

van der Waals Interactions in Density-Functional Theory: Intermolecular Complexes

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Abstract: In previous work (*J. Chem. Theory Comput.* **2009**, *5*, 719), we assessed the performance of standard semilocal exchange-correlation density functionals plus the nonempirical dispersion model of Becke and Johnson (*J. Chem. Phys.* **2007**, *127*, 154108) on binding energy curves of rare-gas diatomics. The results were encouraging. In this work, we extend our study to 65 intermolecular complexes representing a wide variety of van der Waals interactions including dispersion, hydrogen bonding, electrostatic, and stacking. Comparisons are made with other density-functional methods for van der Waals interactions in the literature.

1. Introduction

An accurate description of van der Waals (vdW) interactions is required for electronic structure calculations on biomolecules, intermolecular complexes, molecular crystals, and polymers. Although conventional semilocal density-functional theory (DFT) gives accurate predictions for many molecular and solid-state properties, semilocal functionals are inherently unable to describe dispersion, a nonlocal correlation effect.¹ Thus, generalized gradient approximation (GGA), meta-GGA, and hybrid functionals are unreliable for systems where van der Waals interactions are important, even though they may give accidentally good results in limited cases.

Many methods have been developed to treat van der Waals interactions with DFT. These range from physically rigorous dispersion functionals derived from first principles to entirely empirical corrections or parametrizations. A comprehensive review of such methods is given by Johnson et al.² We provide an overview of the established methods and mention more recent approaches not covered in the review of Johnson et al.

The most rigorous description of dispersion interactions is provided by explicitly nonlocal correlation functionals. However, these methods are more computationally demanding and complicated than standard DFT. An example is the Andersson–Langreth–Lundqvist (ALL) functional³ for non-overlapping systems, also derived by Dobson and Dinte (DD),⁴ which has been applied to intermolecular complexes

in conjunction with long-range corrected (LC) exchange-correlation functionals.^{5,6} A seamless van der Waals density functional (vdW-DF), valid at all interatomic distances, has been developed by Langreth and co-workers^{7,8} and applied to many molecular, solid-state, and biochemical systems.⁹ Other approaches use *ab initio* methods such as MP2 or CCSD(T) to describe long-range electron correlation, which is combined with short-range DFT.^{10–13} The advantages of these range-separated hybrid (RSH) methods compared to standard MP2 or CCSD(T) are reduced basis-set dependence and smaller basis-set superposition error (BSSE).

An entirely empirical approach to dispersion interactions involves the parametrization of highly flexible density functionals by including van der Waals complexes in their fitting sets, in spite of the failure of semilocal DFT to capture dispersion physics. Early functionals of this type such as X3LYP,¹⁴ M05, and M05–2X¹⁵ give large errors for stacking interactions,^{16–18} while the newer M06–2X functional performs better due to additional empirical parameters.¹⁹ Also, these functionals do not improve the description of prototypical vdW systems such as rare-gas diatomics, compared to the standard GGAs B97–1 and PBE.²⁰ Neither are they able to reproduce the asymptotic R^{-6} behavior of the dispersion energy at large separation.^{2,17}

Theoretically more sound, but still highly empirical, is the addition of explicit dispersion corrections to conventional functionals. These can take the form of C_6R^{-6} corrections (DFT-D)^{21–27} or atom-centered dispersion-correcting pseudopotentials (DCP).^{28–31} Both approaches are easy to implement in existing electronic structure codes and have negli-

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gible computational cost. However, the necessary C_6 coefficients and vdW radii (DFT-D), or pseudopotential parameters (DCP), must be empirically determined for each element and have limited transferability. Real dispersion coefficients depend on the oxidation state of an atom and its molecular environment, which is disregarded in the DFT-D and DCP approaches.^{2,32}

Much more satisfying dispersion corrections are now available using system-dependent dispersion coefficients calculated from first principles. Three recently proposed methods provide dispersion coefficients from the ground-state electron density of the system. Tkatchenko and Scheffler³² use Hirshfeld atomic volumes to calculate atom-in-molecule dispersion coefficients from corresponding free-atom dispersion coefficients. Their method yields accurate C_6 coefficients but relies on free-atom reference data for dispersion coefficients and polarizabilities. Sato and Nakai³³ have formulated the local response dispersion (LRD) method, which evaluates polarizabilities and dispersion coefficients from first principles without the need for free-atom reference data. It uses the same local density approximation to the response function as in the DD/ALL and vdW-DF approaches. A multipole expansion of the dispersion energy is introduced, and numerical evaluation of a Casimir–Polder imaginary frequency integral is used to obtain dispersion coefficients,³³ replacing the double numerical integrations required in the ALL and vdW-DF methods.

Preceding both the Tkatchenko–Scheffler and LRD methods is the nonempirical dispersion model of Becke and Johnson.³⁴ This model generates dispersion coefficients from the exchange-hole dipole moment (XDM)³⁵ using occupied orbitals or the electron density.³⁶ Its theoretical foundations have been investigated by various other authors.^{37–39} In addition to the exchange-hole dipole moment, the method uses atom-in-molecule polarizabilities derived from atomic reference data and Hirshfeld atomic volumes.³⁴ A modification introduced by Krishtal et al.⁴⁰ employs intrinsic atomic polarizabilities, obtained by a Hirshfeld partitioning of molecular polarizability tensors, which also gives anisotropy corrections. Kong et al.⁴¹ recently implemented the XDM model self-consistently and assessed the importance of self-consistency on the calculation of dispersion energies and forces.

