Density-functional approach to the three-body dispersion interaction based on the exchange dipole moment

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(Received 30 March 2015; accepted 14 August 2015; published online 31 August 2015)

We implement and compute the density functional nonadditive three-body dispersion interaction using a combination of Tang-Karplus formalism and the exchange-dipole moment model of Becke and Johnson. The computation of the C_9 dispersion coefficients is done in a non-empirical fashion. The obtained C_9 values of a series of noble atom triplets agree well with highly accurate values in the literature. We also calculate the C_9 values for a series of benzene trimers and find a good agreement with high-level *ab initio* values reported recently in the literature. For the question of damping of the three-body dispersion at short distances, we propose two damping schemes and optimize them based on the benzene trimers data, and the fitted analytic potentials of He_3 and Ar_3 trimers fitted to the results of high-level wavefunction theories available from the literature. Both damping schemes respond well to the optimization of two parameters. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4929581>]

I. INTRODUCTION

Extending Density Functional Theory (DFT) to van-der-Waals (VDW) dispersion interactions from first principles is paramount. *Ab initio* correlation methods, such as coupled-cluster with single, doubles, and perturbative triple excitations (CCSD(T)) and symmetry-adapted perturbation theory (SAPT) are capable of estimating accurately the dispersion interaction. But they are computationally expensive. In recent years, models based on density functional theory have been proposed, mostly focusing on the two-body dispersion interaction. Some of those models follow an empirical approach, adding to the density functional empirical dispersion terms similar to those used in classical force fields.¹ Non-empirical DFT models have also been put forward based on response formalism,² model exchange hole,³ exchange-correlation (XC) hole,⁴ and ground-state electron density with reference values for the free atoms.² The exchange dipole moment (XDM) model of Becke and Johnson^{3,5,6} is a nonempirical density functional model of dispersion, in which the dipole moment of a model exchange hole centered on one system induces an instantaneous dipole moment in a weakly interacting neighboring system.

In most cases, the two-body contribution is expected to count for most of the dispersion interactions. The significance of the non-additive three-body dispersion term is still not quite clear and is being debated.⁷⁻⁹ It was estimated to be as large as 10% of the stabilization energy in some molecular crystals¹⁰ and about 46% of the energy difference between folded and elongated polyalanine decamers.⁷ The three-body dispersion contribution was also shown to be crucial to the

third virial coefficient.^{7,10-12} Current DFT methods tend to overestimate the two-body dispersion interaction partly due to the omission of the three-body contribution that is often of the opposite sign.⁷ The general formulas for the nonadditive three-body dispersion were derived long ago based on perturbation theory and dynamic polarizabilities,¹³⁻¹⁵ but were not applied in DFT studies of VDW systems until recent years.^{1,7,8} Grimme *et al.* added an empirical, molecular-mechanic-like dispersion term to the DFT functional that includes nonadditive three-body dispersion components.¹ The three-body dispersion coefficient C_9 was evaluated as a geometric mean of the three empirical two-body coefficients C_6 in a given triatomic group ABC. Lilienfeld and Tkatchenko⁷ (LT) proposed a DFT approach to the three-body dispersion based on a two-body dispersion model using the electron density of the system and frequency-dependent atomic polarizability data.⁸ They evaluated the C_9 coefficient employing formulas from Tang's work.¹⁵ An alternative approach to handling the many-body dispersion beyond the triple-dipole level was later on proposed by Tkatchenko and Co. based on microscopic description of the frequency-dependent polarizability.¹⁶ Recently, Otero-de-la-Roza and Johnson (OJ) proposed an XDM-based expression of the nonadditive three-body dispersion interaction⁸ that satisfies the Midzuno-Kihara relations.¹⁷ Their C_9 coefficients were calculated with numerical basis, using the post-Hartree-Fock XDM mean-squared dipole atomic moments and effective atomic polarizabilities. They concluded that a three-body addition to the XDM dispersion model may be prematured mainly due to difficulties of finding a suitable damping formula for it.

The development of dispersion models relies on accurate data for benchmarking and optimization, which has been scarce for three-body nonadditive dispersion interaction compared with the situation for two-body dispersion. Kumar and

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Thakkar (KT) reported highly accurate estimates of this interaction in well-separated noble atom triplets based on the dipole oscillator strength distribution calculated from theoretical and experimental photo-absorption cross sections.¹⁸ They contain less approximations and are considered highly accurate. Another recent accurate benchmark results are Tang's^{12,19} based on explicit evaluation of oscillator strength sum rules and are in very good agreement with KT's work. These studies are useful for estimating the accuracy of the C_9 coefficient from approximate DFT models. The atoms in those triplets are not close in space and thus are not suitable for the optimization of a damping formula. Very recently, Sherrill and Co.⁹ have reported accurate coupled-cluster theory values of the three-body interaction in crystalline benzene. They proposed that the non-additive three-body dispersion component can be deduced by subtracting the Møller–Plesset perturbation theory (MP2) energy from the energy of the CCST(T). Accurate estimates of the three-body nonadditive interaction potential in He_3 and Ar_3 trimers have been recently reported as well by Szalewicz and Co.,^{12,20,21} based on fitting the terms of SAPT to the results of full configuration interaction (FCI) for He_3 and high-order coupled-cluster method for Ar_3 .

