

Van der Waals Interactions in Density-Functional Theory: Rare-Gas Diatomics

Felix O. Kannemann and Axel D. Becke*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia,
Canada B3H 4J3

Received December 1, 2008

Abstract: The application of conventional GGA and meta-GGA density functionals to van der Waals interactions is fraught with difficulties. Conventional functionals do not contain the physics of the dispersion interaction. To make matters worse, the exchange part alone can yield anything from severe overbinding to severe over-repulsion depending on the choice of functional. We have assessed a variety of exchange GGAs for their ability to reproduce exact Hartree–Fock repulsion energies in rare-gas systems, and we find that PW86 [*Phys. Rev. B* 1986, 33, 8800] performs remarkably well. The addition of a dynamical correlation GGA and the nonempirical dispersion model of Becke and Johnson [*J. Chem. Phys.* 2007, 127, 154108] to PW86 gives a simple GGA plus dispersion theory yielding excellent rare-gas interaction curves for pairs involving He through Kr, with only two adjustable parameters for damping of the dispersion terms.

1. Introduction

Density functional theory (DFT) is a successful and accurate method for electronic structure calculations of atoms, molecules, and solids. Its application to soft matter and weakly bound systems, including intermolecular complexes, biomolecules, molecular crystals, and polymers, depends on a realistic description of van der Waals (vdW) interactions including the London dispersion force. Dispersion arises from correlated motions of electrons on well-separated systems and is an inherently nonlocal electron correlation effect. Density functionals based on the local density approximation (LDA) or the semilocal generalized gradient approximation (GGA) do not account for such long-range correlations and, consequently, fail to reproduce the attractive R^{-6} behavior of the interatomic potential between closed-shell atoms at large separation R .¹

Problems with LDA and GGA functionals in vdW interactions arise not only in the asymptotic region, however. At the equilibrium separation of typical dispersion-bound van der Waals complexes, such as rare-gas diatomics or stacked aromatic rings, there is a weak wave function overlap leading to considerable Hartree–Fock (HF) repulsion between the monomers. Lacks and Gordon² found that LDA and GGA

exchange functionals applied to the helium and neon dimers give widely varying interaction energies, from too repulsive (B88)³ to spurious binding (LDA, PW91^{4,5}), when compared to exact Hartree–Fock repulsion.

A DFT treatment of vdW interactions should address both issues, the erratic behavior of approximate exchange functionals near equilibrium separations, as well as the missing long-range attraction caused by dispersion.⁶ Many different approaches have been used in the literature and only a superficial overview is given here. For more complete discussions, see refs 1 and 6–8.

The van der Waals density functional (vdW-DF) approach of Langreth et al.^{9,10} uses an approximate nonlocal correlation functional derived from response theory to account for long-range dispersion interactions. It is combined with revPBE¹¹ exchange and LDA correlation to give a seamless functional valid at all interatomic distances. The revPBE GGA was chosen for exchange as it does not produce artificial binding in vdW complexes.^{12,13} The original vdW-DF method consistently overestimated the separation in vdW complexes, which was ascribed to the overestimation of Hartree–Fock repulsion by revPBE.¹⁰ The substitution of revPBE by HF exchange indeed improves the separations and establishes the correct relative stability of different benzene dimer conformations but leads to significant overestimation of

* To whom correspondence should be addressed. E-mail: axel.becke@dal.ca.

binding energies,^{14–16} suggesting that the nonlocal correlation part in vdW-DF is not fully compatible with HF exchange.

Other nonempirical approaches circumvent the problems associated with approximate exchange functionals by using a separation of the electron–electron interaction into a long-range part treated exactly and a short-range part described by an exchange GGA. The method of Hirao et al.^{17,18} combines long-range HF with short-range B88³ exchange. Short-range correlation is treated by the OP¹⁹ functional, while the long-range correlation comes from the nonlocal Andersson–Langreth–Lundqvist²⁰ (ALL) vdW functional multiplied by a damping function depending on empirical atomic radii. The range-separated hybrid (RSH+MP2) method of Ángyán et al.^{6,21} employs the LDA for short-range exchange and correlation, HF for long-range exchange, and second-order perturbation theory (MP2) to account for the dispersion interaction in a seamless manner.

The three methods mentioned so far have in common that long-range dispersion is treated by explicitly nonlocal correlation functionals of the vdW-DF, ALL, or MP2 type. These are inherently more computationally demanding than the (semi)local functionals of conventional DFT. To retain the computational efficiency of DFT, empirical dispersion terms of the form $-C_6/R^6$ have been added to conventional density functionals to give methods collectively known as DFT-D.^{8,22–24} The C_6 coefficients are empirical parameters derived from fits, atomic calculations, or approximate formulas. In addition, the dispersion term must be attenuated at small separations R by damping functions depending on empirical vdW radii. Some DFT-D methods use additional global scaling factors that depend on the underlying density functional to account for differences in the description of Hartree–Fock repulsion^{8,24} and may include reparametrization.²⁴

Another approach involves modifying standard DFT functionals to give a good description of van der Waals interactions without an explicit dispersion or nonlocal correlation correction. This is done by refitting the exchange–correlation functional while including van der Waals complexes in the training set.^{25–29} An exception is the Wilson–Levy correlation functional³⁰ combined with HF exchange, which gives good results for various vdW complexes near their equilibrium distances without adjustment, although lacking theoretical justification.³¹

In summary, previous attempts to make DFT applicable to van der Waals complexes either (a) include explicitly nonlocal correlation which is computationally demanding, (b) introduce highly empirical dispersion corrections, or (c) refit functionals that are fundamentally unable to account for dispersion interactions to van der Waals data nevertheless.