The XDM dispersion model is part of the DF07 functional,⁴² a universal DFT for thermochemistry, kinetics, and van der Waals interactions.⁴³ DF07 is exact-exchange-based, using 100% Hartree–Fock (HF) exchange. HF exchange is computationally expensive, however, and a combination of XDM dispersion with a pure GGA functional is desirable. Unfortunately, standard exchange GGAs give everything from artificial binding (e.g., LDA, PW91,^{44,45} PBE,⁴⁶ and B86⁴⁷) to strong over-repulsion (B88⁴⁸) in rare-gas diatomic tests, compared to HF repulsion.⁴⁹

In a previous paper,⁵⁰ we benchmarked standard exchange GGAs for their ability to reproduce HF repulsion in 10 rare-gas diatomics and found that the nonempirical exchange GGA of Perdew and Wang (PW86)^{51,52} performs best. This conclusion was reached by comparing GGA exchange-only interaction energies, at equilibrium separations, to exact

Hartree–Fock interaction energies. More recently, Murray, Lee, and Langreth⁵³ have examined standard exchange GGAs in interacting molecular systems (dimers of H₂, N₂, CO₂, ammonia, methane, ethene, benzene, and pyrazine). They also find that PW86 best reproduces Hartree–Fock repulsion energies over a range of intermolecular separations.

We then combined⁵⁰ the PW86 exchange functional with the PBE⁴⁶ correlation functional and the XDM dispersion model as follows,

$$E_{\text{XC}} = E_{\text{X}}^{\text{PW86}} + E_{\text{C}}^{\text{PBE}} + E_{\text{disp}}^{\text{XDM}} \quad (1)$$

and obtained excellent binding energy curves for our 10 rare-gas diatomics. In the present work, we extend the benchmarking of eq 1 from rare-gas diatomics to intermolecular complexes. A comprehensive test set of 65 complexes has been assembled (see section 2), containing vdW interactions from He₂ through electrostatic, hydrogen bonding, and stacking interactions of importance in biochemistry. With only two parameters, an excellent fit is obtained to binding energies spanning 3 orders of magnitude in strength.

In section 3, we compare our results with results from a variety of other methods in the literature. Our method compares quite favorably, especially considering its small number (2) of fitted parameters.

2. Fitting of Dispersion Damping Parameters

In the XDM model of Becke and Johnson, the dispersion energy is given by

$$E_{\text{disp}}^{\text{XDM}} = -\frac{1}{2} \sum_{i \neq j} \left(\frac{C_{6,ij}}{R_{\text{vdW},ij}^6 + R_{ij}^6} + \frac{C_{8,ij}}{R_{\text{vdW},ij}^8 + R_{ij}^8} + \frac{C_{10,ij}}{R_{\text{vdW},ij}^{10} + R_{ij}^{10}} \right) \quad (2)$$

The nonempirical, system-dependent dispersion coefficients $C_{6,ij}$, $C_{8,ij}$, and $C_{10,ij}$ are obtained from the exchange-hole dipole moment and atom-in-molecule polarizabilities using second-order perturbation theory.³⁵ In the “exact-exchange” (XX) version of the XDM model, the dipole moment of the exchange hole is calculated using occupied orbitals.³⁴ Alternatively, the Becke–Roussel density-functional model of the exchange hole⁵⁴ can be used to calculate an approximate dipole moment, giving the “BR” variant of the XDM model.³⁶

The van der Waals separations $R_{\text{vdW},ij}$ in eq 2 are assumed to be linearly related to “critical” interatomic separations $R_{\text{c},ij}$ by

$$R_{\text{vdW},ij} = a_1 R_{\text{c},ij} + a_2 \quad (3)$$

where a_1 and a_2 are universal parameters and $R_{\text{c},ij}$ is the average value of the ratios $(C_{8,ij}/C_{6,ij})^{1/2}$, $(C_{10,ij}/C_{6,ij})^{1/4}$, and $(C_{10,ij}/C_{8,ij})^{1/2}$. At this separation, the three asymptotic dispersion terms are approximately equal to each other:

$$\frac{C_{6,ij}}{R_{\text{c},ij}^6} \approx \frac{C_{8,ij}}{R_{\text{c},ij}^8} \approx \frac{C_{10,ij}}{R_{\text{c},ij}^{10}} \quad (4)$$

and the asymptotic expansion of the dispersion energy is no longer valid.³⁴

In our previous work,⁵⁰ the a_1 and a_2 parameters in eq 3 were fit to the binding energies of 10 rare-gas diatomics. Good performance in rare-gas systems does not, however, guarantee good performance in intermolecular complexes.^{16,55} In this work, we therefore fit the damping parameters to a larger set of 65 complexes. This set includes the following:

- The 22 complexes of the “S22” biochemical benchmark set.⁵⁵ S22 uses CCSD(T) or MP2 geometries, and the binding energies are CCSD(T)/complete basis-set estimates. Monomer deformations are not considered.

