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Universal Correction of Density Functional Theory to Include London Dispersion (up to Lr, Element 103)

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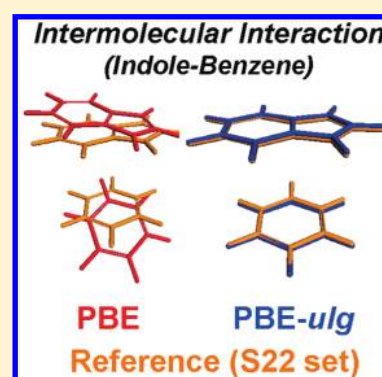
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S Supporting Information

ABSTRACT: Conventional density functional theory (DFT) fails to describe accurately the London dispersion essential for describing molecular interactions in soft matter (biological systems, polymers, nucleic acids) and molecular crystals. This has led to several methods in which atom-dependent potentials are added into the Kohn–Sham DFT energy. Some of these corrections were fitted to accurate quantum mechanical results, but it will be tedious to determine the appropriate parameters to describe all of the atoms of the periodic table. We propose an alternative approach in which a single parameter in the low-gradient (*lg*) functional form is combined with the rule-based UFF (universal force-field) nonbond parameters developed for the entire periodic table (up to Lr, *Z* = 103), named as a DFT-*ulg* method. We show that DFT-*ulg* method leads to a very accurate description of the properties for molecular complexes and molecular crystals, providing the means for predicting more accurate weak interactions across the periodic table.

SECTION: Molecular Structure, Quantum Chemistry, General Theory



London dispersion forces^{1–3} (van der Waals (vdW) attraction) are responsible for the long-range attractions critical to determining the physical and chemical properties of soft matter (biological systems, polymers, nucleic acids) and molecular crystals. However, density functional theory (DFT), the practical method of choice for accurate quantum mechanics calculations on large systems, generally fails to describe accurately systems where vdW interactions are dominant.^{4–6} Therefore, in the Perdew–Burke–Ernzerhof (PBE) flavor of DFT, graphite falls apart into graphene sheets, and benzene crystal has heat of vaporization that is 92% too small and a density that is 20% too small.

Such gross errors are unacceptable, which has led to a number of methods aimed at giving more accurate properties. One approach is to develop new DFT functionals that predict London dispersion interactions more accurately. This includes the double hybrid functional,⁷ nonlocal vdW functional,^{8–10} implicit exchange–correlation energy functionals,^{11,12} local atomic potentials,^{13,14} and hybrid meta exchange–correlation functionals.^{15,16} However, most of these methods require substantial additional computational cost, making impractical their direct applications to many crystal systems of interest.

An alternative method with almost no additional computational cost is to add an ad hoc atom-based pairwise potential (E_{disp}) to the conventional Kohn–Sham DFT energy ($E_{\text{KS-DFT}}$) aimed at improving the description of the long-range London dispersion forces. These are referred to as DFT-D methods, but a variety of choices for the form of E_{disp} and for the parameters

have been proposed.^{17–24} Most DFT-D methods assume the asymptotic form, $E_{\text{disp}} \propto -C_6/R^6$ expected from the London analysis of He atoms in the limit of no overlap. Clearly this form has problems as $R \rightarrow 0$, which has led to several suggestions for damping this singularity.

We adopt here the low-gradient functional form for E_{disp} , suggested by Liu and Goddard²⁴ and denoted as (DFT-*lg*).

$$E_{\text{disp-}lg} = - \sum_{i,j,i < j}^{N_{\text{atom}}} \frac{C_6^{ij}}{(r_{ij})^6 + b_{lg}(R_0^{ij})^6} \quad (1)$$

The *lg* correction has the proper asymptotic $-C_6/R^6$ description but transforms smoothly to a flat bottom (negligible forces) at normal bond distances (smaller than the vdW radius) with the forces remaining always attractive. With DFT-*lg*, ref 24 found that three independent parameters C_6^{HH} , C_6^{HC} , and C_6^{CC} could be adjusted to give a nearly exact fit to the coupled cluster results on benzene dimer. Ref 24 showed that PBE-*lg* with these parameters leads to an excellent description of crystalline graphite and the crystals of benzene, naphthalene, and anthracene. Unfortunately, parameters are available only for carbon and hydrogen, although they could be fitted to other prototype dimers.