We have developed previously an efficient self-consistent implementation of the XDM model and its energy gradient in DFT realization.²² We have shown that this model leads to improved isomerization energies of alkanes and the optimal geometry of a tyrosine-glycine peptide. The purpose of the present study is to extend our implementation of the XDM method to include the nonadditive three-body dispersion component. Our formalism for the C_9 coefficients is based on Tang's work on three-body dispersion¹⁵ and the two-body XDM model, which is equivalent to OJ's work⁸ apart from the present DFT realization of XDM. We calculate the C_9 values of a series of noble atom triplets and compare with accurate reference data in the literature and the reported results of other recent methods. Furthermore, we propose two damping functions for the nonadditive three-body dispersion and optimize and test them against the combined reference data for a series of benzene trimers from Sherrill and Co. and trimers of He and Ar from Szalewicz and Co. We then calculate the three-body dispersion contribution to the binding energies of the S22 set of VDW complexes using our new damping terms and compare with the results of LT, Ref. 7.

II. THEORY

The dispersion energy of a group of atoms (A, B, C, ...) at positions $\mathbf{R}_A, \mathbf{R}_B, \mathbf{R}_C, \dots$ can be represented as a many-body series expansion,¹⁵

$$E_{\text{disp}} = \frac{1}{2} \sum_{A,B} E_{(2)}(\vec{R}_A, \vec{R}_B) + \frac{1}{6} \sum_{A,B,C} E_{(3)}(\vec{R}_A, \vec{R}_B, \vec{R}_C) + \dots \quad (1)$$

For spherical neutral atoms with non-overlapping densities, the expression for the two-body term is

$$E_{(2)}(\vec{R}_A, \vec{R}_B) = -\frac{C_6^{AB}}{R_{AB}^6} - \frac{C_8^{AB}}{R_{AB}^8} - \frac{C_{10}^{AB}}{R_{AB}^{10}} - \dots \quad (2)$$

The XDM model of Becke and Johnson used in this work provides nonempirical formulas for each dispersion coefficient in Eq. (2). Using similar physical arguments, one can express the non-additive three-body interaction with a series expansion, the leading term of which is given by the Axilrod-Teller formula,⁹

$$E_{(3)}(\vec{R}_A, \vec{R}_B, \vec{R}_C) = C_9^{ABC} \frac{(3 \cos(\phi_A) 3 \cos(\phi_B) 3 \cos(\phi_C) + 1)}{R_{AB}^3 R_{AC}^3 R_{BC}^3}, \quad (3)$$

where ϕ_A, ϕ_B, ϕ_C are the internal angles of the triangle ABC.

A three-body dispersion correction to the XDM model in its post-Hartree-Fock version was suggested very recently by OJ⁸ using atomic squared dipole moments and polarizabilities. In the present work (PW), we develop an extension of the XDM model to include the three-body dispersion term, following a somewhat different route. We start with the XDM expression of the two-body dispersion coefficient C_6 for an interaction between two identical atoms A–A,³

$$C_6^{AA} = \frac{1}{2} \langle d_X^2 \rangle_A \alpha_A. \quad (4)$$

In the above equations, α_A is an effective atomic polarizability that will be specified later. $\langle d_X^2 \rangle_A$ is the averaged squared atomic dipole moment of the exchange-hole. One can use either the HF exchange hole or the Becke-Roussel (BR89) model exchange hole.²³ In the latter case, the averaged squared dipole moment is calculated as the integral of the squared local dipole moment of the BR89 hole function,

$$d_{X\sigma}^2(\mathbf{r}) = b_\sigma^2(\mathbf{r}), \quad (5)$$

$$\langle d_X^2 \rangle_A = \sum_\sigma \int w_A(\mathbf{r}) \rho_\sigma(\mathbf{r}) d_{X\sigma}^2(\mathbf{r}) d^3\mathbf{r}, \quad (6)$$

where b_σ is a function derived in the BR89 exchange model that depends on the electron density, the first and second order derivatives of the electron density, and the electron kinetic-energy density. Note that the original BR89 functional was not given in a closed analytic form. It required solving a non-linear algebraic equation numerically at each grid point. We have developed the BR89 exchange model in closed analytic form,²⁴ which is used in this work to evaluate efficiently Eq. (6). The analytical representation allows exploring the full capabilities of the XDM DFT model. It also avoids potential instabilities associated with numerical solutions particularly for small argument values.