- Ten rare-gas diatomics involving He through Kr. We use the experimentally derived data of Tang and Toennies (TT).⁵⁶

- Twelve complexes from the NC31/05 “non-covalent” database of Zhao and Truhlar,^{20,57} excluding those systems duplicated in the S22 and TT sets. The NC31/05 database uses mainly MC-QCISD/3 geometries and W1 binding energies, including monomer deformation energies. We also exclude charge-transfer complexes from our training set, as GGAs strongly overestimate charge-transfer interactions due to severe self-interaction error.^{58,59} This error is partly removed by hybrid functionals that mix in a fraction of HF exchange,^{58,59} and more completely by LC-hybrid methods that use 100% long-range HF exchange.^{27,60} However, the focus of the present work is on a pure GGA functional without inclusion of HF exchange.

- Twenty-one systems from the 45 vdW complexes of Johnson and Becke (JB),³⁴ excluding systems contained in the preceding databases. Binding energies for the JB systems are mainly at the estimated CCSD(T)/complete basis-set limit and do not include monomer deformation energies.

This compilation of reference data from various sources comprises a diverse set of intermolecular complexes with binding energies ranging from 0.022 kcal/mol (He₂) to 20.65 kcal/mol (hydrogen bonded uracil dimer) and including dispersion, hydrogen bonding, electrostatic, and stacking interactions.

The damping parameters a_1 and a_2 are determined by minimizing the root-mean-square percent error (RMS%E)

$$\text{RMS}\%E = 100 \times \sqrt{\frac{1}{N} \sum_i \left(\frac{\text{BE}_i^{\text{calc}} - \text{BE}_i^{\text{ref}}}{\text{BE}_i^{\text{ref}}} \right)^2}$$

of our calculated binding energies $\text{BE}_i^{\text{calc}}$ with respect to the reference binding energies BE_i^{ref} at the reference geometries. Cartesian coordinates for the complexes and monomers of this training set are provided in the Supporting Information. Our calculations were performed with the fully numerical, basis-set-free Numol program of Becke and Dickson^{61–63} using LDA orbitals (i.e., “post-LDA”) and the Perdew–Wang uniform-electron-gas exchange–correlation parametrization.⁶⁴ We use numerical grids of 302 angular points per atom and 80 ($Z \leq 2$), 120 ($2 < Z \leq 10$), 160 ($10 < Z \leq 18$), and 200 ($18 < Z \leq 36$) radial shells per atom.

The binding energies of the 65 complexes are shown in Table 1. Binding energies are taken to be positive quantities, i.e., negative values indicate a repulsive interaction. Table 1

also lists the dispersion contribution to the binding energy, calculated as

$$\% \text{disp} = 100 \times \frac{\text{BE}(\text{PW86PBE-XDM}) - \text{BE}(\text{PW86PBE})}{\text{BE}(\text{PW86PBE-XDM})}$$

Hydrogen bonded complexes have dispersion contributions < 20% and dipolar and “mixed” interactions < 75% (with the exception of the T-shaped benzene dimer), while in dispersion-bound and “stacked” complexes, the contribution of the dispersion energy exceeds 50%.

Table 2 contains the optimized a_1 and a_2 values and error statistics. As can be seen from Tables 1 and 2, PW86PBE describes hydrogen bonding and dipolar (electrostatic) interactions well but fails for dispersion. The addition of the XDM dispersion energy gives accurate binding energies for the whole set of 65 complexes. A few systems (C₂H₄•HF, HF•HF, NH₃•H₂O, H₂S•HCl, and CH₃SH•HCl) are slightly overbound by PW86PBE itself, and addition of the dispersion energy worsens the agreement with the reference binding energies.

Table 2 also shows that, for this set of 65 complexes, the BR variant of the XDM dispersion model is significantly more accurate than the XX version. The opposite result was found in our work on rare-gas diatomics.⁵⁰ This can be understood by considering how well the exchange hole in the XDM dispersion model actually approximates the full exchange–correlation (XC) hole.^{37,38} In rare-gas systems, which do not have nondynamical correlation, the exact-exchange hole (XX) is apparently a better approximation of the XC hole than the approximate BR hole. In molecular systems, however, nondynamical (left–right) correlation leads to a multicenter-to-single-center localization of the XC hole.^{65,66} As the localized XC holes in molecules are more effectively modeled by semilocal (meta-)GGAs such as BR than by the delocalized exact-exchange hole, the BR version of the XDM dispersion model can be expected to work better in intermolecular complexes. Dynamical correlation also contributes to the XC hole, but the dipole moment of the XC hole should be rather insensitive to the effects of dynamical correlation,³⁸ thus justifying the use of the exchange-only hole in the XDM dispersion model.

Table 3 contains the a_1 and a_2 damping parameters for the PW86PBE-XDM functional obtained in our previous work⁵⁰ on rare-gas diatomics. Using these rare-gas-optimized parameters to calculate binding energies for the current set of 65 vdW complexes, we obtain similar error statistics (Table 3) compared to the fit in Table 2. In other words, the damping parameters optimized for rare-gas systems are transferable to more complex intermolecular interactions. Conversely, the damping parameters obtained in this work give good results for the binding energies of rare-gas diatomics, with mean absolute percentage errors (MA%E) of 24.7% for XDM(XX) and 10.3% for XDM(BR). This is very gratifying. The functional of eq 1, with the damped XDM dispersion model of eq 2, is apparently universally applicable to vdW interactions spanning 3 orders of magnitude in strength, with only two fitted parameters.