The nonempirical dispersion model of Becke and Johnson^{32–37} has previously been used in conjunction with exact Hartree–Fock exchange^{38,39} to give an accurate treatment of vdW interactions. In this work, we replace Hartree–Fock exchange with an exchange GGA that well reproduces Hartree–Fock repulsion in rare-gas diatomics. This functional is then combined with various correlation GGAs and the Becke–Johnson dispersion model. The

method is calibrated on all pair interactions between the atoms He, Ne, Ar, and Kr and yields excellent equilibrium separations, binding energies, and interatomic potential energy curves.

2. Hartree–Fock Repulsion in Rare-Gas Diatomics

Hartree–Fock theory gives (in the complete basis set limit) repulsive potentials for rare-gas diatomics. Exchange functionals should accurately reproduce this Hartree–Fock repulsion if DFT is to be applied to vdW interactions.

The only systematic benchmark study of the ability of exchange functionals to reproduce Hartree–Fock repulsion in rare-gas diatomics is by Lacks and Gordon.² They showed that most exchange functionals give large errors, over 100%, for the exchange-only interaction energy in He₂ and Ne₂, even though total atomic exchange energies are within 1%. Some functionals such as B88 are too repulsive, others such as PW91 or the LDA give an artifactual *attractive* interaction.

The broad range of exchange-only interaction energies obtained from approximate functionals is illustrated in Figure 1 for the neon dimer. The interaction energy of two Ne atoms is plotted as a function of interatomic separation for exact HF exchange, the exchange-only LDA (xLDA), and the GGA exchange functionals B86,⁴⁰ B86b,⁴¹ B88,³ PW86,⁴² PW91,^{4,5} PBE,^{43,44} and revPBE.¹¹ The HF and xLDA curves are self-consistent. The GGA curves are evaluated using the xLDA orbitals (i.e., post-xLDA). All calculations are performed with the fully numerical, basis-set-free Numol program of Becke and Dickson.^{45,46}

Van der Waals interaction curves are extremely sensitive to the choice of GGA exchange functional.^{47–50} We obtain in Figure 1 everything from massive “binding” of $\sim 500 \mu\text{H}$ (xLDA and PW91) to repulsion of $\sim 800 \mu\text{H}$ (B88) compared to the exact Hartree–Fock repulsion energy of $\sim 100 \mu\text{H}$ at the experimental equilibrium separation of Ne₂.⁵¹ The curves can be ordered according to the behavior of the exchange GGA at large reduced density gradient χ

$$\chi(\mathbf{r}) = \frac{|\nabla p(\mathbf{r})|}{p(\mathbf{r})^{4/3}} \quad (1)$$

GGA exchange functionals can be expressed in the form

$$E_X^{\text{GGA}} = \int e_X^{\text{LDA}}(\mathbf{r}) F[\chi(\mathbf{r})] \quad (2)$$

where e_X^{LDA} is the LDA exchange energy density, and $F[\chi(\mathbf{r})]$ is the “exchange enhancement factor”. Standard exchange GGAs, such as those in Figure 1, all have similar behavior for small χ . However, they behave very differently at large χ (see Figure 1 in ref 47), corresponding in real space to the region very far from nuclei (i.e., the asymptotic tail density). The functionals displaying artifactual binding in Figure 1 are those with relatively small enhancement factor at large χ ; those being overly repulsive have relatively large enhancement factor at large χ . Inspection of Figure 1 suggests that PW86 best reproduces the exact Hartree–Fock repulsion curve in Ne₂, especially near the equilibrium separation.

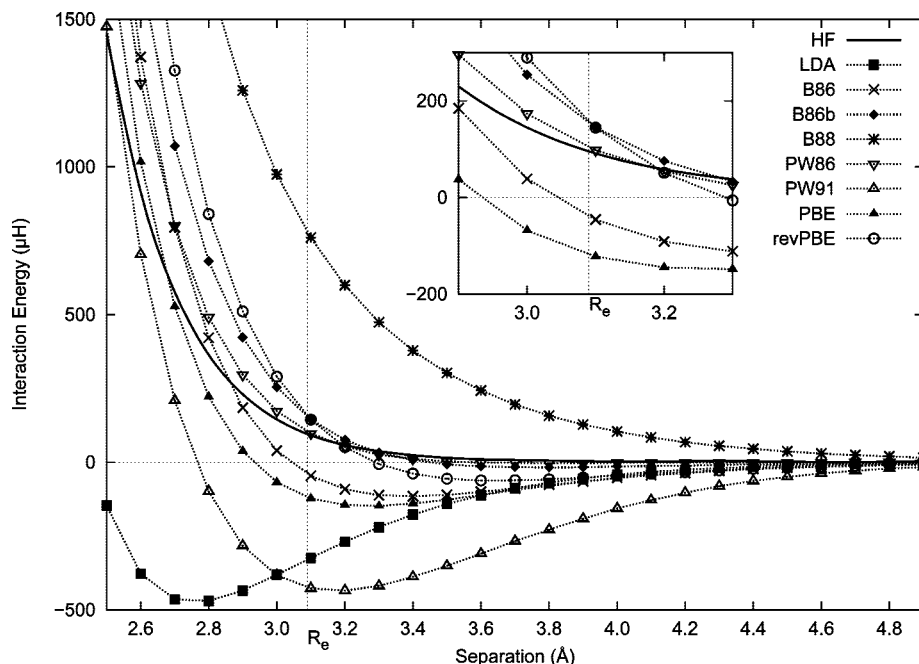


Figure 1. Hartree–Fock repulsion, xLDA, and exchange-only GGA interaction energies of Ne_2 .

