

Extension of the D3 dispersion coefficient model

Eike Caldeweyher, Christoph Bannwarth, and Stefan Grimme

Citation: *J. Chem. Phys.* **147**, 034112 (2017); doi: 10.1063/1.4993215

View online: <https://doi.org/10.1063/1.4993215>

View Table of Contents: <http://aip.scitation.org/toc/jcp/147/3>

Published by the [American Institute of Physics](#)

Articles you may be interested in

[A general intermolecular force field based on tight-binding quantum chemical calculations](#)

The Journal of Chemical Physics **147**, 161708 (2017); 10.1063/1.4991798

[B97-3c: A revised low-cost variant of the B97-D density functional method](#)

The Journal of Chemical Physics **148**, 064104 (2018); 10.1063/1.5012601

[Consistent structures and interactions by density functional theory with small atomic orbital basis sets](#)

The Journal of Chemical Physics **143**, 054107 (2015); 10.1063/1.4927476

[Density-functional thermochemistry. III. The role of exact exchange](#)

The Journal of Chemical Physics **98**, 5648 (1993); 10.1063/1.464913

[Evaluation of DFT-D3 dispersion corrections for various structural benchmark sets](#)

The Journal of Chemical Physics **146**, 044115 (2017); 10.1063/1.4974840

[Perspective: Found in translation: Quantum chemical tools for grasping non-covalent interactions](#)

The Journal of Chemical Physics **146**, 120901 (2017); 10.1063/1.4978951

PHYSICS TODAY

WHITEPAPERS

ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these environmentally friendly adhesive systems can do

READ NOW

PRESENTED BY
 **MASTERBOND**
ADHESIVES | SEALANTS | COATINGS

Extension of the D3 dispersion coefficient model

Eike Caldeweyher, Christoph Bannwarth, and Stefan Grimme^{a)}

Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie der Universität Bonn, Beringstr. 4, D-53115 Bonn, Germany

(Received 25 April 2017; accepted 22 June 2017; published online 21 July 2017)

A new model, termed D4, for the efficient computation of molecular dipole-dipole dispersion coefficients is presented. As in the related, well established D3 scheme, these are obtained as a sum of atom-in-molecule dispersion coefficients over atom pairs. Both models make use of dynamic polarizabilities obtained from first-principles time-dependent density functional theory calculations for atoms in different chemical environments employing fractional atomic coordination numbers for interpolation. Different from the D3 model, the coefficients are obtained on-the-fly by numerical Casimir-Polder integration of the dynamic, atomic polarizabilities $\alpha(i\omega)$. Most importantly, electronic density information is now incorporated via atomic partial charges computed at a semi-empirical quantum mechanical tight-binding level, which is used to scale the polarizabilities. Extended statistical measures show that errors for dispersion coefficients with the proposed D4 method are significantly lower than with D3 and other, computationally more involved schemes. Alongside, accurate isotropic charge and hybridization dependent, atom-in-molecule static polarizabilities are obtained with an unprecedented efficiency. Damping function parameters are provided for three standard density functionals, i.e., TPSS, PBE0, and B3LYP, allowing evaluation of the new DFT-D4 model for common non-covalent interaction energy benchmark sets. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4993215>]

I. INTRODUCTION

Due to its excellent accuracy-cost ratio, Kohn-Sham density functional theory (KS-DFT, or DFT in the following)^{1,2} is the workhorse of modern electronic structure calculations. Especially for the chemistry or physics of large or condensed-phase systems, the inclusion of long-range electron correlation interactions is indispensable in order to reach the so-called chemical accuracy (~ 1 kcal/mol) in theoretical simulations. Semi-local or hybrid density functional approximations (DFAs) do not describe such correlation effects,³ hence they cannot account for the important London dispersion interactions.⁴ In order to correct for this shortcoming, semi-classical methods were developed to enable the computation of the long-range (London) dispersion energy in molecules and solids. The computationally efficient atom pairwise D3(BJ) scheme⁵ requires only the molecular geometry as input to calculate the inter- and intramolecular dispersion energy based on pre-computed linear-response time-dependent DFT (TD-DFT) data. Aside from this geometrical dispersion model, electron density dependent approaches like the Tkatchenko-Scheffler (TS) model,⁶ the exchange dipole moment (XDM) model of Becke and Johnson,^{7–9} or the local-response dispersion (LRD) model by Sato and Nakai exist.^{10,11} Conceptually somewhat different are the nonlocal density functional based dispersion corrections for which the family of van der Waals density functionals^{12–17} (vdW-DFs) and VV10^{18,19} are noteworthy

examples. While the D3 approach is by far the fastest dispersion correction, one disadvantage of this geometrical scheme is that changes in the underlying electron density are not reflected in the dispersion coefficients. Whenever the density around an atom in a molecule or solid is significantly different from the one present in the reference compound, larger errors can occur.^{20,21} This is in particular relevant for applications involving metal centers (ions), which often change their effective electron number (atomic charge) and corresponding dipole-dipole dispersion coefficients (C_6). Density dependent approaches are, however, computationally more expensive compared to the D3 model and often neglect atomic hybridization effects (for respective modification of the hybridization devoid TS model, see Ref. 22). With this in mind, an extension of the well established and widely used D3 method is proposed here.