3. Performance on the S22 Benchmark Set

The “S22” database of Jurecka et al.⁵⁵ contains 22 intermolecular complexes of biochemical interest and covers hy-

Table 1. Binding Energies (kcal/mol), Binding Energy Errors (kcal/mol), and Dispersion Contribution to Binding Energy (%) for the Training Set of 65 vdW Complexes

complex	database	type	PW86PBE			PW86PBE-XDM(XX)			PW86PBE-XDM(BR)		
			BE _{ref}	BE _{calc}	error	BE _{calc}	error	% disp	BE _{calc}	error	% disp
He•He	TT	dispersion	0.022	-0.016	-0.038	0.018	-0.004	189	0.018	-0.004	189
He•Ne	TT	dispersion	0.041	-0.012	-0.053	0.046	0.005	126	0.048	0.007	125
He•Ar	TT	dispersion	0.059	-0.023	-0.082	0.070	0.011	133	0.059	0.000	139
He•Kr	TT	dispersion	0.062	-0.020	-0.082	0.082	0.020	124	0.065	0.003	131
Ne•Ne	TT	dispersion	0.084	-0.007	-0.091	0.094	0.010	107	0.100	0.016	107
Ne•Ar	TT	dispersion	0.132	-0.016	-0.148	0.165	0.033	110	0.143	0.011	111
Ne•Kr	TT	dispersion	0.141	-0.008	-0.149	0.199	0.058	104	0.164	0.023	105
Ar•Ar	TT	dispersion	0.285	-0.063	-0.348	0.345	0.060	118	0.255	-0.030	125
Ar•Kr	TT	dispersion	0.333	-0.065	-0.398	0.435	0.102	115	0.311	-0.022	121
Kr•Kr	TT	dispersion	0.400	-0.071	-0.471	0.552	0.152	113	0.381	-0.019	119
He•N ₂ L-shaped	JB	dispersion	0.053	-0.026	-0.079	0.041	-0.012	163	0.040	-0.013	165
He•N ₂ T-shaped	JB	dispersion	0.066	-0.033	-0.099	0.064	-0.002	152	0.062	-0.004	153
He•FCI	JB	dispersion	0.097	-0.031	-0.128	0.074	-0.023	142	0.077	-0.020	140
FCI•He	JB	dispersion	0.182	0.016	-0.166	0.187	0.005	91	0.157	-0.025	90
CH ₄ •C ₂ H ₄	JB	dispersion	0.50	0.11	-0.39	0.63	0.13	83	0.67	0.17	84
CF ₄ •CF ₄	JB	dispersion	0.78	-0.41	-1.19	0.50	-0.28	181	0.70	-0.08	158
SiH ₄ •CH ₄	JB	dispersion	0.81	-0.06	-0.87	0.89	0.08	106	0.88	0.07	106
CO ₂ •CO ₂	JB	dispersion	1.37	0.28	-1.09	1.19	-0.18	76	1.15	-0.22	76
OCS•OCS	JB	dispersion	1.40	-0.10	-1.50	1.69	0.29	106	1.38	-0.02	107
C ₁₀ H ₈ •C ₁₀ H ₈ parallel	JB	dispersion (stacking)	3.78	-2.70	-6.48	2.87	-0.91	194	4.50	0.72	160
C ₁₀ H ₈ •C ₁₀ H ₈ parallel crossed	JB	dispersion (stacking)	5.28	-2.46	-7.74	3.95	-1.33	162	5.85	0.57	142
C ₁₀ H ₈ •C ₁₀ H ₈ T-shaped	JB	dispersion (stacking)	4.34	-0.39	-4.73	3.38	-0.96	112	4.46	0.12	109
C ₁₀ H ₈ •C ₁₀ H ₈ T-shaped crossed	JB	dispersion (stacking)	3.09	-0.21	-3.30	2.62	-0.47	108	3.50	0.41	106
CH ₄ •NH ₃	JB	dipole-induced dipole	0.73	0.54	-0.19	0.95	0.22	43	0.97	0.24	45
SiH ₄ •HF	JB	dipole-induced dipole	0.73	0.17	-0.56	0.63	-0.10	73	0.62	-0.11	73
CH ₄ •HF	JB	dipole-induced dipole	1.65	1.29	-0.36	1.77	0.12	27	1.76	0.11	27
C ₂ H ₄ •HF	JB	dipole-induced dipole	4.47	4.50	0.03	5.16	0.69	13	5.16	0.69	13
CH ₃ F•CH ₃ F	JB	dipole-dipole	2.33	1.32	-1.01	2.11	-0.22	37	2.16	-0.17	39
H ₂ CO•H ₂ CO	JB	dipole-dipole	3.37	1.95	-1.42	3.03	-0.34	36	2.99	-0.38	35
CH ₃ CN•CH ₃ CN	JB	dipole-dipole	6.16	4.40	-1.76	6.16	0.00	29	6.13	-0.04	28
HCN•HF	JB	hydrogen bonding	7.3	7.27	-0.03	7.75	0.45	6	7.71	0.41	6
(NH ₃) ₂ [C ₂ h]	S22	hydrogen bonding	3.17	2.60	-0.57	3.28	0.11	21	3.24	0.07	20
(H ₂ O) ₂ [Cs]	S22	hydrogen bonding	5.02	4.73	-0.29	5.26	0.24	10	5.23	0.21	9
formic acid dimer [C ₂ h]	S22	hydrogen bonding	18.61	17.38	-1.23	19.08	0.47	9	19.13	0.52	9
formamide dimer [C ₂ h]	S22	hydrogen bonding	15.96	14.30	-1.67	16.04	0.08	11	16.09	0.13	11
uracil dimer [C ₂ h]	S22	hydrogen bonding	20.65	17.98	-2.68	19.91	-0.74	10	20.28	-0.37	11
2-pyridoxine•2-aminopyridine [C ₁]	S22	hydrogen bonding	16.71	14.68	-2.03	16.97	0.26	13	17.44	0.72	16
adenine•thymine WC [C ₁]	S22	hydrogen bonding	16.37	13.65	-2.72	16.11	-0.26	15	16.68	0.31	18
(CH ₄) ₂ [D ₃ d]	S22	dispersion	0.53	-0.14	-0.67	0.52	-0.01	128	0.54	0.01	127
(C ₂ H ₄) ₂ [D ₂ d]	S22	dispersion	1.51	0.01	-1.50	1.41	-0.10	99	1.36	-0.15	99
benzene•CH ₄ [C ₃]	S22	dispersion	1.50	-0.18	-1.68	1.25	-0.25	114	1.48	-0.02	112
benzene dimer parallel displaced [C ₂ h]	S22	dispersion (stacking)	2.73	-2.22	-4.95	1.85	-0.88	220	2.63	-0.10	184
pyrazine dimer [Cs]	S22	dispersion (stacking)	4.42	-1.02	-5.44	3.13	-1.29	133	3.69	-0.73	128
uracil dimer stack [C ₂]	S22	dispersion (stacking)	10.12	2.38	-7.74	7.62	-2.50	69	8.78	-1.35	73
indole•benzene stack [C ₁]	S22	dispersion (stacking)	5.22	-2.55	-7.77	3.02	-2.20	184	4.27	-0.95	160
adenine•thymine stack [C ₁]	S22	dispersion (stacking)	12.23	0.95	-11.28	8.30	-3.93	89	10.07	-2.16	91
ethene•ethyne [C ₂ v]	S22	mixed	1.53	0.97	-0.57	1.72	0.19	44	1.71	0.18	43
benzene•H ₂ O [Cs]	S22	mixed	3.28	1.69	-1.59	3.01	-0.27	44	3.17	-0.11	47
benzene•NH ₃ [Cs]	S22	mixed	2.35	0.65	-1.70	2.05	-0.30	68	2.22	-0.13	71