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Table 1. Calculated Equilibrium Cell Volume, Heat of Sublimation, ΔH_{sub} , and Bulk Modulus, B_0 , of Benzene Compared with Experiment (Where Zero-Point Energy (ZPE) and Lattice Vibration (VIB) Corrections Are Used to Estimate ΔH_{sub} at 0 K)

	volume ($\text{\AA}^3/\text{cell}$)	ΔH_{sub} (kcal/mol)	B_0 (GPa)
experiment	461.8 (4.2 K) ²⁹	10.0–11.1 (RT + ZPE) ³⁰ 12.1–13.3 (0 K) ^a	$\sim 8^4$
PBE- <i>ulg</i>	452.1 (–2.1%)	12.81	8.83
PBE-Grimme	420.3 (–9.0%)	12.84	10
PBE	620.2 (34.3%)	2.47	1.49
ACFDT ⁴⁰	461.9 (0.02%)	11.23	7.50

^aZPE = 0.67 kcal/mol 46, VIB = 13.99%. ACFDT is the adiabatic-connection fluctuation–dissipation theorem method (computationally expensive).

We propose an alternative universal low gradient approach, DFT-*ulg*, where with a single new parameter, we can correct the vdW interactions for all elements of the periodic table (up to Lr, $Z = 103$). We demonstrate that the DFT-*ulg* leads to excellent results when compared to the highest quality CCSD(T) calculations on finite molecules and leads to excellent structures, heats of vaporization, and elastic constants for crystals.

The basis for *ulg* is the rule-based universal force field (UFF) developed by Rappé, Goddard, and coworkers in 1992. They combined experimental valence-averaged ionization potentials (IPs), experimental atomic bond radii, and computed Hartree–Fock atomic polarizabilities to fit exponential-6 vdW interatomic vdW potentials for all elements up to $Z = 103$, from which they determined the vdW well-depth (D_0) and vdW equilibrium distance (R_0) for all atoms, assuming the standard geometric combination rule for cross terms. Extracting the C_6 term from the UFF force field leads to

$$C_6^{ij} = 2D_0^{ij}(R_0^{ij})^6 \quad (2)$$

Inserting eq 2 into the *lg* form leads to

$$E_{\text{ulg}} = -s_{\text{lg}} \sum_{i,j,i < j}^{N_{\text{atom}}} \frac{2D_0^{ij}(R_0^{ij})^6}{(r_{ij})^6 + b_{\text{lg}}(R_0^{ij})^6} \quad (3)$$

where D_0^{ij} and R_0^{ij} are the vdW UFF parameters (tabulated for all atoms up to Lr in Table S1 of the Supporting Information). Equation 3 includes two universal correction parameters s_{lg} and b_{lg} .

The value of b_{lg} depends on how fast the overlap effects dampen the London forces. Figure S1 of the Supporting Information shows that E_{ulg} with $b_{\text{lg}} = 0.7$ matches the full LJ 12–6 curve at $R = 1.1R_0$ and beyond. Therefore, we adopt the quantitative condition of making E_{disp} match the 12–6 LJ potential at $R = 1.1R_0$, which leads $b_{\text{lg}} = 0.6966$.

The global scaling parameter s_{lg} is introduced because a particular flavor of DFT may already describe some aspect of the long-range attraction. For the HF-*ulg* in which the wave function contains no London forces, we expect $s_{\text{lg}} = 1$. In *ulg*, we assume that s_{lg} is independent of element type so that the DFT-*ulg* method requires only a single adjustable parameter, s_{lg} , to describe London forces between all pairs of atoms (up to $Z = 103$).

Figure S2 of the Supporting Information shows that with $s_{\text{lg}} = 0.7012$, PBE-*ulg* gives essentially an exact fit of the CCSD(T) potential energy curve of benzene dimers,²⁵ just as good as the Liu–Goddard fit using three parameters (C_6^{HH} , C_6^{HC} , and C_6^{CC}).