Table 1. Hartree–Fock Repulsion Energies (μH) for Rare-Gas Diatomics at Tang–Toennies Reference Equilibrium Separations $r_{\text{ref}}^{\text{TT}}$ (Å)

	$r_{\text{ref}}^{\text{TT}51}$	ΔE^{HF}
He_2	2.97	28
He–Ne	3.05	47
He–Ar	3.50	85
He–Kr	3.69	103
Ne_2	3.09	96
Ne–Ar	3.48	190
Ne–Kr	3.65	227
Ar_2	3.76	435
Ar–Kr	3.89	538
Kr_2	4.01	674

Table 2. Hartree–Fock Repulsion Energy Errors (%) of Exchange GGAs at Reference Equilibrium Separations $r_{\text{ref}}^{\text{TT}}$ (Post-HF)

	B86	B86b	B88	PW86	PW91	PBE	revPBE
MPE	−76	32	374	34	−337	−106	2
MAPE	85	34	374	34	337	106	60
MaxAPE	239	57	679	53	832	259	153

Table 3. Hartree–Fock Repulsion Energy Errors (%) of Exchange GGAs at Reference Equilibrium Separations $r_{\text{ref}}^{\text{TT}}$ (Post-xLDA)

	B86	B86b	B88	PW86	PW91	PBE	revPBE
MPE	−96	53	542	20	−418	−158	51
MAPE	111	53	542	22	418	158	75
MaxAPE	309	72	1126	82	1133	381	124

Lacks and Gordon concluded that PW86 and B86b best reproduced Hartree–Fock repulsion in He_2 and Ne_2 on the basis of post-HF calculations with the xLDA, PW86, PW91, B86, B86b, B88, and DK87⁵² functionals.

We have extended their assessment to all pair interactions between the rare-gas atoms He, Ne, Ar, and Kr, using both

Table 4. Exact (Hartree–Fock) and PW86 Repulsion Energies (μH) for Rare-Gas Diatomics at Equilibrium Separations. Worst Cases (MaxAPE) in Bold

	ΔE^{HF} SCF, numerical	ΔE^{PW86} post-xLDA, numerical	ΔE^{PW86} SCF, aug-cc-pV5Z (aug-cc-pV6Z, aug-pc-4) CP
He_2	28	51	29 (30, 30)
He–Ne	47	64	52 (50, 51)
He–Ar	85	107	87 (89, 88)
He–Kr	103	116	98
Ne_2	96	104	117 (113, 115)
Ne–Ar	190	189	198 (197, 198)
Ne–Kr	227	201	219
Ar_2	435	505	503 (507, 512)
Ar–Kr	538	611	626
Kr_2	674	764	796
MPE		20	8 (6, 6)
MAPE		22	10 (6, 6)
MaxAPE		82	22 (18, 20)

Hartree–Fock and xLDA orbitals, and including the exchange functionals PBE^{43,44} and revPBE.¹¹ Table 1 shows exact Hartree–Fock repulsion energies ΔE^{HF} computed with Numol at the reference equilibrium separations of Tang and Toennies.⁵¹ Table 2 gives the mean percent error (MPE), mean absolute percent error (MAPE) and maximum absolute percent error (MaxAPE) of GGA exchange functionals with respect to ΔE^{HF} , evaluated using Hartree–Fock orbitals (i.e., post-HF). In agreement with Lacks and Gordon, B86b and PW86 best reproduce Hartree–Fock repulsion. With xLDA orbitals however, we find that PW86 is superior to all other functionals tested (Table 3). Self-consistent GGA calculations are currently not possible with Numol.

We then used Gaussian03⁵³ to obtain fully self-consistent interaction energies with the PW86 functional using the keyword iop(3/74=800). A numerical integration grid of 400 radial shells and 590 angular points per atom was used, the SCF convergence criterion was set to 10^{-8} with full integral accuracy during the SCF cycles. We used the aug-cc-pV5Z^{54–57}

basis set throughout as well as aug-cc-pV6Z^{58,59} and aug-pc-4⁶⁰ for the subset of systems containing only He, Ne, and Ar atoms because these basis sets are not available for Kr. Basis sets were obtained from the EMSL basis-set library.^{61,62} The counterpoise (CP)⁶³ procedure was used to correct for basis set superposition error, which was found to be up to 5% of ΔE^{PW86} for He–Ne and Ne₂ with the aug-cc-pV5Z basis set. The resulting PW86/aug-cc-pV5Z-CP interaction energies are given in Table 4, with results for aug-cc-pV6Z and aug-pc-4 in parentheses. The self-consistent PW86 interaction energies are even more accurate than the post-HF and post-xLDA results. In particular, the overestimation of Hartree–Fock repulsion in He₂ is significantly improved.

PW86 is a remarkably accurate exchange GGA for reproducing Hartree–Fock repulsion energies in rare-gas diatomics. Compared to more sophisticated approaches to correct for deficiencies in approximate exchange functionals when applied to van der Waals complexes, such as the use of long-range Hartree–Fock exchange^{6,17,18,21} or exact-exchange-based functionals themselves,^{31,36,37} it has the obvious benefit of computational efficiency.

PW86 is also appealing because of its simple functional form and the absence of any empirical parameters.⁴² As with any typical GGA, it gives atomic exchange energies accurate to within 1%,^{2,42} and is therefore of similar utility for general quantum chemistry as the more popular functionals B88, PW91, or PBE (see section 5).