The local function w_A is an atomic weight function of Hirshfeld type,

$$w_A(\mathbf{r}) = \frac{\rho_A^{\text{at}}(\mathbf{r})}{\sum_B \rho_B^{\text{at}}(\mathbf{r})}, \quad (7)$$

where ρ_A^{at} is free spherical atomic density placed at nucleus A. Using the Hirshfeld atomic weights, the effective atomic polarizability of an atom A in a molecule is given in the XDM model as⁵

$$\alpha_A = \frac{\langle r^3 \rangle_A}{\langle r^3 \rangle_{A, \text{free}}} \alpha_{A, \text{free}}, \quad (8)$$

$$\langle r^3 \rangle_A = \int r^3 w_A(\mathbf{r}) \rho(\mathbf{r}) d^3\mathbf{r}, \quad (9)$$

$$\langle r^3 \rangle_{A,\text{free}} = \int r^3 \rho_A^{\text{at}}(\mathbf{r}) d^3\mathbf{r}, \quad (10)$$

where α_A and $\alpha_{A,\text{free}}$ are effective atomic polarizability in a molecule and free-atomic polarizability, respectively, $\langle r^3 \rangle_A$ and $\langle r^3 \rangle_{A,\text{free}}$ are measures of effective atomic volume of atom in a molecule and in free atom, respectively.

For the nonadditive three-body term, we start with Eq. (2.16) in Tang's paper,¹⁵

$$C_9^{ABC} = \frac{3}{2} \alpha_A \alpha_B \alpha_C \frac{\eta_A \eta_B \eta_C (\eta_A + \eta_B + \eta_C)}{(\eta_A + \eta_B)(\eta_B + \eta_C)(\eta_C + \eta_A)}, \quad (11)$$

where η_i are constants that have the meaning of an average atomic excitation energy. The best approximation for these constants was given by Tang as a function of the two-body interaction coefficients in the form

$$\eta_A = \frac{4}{3} \frac{C_6^{AA}}{\alpha_A^2}. \quad (12)$$

Inserting in Eq. (12) the XDM formula for C_6^{AA} given by Eq. (4), we obtain a link between the XDM model and the three-body dispersion model of Tang and Karplus,

$$\eta_A = \frac{2}{3} \frac{\langle d_X^2 \rangle_A}{\alpha_A}. \quad (13)$$

Using expression (13) back in the general Tang-Karplus formula, Eq. (11), gives us a nonempirical estimate of the nonadditive three-body interaction contribution to the dispersion energy within the XDM model. We note that an expression analogous to Eq. (13) has been mentioned in XDM works before (Eq. (29) in Ref. 5), where it was explained as an ‘‘averaged’’ excitation energy. We note also that Tang¹⁵ has shown long time ago the formal equivalence of the three-body formula used in the present work, Eq. (11), with that used by LT (Eq. (6) of Ref. 7) and with the formula used by OJ (Eq. (41) of Ref. 8). In practice, values from each of these three formulas may differ somewhat due to differences

in implementation. In particular, OJ used HF exchange hole for the computation of the averaged atomic exchange dipole moment, whereas we use BR89 exchange hole for the present work.

To make the model applicable to molecules, one needs suitable damping factors (f) to prevent the dispersion energy from collapsing at small inter-nuclear distances. Damping functions are needed not only to avoid the divergence of the R^{-n} terms at short range but also to correct the errors from using the multipole expansion of the electrostatic interaction.⁸ Equation (1) is then rewritten as

$$E_{\text{disp}} = \frac{1}{2} \sum_{A,B} E_{(2)}(\vec{R}_A, \vec{R}_B; f_{AB}(R_{AB})) + \frac{1}{6} \sum_{A,B,C} E_{(3)}(\vec{R}_A, \vec{R}_B, \vec{R}_C; f_{ABC}(\bar{R}_{ABC})) + \dots, \quad (14)$$

where f_{AB} and f_{ABC} are damping functions for two-body and nonadditive three-body dispersion interactions, respectively. $\bar{R}_{ABC}$ is certain geometrically averaged effective distance to be specified. It depends on more than one interatomic distance, which complicates the modelling of such damping functions. Two-body damping has been well studied in the literature.^{1,3,5,8} For the three-body damping, LT⁷ suggested a triple-product of two-body damping function for their three-body term, which corresponds to damping each of the three distances separately and independently from each other. OJ⁸ also proposed a triple-product of the two-body XDM damping functions for their three-body term, using the two damping parameters optimized for the two-body XDM. In general, it is not well established yet how to properly model the damping of the non-additive three-body dispersion.

