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

Hyungjun Kim,†,* Jeong-Mo Choi,‡,∥ and William A. Goddard, III*§

1Graduate School of Energy Environment Water Sustainability (EEWS), World Class University (WCU) program and 4Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 305-701 Republic of Korea
2Materials and Process Simulation Center, Beckman Institute, California Institute of Technology, Pasadena, California 91125, United States

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_{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_{disp} \propto -C_{r}/R^6 expected from the London analysis of He atoms in the limit of no overlap. Clearly this form has problems as R \to 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).

\[ E_{\text{disp}-lg} = - \sum_{i,j,i<j}^{N_{\text{atom}}} \frac{C^i_j}{R_{ij}^6} + b_j(R_{ij}^6) \]  

The lg correction has the proper asymptotic \(-C_{r}/R^6\) 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_{HH}, C_{H}, and C_{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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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 (D0) and vDw equilibrium distance (R0) for all atoms, assuming the standard geometric combination rule for cross terms. Extracting the C6 term from the UFF force field leads to

\[
C_{ij} = 2D_0^6(R_0^6)^6
\]  

Inserting eq 2 into the ulg form leads to

\[
E_{ulg} = -s_g \sum_{i,j,r<s} \frac{2D_0^6(R_0^6)^6}{(r_{ij}^6 + b_{lg}(R_{ij}^6))^6}
\]

where D0 and R0 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 sg and bg.

The value of bg depends on how fast the overlap effects dampen the London forces. Figure S1 of the Supporting Information shows that Eulg with bg = 0.7 matches the full LJ 12–6 curve at R = 1.1R0 and beyond. Therefore, we adopt the quantitative condition of making Eulg match the 12–6 LJ potential at R = 1.1R0, which leads bg = 0.6966.

The global scaling parameter sg 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 sg = 1. Since ulg, we assume that sg is independent of element type so that the DFT-ulg method requires only a single adjustable parameter, sg, to describe London forces between all pairs of atoms (up to Z = 103).

Figure S2 of the Supporting Information shows that with sg = 0.7012, PBE-ulg gives essentially an exact fit of the CCSD(T) potential energy curve of benzene dimers just as good as the Liu–Goddard fit using three parameters (C6H10F, C6H10C, and C6H10).

To test the accuracy for the PBE-ulg on various molecular systems, we used the Hobza 22 set of noncovalent molecular complexes26 for which 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, 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), we find excellent results. Therefore

1 The optimized cell volume with PBE-ulg is 452.1 Å3, compared with 461.8 Å3 experiment and 620.2 Å3 PBE (Table 1). DFT-Grimme leads to a volume of 420.3 Å3.
2 PBE-ulg gives ΔHsub = 12.81 kcal/mol, which agrees well with experiment (12.1 to 13.3 kcal/mol) after adding zero-point energy (0.67 kcal/mol) and thermal vibration corrections. In contrast, PBE gives ΔHsub = 2.47 kcal/mol (1/5 of experiment). DFT-Grimme leads to ΔHsub = 12.84 kcal/mol.
3 The bulk modulus, B0, from PBE-ulg is 8.83 GPa, which compares well with experimental, B0 ≈ 8 GPa. In contrast, PBE leads to B0 = 1.49 GPa (1/6 of experiment) and DFT-Grimme leads to B0 = 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.25–28 The PBE-ulg EOS agrees well with the experimental EOS, whereas the PBE EOS systematically leads to volumes ~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 ΔHsub 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 (C6K). 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 (C6K).

For graphite, PBE-ulg leads to c = 6.75 Å (0.07 Å or 1.0% larger than experiment) and a sheet–sheet binding energy (E0 = 1.35 kcal/mol, Table 2). In comparison, PBE leads to c ≈ 9 Å (35% error) and E0 ≈ 0.06 kcal/mol (96% error). The available experimental E0 values all are indirect and range from

Table 1. Calculated Equilibrium Cell Volume, Heat of Sublimation, ΔHsub, and Bulk Modulus, B0, of Benzene Compared with Experiment (Where Zero-Point Energy (ZPE) and Lattice Vibration (VIB) Corrections Are Used to Estimate ΔHsub at 0 K)

<table>
<thead>
<tr>
<th>Method</th>
<th>Volume (Å3/cell)</th>
<th>ΔHsub (kcal/mol)</th>
<th>B0 (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment</td>
<td>461.8 (4.2 K)</td>
<td>10.0–11.1 (RT + ZPE)</td>
<td>~8*</td>
</tr>
<tr>
<td>PBE-ulg</td>
<td>452.1 (−2.1%)</td>
<td>12.81</td>
<td>8.83</td>
</tr>
<tr>
<td>PBE-Grimme</td>
<td>420.3 (−9.0%)</td>
<td>12.84</td>
<td>10</td>
</tr>
<tr>
<td>PBE</td>
<td>620.2 (34.3%)</td>
<td>2.47</td>
<td>1.49</td>
</tr>
<tr>
<td>ACFDT*</td>
<td>461.9 (0.02%)</td>
<td>11.23</td>
<td>7.50</td>
</tr>
</tbody>
</table>