3. Dynamical Correlation and Dispersion Corrections

Having found a suitable exchange GGA for use with van der Waals interactions, we now consider the correlation functional. Typical semilocal correlation functionals account for short-range dynamical correlation arising from interelectronic cusp conditions.⁶⁴ Semilocal functionals are inherently unable to describe the long-range electron correlations between *nonoverlapping* fragments that give rise to the asymptotic dispersion interaction.^{1,6,12,65} The application of GGAs to van der Waals interactions therefore requires an explicit long-range dispersion correction. Empirical corrections have been used successfully but suffer from limited applicability and transferability.^{7,8,22–24,66–68} The recent dispersion model of Becke and Johnson,³⁵ however, is nonempirical.

The Becke–Johnson model employs the dipole moment of an electron and its associated exchange hole (as an approximation to the full exchange–correlation hole) as the

source of position-dependent multipole moments leading to the dispersion interaction.^{32,35,69} System-dependent interatomic dispersion coefficients $C_{6,ij}$, $C_{8,ij}$, and $C_{10,ij}$ are thus obtained from the exchange-hole dipole moment, effective atomic polarizabilities, and second-order perturbation theory. The dispersion model has two variants, an exact-exchange version where the dipole moment of the exchange hole and its reference electron is calculated using occupied orbitals (XX), and a density-functional version based on the Becke–Roussel model of the exchange hole (BR).⁷⁰

The asymptotic dispersion terms need to be damped at small separations R . The Becke–Johnson scheme³⁷ uses

$$E_{\text{disp}} = -\frac{1}{2} \sum_{i \neq j} \left(\frac{C_{6,ij}}{R_{\text{vdW},ij}^6 + R_{ij}^6} + \frac{C_{8,ij}}{R_{\text{vdW},ij}^8 + R_{ij}^8} + \frac{C_{10,ij}}{R_{\text{vdW},ij}^{10} + R_{ij}^{10}} \right) \quad (3)$$

where the sum is over all pairs of atoms i and j , and the effective interatomic van der Waals separation $R_{\text{vdW},ij}$ is related to a “critical” interatomic separation $R_{c,ij}$ by

$$R_{\text{vdW},ij} = a_1 R_{c,ij} + a_2 \quad (4)$$

The critical separation $R_{c,ij}$ is given by the average value of the ratios $(C_{8,ij}/C_{6,ij})^{1/2}$, $(C_{10,ij}/C_{6,ij})^{1/4}$, and $(C_{10,ij}/C_{8,ij})^{1/2}$, and corresponds to the separation where the three asymptotic dispersion terms are approximately equal in magnitude

$$\frac{C_{6,ij}}{R_{ij}^6} \approx \frac{C_{8,ij}}{R_{ij}^8} \approx \frac{C_{10,ij}}{R_{ij}^{10}} \quad (5)$$

This is where the asymptotic series expansion is expected to break down. The two coefficients a_1 and a_2 in eq 4 are empirical parameters assumed to be universal and determined as described below.

We combine the PW86 exchange functional with various GGA functionals for dynamical correlation $E_{\text{C}}^{\text{GGA}}$ and the Becke–Johnson dispersion model as follows:

$$E_{\text{XC}} = E_{\text{X}}^{\text{PW86}} + E_{\text{C}}^{\text{GGA}} + E_{\text{disp}}^{\text{BJ}} \quad (6)$$

We use the standard correlation GGAs P86,^{71,72} PW91,^{4,5} and PBE.^{43,44} All following calculations were performed with the Numol program using LDA orbitals and the Perdew–Wang uniform-gas exchange–correlation parametrization⁷³ (i.e., post-xcLDA). We used numerical grids of 302 angular points per atom, and 80, 120, 160, and 200 radial shells for the He, Ne, Ar, and Kr atoms, respectively.

The coefficients a_1 and a_2 in eq 4 were determined by minimizing the root-mean-square percent error (RMSPE) for the interaction energies of the ten rare-gas pairs involving He, Ne, Ar, and Kr with respect to reference binding energies at the experimental equilibrium separations of Table 1. We chose the rare-gas reference data of Tang and Toennies (TT)⁵¹ following the suggestion by Gerber and Ángyán.⁶

Results of our fits are shown in Table 5. The exact-exchange version (XX) of the dispersion model gives somewhat better fits than the density-functional version (BR) for all correlation GGAs. The PW91 and PBE correlation

Table 5. Best-Fit Dispersion Damping Parameters and Interaction-Energy RMS Percent Errors for Various Combinations of Correlation GGA and Becke–Johnson Dispersion

	a_1	$a_2/\text{\AA}$	RMSPE
P86-XX	1.80	−1.16	20.5
P86-BR	1.54	−0.53	28.7
PW91-XX	0.96	0.87	8.1
PW91-BR	0.76	1.35	12.5
PBE-XX	0.95	0.87	7.8
PBE-BR	0.75	1.25	12.0

functionals give almost identical results, not surprising given that PBE generally behaves very much like PW91.⁴³ P86, however, yields errors more than twice as large compared to PW91 and PBE. We therefore omit P86 from further consideration.

4. Binding Energy Curves

We have calculated binding energy curves using PW86x and PBEC and the dispersion damping parameters in Table 5. These are shown for the homonuclear dimers of He, Ne, Ar, and Kr in Figures 2–5, together with the TT reference potentials. The PW91c curves are essentially identical to the

PBEC binding energy curves. For clarity, we also omit the curves for the BR version of the Becke–Johnson dispersion model. They are qualitatively similar to the XX-based curves and only slightly inferior. PW86xPBEC+disp gives binding energy curves that closely reproduce the reference curves. The largest deviations are observed for the heavier diatomics Ne–Kr, Ar–Ar, Ar–Kr, and Kr–Kr.

