13113 (1993).

23^L. Pollack and J. P. Perdew, "Evaluating density functional performance for the quasi-two-dimensional electron gas," J. Phys. Condens. Matter 12, 1259–1252 (2000).

24^P. Svendsen and U. von Barth, "Gradient expansion of the exchange energy from second-order density response theory," Phys. Rev. B 54, 17402–17413 (1996).

25^J. P. Perdew and Y. Wang, "Accurate and Simple Analytic Representation of the Electron-Gas Correlation-Energy," Phys. Rev. B 45, 13244–13249 (1992).

26^T. Aschenbrock and S. Kömmel, "Ultranonlocality and accurate band gaps from a meta-generalized gradient approximation," Phys. Rev. Research 1, 013082 (2019).

27^F. Hofmann and S. Kömmel, "Molecular excitations from meta-generalized gradient approximations in the Kohn–Sham scheme. Molecular excitations from meta-generalized gradient approximations in the Kohn–Sham scheme," J. Chem. Phys. 153, 114106 (2020).

28^D. Mejía-Rodríguez and S. B. Trickey, "Meta-GGA performance in solids at almost GGA cost," Phys. Rev. B 102, 121109 (2020).

29^R. Sure and S. Grimme, J. Chem. Theory Comput. 11, 3785–3801 (2015).

30^Running on Intel(R) Xeon(R) CPU E3-1270 v5 @ 3.60GHz using four cores.

31^The 6 radial points correspond to the default settings of Turbomole's grid m4.

32^J. Klimeš and A. Michaelides, "Perspective: Advances and challenges in treating van der Waals dispersion forces in density functional theory," J. Chem. Phys. 137, 120901 (2012).

33^J. Herrmann, R. A. DiStasio, and A. Tkatchenko, "First-principles models for van der Waals interactions in molecules and materials: Concepts, theory, and applications," Chem. Rev. 117, 4714–4758 (2017).

34^K. Berland, V. R. Cooper, K. Lee, E. Schröder, T. Thonhauser, P. Hyldgaard, and B. J. Lundqvist, "van der Waals forces in density functional theory: a review of the vdW-DF method," Rep. Prog. Phys. 78, 066501 (2015).

35^O. A. Yudov and T. Van Voorhis, "Nonlocal van der Waals density functional: The simpler the better," J. Chem. Phys. 133, 244103 (2010).

36^R. Sabatini, T. Gorni, and S. de Gironcoli, "Nonlocal van der Waals density functional made simple and efficient," Phys. Rev. B 87, 041108 (2013).

37^E. R. Johnson and A. D. Becke, "A post-Hartree–Fock model of intermolecular interactions," J. Chem. Phys. 123, 024101 (2005).

38^F. R. Johnson and A. D. Becke, "A post-Hartree-Fock model of intermolecular interactions: Inclusion of higher-order corrections," J. Chem. Phys. 124, 174104 (2006).

39^B. M. Axilrod and E. Teller, "Interaction of the van der Waals Type Between Three Atoms," J. Chem. Phys. 11, 299–300 (1943).

40^Y. Muto, "Force between nonpolar molecules," Proc. Phys. Soc. Jpn. 17, 629 (1943).

41^J. Úherzal, K. E. Riley, and P. Hörbä, "S66: A well-balanced database of benchmark interaction energies relevant to biomolecular structures," J. Chem. Theory Comput. 7, 2427 (2011).

42^M. S. Marshall, L. A. Burns, and C. D. Sherrill, "Basis set convergence of the coupled-cluster correction, 6MP2CCS(D): Best practices for benchmarking non-covalent interactions and the attendant revision of the S22, NBC10, HBC6, and HSG databases," J. Chem. Theory Comput. 15, 194102 (2017).

43^D. E. Taylor, J. G. Angyán, G. Galli, C. Zhang, F. Gygi, K. Hirao, J. W. Song, K. Rahul, O. Anahite von Lilienfeld, R. Podeszwa, et al., "Blind test of density-functional-based methods on intermolecular interaction energies," J. Chem. Phys. 145, 124105 (2016).

44^F. Furche, R. Ahlrichs, C. Hättig, W. Klopfer, M. Sierka, and F. Weigend,
“TurboMol,” WIREs Comput Mol Sci 4, 91–100 (2014).