II. THEORY

A. General

The new model introduced here, termed D4, calculates charge dependent dispersion coefficients efficiently and in a black box manner by incorporation of molecular input coordinates [for coordination numbers (CN_s)] and also by semi-empirical quantum mechanical (QM) tight-binding (TB) computation (for atomic charges). The Mulliken charges²³ from a (partially polarized) minimal basis tight-binding scheme were shown to agree rather well with DFT Hirshfeld charges.²⁴ By using the same (semi-empirical) QM method (GFN-xTB²⁵) throughout to obtain the charges for our new model, we avoid complications arising solely from the fact that

^{a)} Author to whom correspondence should be addressed: grimme@thch.uni-bonn.de

various functionals (e.g., hybrid vs. GGA) yield different charges. This choice furthermore reduces the number of necessary fit procedures and facilitates interfacing the model to existing QM codes. A related atom pairwise dispersion correction, denoted as dDMC,²⁶ also incorporated TB based Mulliken charges from the self-consistent charge density functional tight-binding (SCC-DFTB)^{27,28} method. The general applicability of TB charge based dispersion models depends on the availability of parameters for different elements. Since all elements up to $Z = 86$ are parameterized for GFN-xTB, the new D4 method has practically no limitations regarding the applicability to various chemical problems. Starting from the D3 scheme, conceptually minimal changes are applied such that for neutral (non-polar) molecules only small differences (mostly small improvements) between D3 and D4 are found. The new model is intended to be combined with various, predominantly mean-field electronic structure methods³ similar to D3 (for a recent successful use of D3 dispersion in SAPT, see Ref. 29). The D4 dispersion coefficients and static dipole polarizabilities are already used in a newly developed intermolecular force-field (FF).³⁰

B. Dispersion coefficients

The calculated Mulliken charges serve as descriptors to scale pre-computed reference TD-DFT polarizabilities at imaginary frequencies $\alpha(i\omega)$. These are then used to obtain charge and coordination number (see below) dependent C_6^{AB} coefficients via numerical on-the-fly Casimir-Polder integration³¹

$$C_6^{AB} = \sum_{A,ref=1}^{N^{A,ref}} \sum_{B,ref=1}^{N^{B,ref}} \frac{3}{\pi} \int_0^\infty d\omega \alpha^{A,ref}(i\omega, z^A) \times W_A^{A,ref} \alpha^{B,ref}(i\omega, z^B) W_B^{B,ref} \quad (1)$$

with

$$\alpha^{A,ref}(i\omega, z^A) = \frac{1}{m} \left[\alpha^{A_m H_n}(i\omega) - \frac{n}{2} \alpha^{H_2}(i\omega) \right] \times \zeta(z^{H_A,ref}, z^{H_2}) \zeta(z^A, z^{A,ref}) \quad (2)$$

and

$$\zeta(z^A, z^{A,ref}) = ba \left[1.47 \exp(z^A / z^{A,ref}) \log_{10}(z^{A,ref} / z^A) \right]. \quad (3)$$

The reference polarizabilities $\alpha^{A_m H_n}$, describing the molecular polarizabilities of the symmetric hydride systems $A_m H_n$ (i.e., containing m chemically equivalent atoms A), incorporate hybridization in the D3 model (e.g., for carbon, the reference system with $CN^C = 2$ is $C_2 H_2$). Polarizabilities were calculated at the same level of theory as for D3 (hybrid TD-DFT with augmented quadruple- ζ AO basis set).⁵ In Eq. (1), $W_A^{A,ref/B,ref}$, are weighting factors to determine the contributions of all element specific reference systems $N^{A,ref/B,ref}$ (for further details see the [supplementary material](#)). In Eq. (2), z^{H_A} describes the effective charge of hydrogen bound to atom A in the particular reference system $A_m H_n$ while z^{H_2} describes the effective charge of hydrogen in the H_2 molecule. The effective charge z^A of an atom A within a molecule equals the sum of its nuclear charge Z^A and its self-consistently derived Mulliken

charge q^A ,

$$z^A = Z^A + q^A. \quad (4)$$

Thus, a negatively charged atom is treated as having an effectively smaller nuclear charge. Equation (3) introduces the atom specific charge-function ζ . Here, the parameter b has been parametrized first to match the TD-DFT derived molecular dispersion coefficients of the reference systems (i.e., $z^A = z^{A,ref}$). Then parameter a is parametrized to match cationic static polarizabilities ($z^A \neq z^{A,ref}$) for all elements with $Z = 2-86$. The whole training set is given within the [supplementary material](#). In principle, the atomic charges could also be provided individually by the underlying DFT calculation. This, however, would introduce many empirical parameters (one set for each DFA) and would furthermore complicate interfacing the method with existing computer codes (in particular for nuclear gradients) and charge devoid methods like force-fields. We thus continue the successful D3 strategy to provide only a single, well-defined and general “set” of dispersion coefficients. For the very rare case of GFN-xTB not providing a reasonable electronic structure, we provide a fall-back option to resort to PBE0/TZVP Hirshfeld charges.

Figure 1 illustrates the effect of the introduced scaling function for hydrogen in two extreme bonding situations. The radii of the atoms directly correspond to the calculated homoatomic C_6^{AA} dispersion coefficients derived with D3 (left side) and D4 (right side).