Equilibrium separations were found by potential-energy scans in steps of 0.01 Å and are shown in Table 6, together with the TT reference values (Å). Our results are reported as reduced quantities, defined as equilibrium separation divided by the reference value. The methods using either

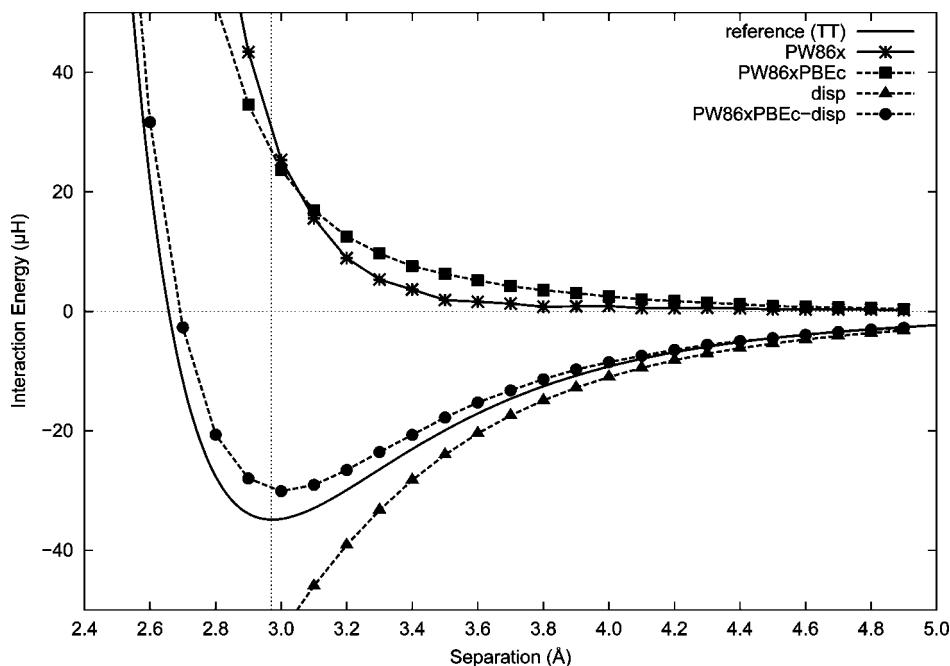


Figure 2. He₂ binding energy curves.

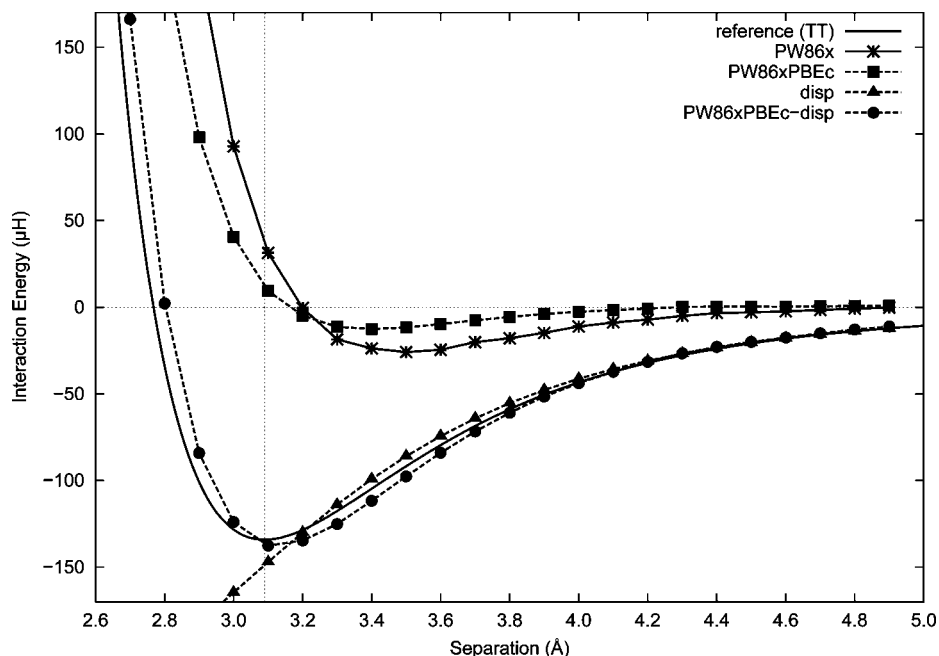


Figure 3. Ne₂ binding energy curves.