Table 1. Continued

complex	database	type	PW86PBE			PW86PBE-XDM(XX)			PW86PBE-XDM(BR)		
			BE ^{ref}	BE ^{calc}	error	BE ^{calc}	error	% disp	BE ^{calc}	error	% disp
benzene•HCN [Cs]	S22	mixed	4.46	2.35	-2.12	4.01	-0.45	42	4.15	-0.31	43
benzene dimer T-shaped [C2v]	S22	mixed	2.74	-0.24	-2.98	1.94	-0.80	112	2.40	-0.34	110
indole-benzene T-shaped [C1]	S22	mixed	5.73	1.45	-4.28	4.31	-1.42	66	4.95	-0.79	71
phenol dimer [C1]	S22	mixed	7.05	3.62	-3.43	6.00	-1.05	40	6.52	-0.53	45
HF•HF	HB6/04	hydrogen bonding	4.57	4.59	0.02	4.92	0.35	7	4.91	0.34	7
NH3•H2O	HB6/04	hydrogen bonding	6.41	6.52	0.11	7.14	0.73	9	7.12	0.71	8
H2S•H2S	D16/04	dipole-dipole	1.66	1.29	-0.37	2.22	0.56	42	2.02	0.36	36
HCl•HCl	D16/04	dipole-dipole	2.01	1.81	-0.21	2.66	0.65	32	2.43	0.42	26
H2S•HCl	D16/04	dipole-dipole	3.35	3.66	0.31	4.70	1.35	22	4.43	1.08	17
CH3Cl•HCl	D16/04	dipole-dipole	3.55	2.97	-0.58	4.34	0.79	32	4.06	0.51	27
HCN•CH3SH	D16/04	dipole-dipole	3.59	3.11	-0.48	4.33	0.74	28	4.20	0.61	26
CH3SH•HCl	D16/04	dipole-dipole	4.16	4.89	0.73	6.46	2.30	24	6.14	1.98	20
CH4•Ne	W17/05	dispersion	0.22	-0.04	-0.26	0.14	-0.08	126	0.14	-0.08	124
C6H6•Ne	W17/05	dispersion	0.47	-0.14	-0.61	0.27	-0.20	152	0.35	-0.13	140
C2H2•C2H2	PPS5/05	dispersion (stacking)	1.34	0.88	-0.46	1.73	0.39	49	1.64	0.30	46
C6H6•C6H6 parallel	PPS5/05	dispersion (stacking)	1.81	-2.02	-3.83	0.82	-0.99	347	1.49	-0.32	235