To test the accuracy for the PBE-*ulg* on various molecular systems, we used the Hobza 22 set of noncovalent molecular complexes²⁶ for which very extensive CCSD(T) calculations

with large basis sets have been tabulated. We find an overall mean absolute error (MAE) = 0.70 kcal/mol for PBE-*ulg*. This can be compared with the most accurate double-hybrid DFT including explicit virtuals, XYGJ-OS,²⁷ which leads to MAE = 0.46 kcal/mol and PBE-Grimme (with 72 fitted parameters), which leads to MAE = 0.65 kcal/mol. The van der Waals functional (vdW-DF) method (which attempts a more rigorous inclusion of London-like terms) leads to MAE = 1.20 kcal/mol.²⁸

However, our main point to developing PBE-*ulg* is to do crystals, which is not practical for CCSD and is not yet possible for XYGJ-OS.

For benzene crystal (*Pbca* orthorhombic phase I),²⁹ we find excellent results. Therefore

- 1 The optimized cell volume with PBE-*ulg* is 452.1 \AA^3 , compared with 461.8 \AA^3 experiment and 620.2 \AA^3 PBE (Table 1). DFT-Grimme leads to a volume of 420.3 \AA^3 .
- 2 PBE-*ulg* gives $\Delta H_{\text{sub}} = 12.81$ kcal/mol, which agrees well with experiment (12.1 to 13.3 kcal/mol³⁰ after adding zero-point energy (0.67 kcal/mol)³¹ and thermal vibration corrections). In contrast, PBE gives $\Delta H_{\text{sub}} = 2.47$ kcal/mol (1/5 of experiment). DFT-Grimme leads to $\Delta H_{\text{sub}} = 12.84$ kcal/mol.
- 3 The bulk modulus, B_0 , from PBE-*ulg* is 8.83 GPa, which compares well with experimental, $B_0 \approx 8$ GPa⁴. In contrast, PBE leads to $B_0 = 1.49$ GPa (1/6 of experiment) and DFT-Grimme leads to $B_0 = 10$ GPa.

Figure 1 shows the cold compression (0 K) equation of state (EOS) for benzene crystal. Here the “experimental” zero-temperature EOS²⁴ is based on the benzene crystal structures down to 15 K and at pressures up to 1.1 GPa from X-ray and neutron scattering spectroscopy.^{32–35} The PBE-*ulg* EOS agrees well with the experimental EOS, whereas the PBE EOS systematically leads to volumes $\sim 9\%$ too large for each pressure (Figure 1). Tables S9 and S10 of the Supporting Information show results for other polyaromatic hydrocarbons: naphthalene, anthracene, and phenanthrene crystals where PBE-*ulg* reproduces the experimental cell volume within 0.6% and ΔH_{sub} values within the experimental error bars of 3–5 kcal/mol.

Tables 2 and 3 show the results for layered structures: graphite, hexagonal boron nitride (*h*-BN), and potassium intercalated graphite (C_8K). These systems have interlayer bonding dominated by London dispersion interactions (graphite), by mixed interaction of electrostatic and dispersive interactions (*h*-BN), and by intercalated metals inducing strong electrostatic interactions (C_8K).

For graphite, PBE-*ulg* leads to $c = 6.75$ \AA (0.07 \AA or 1.0% larger than experiment) and a sheet–sheet binding energy ($E_b = 1.35$ kcal/mol, Table 2). In comparison, PBE leads to $c \approx 9$ \AA (35% error) and $E_b \approx 0.06$ kcal/mol (96% error). The available experimental E_b values all are indirect and range from

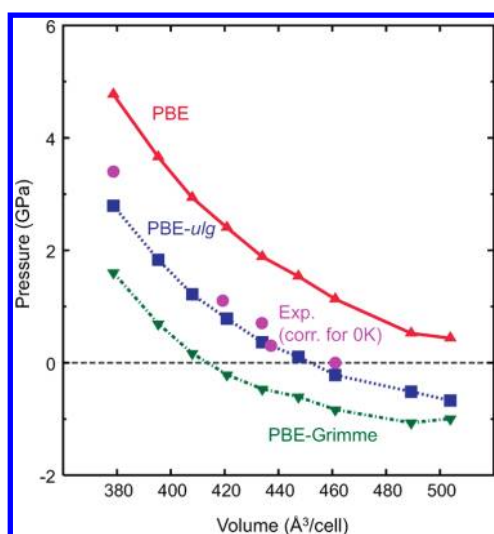


Figure 1. Equation of states (EOS) of benzene crystal (orthorhombic phase I) calculated using PBE-ulg compared with the conventional PBE and PBE-Grimme. The experimental data at 15 K has been corrected to obtain the EOS at 0 K (purple circles).^{32–35}