Fractional coordination numbers of all atoms are calculated to obtain atomic polarizabilities by weighting over all element specific reference systems $A_m H_n$ with respect to those CNs . In D3, a two-dimensional interpolation scheme for different atoms A and B is used to compute C_6^{AB} , while in D4 this function is four-dimensional, i.e., two atomic charges and two CN values. The use of CNs is in accordance with chemical intuition regarding different hybridization situations for each atom within the molecule. Compared to D3, the calculation of the CN has been slightly modified. The atomic

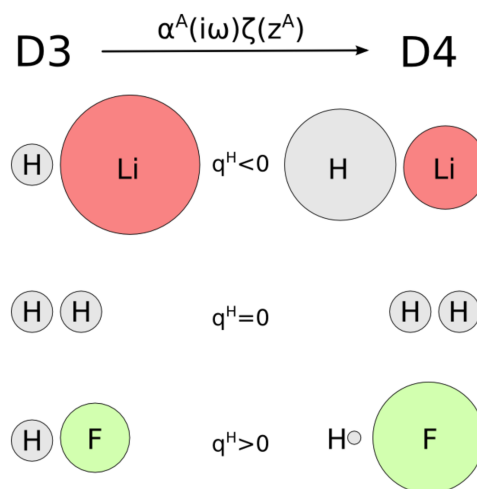


FIG. 1. Schematic representation of the ζ -functionality which rescales atomic polarizabilities based on input Mulliken charges q . The left side shows the standard partitioning of atomic polarizabilities in D3. On the right side, the scaled atomic polarizabilities are shown. The depicted radii of the atoms directly correspond to the calculated atomic C_6^{AA} coefficients.

electronegativities of the two atoms enter the calculation in order to distinguish between covalent and ionic bonding. The CN s are adjusted to approximately match Wiberg bond orders³² of single bonds. Therefore, additional reference systems are included in the D4 Gaussian interpolation of polarizabilities describing non-polar (e.g., fluorine with $CN^{F_2}=0.96$) as well as polar (e.g., hydrogen fluoride with $CN^{HF}=0.74$) cases resulting in a better description of the individual bonding and hybridization situation. For details of the determination of the few relevant model parameters, see the [supplementary material](#). Furthermore, we changed the Gaussian weighting from interpolating precalculated C_6^{AB} dispersion coefficients between atoms having different CN s to a scheme which interpolates reference polarizabilities between atoms having different CN s and different charges instead (i.e., each polarizability is a two-dimensional function).

C. Dispersion energy

The D4 dispersion coefficients are used to compute the atom pairwise dispersion energy in complete analogy to DFT-D3(BJ) by coupling to a damping scheme to be used with standard density functionals. The DFT-D4 dispersion energy is given by

$$E_{\text{disp}}^{D4} = - \sum_{AB} \sum_{n=6,8} s_n \frac{C_6^{AB(n)}}{R^n} f_{\text{damp}}^{(n)}(R), \quad (5)$$

where R is an interatomic distance for atom pair AB , and $f_{\text{damp}}^{(n)}$ denotes the rational Becke-Johnson damping³³ function (denoted BJ-damping or simply damping in the following). The factors s_n scale the individual multipolar contributions. Due to its physically reasonable behavior at short interatomic distances, the BJ-damping function given by

$$f_{\text{damp}}^{(n)}(R) = \frac{R^n}{R^n + (a_1 R_0 + a_2)^n} \quad (6)$$

has become the default in combination with D3.³³ It incorporates functional-specific parameters a_1 and a_2 as well as the radii $R_0 = \sqrt{C_8^{AB}/C_6^{AB}}$. The atom pairwise dipole-quadrupole contribution $E_{\text{disp}}^{(8)}$ is included with the respective C_8^{AB} dispersion coefficient, which is computed recursively as in D3 from the dipole-dipole dispersion coefficient

$$C_8^{AB} = 3C_6^{AB} \sqrt{Q_A Q_B} \quad (7)$$

with

$$Q_A = \sqrt{Z^A} \frac{\langle r_A^4 \rangle}{\langle r_A^2 \rangle}. \quad (8)$$

Here, $\langle r_A^4 \rangle$ and $\langle r_A^2 \rangle$ are multipole-type expectation values derived from atomic densities. For more details, see Ref. 5.

D. Technical details

We have coupled three established DFAs to the new D4 dispersion model (meta-GGA: TPSS,³⁴ hybrid: B3LYP^{35,36} and PBE0³⁷) as usual by fitting to common interaction energy benchmark sets, namely, S66x8,³⁸ S22x5,³⁹ and

NCIBLIND10.⁴⁰ We used the TURBOMOLE suite of programs^{41–43} (version 7.0.2) to conduct all ground-state DFT calculations. Within the DFT calculations, we applied standard exchange-correlation functional integration grids ($m4$) and typical self-consistent field convergence criteria (10^{-7} E_h) as well as the resolution of the identity integral approximation.^{44–46} Ahlrich's type quadruple-zeta basis sets (def2-QZVP) are used for all single-point calculations. The density functional specific damping parameters are obtained by least-squares Levenberg-Marquardt minimization to the reference interaction energies in the three investigated benchmark sets.