Table 2. Optimized Dispersion Damping Parameters and Error Statistics for the Training Set of 65 vdW Complexes

dispersion	none	XDM(XX)	XDM(BR)
a_1		0.68	0.82
a_2 (Å)		1.43	1.16
RMS%E (%)	96.8	24.0	15.8
MA%E (%)	79.1	19.9	12.6
MAE (kcal/mol)	1.72	0.53	0.33
MaxE(-) (kcal/mol)	-11.28	-3.93	-2.16
MaxE(+) (kcal/mol)	0.73	2.30	1.98
	(A•T stack)	(A•T stack)	(A•T stack)
	(CH3SH•HCl)	(CH3SH•HCl)	(CH3SH•HCl)

Table 3. Error Statistics for the Current Set of 65 vdW Complexes Using Rare-Gas-Optimized Damping Parameters⁵⁰

dispersion	XDM(XX)	XDM(BR)
a_1	0.95	0.75
a_2 (Å)	0.87	1.25
RMS%E (%)	30.5	18.9
MA%E (%)	23.3	14.2
MAE (kcal/mol)	0.73	0.35
MaxE(-) (kcal/mol)	-5.95 (A•T stack)	-0.76 (A•T stack)
MaxE(+) (kcal/mol)	1.74 (CH3SH•HCl)	2.26 (CH3SH•HCl)

drogen bonding, dispersion, and stacking interactions. It provides CCSD(T) binding energies at the estimated complete basis-set limit and has been widely adopted to assess the performance of electronic structure methods for intermolecular interactions. In Table 4, we list mean absolute errors (MAE, kcal/mol) and mean absolute percent errors (MA%E) for a variety of DFT methods for which benchmark data on the S22 set are available in the literature.^{17,19,27,30,32,33,67-71}

The Becke–Roussel variant of the XDM dispersion model, XDM(BR), gives excellent binding energies for the S22 set as demonstrated by its low MAE and MA%E values. Its accuracy is comparable to the empirical DFT-D methods, the highly parametrized M06-2X and ω B97X functionals, and the much more expensive “double hybrid” functionals (which include nonlocal correlation through second order MP2 perturbation theory). By coincidence, our previous damping parameter fit to rare-gas systems⁵⁰ (denoted as “TT” in Table 4) gives slightly better error statistics than the current fit to 65 intermolecular complexes. We also note that the exact-exchange version of the XDM dispersion model, XDM(XX), is much less accurate for the S22 set for reasons explained in section 2. Given its higher accuracy and lower computational cost, we prefer the XDM(BR) variant over XDM(XX). XDM(BR) is also the method which was recently implemented self-consistently.⁴¹

The nonempirical dispersion approaches of Sato and Nakai (LRD) and Tkatchenko and Scheffler (TS) also give excellent binding energies for the S22 set, as do the empirical (DFT-D) dispersion corrections. The van der Waals density functional (vdW-DF) is less accurate, and as shown by Gulans et al.⁶⁷ and Klimes et al.,⁶⁸ the results depend on the underlying exchange functional. With revPBE⁷² exchange, the complexes of the S22 set are systematically underbound,^{67,68}

Table 4. Mean Absolute Errors (MAE, kcal/mol) of Various DFT Methods for the S22 Set and the Subsets of Hydrogen-Bonded (HB), Dispersion-Dominated (disp), and Mixed (mix) Complexes, As Well As Mean Absolute Percentage Errors (MA%E) for the S22 Set^a

method	type	MAE (S22)	MAE (HB)	MAE (disp)	MAE (mix)	MA%E
PW86PBE-XDM(BR)	GGA-XDM	0.46	0.33	0.68	0.34	7.4
PW86PBE-XDM(BR) TT ⁵⁰	GGA-XDM	0.31	0.52	0.27	0.14	6.2
PW86PBE-XDM(XX)	GGA-XDM	0.81	0.31	1.39	0.64	14.3
PW86PBE-XDM(XX) TT ⁵⁰	GGA-XDM	1.33	0.43	2.39	1.03	26.7
vdW-DF(revPBE) ⁶⁷	GGA+vdW-DF	1.39	2.81	0.79	0.65	18.3
vdW-DF(B86) ⁶⁸	GGA+vdW-DF	0.53	0.76	0.58	0.23	na
LC-BOP+LRD(6 + 8+10) ³³	LC hybrid GGA+LRD	0.27	0.35	0.20	0.28	5.7
PBE+TS ³²	GGA+TS	0.30	0.46	0.30	0.14	na
<i>ω</i> B97X-D ²⁷	LC hybrid GGA-D	0.22	0.24	0.26	0.17	5.4
B97-D ²⁷	GGA-D	0.50	0.84	0.43	0.24	6.4
B3LYP-D ²⁷	hybrid GGA-D	0.48	0.81	0.35	0.28	8.5
BLYP-D ²⁷	GGA-D	0.33	0.28	0.52	0.16	8.6
revPBE+LAP ³⁰	GGA-DCP(LAP)	0.57	1.11	0.42	0.22	7.0
B3LYP-DCP ⁶⁹	hybrid GGA-DCP	0.93	1.34	0.90	0.56	20.4
M06-2X ¹⁹	hybrid meta-GGA	0.40	0.70	0.17	0.35	6.4
M05-2X ¹⁷	hybrid meta-GGA	0.86	0.75	1.26	0.53	14.8
mPW2PLYP-D ⁷¹	double hybrid GGA-D	0.46	0.50	0.70	0.16	8.4
B2PLYP-D ⁷¹	double hybrid GGA-D	0.27	0.18	0.48	0.12	6.6
<i>ω</i> B97X-2(LP) ⁷⁰	LC double hybrid GGA	0.24	0.21	0.30	0.22	7.4