Table 2. Equilibrium c_0 Lattice Parameters and Interlayer Binding Energies (E_b) of Graphite^a

	c_0 (Å)	E_b (kcal/mol/atom)
experiments	6.7063 (RT + ZPE) ⁴¹ 6.6792 (0 K) ^b	0.8–1.2 ^{36–38}
PBE-ulg	6.75	1.35
PBE	8.49, ⁴² 8.84 ⁴³	0.06 ⁴²
vdW-DF ⁹	7.52	0.78
QMC ³⁹	6.8527	1.38 ± 0.23

^aQMC denotes quantum Monte Carlo (QMC) and vdW-DF is the van der Waals density functional that is a non-local DFT.⁹

^bVIB = −6.17%.

Table 3. Equilibrium Lattice Parameters (a_0 and c_0) and Layer–Layer Elastic Constant (C_{33}) of Layered Structures: Graphite, Hexagonal Boron Nitride (h -BN), and Potassium Intercalated Graphite (C_8K)^a

		a_0 (Å)	c_0 (Å)	C_{33} (GPa)
graphite	experiments ^b	2.6034 ⁴¹	6.7063 ⁴¹	36.5 ± 0.1 ⁴⁴ 37.1 ± 0.05 ⁴⁵
	PBE-ulg	2.46 (−5.5%)	6.75 (0.65%)	33.7 (−8.4%)
	PBE-Grimme	2.46 (−5.5%) ⁴³	6.45 (−3.8%) ⁴³	42.0 (14%)
	vdW-DF ⁹	2.47 (−6.5%)	7.52 (12%)	13
	experiments ^b	2.503	6.661	32.4 ± 0.3 ⁴⁶
h -BN	PBE-ulg	2.50 (−0.12%)	6.47 (−2.9%)	29.8 (−8.0%)
	PBE-Grimme	2.51 (−0.28%)	6.17 (−7.4%)	69.0 (110%)
	vdW-DF ⁹	2.51 (−0.28%)	7.26 (9.0%)	11
	experiments ^b	4.960	21.400	48.5 ± 0.14 ⁴⁷
C_8K	PBE-ulg	4.96 (0%)	21.23 (−0.79%)	50.0 (3.1%)
	PBE-Grimme	4.97 (0.20%)	21.12 (−1.3%)	74.8 (54%)

^avdW-DF is the van der Waals density functional that is a non-local DFT.⁹ ^bRoom-temperature data.

0.58 to 1.32 kcal/mol.^{36–38} The most reliable may be E_b = 1.38 kcal/mol from Quantum Monte Carlo (QMC values),³⁹ which is 0.03 kcal/mol or 2.1% larger than the PBE-ulg value.

Table 3 compares the optimized cell parameters and sheet–sheet elastic constants, C_{33} , of graphite, h -BN, and C_8K with experiment and with PBE-Grimme. For graphite, C_{33} from PBE-ulg leads to 33.7 GPa, which is 8.4% too small, whereas C_{33} from PBE-Grimme is 14% too high and that from vdW-DF is 37% too small.

For h -BN, the c = 6.47 Å from PBE-ulg just 3% below experiment while C_{33} = 29.8 GPa, just 8% below experiment. Here DFT-Grimme leads to C_{33} = 69.0 GPa, an error of 110%. We speculate that this arises from the high gradient in the nonmonotonic E_{disp} in PBE-Grimme (Table S11 of the Supporting Information) (the forces change from attractive to repulsive and back to attractive as R increases).