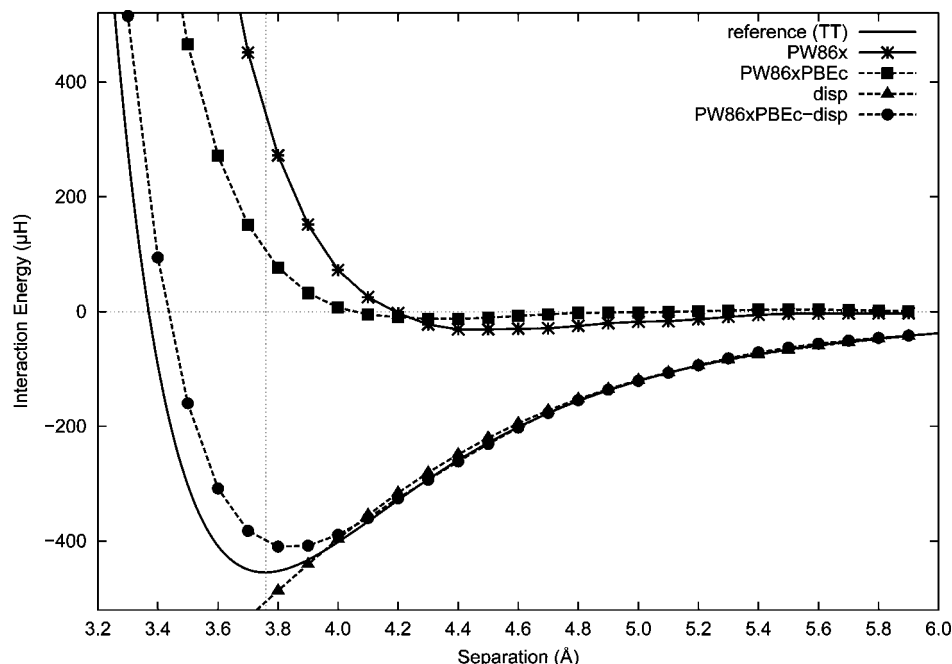


Figure 4. Ar₂ binding energy curves.

Table 6. Reference Equilibrium Separations (Å) and Calculated Reduced Equilibrium Separations for Various Combinations of Correlation GGA and Becke–Johnson Dispersion

	reference (TT) ⁵¹	PW91-XX	PW91-BR	PBE-XX	PBE-BR
He ₂	2.97	1.009	1.019	1.012	1.022
He–Ne	3.05	0.994	0.994	0.997	0.997
He–Ar	3.50	0.995	0.998	0.998	1.001
He–Kr	3.69	0.988	0.991	0.994	0.996
Ne ₂	3.09	1.006	1.000	1.010	1.003
Ne–Ar	3.48	1.007	0.998	1.010	1.004
Ne–Kr	3.65	0.993	0.990	0.996	0.993
Ar ₂	3.76	1.019	1.014	1.022	1.017
Ar–Kr	3.89	1.018	1.010	1.018	1.013
Kr ₂	4.01	1.012	1.007	1.015	1.010
MPE		0.4	0.2	0.7	0.6
MAPE		1.0	0.8	1.0	0.8
MaxAPE		1.9	1.9	2.2	2.2

PW91 or PBE dynamical correlation are very accurate, with mean absolute and maximum errors of about 1% and 2%, respectively.

Binding energies obtained at the equilibrium separations are given in Table 7 as reduced quantities, along with the TT reference values (μH). For comparison, we also include CCSD(T),⁶ DFT+CCSD(T),⁷⁴ and RSH+MP2⁶ results. We obtain excellent binding energies with the dispersion-corrected GGA functionals, surpassing even CCSD(T) in accuracy, though our results are admittedly *fits* to the reference data.

5. Conclusions

Standard semilocal density functionals without an explicitly nonlocal correlation part or an asymptotic dispersion correction are unable to describe van der Waals interactions. Not only do they miss the attractive R^{-6} behavior at long-range but those that give vdW binding at shorter separations

do so as a result of artifactual binding in their exchange parts. We have examined a variety of exchange GGAs for their ability to reproduce exact Hartree–Fock repulsion in rare-gas diatomics. While the selected functionals gave widely differing results, the PW86 exchange functional was found to be the most accurate.

PW86x was then combined with dynamical correlation functionals P86, PW91, and PBE and the nonempirical dispersion model of Becke and Johnson to give binding energy curves for the diatomics of the rare-gas atoms He, Ne, Ar, and Kr. The P86 correlation functional yielded poor results in these systems. The PW91 and PBE correlation functionals gave binding energy curves of excellent quality. Our scheme contains only two empirical parameters in the dispersion damping function. In future work, the method will be tested on vdW complexes beyond rare-gas diatomics.

We expect that functionals like eq 6, containing PW86 for exchange, will have wide applicability beyond van der Waals systems. PW86x has not been extensively benchmarked in the past but should perform similar to other exchange GGAs. The results of atomization-energy calculations on the 222 molecules of the G3/99 benchmark set of Curtiss et al.⁷⁵ are presented in Table 8. The computations are done post-xcLDA with the Numol program. We compare mean errors (ME), mean absolute errors (MAE), and maximum absolute errors (MaxAE) for the functional

$$E_{\text{XC}} = E_{\text{X}}^{\text{GGA}} + E_{\text{C}}^{\text{PBE}} + E_{\text{disp}}^{\text{BJ}} \quad (7)$$

using the exchange GGAs B86, B86b, B88, PW86, and PBE. We use the exact-exchange version of the Becke–Johnson dispersion model (XX) with the optimized damping parameters from Table 5, $a_1 = 0.95$ and $a_2 = 0.87$ Å.