^a Methods using optimized geometries instead of the S22 reference geometries are shown in *italics*.

while the combination of B86⁴⁷ exchange and vdW-DF gives substantially improved results.⁶⁸

A similar case is B3LYP-DCP,⁶⁹ which combines the dispersion-correcting pseudopotentials of DiLabio and Mackie⁷³ with the B3LYP^{74,75} functional. Due to the use of overly repulsive B88 exchange⁴⁸ in B3LYP, B3LYP-DCP underbinds all systems in the S22 database except for the water dimer.⁶⁹ The revPBE+LAP³⁰ method, which combines the revPBE⁷² exchange-correlation functional with a dispersion-correcting local atomic potential (LAP),³⁰ does not suffer from this deficiency but is still rather inaccurate for hydrogen-bonded complexes.

A variety of DFT methods reproduce the binding energies of the intermolecular complexes in the S22 database very well. Those that use nonempirical dispersion coefficients and only a few parameters in their damping functions are the present XDM(BR), the LRD of Sato and Nakai, and the Tkatchenko–Scheffler methods. The nonempirical vdW-DF is comparably less accurate with the original revPBE exchange but can be improved by changing the underlying exchange functional.⁶⁸ The influence of the exchange functional is well-known^{49,76,77} but has been somewhat overlooked until the recent studies of refs 50, 53, and 68 and the present work.

4. Conclusions

We have shown that the XDM dispersion model of Becke and Johnson can be combined with standard GGAs for exchange (PW86) and correlation (PBE) to give an excellent description of van der Waals interactions. The XDM dispersion model contains only two empirical parameters in the damping function. These have been fit to a set of 65 complexes ranging from rare-gas systems to nucleic acid base pairs and spanning 3 orders of magnitude in binding energy strength. Also, the dispersion damping parameters optimized for rare-gas diatomics in our previous work⁵⁰ are found to be highly transferable to the larger set of intermolecular interactions.

The Becke–Roussel variant of XDM, XDM(BR), is more accurate for intermolecular complexes than the exact-exchange-hole variant, XDM(XX), and we have rationalized this result. The performance of the XDM dispersion model on the S22 database has been compared to a variety of alternative DFT methods that account for dispersion, and the XDM(BR) method compares very favorably. In future work, we will explore geometry optimizations of intermolecular complexes using XDM-derived dispersion forces.

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Supporting Information Available: Cartesian coordinates and reference binding energies for the training set of 65 intermolecular complexes (XYZ file format). This material is available free of charge via the Internet at <http://pubs.acs.org/>.

References

- (1) Kristyán, S.; Pulay, P. *Chem. Phys. Lett.* **1994**, *229*, 175.
- (2) Johnson, E. R.; Mackie, I. D.; DiLabio, G. A. *J. Phys. Org. Chem.* **2009**, *22*, 1127.
- (3) Andersson, Y.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **1996**, *76*, 102.
- (4) Dobson, J. F.; Dinte, B. P. *Phys. Rev. Lett.* **1996**, *76*, 1780.
- (5) Kamiya, M.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2002**, *117*, 6010.
- (6) Sato, T.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2007**, *126*, 234114.
- (7) Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2004**, *92*, 246401.
- (8) Thonhauser, T.; Cooper, V. R.; Li, S.; Puzder, A.; Hyldgaard, P.; Langreth, D. C. *Phys. Rev. B* **2007**, *76*, 125112.