We suggest here two damping functions for the XDM three-body term. One of these (denoted as Scheme A) is similar to the triple-product form in Ref. 8 apart from the different numerators,

$$E_{(3)}(\vec{R}_A, \vec{R}_B, \vec{R}_C; f_{ABC}) = C_9^{ABC} \frac{(3 \cos(\phi_A) 3 \cos(\phi_B) 3 \cos(\phi_C) + 1)}{(\bar{R}_{vdW,AB}^3 + R_{AB}^3)(\bar{R}_{vdW,BC}^3 + R_{BC}^3)(\bar{R}_{vdW,CA}^3 + R_{CA}^3)}. \quad (15)$$

Here, $R_{vdW,AB}$ is a sum of effective atomic VDW radii of atoms A and B related to the critical interatomic distance ($R_{c,AB}$) as defined in the two-body XDM model. It is the distance where the three components of the two-body dispersion energy become roughly equal in magnitude,⁶ which is when

$$R_{c,ij} = \frac{1}{3} \left[\left(\frac{C_{8,ij}}{C_{6,ij}} \right)^{1/2} + \left(\frac{C_{10,ij}}{C_{6,ij}} \right)^{1/4} + \left(\frac{C_{10,ij}}{C_{8,ij}} \right)^{1/2} \right], \quad (16)$$

$$\bar{R}_{vdW,ij} = \alpha_1 R_{c,ij} + \alpha_2, \quad (17)$$

α_1 and α_2 are two adjustable damping parameters that can be optimized for three-body dispersion interaction separately from the two-body interaction.

The second damping function that we propose and test (Scheme B) uses a geometric-mean of the XDM effective VDW radii, Eq. (19),

$$E_{(3)}(\vec{R}_A, \vec{R}_B, \vec{R}_C; f_{ABC}(\bar{R}_{ABC})) = C_9^{ABC} \frac{(3 \cos(\phi_A) 3 \cos(\phi_B) 3 \cos(\phi_C) + 1)}{(\bar{R}_{vdW,ABC}^9 + R_{AB}^3 R_{AC}^3 R_{BC}^3)}, \quad (18)$$

$$\bar{R}_{vdW,ABC} = \sqrt[3]{R_{vdW,AB} R_{vdW,BC} R_{vdW,CA}}. \quad (19)$$

This form bares some analogy with the single two-body damping formula used in XDM, and it is not of triple-product form. The damping along each of the three interatomic distances is now inter-related via the three-body

effective mean radius $\bar{R}_{vdW,ABC}$, introduced here by Eqs. (18) and (19).

III. RESULTS AND DISCUSSION

The present model is an extension of the XDM algorithm implemented by us earlier in a fully analytic form.²² All calculations are done with unpruned grid (194 590) consisting of 194 radial and 590 angular points, which provides the desired accuracy of the numerical integration in all studied cases. The dispersion energy is calculated here in a post-self-consistent field (SCF) fashion. The electron density and the non-dispersion part of the DFT energy are calculated with the XC DFT scheme P86 (X) + PBE (C) as recommended in Ref. 25. We have shown earlier²² that post-SCF solution of XDM brings an error in the order of only 10^{-5} in the density matrix, which is negligible in most applications.

We first test the basis set dependence of C_6 and C_9 . Table I contains the C_6 and C_9 estimates of a set of well-separated homonuclear triplets of H, N, O, F, Si, P, S, Cl, Ne, He, Ar, Kr using aug-cc-PVQZ, G3LARGE²⁶ (in round brackets) and 6-311+G(3df,3p) (in square brackets). There is a small to moderate dependence of the results on the basis set (percentage deviations in single digits) with the exception of H and He triplets where the basis set dependence is more noticeable, especially for C_9 .

The C_9 values of those triplets have been also reported in the works of LT and OJ.^{7,8} They are listed in Table II along with our results done with as large basis set as aug-cc-PVQZ. We note that the results of Ref. 7 are obtained with the PBE(X) + PBE(C) functional and a different basis set and method; the results of Ref. 8 are from fully numerical Hartree-Fock implementation of the XDM method. The C_9 values between those three methods are in good agreement with each other, considering the differences in the basis sets and XC functionals. The C_6 values of the XDM calculated in the present work are also compared with those reported in Ref. 7. The agreement is somewhat better than for C_9 , indicating a stronger dependency on the choice of method for the latter. We note that the XDM method used here also includes higher-order two-body terms up to R^{-10} .^{1,3,5,8}