Figure 2 shows how the cell parameters of h -BN change with pressure up to ~7 GPa. PBE-ulg predicts lattice parameters

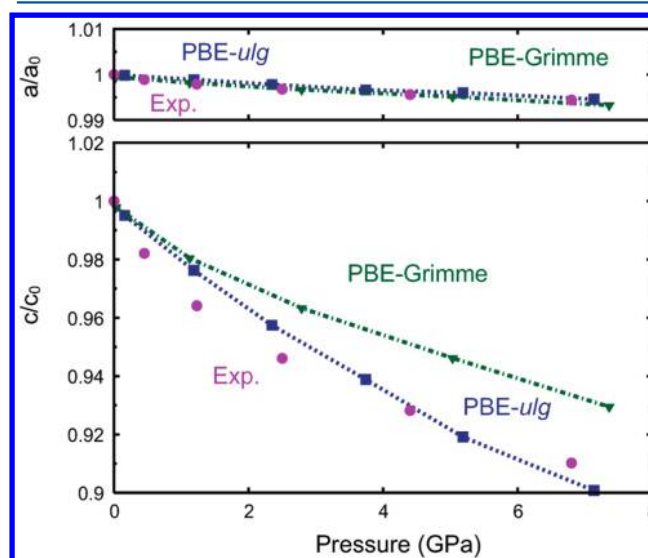


Figure 2. Dependence of hexagonal boron nitride (h -BN) cell parameters on compression. Equilibrium cell parameters (Table 3) are: Experiment: a_0 = 2.503, c_0 = 6.661; PBE-ulg: a_0 = 2.50 and c_0 = 6.40 for method; and PBE-Grimme: a_0 = 2.51 and c_0 = 6.17. The experimental values are from 300 K.

within 4.6% of experiment over the whole pressure regime. These experimental values are for 300K. The 0K value of c would be smaller while a would be larger, making the PBE-ulg errors smaller.

For C_8K , PBE-ulg predicts the cell parameters within <1%, with C_{33} 3.1% too high. In contrast, DFT-Grimme leads to C_{33} too high by 54% (Table 3), again probably from the nonmonotonic form used for E_{disp} .

To benchmark simple crystal systems, Tables S3–S8 of the Supporting Information report the results simple molecular crystals (O_2 , N_2 , CO , and CO_2), halogen molecular crystals (F_2 , Cl_2 , Br_2 , and I_2), and inert gas crystals (Ne , Ar , Kr , and Xe). We find an average error in volume for PBE-ulg of 0.4% compared with an average error of 5.8% for PBE. For these systems, the MAE in sublimation energy, ΔH_{sub} , for PBE-ulg is 0.89 kcal/mol compared with 2.49 kcal/mol for PBE. For the halogen gas crystals, PBE-ulg leads to average errors of 3.4% for volume and 1.02 kcal/mol for ΔH_{sub} . (PBE leads to an 18%

error in volume and a 4.83 kcal/mol error in ΔH_{sub} .) For noble gas crystals, PBE-*ulg* leads to an average error of 5.1% in volume and 0.74 kcal/mol in ΔH . (For PBE, the errors are 11% volume and 1.70 kcal/mol ΔH_{sub} .) Therefore, PBE-*ulg* provides energetics of near chemical accuracy despite the lack of adjustable parameters.

In summary, we show that the PBE-*ulg* method with a single adjustable parameter fixed from benzene dimer calculations predicts reliable structures, binding energies, elastic constants, and EOS for a variety of systems for which vdW interactions dominate. This immediately enables much more accurate calculations on solids for studying soft matter, gas storage, phase diagrams, catalysis, batteries, and nanotech systems involving nanotubes and fullerenes. To enable widespread use of PBE-*ulg*, it has been implemented in VASP for Z up to 103.

We plan to develop other flavors of DFT-*ulg* and indeed HF-*ulg* by choosing the one parameter of *ulg* to fit the benzene dimer data.

Here we made use of the C_6 parameters in the UFF force field, which were based on HF atomic polarizability calculations from the 1970s. We expect that modern methods (e.g., XYGJ-OS) might lead to improved values particularly for high Z. This might lead to improved accuracy for *ulg*.

■ ASSOCIATED CONTENT

■ Supporting Information

Computational details, UFF parameters with C_6 values, and benchmarking data of PBE-*ulg* with molecular and crystal systems. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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