- (9) Langreth, D. C.; Lundqvist, B. I.; Chakarova-Kack, S. D.; Cooper, V. R.; Dion, M.; Hyldgaard, P.; Kelkkanen, A.; Kleis, J.; Kong, L.; Li, S.; Moses, P. G.; Murray, E.; Puzder, A.; Rydberg, H.; Schroder, E.; Thonhauser, T. *J. Phys.: Condens. Matter* **2009**, *21*, 084203.
- (10) Ángyán, J. G.; Gerber, I. C.; Savin, A.; Toulouse, J. *Phys. Rev. A* **2005**, *72*, 012510.
- (11) Gerber, I. C.; Ángyán, J. G. *J. Chem. Phys.* **2007**, *126*, 044103.
- (12) Goll, E.; Werner, H.-J.; Stoll, H. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3917.
- (13) Goll, E.; Leininger, T.; Manby, F. R.; Mitrushchenkov, A.; Werner, H.-J.; Stoll, H. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3353.
- (14) Xu, X.; Goddard, W. A. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 2673.
- (15) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.
- (16) Cerny, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1624.
- (17) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2007**, *3*, 289.
- (18) Sherrill, C. D.; Takatani, T.; Hohenstein, E. G. *J. Phys. Chem. A* **2009**, *113*, 10146.
- (19) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. C* **2008**, *112*, 4061.
- (20) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2005**, *1*, 415.
- (21) Wu, X.; Vargas, M. C.; Nayak, S.; Lotrich, V.; Scoles, G. *J. Chem. Phys.* **2001**, *115*, 8748.
- (22) Wu, Q.; Yang, W. *J. Chem. Phys.* **2002**, *116*, 515.
- (23) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463.
- (24) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.
- (25) Ortmann, F.; Bechstedt, F.; Schmidt, W. G. *Phys. Rev. B* **2006**, *73*, 205101.
- (26) Jurecka, P.; Cerný, J.; Hobza, P.; Salahub, D. R. *J. Comput. Chem.* **2007**, *28*, 555.
- (27) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615.
- (28) von Lilienfeld, O. A.; Tavernelli, I.; Rothlisberger, U.; Sebastiani, D. *Phys. Rev. Lett.* **2004**, *93*, 153004.
- (29) Lin, I.-C.; Coutinho-Neto, M. D.; Felsenheimer, C.; von Lilienfeld, O. A.; Tavernelli, I.; Rothlisberger, U. *Phys. Rev. B* **2007**, *75*, 205131.
- (30) Sun, Y. Y.; Kim, Y.-H.; Lee, K.; Zhang, S. B. *J. Chem. Phys.* **2008**, *129*, 154102.
- (31) DiLabio, G. A. *Chem. Phys. Lett.* **2008**, *455*, 348.
- (32) Tkatchenko, A.; Scheffler, M. *Phys. Rev. Lett.* **2009**, *102*, 073005.
- (33) Sato, T.; Nakai, H. *J. Chem. Phys.* **2009**, *131*, 224104.
- (34) Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2006**, *124*, 174104.
- (35) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2007**, *127*, 154108.
- (36) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2005**, *123*, 154101.
- (37) Ángyán, J. G. *J. Chem. Phys.* **2007**, *127*, 024108.
- (38) Ayers, P. *J. Math. Chem.* **2009**, *46*, 86.
- (39) Heßelmann, A. *J. Chem. Phys.* **2009**, *130*, 084104.
- (40) Krishtal, A.; Vanommeslaeghe, K.; Olasz, A.; Veszpremi, T.; Van Alsenoy, C.; Geerlings, P. *J. Chem. Phys.* **2009**, *130*, 174101.
- (41) Kong, J.; Gan, Z.; Proynov, E.; Freindorf, M.; Furlani, T. R. *Phys. Rev. A* **2009**, *79*, 042510.
- (42) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2007**, *127*, 124108.
- (43) Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2008**, *128*, 124105.
- (44) Perdew, J. P. In *Electronic Structure of Solids '91*; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991.
- (45) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.
- (46) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (47) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524.
- (48) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (49) Lacks, D. J.; Gordon, R. G. *Phys. Rev. A* **1993**, *47*, 4681.
- (50) Kannemann, F. O.; Becke, A. D. *J. Chem. Theory Comput.* **2009**, *5*, 719.
- (51) Perdew, J. P.; Yue, W. *Phys. Rev. B* **1986**, *33*, 8800.
- (52) Perdew, J. P.; Yue, W. *Phys. Rev. B* **1989**, *40*, 3399.
- (53) Murray, E. D.; Lee, K.; Langreth, D. C. *J. Chem. Theory Comput.* **2009**, *5*, 2754.
- (54) Becke, A. D.; Roussel, M. R. *Phys. Rev. A* **1989**, *39*, 3761.
- (55) Jurecka, P.; Sponer, J.; Cerny, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985.
- (56) Tang, K. T.; Toennies, J. P. *J. Chem. Phys.* **2003**, *118*, 4976.
- (57) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 5656.
- (58) Ruiz, E.; Salahub, D. R.; Vela, A. *J. Am. Chem. Soc.* **1995**, *117*, 1141.
- (59) Ruiz, E.; Salahub, D. R.; Vela, A. *J. Phys. Chem.* **1996**, *100*, 12265.
- (60) Chai, J.-D.; Head-Gordon, M. *J. Chem. Phys.* **2008**, *128*, 084106.
- (61) Becke, A. D.; Dickson, R. M. *J. Chem. Phys.* **1988**, *89*, 2993.
- (62) Becke, A. D. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1989**, *23*, 599.
- (63) Becke, A. D.; Dickson, R. M. *J. Chem. Phys.* **1990**, *92*, 3610.
- (64) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
- (65) Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403.
- (66) Becke, A. D. *J. Chem. Phys.* **2005**, *122*, 064101.
- (67) Gulans, A.; Puska, M. J.; Nieminen, R. M. *Phys. Rev. B* **2009**, *79*, 201105.
- (68) Klimes, J.; Bowler, D. R.; Michaelides, A. *J. Phys.: Condens. Matter* **2010**, *22*, 022201.
- (69) Nilsson Lill, S. O. *J. Phys. Chem. A* **2009**, *113*, 10321.
- (70) Chai, J.-D.; Head-Gordon, M. *J. Chem. Phys.* **2009**, *131*, 174105.
- (71) Schwabe, T.; Grimme, S. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3397.

- (72) Zhang, Y.; Yang, W. *Phys. Rev. Lett.* **1998**, 80, 890.
- (73) Mackie, I. D.; DiLabio, G. A. *J. Phys. Chem. A* **2008**, 112, 10968.
- (74) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.
- (75) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.
- (76) Wesolowski, T.; Parisel, O.; Ellinger, Y.; Weber, J. *J. Phys. Chem. A* **1997**, 101, 7818.
- (77) Zhang, Y.; Pan, W.; Yang, W. *J. Chem. Phys.* **1997**, 107, 7921.

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