III. RESULTS

A. Molecular C_6 coefficients

Experimentally, molecular C_6 coefficients are accessible from dipole oscillator strength distributions (DOSDs). Figure 2 displays computed molecular dispersion coefficients in comparison to experimental values and data from related theoretical methods (D3, TS, LRD). The respective statistical evaluation over all calculated dispersion coefficients in Fig. 2 is given in Table I, presenting the mean absolute deviation (MAD), mean deviation (MD), standard deviation (SD), and the absolute maximum (AMAX) error. The deviations are always taken as relative values (in %). It is noteworthy that already the calculation of dispersion coefficients for “normal,” medium-sized inorganic and organic molecules is substantially improved upon the accurate D3 model which has an MAD of 4.7%⁴⁷ for this benchmark set compiled by A. Tkatchenko. The D4 MAD value of 2.9% is remarkable and is well within the accuracy limits of the underlying hybrid TD-DFT quantum chemistry method. To the best of our knowledge, the new D4 model yields the best cost-accuracy ratio for calculating isotropic C_6 dispersion coefficients for arbitrary systems compared to other approaches.^{6–11,48–57}

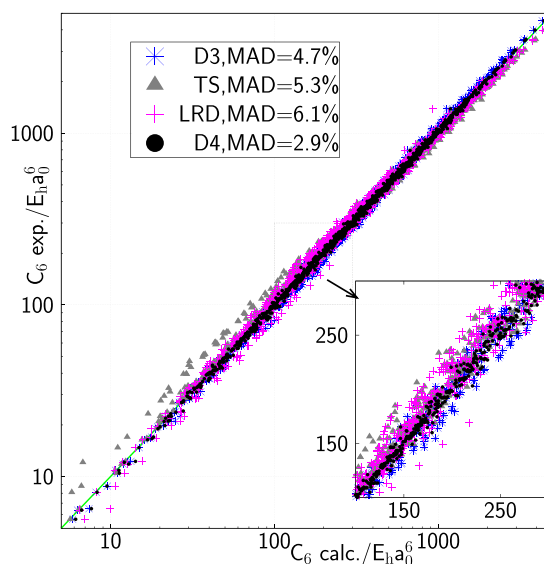


FIG. 2. Comparison of experimentally derived molecular dispersion coefficients (from dipole oscillator strength distributions) with calculated ones (1225 cases, compilation by A. Tkatchenko). Note the logarithmic scale and variation of the coefficients over three orders of magnitude. The test set contains small to medium-sized, inorganic and organic molecules (H_2 – C_8H_{18}).

TABLE I. Statistical measures for the relative deviations (in %) of calculated molecular C_6 dispersion coefficients from different approaches with respect to experimental values for the molecular benchmark set in Fig. 2. All calculated values are given in the electronic structure information.

Method	MAD	MD	SD	AMAX
D3	4.7	-2.4	5.2	23.9
TS	5.3	-2.7	7.3	44.0
LRD	6.1	-2.5	7.7	52.9
D4	2.9	-0.6	3.6	17.5

B. Atoms-in-molecules polarizabilities

As a by-product of the D4 procedure, accurate atomic polarizabilities are obtained which may have a widespread application in classical force-fields (see our parallel work on a GFN-xTB based intermolecular FF³⁰). As an example for a possible large target system, the dispersion coefficients and atomic polarizabilities of the green fluorescent protein⁵⁸ (GFP, PDB entry 1GFL, with 3601 atoms and a total molecular charge of -6) were calculated within 30 minutes on a single desktop computer. Figure 3 shows the charge and coordination dependency of homoatomic C_6^{AA} dispersion coefficients in the chromophore of the GFP exemplifying the relatively big changes between D3 and D4 for very polar bonding situations. Because of the presence of charged side-chains, we used

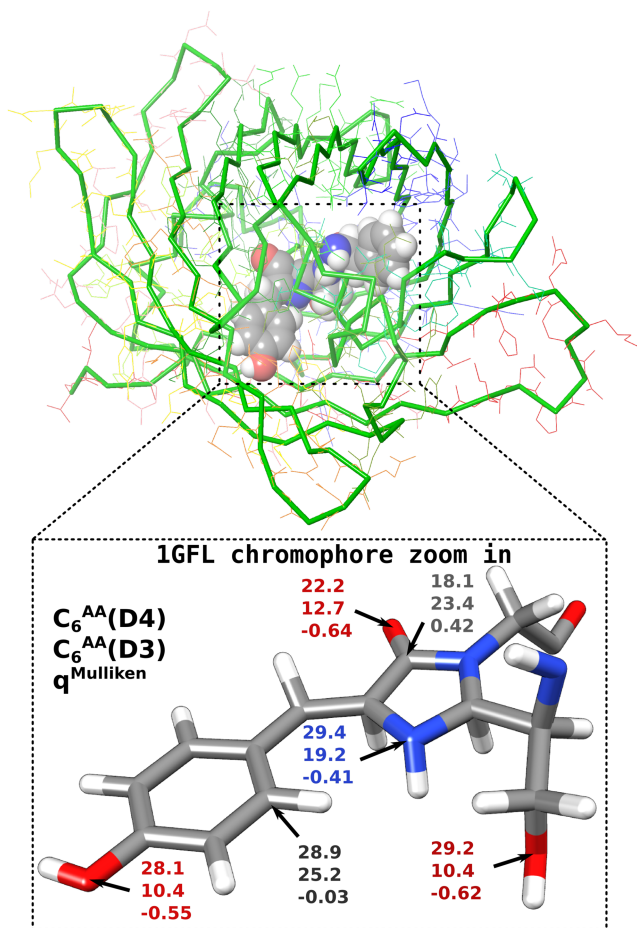


FIG. 3. Chain A of the green fluorescent protein as well as an enlarged display of the chromophore (PHE64, SER65, and TYR66). All homoatomic C_6^{AA} dispersion coefficients were calculated for the whole protein at the D4 and the D3 level of theory.

an implicit generalized Born solvation model⁵⁹ augmented with a solvent accessible surface term for water [GBSA(H_2O), GBSA in the following] in this calculation, while the default D4 procedure employs gas phase Mulliken partial charges. However, GFN-xTB/GBSA provides higher stability in the self-consistent charge procedure for highly charged molecular systems so that we recommend its use in such calculations. The quality of the calculated atomic polarizabilities is estimated by exploiting their additivity property⁶⁰ to compute molecular polarizabilities that are directly comparable to calculated hybrid TD-DFT molecular polarizabilities. For an organic molecule benchmark set (ROT34⁶¹), this results in a small deviation of only 2.5% similar to the one obtained for the molecular C_6 coefficients (see Table I).