50. TURBOMOLE V7.5 2020, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.org.

51. K. Eichkorn, O. Treutler, H. Öhm, M. Häser, and R. Ahlrichs, “Auxiliary basis sets to approximate Coulomb potentials,” Chem. Phys. Lett. 240, 283–289 (1995).

52. K. Eichkorn, F. Weigend, O. Treutler, and R. Ahlrichs, “Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials,” Theor. Chem. Acc. 97, 119–124 (1997).

53. F. Weigend, F. Furche, and R. Ahlrichs, “Gaussian basis sets of quadruple zeta quality for atoms h to kr,” J. Chem. Phys. 119, 12753–12762 (2003).

54. G. Kresse and J. Hafner, “Ab initio molecular dynamics for liquid metals,” Phys. Rev. B 47, 558 (1993).

55. G. Kresse and J. Furthmüller, “Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set,” J. Comp. Mat. Sci. 6, 15 (1996).

56. P. E. Blöchl, “Projector augmented-wave method,” Phys. Rev. B 50, 17953 (1994).

57. G. Kresse and J. Joubert, “From ultrasoft pseudopotentials to the projector augmented-wave method,” Phys. Rev. B 59, 1758 (1999).

58. S. Grimme, G. Brandenburg, C. Bannwarth, and A. Hansen, “Consistent structures and interactions by density functional theory with small atomic orbital basis sets,” J. Chem. Phys. 143, 054107 (2015).

59. M. Bühl and H. Kabrede, “Geometries of transition-metal complexes from density-functional theory,” J. Chem. Theory Comput. 2, 1282–1290 (2006).

60. M. Piccardo, E. Penocchio, C. Puzzarini, M. Biczysko, and V. Barone, “Semi-experimental equilibrium structure determinations by employing B3LYP/SNSD anharmonic force fields: Validation and application to semi-rigid organic molecules,” J. Phys. Chem. B 119, 2058–2082 (2015).

61. E. Brémond, M. Savagee, N. Q. Su, A. J. Pérez-Jiménez, X. Xu, J. C. Sancho-García, and C. Adamo, “Benchmarking density functionals on structural parameters of small-medium-sized organic molecules,” J. Chem. Theory Comput. 12, 459–465 (2016).

62. Optimized r2SCAN-D4/def2-QZVP geometries of the LMB35, HMGB11, and TMC32 sets, statistical performance of the LMB35, HMGB11, TMC32, Ccse2[RH]1, GMKTN55, S30L, L7, C40x10 sets are provided at https://github.com/awwkgk/rr2scan-d4-paper.

63. C. Adamo and V. Barone, “Toward reliable density functional methods without adjustable parameters: The PBE0 model,” J. Chem. Phys. 110, 6158–6170 (1999).

64. J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, “Climbing the density functional ladder: Nonempirical meta generalized gradient approximation designed for molecules and solids,” Phys. Rev. Lett. 91, 146401 (2003).

65. J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” Phys. Rev. Lett. 77, 3865–3868 (1996), erratum Phys. Rev. Lett. 78, 1396 (1997).

66. L. Goeriök, A. Hansen, C. A. Bauer, S. Ehrlich, A. Najibi, and S. Grimme, “A look at the density functional theory zoo with the advanced GMKTN55 database for general main group thermochemistry, kinetics and noncovalent interactions,” Phys. Chem. Chem. Phys. (2017), doi: 10.1039/C7CP04913G.

67. A. Najibi and L. Goeriök, “DFT-D4 counterparts of leading meta-generalized-gradient approximation and hybrid density functionals for energetics and geometries,” J. Comput. Chem. (2020), 10.1002/jcc.26411.

68. For a subset of the GMKTN55 not all of the published benchmark results with the SCAN functional were reproducible. Therefore, we reevaluated SCAN on the complete GMKTN55.

69. S. Dohn, A. Hansen, M. Steinmetz, S. Grimme, and M. P. Checinski, “Comprehensive thermochemical benchmark set of realistic closed-shell metal organic reactions,” J. Chem. Theory Comput. 14, 2596–2608 (2018).

70. R. Sedlák, T. Janowski, M. Pitioňák, J. Rezić, P. Pulay, and P. Hobza, “Accuracy of Quantum Chemical Methods for Large Noncovalent Complexes,” J. Chem. Theory Comput. 9, 3364–3374 (2013).