Accurate theoretical estimates of C_9 values for well-separated triplets of noble gas atoms have been reported in the literature, which are an excellent source of data for benchmarking the results from various DFT methods. Some of them are in Tang's seminal work from 1969 (Tang'69), estimated based on two-point Pade approximant of the atomic dynamic polarizability and dipole oscillator strength data¹⁵ (listed in column 5 of our Table III). The more recent data, listed in column 6 of Table III, are from the work of KT based on the dipole oscillator strength distribution calculated from theoretical and experimental photo-absorption cross sections.¹⁸ They contain less approximations and are considered highly accurate. Very recent accurate benchmark results were also reported¹⁹ (Tang'12) based on explicit evaluation of oscillator strength sum rules and are in very good agreement with KT's work. The data from that benchmark pertaining to this study are listed in column 7 of Table III. The earlier results of Tang

TABLE I. C_6 and C_9 values of homonuclear trimers from the present work using three different basis sets: 6-311+G(3df,3p), G3LARGE, and aug-cc-PVQZ. The signed percentage deviation of the G3LARGE results from the aug-cc-PVQZ results is given in round brackets. The signed percentage deviation of the 6-311+G(3df,3p) results from the aug-cc-PVQZ results is given in square brackets.

Atom	C_6	C_9
H	6.97 (0.18%), [−10.31%]	21.92 (0.00%), [−16.11%]
C	50.54 (0.70%), [0.70%]	448.04 (0.91%), [0.91%]
N	26.16 (−0.34%), [−0.30%]	146.54 (−0.53%), [−0.50%]
O	17.67 (−1.67%), [−1.67%]	71.38 (−2.72%), [−2.72%]
F	11.06 (−2.53%), [−2.53%]	31.19 (−3.94%), [−3.94%]
Si	288.05 (−0.25%), [−0.22%]	7 719.27 (0.87%), [0.91%]
P	164.31 (0.21%), [3.73%]	3 016.07 (0.32%), [5.15%]
S	125.13 (0.20%), [2.04%]	1 825.42 (0.31%), [2.77%]
Cl	85.95 (0.41%), [2.77%]	948.56 (0.52%), [3.63%]
Ne	6.98 (−2.54%), [−2.44%]	14.04 (−3.95%), [−3.75%]
He	1.79 (0.00%), [−11.19%]	1.78 (−0.56%), [−19.68%]
Ar	57.98 (0.42%), [0.02%]	482.46 (0.40%), [−0.10%]
Kr	119.83 (−0.05%), [0.37%]	1 543.72 (−0.20%), [0.60%]
Al	433.57 (−0.79%), [−0.70%]	15 012.94 (−1.48%), [−1.38%]

from 1969¹⁵ are also in good agreement with the more recent benchmark data.

Our results of the present model with aug-cc-PVQZ basis set are listed in column 2 of Table III. Compared with the benchmark data, most of our results are less than 10% different from those of KT (column 6) and Tang'12 (column 7), which well validates the present model. Column 3 contains the estimates of C_9 from the post-Hartree-Fock XDM-based model by OJ.⁸ They are in good agreement with our C_9 estimates except for Ar and Kr triplets, where OJ's results are more undervalued when compared with those of KT and Tang'12. We also list for completeness in column 4 the C_9 estimates of Grimme *et al.* based on mean-geometric form of empirical C_6 values.¹ In addition to accurate C_9 coefficients, three-body damping functions are required for such a dispersion model in order to

TABLE II. Values of the dispersion coefficients of homonuclear trimers obtained in the present work and compared with literature results.

Atom	C_9^a PW	C_9^b LT	C_9^c OJ	C_9^d Tang'12	C_6^a PW	C_6^b LT
H	21.92	21.6	22.78	21.62	6.97	6.5
C	447.98	373.0			50.54	46.6
N	146.61	117.0			26.15	24.2
O	71.41	52.6			17.67	15.6
F	31.19	24.2			11.06	9.5
Si	7820.88	8550.0			288.06	305.0
P	3016.03	3561.0			164.30	185.0
S	1826.05	1925.0			125.08	134.0
Cl	948.75	1014.0			85.92	94.6
Ne	14.04	12.0	12.57	11.95	6.98	6.38
He	1.78	1.47	1.80	1.48	1.79	1.46
Ar	482.45	518.0	453.7	518.3	57.98	64.3
Kr	1543.03	1572.0	1386.0	1572.0	119.84	130.0

^a C_6 and C_9 values of homonuclear trimers from the present work using aug-cc-PVQZ basis set.

^bFrom Ref. 7.

^cFrom Ref. 8.