*ZPE = 0.67 kcal/mol 46, VIB = 13.99%. ACFDT is the adiabatic-connection fluctuation–dissipation theory method (computationally expensive).
0.58 to 1.32 kcal/mol. The most reliable may be \( E_{\text{sub}} = 1.38 \text{ kcal/mol from Quantum Monte Carlo (QMC values)}, \)
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 \( c = 6.47\ \text{Å} \) from PBE-ulg just 3% below experiment while \( C_{33} = 29.8\ \text{GPa} \), just 8% below experiment. Here DFT-Grimme leads to \( C_{33} = 69.0\ \text{GPa} \), an error of 110%. We speculate that this arises from the high gradient in the nonmonotonic \( E_{\text{disp}} \) 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 \(~7\ \text{GPa}\). PBE-ulg predicts lattice parameters

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

<table>
<thead>
<tr>
<th></th>
<th>( c_0 ) (Å)</th>
<th>( E_b ) (kcal/mol/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiments ( (RT + ZPE) ) ( b )</td>
<td>6.7063 ( b )</td>
<td>6.6792 ( b )</td>
</tr>
<tr>
<td>PBE-ulg</td>
<td>6.75</td>
<td>1.35</td>
</tr>
<tr>
<td>PBE</td>
<td>8.49,48,8.8443</td>
<td>0.0645</td>
</tr>
<tr>
<td>vdW-DF( g )</td>
<td>7.52</td>
<td>0.78</td>
</tr>
<tr>
<td>QMC( 39 )</td>
<td>6.8527</td>
<td>1.38 ± 0.23</td>
</tr>
</tbody>
</table>

\( \nu \) denotes quantum Monte Carlo (QMC) and vdW-DF is the van der Waals density functional that is a non-local DFT, \( b \).

\( \nu \) is the \( \nu \)-value.

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 (\( C_8K \))

<table>
<thead>
<tr>
<th></th>
<th>( a_0 ) (Å)</th>
<th>( c_0 ) (Å)</th>
<th>( C_{33} ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphite</td>
<td>( b ) 2.603443</td>
<td>6.706343</td>
<td>36.5 ± 0.1465</td>
</tr>
<tr>
<td>PBE-ulg</td>
<td>2.46 (–5.5%)</td>
<td>6.75 (0.65%)</td>
<td>33.7 (–8.4%)</td>
</tr>
<tr>
<td>PBE-Grimme</td>
<td>2.46 (–5.5%)53</td>
<td>6.45 (–3.8%)43</td>
<td>42.0 (14%)</td>
</tr>
<tr>
<td>vdW-DF( g )</td>
<td>2.47 (–6.5%)</td>
<td>7.52 (12%)</td>
<td>13</td>
</tr>
<tr>
<td>( h)-BN</td>
<td>( b ) 2.503</td>
<td>6.661</td>
<td>32.4 ± 0.466</td>
</tr>
<tr>
<td>PBE-ulg</td>
<td>2.50 (–0.12%)</td>
<td>6.47 (–2.9%)</td>
<td>29.8 (–8.0%)</td>
</tr>
<tr>
<td>PBE-Grimme</td>
<td>2.51 (–0.28%)</td>
<td>6.17 (–7.4%)</td>
<td>69.0 (110%)</td>
</tr>
<tr>
<td>vdW-DF( g )</td>
<td>2.51 (–0.28%)</td>
<td>7.26 (9.0%)</td>
<td>11</td>
</tr>
<tr>
<td>( C_8K )</td>
<td>( b ) 4.980</td>
<td>21.400</td>
<td>48.5 ± 0.1467</td>
</tr>
<tr>
<td>PBE-ulg</td>
<td>4.96 (0%)</td>
<td>21.23 (–0.79%)</td>
<td>50.0 (3.1%)</td>
</tr>
<tr>
<td>PBE-Grimme</td>
<td>4.97 (0.20%)</td>
<td>21.12 (–1.3%)</td>
<td>74.8 (54%)</td>
</tr>
</tbody>
</table>

vdW-DF is the van der Waals density functional that is a non-local DFT. \( b \) is room-temperature data.
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 and EOS for a variety of systems for which vdW interactions 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 C₆ parameters in the UFF force field, which were based on HF atomic polarizability calculations form the 1970s. We expect that modern methods (e.g., XYGJ-O5) 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 C₆ 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.

**AUTHOR INFORMATION**

*E-mail: linus16@kaist.ac.kr (H.K.); wag@wag.caltech.edu (W.A.G.).

**Present Address**

†Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street Cambridge, MA 02138.

**Author Contributions**

These authors contributed equally.

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