C. Li^+ -benzene: An electronically complicated example system

As a cross-check and an example for a more difficult case involving a charged, organometallic system, the cation- π dissociation of a lithium cation and benzene is considered. Figure 4 depicts the dissociation curve of the complex. The calculated molecular dispersion coefficient is plotted against the center-of-mass distance $R(Li^+-Bz)$ (shown as a black arrow in the inset).

With increasing $R(Li^+-Bz)$, the coordination number of the lithium cation CN^{Li^+} is decreasing to zero in the asymptotic region. This leads to an overestimation of the C_6 coefficient in D3, which essentially coincides with the huge dispersion coefficient of the free lithium atom. A charge dependent method

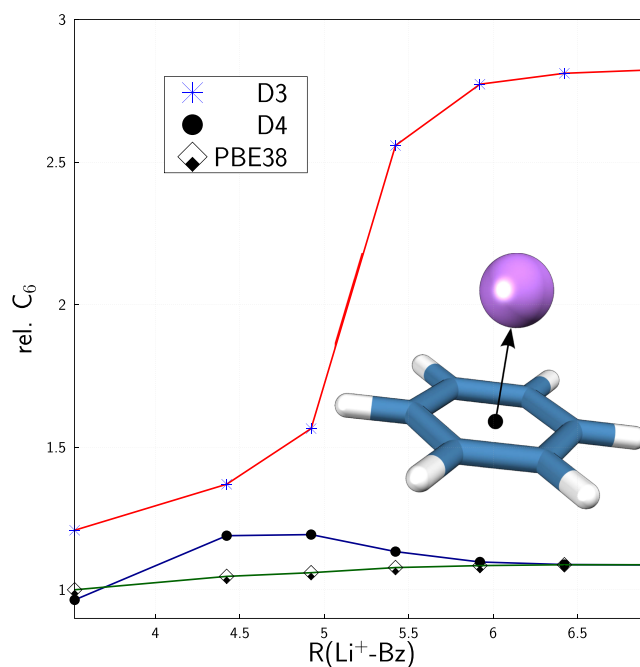


FIG. 4. Molecular dispersion coefficient C_6^{mol} for the dissociating lithium cation-benzene complex. The initial structure is optimized at the PBE0-D3(BJ)/def2-QZVP level of theory. All values are divided by the calculated TD-DFT molecular dispersion coefficient for the optimized minimum structure $C_6^{mol,ref}$. The reference TD-DFT curve is plotted in green while D3 and D4 data are shown in red and blue, respectively. The black arrow corresponds to the distance of the lithium cation to the center-of-mass of the benzene molecule denoted $R(Li^+-Bz)$.

like D4 is able to correct this deficiency by considering the electronic structure. The implemented charge function scales neutral reference polarizabilities to values that agree well with the ones in cationic or anionic situations. An MAD of 5% is calculated with D4 for the entire dissociation curve with respect to TD-DFT reference molecular dispersion coefficients. The maximum deviation is found at $CN^{Li^+} \approx 0.5$, with an error of 12.1%. Upon ionization, the static polarizability of a lithium atom [$\alpha_{ref}^{Li}(0) = 149.6 \text{ E}_h/\text{bohrs}^6$] is decreased by three orders of magnitude compared to the value of the free cation [$\alpha_{ref}^{Li^+}(0) = 0.2 \text{ E}_h/\text{bohrs}^6$]. Thus the residual error is comparably small in this extreme case. The direct comparison to D3 demonstrates the major improvement and shows that the description of charged and neutral systems is more consistent in D4. This is important for many organometallic systems in chemistry (see Ref. 21, for example). For atomic dispersion coefficients calculated by the XDM method for related systems, see Ref. 62.

D. Non-covalent interaction energies

In Table II, we directly compare DFT-D4 and DFT-D3(BJ) derived interaction energies for three density functionals. Here, the DFT-D3(BJ) damping parameters are re-fitted by the same procedure on the same benchmark sets for a fair comparison between both models. As can be seen from the table, the DFT interaction energies are mostly improved by using

TABLE II. Interaction energies calculated with three dispersion corrected DFAs (meta-GGA: TPSS,³⁴ hybrid: B3LYP^{35,36} and PBE0³⁷) and Ahlrich's type def2-QZVP basis set (not counter-poise corrected). All statistical measures are given in kcal/mol relative to the reference energies. The best result for each measure is highlighted in bold-face.