^dBenchmark values from Ref. 19.

be applied to molecular systems, where atoms and molecules are often close to each other. Indeed, OJ⁸ concluded that the three-body extension of the XDM model would not be useful for production mainly because of the unsettled performance of the three-body damping forms they have tested. Part of the difficulty comes from the lack of diversified accurate

benchmark data for the three-body dispersion such that the damping form could be properly calibrated. Very recently, Sherrill and Co.⁹ applied accurate coupled-cluster theory calculations in an attempt to resolve discrepancies in previously reported values of the non-additive three-body intermolecular dispersion interaction in crystalline benzene. They consider a series of 66 symmetry unique benzene trimers with gradually increased average distance between the monomers. The non-additive intermolecular three-body dispersion is estimated by the difference between the CCSD(T) and MP2 total three-body energy contributions ($E(\text{CCSD(T)}) - E(\text{MP2})$), with an assumption that the two-body and additive three-body interactions in CCSD(T) are mostly recovered by the MP2 energy. We use these data to optimize and test the three-body damping functions proposed here, along with other two data sets available in the literature: highly accurate nonadditive three-body interaction analytical potential fitted to FCI results for He₃ trimers²¹ and to coupled-cluster results using single, double, triple, and noniterative quadruple excitations (CCSDT(Q)) for Ar₃ trimers.¹² In the latter two cases, we use the supplied routines in these references to calculate a series of symmetry unique He₃ and Ar₃ trimers. The geometries of this series are generated by even-spaced increments starting from the equilibrium bond lengths (5.6 bohrs for He₃ and 7.1 bohrs for Ar₃) and ending to 2.5 times longer lengths. We use the provided routines to extract the (111) term of the analytical potential (Eqs. (15)–(18) of Ref. 20) that corresponds to the triple-dipole dispersion calculated in our model.

TABLE III. Results for C_9 of Noble atom triplets.

Triplet	C_9^a PW	C_9^b OJ	C_9^c Grimme'10	C_9^d Tang'69	C_9^e KT	C_9^f Tang'12
H H H	21.92	22.78		21.94		21.62
Ne Ne Ne	14.04	12.57	15.8	11.84	11.92	11.95
Ar Ar Ar	482.45	453.70	519.8	542.9	519.0	518.30
Kr Kr Kr	1543.03	1386.0	1489.0	1640.1	1577.0	1572.0
He He He	1.78	1.80		1.51		1.48
Ne Ne Ar	42.36			40.54	40.41	
Ne Ar Ar	138.94			143.95	142.70	
Ne Ar Kr	201.50		219.1	213.89	204.8	
Ne Ne Kr	60.35			60.14	57.48	
Ne Kr Kr	293.46			306.68	294.6	
Kr Ar Ar	708.65			756.0	750.2	
Kr Kr Ar	1044.18		1047.0	1091.0	1087.0	
He He Ne	3.54	3.44		2.94		2.96
He He Ar	10.57	10.59		10.23		10.25
He He Kr	15.03	14.93		15.03		14.62
He Ne Ne	7.05			5.89		
He Ar Ar	69.19			74.95		
He Kr Kr	145.96			154.84		
He Ne Kr	30.12			29.95		28.93
He Ar Kr	100.28			107.35		103.8

^aResults of the present work (PW) using aug-cc-PVQZ basis set with (194 590) grid mesh.

^bResults of Ref. 8.

^cResults of Ref. 1.

^dResults of Ref. 15.

^eBenchmark results of Ref. 18.

^fBenchmark results of Ref. 19.

FIG. 1. The nonadditive three-body intermolecular dispersion interaction estimated as $E(\text{CCSD(T)}) - E(\text{MP2})$ for a series of benzene trimers⁹ as a function of our $R_{ABC} \equiv R_{AB}^3 R_{AC}^3 R_{BC}^3$ normalized by the smallest R_{ABC} value in the series. The numerical values are listed in Table S1.²⁷

We first consider in detail the case of benzene trimers. The data shown in Figure 1 are the intermolecular part of $E(\text{CCSD(T)}) - E(\text{MP2})$ values of 66 symmetry-unique benzene trimers deduced from Ref. 9. The three-body dispersion values calculated using our models are also for intermolecular interactions only. The benzene trimers are indexed here by normalized $\bar{R}_{ABC} \equiv R_{AB}^3 R_{AC}^3 R_{BC}^3$ with the normalization factor being the smallest R_{ABC} value in the series. Note that R_{ABC} is a part of our damping scheme denoted as Scheme B, see Eq. (18). These data are also contained

in Table S1 in the supplementary material.²⁷ We first wish to establish the accuracy of $E(\text{CCSD(T)}) - E(\text{MP2})$ as an estimate of the nonadditive three-body intermolecular dispersion. We use the C_9 values calculated with our model, the accuracy of which has already been demonstrated above. We choose the last 7 most distant symmetry-unique trimers measured by R_{ABC} among the 66 symmetry-unique trimers and compare their $E(\text{CCSD(T)}) - E(\text{MP2})$ values with the calculated nondamped $E_{(3)}(\vec{R}_A, \vec{R}_B, \vec{R}_C)$ (Eq. (3)), assuming that the damping effect is negligible for these well-separated