71. M. K. Kesharwani, D. Manna, N. Sylvesters, and J. M. L. Martin, “The x40-10 halogen bonding benchmark revisited: Surprising importance of (n–1)vdw correlation,” J. Phys. Chem. A 122, 2184–2197 (2018).

72. Y. S. Al-Hamdani, P. R. Nagy, D. Barton, M. Källay, J. G. Brandenburg, and A. Tkatchenko, “Interactions between large molecules: Puzzle for reference quantum-mechanical methods,” (2020), arXiv:2009.08927 [physics.chem-ph].

73. A. Otero-de-la-Roza, B. H. Cao, I. K. Price, J. E. Hein, and E. R. Johnson, “Predicting the relative solubilities of racemic and enantiopure crystals by density-functional theory,” Angew. Chem. Int. Ed. 53, 7879–7882 (2014).

74. A. M. Reilly and A. Tkatchenko, “Understanding the role of vibrations, exact exchange, and many-body van der Waals interactions in the cohesive properties of molecular crystals,” J. Chem. Phys. 139, 024705 (2013).

75. G. J. O. Beran, “Modeling Polymorphic Molecular Crystals with Electronic Structure Theory,” Chem. Rev. 116, 5567–5613 (2016).

76. A. Zen, J. G. Brandenburg, J. Klimeš, A. Tkatchenko, D. Alfe, and A. Michaelides, “Fast and accurate quantum Monte Carlo for molecular crystals,” Proceedings of the National Academy of Sciences 115, 1724–1729 (2018).

77. A. Otero-de-la-Roza and E. R. Johnson, “A benchmark for non-covalent interactions in solids,” J. Chem. Phys. 137, 054103 (2012).

78. A. Ambrosetti, A. M. Reilly, R. A. DiStasio, and A. Tkatchenko, “Long-range correlation energy calculated from coupled atomic response functions,” J. Chem. Phys. 140, 18A508 (2014).

79. J. Carpenter and A. L. Rohl, “Benchmarking calculated lattice parameters and energies of molecular crystals using van der Waals density functionals,” J. Chem. Theory Comput. 10, 3423–3437 (2014).

80. J. G. Brandenburg, T. Maas, and S. Grimme, “Benchmarking dft and semiempirical methods on structures and lattice energies for ten ice polymorphs,” J. Chem. Phys. 142, 124104 (2015).

81. E. Caldeywyerh, J.-M. Mewes, S. Ehlerth, and S. Grimme, “Extension and evaluation of the D4 London-dispersion model for periodic systems,” Phys. Chem. Chem. Phys. 22, 8499–8512 (2020).

82. B. Santra, J. Klimeš, A. Tkatchenko, D. Alfe, B. Slater, A. Michaelides, R. Car, and M. Scheffler, “On the accuracy of van der Waals inclusive density-functional theory exchange-correlation functionals for ice at ambient and high pressures,” J. Chem. Phys. 139, 154702 (2013).

83. G. Brandenburg, A. Zen, D. Alfe, and A. Michaelides, “Interaction between water and carbon nanostructures: How good are current density functional approximations?” J. Chem. Phys. 151, 164702 (2019).

84. K. Sharks, K. Wagle, B. Santra, S. Al-Hamdani, R. R. Zope, T. Baruah, K. A. Jackson, J. P. Perdew, and J. E. Perdahl, “Self-interaction error overbids water clusters but cancels in structural energy differences,” Proc. Natl. Acad. Sci. U.S.A. 117, 11283–11288 (2020).

85. S. Wen and J. G. O. Beran, “Accurate Molecular Crystal Lattice Energies from a Fragment QM/MM Approach with On-the-Fly Ab Initio Force Field Parameterization,” J. Chem. Theory Comput. 7, 3733–3742 (2011).

86. M. R. Kennedy, A. R. McDonald, A. E. DePrince, M. S. Marshall, R. Podeszwa, and C. D. Sherrill, “Communication: Resolving the three-body contribution to the lattice energy of crystalline benzene: Benchmark results from coupled-cluster theory,” J. Chem. Phys. 140, 121104 (2014).

87. W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. 56, 2257 (1972).