S66x8						
Measure	TPSS		B3LYP		PBE0	
	D3	D4	D3	D4	D3	D4
MAD	0.29	0.26	0.20	0.22	0.33	0.30
MD	0.07	-0.03	-0.14	-0.10	-0.17	-0.15
SD	0.37	0.33	0.26	0.27	0.42	0.39
AMAX	1.06	1.00	0.99	0.82	1.61	1.52
S22x5						
Measure	TPSS		B3LYP		PBE0	
	D3	D4	D3	D4	D3	D4
MAD	0.32	0.29	0.28	0.26	0.42	0.37
MD	-0.11	-0.21	-0.14	-0.14	-0.23	-0.27
SD	0.51	0.41	0.46	0.42	0.67	0.56
AMAX	2.54	1.95	2.39	1.66	3.04	2.70
NCIBLIND10						
Measure	TPSS		B3LYP		PBE0	
	D3	D4	D3	D4	D3	D4
MAD	0.90	0.56	0.22	0.20	0.28	0.24
MD	0.72	0.28	0.06	-0.04	-0.04	-0.08
SD	1.98	1.10	0.47	0.32	0.54	0.42
AMAX	9.40	4.77	2.23	1.55	2.10	1.69

D4, even for neutral systems. This is noteworthy because the DFT-D3(BJ) model is usually considered as being already rather accurate. It furthermore indicates that a part of the residual DFT-D3(BJ) interaction energy error is rooted in the dispersion coefficients although the DFT part is also significant at this accuracy level.

IV. SUMMARY AND CONCLUSION

We have presented an atomic charge and coordination number dependent scheme, termed D4, to compute C_6 dispersion coefficients, which can be coupled to standard density functional approximations in a DFT-D4 sense. Atomic Mulliken charges are taken from a recently published semi-empirical tight-binding method (GFN-xTB),²⁵ which is available for all elements with $Z = 1-86$. The dispersion model is based on the well-established D3 scheme and, by incorporating the atomic charge information, basically corrects for some failures for polar, organometallic, and ionic systems. The accuracy of the dispersion coefficients is slightly improved for the "normal" cases which were already good with D3. Importantly, the general black-box philosophy of the approach and the coupling of a single dispersion coefficient model to various standard DFAs is equivalent to the one of D3, which allows a broad application to quantum chemical problems. Compared to the purely geometrical D3 model, the computational cost of D4 is increased due to the semi-empirical tight-binding procedure. Since the entire D4 procedure is orders of magnitude faster compared to a Hartree-Fock or DFT treatment, the cost of D4 is negligible in a DFT-D4 scheme. Preliminary DFT-D4 interaction energy benchmarks for non-covalently bound systems (S66x8, S22x5, NCIBLIND10) show small but consistent improvements for the TPSS, PBE0, and B3LYP DFAs. Prospective works will couple D4 to more contemporary DFAs leading to a general and widely applicable DFT-D4 approach. Current work is devoted to an efficient implementation of analytical D4 nuclear gradients, which are necessary for geometry optimizations. Furthermore, a periodic implementation of GFN-xTB will be developed to treat dispersion interactions of bulk materials and surfaces under periodic boundary conditions. In the current form, the D4 dispersion energy program can be downloaded from the authors' website and used in a single-point energy mode for checking results of other pairwise dispersion corrections and due to its high accuracy even approximate wave function theory calculations.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for further details about the D4 model, parametrization details of the charge function, the training set, and a compilation of all theoretically derived data (molecular dispersion coefficients and BJ-damping parameters for TPSS, B3LYP, and PBE0).

ACKNOWLEDGMENTS

This work was supported by the DFG in the framework of the priority Program No. SPP 1807, "Control of Dispersion Interactions in Chemistry."