FIG. 2. Comparison of the nonadditive three-body intermolecular dispersion interaction estimated as $E(\text{CCSD(T)}) - E(\text{MP2})$ versus nondamped values calculated in the present work (PW) for a series of benzene trimers⁹ as a function of $R_{ABC} \equiv R_{AB}^3 R_{AC}^3 R_{BC}^3$ normalized by the smallest R_{ABC} value in the series. The numerical values are listed in Table S1.²⁷

trimers. The sum of the former for these 7 trimers is 0.001 20 kcal/mol and the sum of the latter is 0.001 25 kcal/mol, with a mean absolute deviation (MAD) on these trimers of 0.000 05 kcal/mol. The accuracy of our non-damped three-body dispersion interaction was verified above in comparison

with highly accurate benchmarks^{18,19} (see Table III). The observed good agreement with respect to this energy component shows in turn that the energy difference $E(\text{CCSD(T)}) - E(\text{MP2})$ is indeed mostly due to the three-body dispersion here.

FIG. 3. Comparison of the nonadditive three-body intermolecular dispersion interaction estimated as $E(\text{CCSD(T)}) - E(\text{MP2})$ versus the values calculated with the present method for a series of benzene trimers. (a) Using damping Scheme A with the original XDM two-body values of the damping parameters. (b) Using damping Scheme B with the original XDM two-body values of the damping parameters.

TABLE IV. Mean absolute deviations (kcal/mol) of our results for the nonadditive 3-body intermolecular dispersion energy for the set of 62 benzene trimers, 203 He₃ trimers, and 203 Ar₃ trimers (benchmark data from Refs. 9, 12, and 21). The mean unsigned relative error is given in square brackets. For the series of benzene trimers, the deviations are estimated with respect to the energy difference $E(\text{CCSD(T)}) - E(\text{MP 2})$ reported in Ref. 9. For the series of He₃ and Ar₃ trimers, the deviations are with respect to the triple-dipole part of the damped dispersion component of the SAPT nonadditive three-body interaction potential fitted to FCI and CCSDT(Q), respectively (the 111 term in Eqs. (15)-(18) in Ref. 20).

Scheme	α_1	α_2 (Å)	(C ₆ H ₆) ₃	He ₃	Ar ₃
No damping	...	...	0.003 72 [0.5690]	3.849×10^{-6} [0.3927]	0.000 050 [0.0946]
A (noopt)	0.80	1.49	0.006 0 [3.9747]	9.606×10^{-7} [0.2300]	0.000 116 [1.2742]
B (noopt)	0.80	1.49	0.002 1 [0.5948]	2.591×10^{-6} [0.3810]	0.000 015 61 [0.0725]
A (opt)	0.084 384 9	1.938 087 2	0.001 9 [0.5687]	9.748×10^{-7} [0.2108]	0.000 014 635 [0.1520]
B (opt)	0.252 548 0	2.927 331 5	0.002 053 [0.5770]	1.432×10^{-6} [0.3547]	0.000 015 306 [0.0779]

When the benzene molecules in a trimer become closer to each other, the above agreement starts to deteriorate, as shown in Figure 2, which highlights the necessity of damping. We test the two damping schemes, Schemes A and B described in Section II. We try first the original XDM values of the two parameters from the damping formula for two-body dispersion, $\alpha_1 = 0.80$ and $\alpha_2 = 1.49$ Å recommended in Ref. 25 for the same basis set (aug-cc-PVDZ) and density functional (P86 X + PBE C) used here for the benzene trimers. The MAD of the two schemes with the original damping parameters with respect to the values of $E(\text{CCSD(T)}) - E(\text{MP 2})$ is 0.006 kcal/mol with Scheme A and 0.0021 kcal/mol with Scheme B (after the removal of four extreme outliers). Figure 3 illustrates the performance of our model with each of the two damping schemes using the original damping parameters optimized for two-body interactions. In this instance, Scheme B is better than Scheme A as far as the benzene trimers are concerned. However, the original damping parameters yield less accurate results for the He₃ and Ar₃ trimers when compared to the fitted analytical potential of Szalewicz and Co. (see Table IV). This shows the need for a combined optimization of our three-body damping parameters using the three different data sets altogether. We have optimized this way the damping parameters, respectively, for each damping scheme. The MAD on this combined data of three different trimer sets is minimized using the genetic algorithm. Each data set was given a relative weight during the optimization so as to bring the weighted three-body dispersion energy values to approximately similar magnitude. The results of this optimization are summarized in Table IV along with the optimized parameters. Concerning first the benzene trimers, the MAD with optimized Scheme B (0.002 05 kcal/mol) remains about the same as in the case of using the original damping parameters α_1 and α_2 (0.0021 kcal/mol). Scheme A benefits more from the optimization here with MAD reduced from 0.006 kcal/mol to 0.0019 kcal/mol. Figure 4 illustrates the performance of