All exchange GGAs perform similarly with the exception of PBE, which gives noticeably larger atomization energy

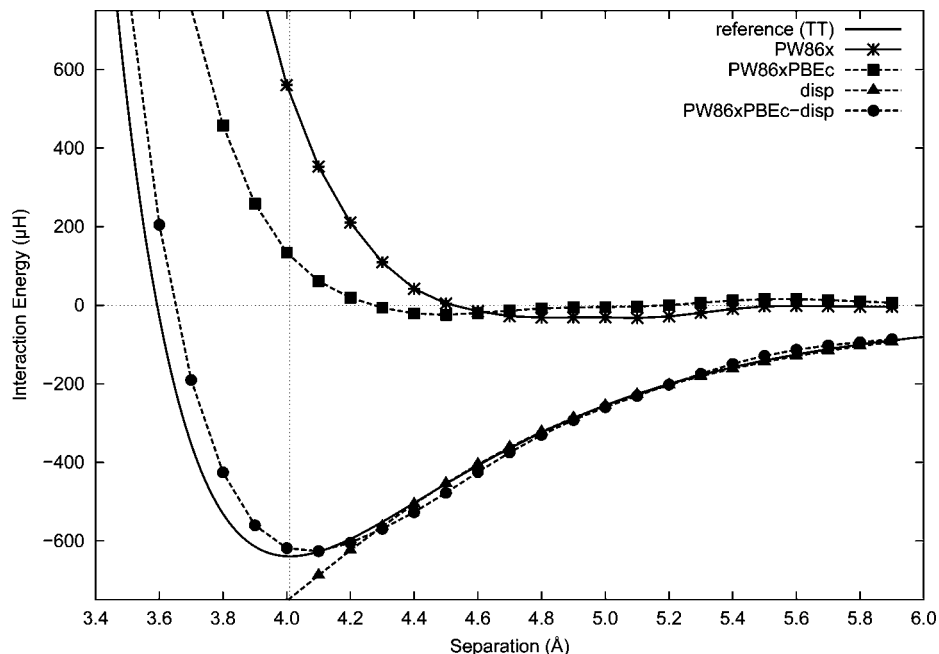


Figure 5. Kr₂ binding energy curves.

Table 7. Reference Binding Energies (μH) and Calculated Reduced Equilibrium Binding Energies for Various Combinations of Correlation GGA and Becke–Johnson Dispersion

	reference (TT) ⁵¹	CCSD(T) ⁶	DFT + CCSD(T) ⁷⁴	RSH + MP2 ⁶	PW91-XX	PW91-BR	PBE-XX	PBE-BR
He ₂	34.8	0.85	0.62	0.58	0.86	0.77	0.87	0.78
He–Ne	66	0.85	0.75	0.68	1.09	1.11	1.08	1.10
He–Ar	93.7	0.86	0.84	0.85	1.03	0.97	1.02	0.96
He–Kr	99.6	0.85	0.82	0.85	1.04	0.94	1.02	0.93
Ne ₂	134	0.79	0.86	0.73	1.05	1.19	1.03	1.17
Ne–Ar	211	0.81	0.97	0.87	1.04	1.09	1.02	1.07
Ne–Kr	224	0.81	1.02	0.89	1.15	1.16	1.13	1.14
Ar ₂	454	0.83	1.00	1.00	0.92	0.93	0.91	0.92
Ar–Kr	531	0.84	1.02	1.00	0.97	0.96	0.95	0.95
Kr ₂	638	0.83	1.04	1.00	0.99	0.98	0.98	0.96
MPE		−16.8	−10.5	−15.5	1.3	0.9	0.1	−0.3
MAPE		16.8	12.3	15.6	6.5	10.1	5.9	10.0
MaxAPE		21.1	37.8	41.9	14.6	23.2	13.4	22.4

Table 8. Atomization-Energy Errors (kcal/mol) for the Exchange–Correlation Functional of eq 7

E_X^{GGA}	ME	MAE	MaxAE
B86	6.8	9.2	37.4
B86b	11.1	12.2	50.5
B88	6.9	9.5	37.4
PW86	7.1	10.0	41.8
PBE	23.3	23.7	87.0

errors compared to the other functionals. These results are consistent with previous atomization energy benchmarks for plain GGAs without a dispersion correction.⁷⁶ We conclude that PW86 exchange, combined with a dynamical correlation GGA and the Becke–Johnson dispersion model, yields excellent results for vdW interactions in rare-gas diatomics, and its performance for atomization energies is comparable to other standard GGAs.

Acknowledgment. This work is supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Killam Trust of Dalhousie

University. Computational facilities are provided by ACEnet, the Atlantic Computational Excellence network.

References

- (1) Dobson, J. F.; McLennan, K.; Rubio, A.; Wang, J.; Gould, T.; Le, H. M.; Dinte, B. P. *Aust. J. Chem.* **2001**, *54*, 513.
- (2) Lacks, D. J.; Gordon, R. G. *Phys. Rev. A* **1993**, *47*, 4681.
- (3) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (4) Perdew, J. P. In *Electronic Structure of Solids*; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991; p 11.
- (5) 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.
- (6) Gerber, I. C.; Ángyán, J. G. *J. Chem. Phys.* **2007**, *126*, 044103.
- (7) Grimme, S.; Antony, J.; Schwabe, T.; Mück-Lichtenfeld, C. *Org. Biomol. Chem.* **2007**, *5*, 741.
- (8) Jurecka, P.; Cerný, J.; Hobza, P.; Salahub, D. R. *J. Comput. Chem.* **2007**, *28*, 555.
- (9) Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2004**, *92*, 246401.