- ¹R. G. Parr and Y. Weitao, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, 1994), Vol. 16.
- ²W. Kohn, "Nobel lecture: Electronic structure of matterwave functions and density functionals," *Rev. Mod. Phys.* **71**, 1253 (1999).
- ³S. Grimme, A. Hansen, J. G. Brandenburg, and C. Bannwarth, "Dispersion-corrected mean-field electronic structure methods," *Chem. Rev.* **116**, 5105–5154 (2016).
- ⁴R. Eisenschitz and F. London, "Über das verhältnis der van der Waalschen kräfte zu den homöopolaren bindungskräften," *Z. Phys.* **60**, 491–527 (1930).
- ⁵S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, "A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu," *J. Chem. Phys.* **132**, 154104 (2010).
- ⁶A. Tkatchenko and M. Scheffler, "Accurate molecular van der Waals interactions from ground-state electron density and free-atom reference data," *Phys. Rev. Lett.* **102**, 073005 (2009).
- ⁷A. D. Becke and E. R. Johnson, "Exchange-hole dipole moment and the dispersion interaction," *J. Chem. Phys.* **122**, 154104 (2005).
- ⁸A. D. Becke and E. R. Johnson, "A density-functional model of the dispersion interaction," *J. Chem. Phys.* **123**, 154101 (2005).
- ⁹A. D. Becke and E. R. Johnson, "Exchange-hole dipole moment and the dispersion interaction: High-order dispersion coefficients," *J. Chem. Phys.* **124**, 014104 (2006).
- ¹⁰T. Sato and H. Nakai, "Density functional method including weak interactions: Dispersion coefficients based on the local response approximation," *J. Chem. Phys.* **131**, 224104 (2009).
- ¹¹T. Sato and H. Nakai, "Local response dispersion method. II. Generalized multicenter interactions," *J. Chem. Phys.* **133**, 194101 (2010).
- ¹²M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, "Van der Waals density functional for general geometries," *Phys. Rev. Lett.* **92**, 246401 (2004).
- ¹³M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, "Erratum: Van der Waals density functional for general geometries [Phys. Rev. Lett. **92**, 246401 (2004)]," *Phys. Rev. Lett.* **95**, 109902 (2005).
- ¹⁴K. Berland and P. Hyldgaard, "Exchange functional that tests the robustness of the plasmon description of the van der Waals density functional," *Phys. Rev. B* **89**, 035412 (2014).
- ¹⁵D. Langreth, B. I. Lundqvist, S. D. Chakarova-Käck, V. Cooper, M. Dion, P. Hyldgaard, A. Kelkkanen, J. Kleis, L. Kong, and S. Li, "A density functional for sparse matter," *J. Phys.: Condens. Matter* **21**, 084203 (2009).
- ¹⁶K. Berland, V. R. Cooper, K. Lee, E. Schröder, T. Thonhauser, P. Hyldgaard, and B. I. Lundqvist, "Van der Waals forces in density functional theory: A review of the vdW-DF method," *Rep. Prog. Phys.* **78**, 066501 (2015).
- ¹⁷G. A. DiLabio and A. Otero-de-la-Rozza, "Noncovalent interactions in density-functional theory," in *Wiley Reviews in Computational Chemistry*, Vol. 29 (Wiley, 2014), p. 1.
- ¹⁸O. A. Vydrov and T. Van Voorhis, "Improving the accuracy of the nonlocal van der Waals density functional with minimal empiricism," *J. Chem. Phys.* **130**, 104105 (2009).
- ¹⁹O. A. Vydrov and T. Van Voorhis, "Nonlocal van der Waals density functional made simple," *Phys. Rev. Lett.* **103**, 063004 (2009).
- ²⁰S. Ehrlich, J. Moellmann, W. Reckien, T. Bredow, and S. Grimme, "System-dependent dispersion coefficients for the DFT-D3 treatment of adsorption processes on ionic surfaces," *ChemPhysChem* **12**, 3414–3420 (2011).
- ²¹A. Hansen, C. Bannwarth, S. Grimme, P. Petrović, C. Werlé, and J.-P. Djukic, "The thermochemistry of London dispersion-driven transition metal reactions: Getting the 'right answer for the right reason'," *ChemistryOpen* **3**, 177–189 (2014).
- ²²M. Stöhr, G. S. Michelitsch, J. C. Tully, K. Reuter, and R. J. Maurer, "Communication: Charge-population based dispersion interactions for molecules and materials," *J. Chem. Phys.* **144**, 151101 (2016).
- ²³R. Mulliken, "Electronic population analysis on LCAO–MO molecular wave functions. II. Overlap populations, bond orders, and covalent bond energies," *J. Chem. Phys.* **23**, 1841–1846 (1955).
- ²⁴S. Grimme and C. Bannwarth, "Ultra-fast computation of electronic spectra for large systems by tight-binding based simplified Tamm-Dancoff approximation (sTDA-xTB)," *J. Chem. Phys.* **145**, 054103 (2016).
- ²⁵S. Grimme, C. Bannwarth, and P. Shushkov, "A robust and accurate tight-binding quantum chemical method for structures, vibrational frequencies, and non-covalent interactions of large molecular systems parameterized for all spd-block elements ($z = 1-86$)," *J. Chem. Theory Comput.* **13**, 1989–2009 (2017).
- ²⁶R. Petraglia, S. N. Steinmann, and C. Corminboeuf, "A fast charge-dependent atom-pairwise dispersion correction for DFTB3," *Int. J. Quantum Chem.* **115**, 1265–1272 (2015).
- ²⁷M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, Th. Frauenheim, S. Suhai, and G. Seifert, "Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties," *Phys. Rev. B* **58**, 7260–7268 (1998).
- ²⁸Y. Yang, H. Yu, D. York, Q. Cui, and M. Elstner, "Extension of the self-consistent-charge density-functional tight-binding method: Third-order expansion of the density functional theory total energy and introduction of a modified effective Coulomb interaction," *J. Phys. Chem. A* **111**, 10861–10873 (2007).
- ²⁹R. Sedlak and J. Řezáč, "Empirical D3 dispersion as a replacement for *ab initio* dispersion terms in density functional theory-based symmetry-adapted perturbation theory," *J. Chem. Theory Comput.* **13**, 1638–1646 (2017).
- ³⁰S. Grimme, C. Bannwarth, E. Caldeweyher, J. Pisarek, and A. Hansen, "A general intermolecular force field based on tight-binding quantum chemical calculations," *J. Chem. Phys.* **147**, 161708 (2017).
- ³¹H. B. G. Casimir and D. Polder, "The influence of retardation on the London-van der Waals forces," *Phys. Rev.* **73**, 360–372 (1948).
- ³²K. B. Wiberg, "Application of the popple-santry-segal CNDO method to the cyclopropylcarbiny and cyclobutyl cation and to bicyclobutane," *Tetrahedron* **24**, 1083–1096 (1968).
- ³³S. Grimme, S. Ehrlich, and L. Goerigk, "Effect of the damping function in dispersion corrected density functional theory," *J. Comput. Chem.* **32**, 1456–1465 (2011).
- ³⁴J. 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).
- ³⁵A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys.* **98**, 5648–5652 (1993).
- ³⁶P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, "*Ab initio* calculation of vibrational absorption and circular dichroism spectra using density functional force fields," *J. Phys. Chem.* **98**, 11623–11627 (1994).
- ³⁷C. Adamo and V. Barone, "Toward reliable density functional methods without adjustable parameters: The PBE0 model," *J. Chem. Phys.* **110**, 6158–6170 (1999).
- ³⁸B. Brauer, M. K. Kesharwani, S. Kozuch, and J. M. L. Martin, "The S66x8 benchmark for noncovalent interactions revisited: Explicitly correlated *ab initio* methods and density functional theory," *Phys. Chem. Chem. Phys.* **18**, 20905–20925 (2016).
- ³⁹L. Gráfová, M. Pitoňák, J. Řezáč, and P. Hobza, "Comparative study of selected wave function and density functional methods for noncovalent interaction energy calculations using the extended S22 data set," *J. Chem. Theory Comput.* **6**, 2365–2376 (2010).
- ⁴⁰D. E. Taylor, J. G. Ángyán, G. Galli, C. Zhang, F. Gygi, K. Hirao, J. W. Song, K. Rahul, O. Anatole von Lilienfeld, R. Podeszwa *et al.*, "Blind test of density-functional-based methods on intermolecular interaction energies," *J. Chem. Phys.* **145**, 124105 (2016).
- ⁴¹TURBOMOLE V7.0, University of Karlsruhe, Forschungszentrum Karlsruhe GmbH, TURBOMOLE GmbH, Karlsruhe, Germany, 2015, <http://www.turbomole.com>.
- ⁴²R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel, "Electronic structure calculations on workstation computers: The program system turbomole," *Chem. Phys. Lett.* **162**, 165–169 (1989).
- ⁴³F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, and F. Weigend, "Turbomole," *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **4**, 91–100 (2014).
- ⁴⁴O. Vahtras, J. Almlöf, and M. Feyereisen, "Integral approximations for LCAO-SCF calculations," *Chem. Phys. Lett.* **213**, 514–518 (1993).
- ⁴⁵K. 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).
- ⁴⁶F. Weigend, "Accurate Coulomb-fitting basis sets for H to Rn," *Phys. Chem. Chem. Phys.* **8**, 1057–1065 (2006).
- ⁴⁷S. Grimme, "Density functional theory with London dispersion corrections," *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **1**, 211–228 (2011).
- ⁴⁸S. Grimme, "Accurate description of van der Waals complexes by density functional theory including empirical corrections," *J. Comput. Chem.* **25**, 1463–1473 (2004).
- ⁴⁹O. A. von Lilienfeld, I. Tavernelli, U. Röhrlisberger, and D. Sebastiani, "Optimization of effective atom centered potentials for London dispersion forces in density functional theory," *Phys. Rev. Lett.* **93**, 153004 (2004).
- ⁵⁰Q. Wu and W. Yang, "Empirical correction to density functional theory for van der Waals interactions," *J. Chem. Phys.* **116**, 515–524 (2002).
- ⁵¹S. N. Steinmann, G. Csonka, and C. Corminboeuf, "Unified inter- and intramolecular dispersion correction formula for generalized gradient