the present model on the benzene trimers with each damping scheme after optimization. The accuracy achieved after the optimization with both damping schemes is quite reasonable in both cases, with Scheme A performing overall slightly better than Scheme B as can be seen from Table IV. Comparing the MAD and the total errors for each of the three sets obtained with optimized damping and without damping, we can see that damping for the nonadditive three-body is necessary, especially for the case of noble-gas trimers. Listed in Table IV are also mean unsigned relative errors for each scheme. The main contribution to the relative errors is the small interaction energies as a result from the angle factors in the three-body formalism (Eq. (3)) even at relatively close distances.

Finally, we test the optimized nonadditive three-body dispersion model on the well-known S22 set by Hobza *et al.*²⁸ of bi-molecular complexes bound with pronounced dispersion interaction. This test set was also used by Tkatchenko *et al.* to assess their models for nonadditive three-body dispersion.^{7,16} The two-body dispersion between all the atoms is calculated with XDM model with the damping parameters of Ref. 6. The nonadditive three-body dispersion component of the binding energy is calculated with the present method with both Schemes A and B with optimized damping. We find that the nonadditive three-body dispersion is about an order of magnitude smaller than the two-body counterpart here, which is in agreement with the literature.⁷⁻⁹ Damping Scheme A gives in most cases larger weakening of the binding energy (larger positive values) and/or smaller strengthening (larger negative values), compared to Scheme B. The results of LT model⁷ fall mostly between the values obtained with our two damping schemes, with reasonable agreement overall. The results are listed in Table S2 in the supplementary material.²⁷ We note that the VDW dimers included in the S22 set have somewhat limited value for studying the nonadditive three-body interaction since the intermolecular dispersion here is mainly of two-body in nature.

FIG. 4. Comparison of the nonadditive three-body intermolecular dispersion interaction estimated as $E(\text{CCSD(T)}) - E(\text{MP2})$ versus the values calculated with the present method for a series of benzene trimers, after optimizing the damping schemes. (a) Using damping Scheme A with optimized values of the damping parameters. (b) Using damping Scheme B with optimized values of the damping parameters.

IV. CONCLUSIONS

This work presents a density-functional model for the computation of nonadditive three-body VDW interaction for molecules with nonempirical calculation of the C_9 dispersion coefficients. It is an extension of XDM method in its DFT

version for two-body interaction. The preliminary assessment of this model is encouraging, especially concerning the C_9 values of a series of noble atom triplets that agree well with highly accurate values in the literature, including the recent XDM-based post-HF results of Otero-de-la-Roza and Johnson.⁸ Based on the accurate estimate of C_9 with our method, we

confirm the accuracy of the high-level theoretical estimate of the nonadditive three-body intermolecular dispersion interaction for a series of benzene trimers by Sherrill and Co.⁹ For the unsettled question of damping for the nonadditive three-body dispersion,⁸ we propose two new schemes and benchmark and optimize them against a combined set of data including the series of benzene trimers considered by Sherrill and Co., as well as a set of He₃ and Ar₃ trimers for which accurate fitted SAPT data have been reported by Szalewicz and Co.^{12,21} Both schemes respond well to optimization and show comparable performance after the optimization, with Scheme A doing overall slightly better. Besides the data on molecular crystals and noble gas trimers, further improvement on the modeling of the nonadditive three-body interactions can be achieved by computing the third virial coefficients and comparing with theoretical and experimental values.^{8,9,12}

ACKNOWLEDGMENTS

This work was supported by a grant from National Institute of Health (No. R44GM084555) and a grant from National Science Foundation (No. DMR-0913802). Authors E.P. and J.K. would like to thank Matthew Kennedy and David Sherrill at Georgia Institute of Technology for providing data for their benzene trimers. Authors F.L. and J.K. would like to thank Dr. Andrew Schultz and Dr. David Kofke at University at Buffalo for helpful discussions. J.K. would also like to thank Dr. Greg Beran at University of California at Riverside for helpful discussions.

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