- (10) Thonhauser, T.; Cooper, V. R.; Li, S.; Puzder, A.; Hyldgaard, P.; Langreth, D. C. *Phys. Rev. B* **2007**, *76*, 125112.
- (11) Zhang, Y.; Yang, W. *Phys. Rev. Lett.* **1998**, *80*, 890.
- (12) Rydberg, H.; Dion, M.; Jacobson, N.; Schröder, E.; Hyldgaard, P.; Simak, S. I.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2003**, *91*, 126402.
- (13) Langreth, D. C.; Dion, M.; Rydberg, H.; Schröder, E.; Hyldgaard, P.; Lundqvist, B. I. *Int. J. Quantum Chem.* **2005**, *101*, 599.
- (14) Puzder, A.; Dion, M.; Langreth, D. C. *J. Chem. Phys.* **2006**, *124*, 164105.
- (15) Thonhauser, T.; Puzder, A.; Langreth, D. C. *J. Chem. Phys.* **2006**, *124*, 164106.
- (16) Vydrov, O. A.; Wu, Q.; Van Voorhis, T. *J. Chem. Phys.* **2008**, *129*, 014106.
- (17) Kamiya, M.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2002**, *117*, 6010.
- (18) Sato, T.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2007**, *126*, 234114.
- (19) Tsuneda, T.; Suzumura, T.; Hirao, K. *J. Chem. Phys.* **1999**, *110*, 10664.
- (20) Andersson, Y.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **1996**, *76*, 102.
- (21) Ángyán, J. G.; Gerber, I. C.; Savin, A.; Toulouse, J. *Phys. Rev. A* **2005**, *72*, 012510.
- (22) Wu, X.; Vargas, M. C.; Nayak, S.; Lotrich, V.; Scoles, G. *J. Chem. Phys.* **2001**, *115*, 8748.
- (23) Wu, Q.; Yang, W. *J. Chem. Phys.* **2002**, *116*, 515.
- (24) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.
- (25) Kurita, N.; Sekino, H. *Chem. Phys. Lett.* **2001**, *348*, 139.
- (26) Xu, X.; Goddard, W. A. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 2673.
- (27) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 5656.
- (28) Zhao, Y.; Truhlar, D. *J. Phys. Chem. A* **2006**, *110*, 5121.
- (29) Zhang, Y.; Vela, A.; Salahub, D. *Theor. Chem. Acc.* **2007**, *118*, 693.
- (30) Wilson, L. C.; Levy, M. *Phys. Rev. B* **1990**, *41*, 12930.
- (31) Walsh, T. R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 443.
- (32) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2005**, *122*, 154104.
- (33) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2005**, *123*, 154101.
- (34) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2006**, *124*, 014104.
- (35) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2007**, *127*, 154108.
- (36) Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2005**, *123*, 024101.
- (37) Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2006**, *124*, 174104.
- (38) Johnson, E. R.; Becke, A. D. *Chem. Phys. Lett.* **2006**, *432*, 600.
- (39) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2007**, *127*, 124108.
- (40) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524.
- (41) Becke, A. D. *J. Chem. Phys.* **1986**, *85*, 7184.
- (42) Perdew, J. P.; Yue, W. *Phys. Rev. B* **1986**, *33*, 8800.
- (43) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (44) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.
- (45) Becke, A. D.; Dickson, R. M. *J. Chem. Phys.* **1988**, *89*, 2993.
- (46) Becke, A. D.; Dickson, R. M. *J. Chem. Phys.* **1990**, *92*, 3610.
- (47) Zhang, Y.; Pan, W.; Yang, W. *J. Chem. Phys.* **1997**, *107*, 7921.
- (48) Wesolowski, T.; Parisel, O.; Ellinger, Y.; Weber, J. *J. Phys. Chem. A* **1997**, *101*, 7818.
- (49) van Mourik, T.; Gdanitz, R. J. *J. Chem. Phys.* **2002**, *116*, 9620.
- (50) Ruzsinszky, A.; Perdew, J. P.; Csonka, G. I. *J. Phys. Chem. A* **2005**, *109*, 11015.
- (51) Tang, K. T.; Toennies, J. P. *J. Chem. Phys.* **2003**, *118*, 4976.
- (52) DePristo, A. E.; Kress, J. D. *J. Chem. Phys.* **1987**, *86*, 1425.
- (53) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision 05; Gaussian, Inc.: Wallingford, CT, 2004.
- (54) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
- (55) Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H. *J. Chem. Phys.* **1999**, *110*, 7667.
- (56) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.
- (57) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1994**, *100*, 2975.
- (58) van Mourik, T.; Wilson, A. K.; Dunning, T. H. *Mol. Phys.* **1999**, *96*, 529.
- (59) van Mourik, T.; Dunning, T. H. *Int. J. Quantum Chem.* **2000**, *76*, 205.
- (60) Jensen, F. *J. Phys. Chem. A* **2007**, *111*, 11198.
- (61) Feller, D. *J. Comput. Chem.* **1996**, *17*, 1571.
- (62) Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoorhi, V.; Chase, J.; Li, J.; Windus, T. L. *J. Chem. Inf. Model.* **2007**, *47*, 1045.
- (63) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
- (64) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 1053.
- (65) Kristyán, S.; Pulay, P. *Chem. Phys. Lett.* **1994**, *229*, 175.
- (66) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463.

- (67) Antony, J.; Grimme, S. *Phys. Chem. Chem. Phys.* **2006**, 8, 5287.
- (68) Ortmann, F.; Bechstedt, F.; Schmidt, W. G. *Phys. Rev. B* **2006**, 73, 205101.
- (69) Ángyán, J. G. *J. Chem. Phys.* **2007**, 127, 024108.
- (70) Becke, A. D.; Roussel, M. R. *Phys. Rev. A* **1989**, 39, 3761.
- (71) Perdew, J. P. *Phys. Rev. B* **1986**, 33, 8822.
- (72) Perdew, J. P. *Phys. Rev. B* **1986**, 34, 7406.
- (73) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, 45, 13244.
- (74) Goll, E.; Werner, H.-J.; Stoll, H. *Phys. Chem. Chem. Phys.* **2005**, 7, 3917.
- (75) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, 112, 7374.
- (76) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, 119, 12129.

CT800522R