- approximation density functional theory,” *J. Chem. Theory Comput.* **5**, 2950–2958 (2009).
- ⁵²U. Zimmerli, M. Parrinello, and P. Koumoutsakos, “Dispersion corrections to density functionals for water aromatic interactions,” *J. Chem. Phys.* **120**, 2693–2699 (2004).
- ⁵³S. N. Steinmann and C. Corminboeuf, “A system-dependent density-based dispersion correction,” *J. Chem. Theory Comput.* **6**, 1990–2001 (2010).
- ⁵⁴S. N. Steinmann and C. Corminboeuf, “A generalized-gradient approximation exchange hole model for dispersion coefficients,” *J. Chem. Phys.* **134**, 044117 (2011).
- ⁵⁵S. N. Steinmann and C. Corminboeuf, “Comprehensive benchmarking of a density-dependent dispersion correction,” *J. Chem. Theory Comput.* **7**, 3567–3577 (2011).
- ⁵⁶A. Tkatchenko, R. A. DiStasio, R. Car, and M. Scheffler, “Accurate and efficient method for many-body van der Waals interactions,” *Phys. Rev. Lett.* **108**, 236402 (2012).
- ⁵⁷T. Bučko, S. Lebègue, J. Hafner, and J. G. Ángyán, “Improved density dependent correction for the description of London dispersion forces,” *J. Chem. Theory Comput.* **9**, 4293–4299 (2013).
- ⁵⁸F. Yang, L. G. Moss, and G. N. Phillips, “The molecular structure of green fluorescent protein,” *Nat. Biotechnol.* **14**, 1246–1251 (1996).
- ⁵⁹W. C. Still, A. Tempczyk, R. C. Hawley, and T. Hendrickson, “Semianalytical treatment of solvation for molecular mechanics and dynamics,” *J. Am. Chem. Soc.* **112**, 6127–6129 (1990).
- ⁶⁰A. Stone, *The Theory of Intermolecular Forces* (OUP, Oxford, 2013).
- ⁶¹T. Risthaus, M. Steinmetz, and S. Grimme, “Implementation of nuclear gradients of range-separated hybrid density functionals and benchmarking on rotational constants for organic molecules,” *J. Comput. Chem.* **35**, 1509–1516 (2014).
- ⁶²E. R. Johnson, “Dependence of dispersion coefficients on atomic environment,” *J. Chem. Phys.* **135**, 234109 (2011).