

Empirical Correction to Molecular Interaction Energies in Density Functional Theory (DFT) for Methane Hydrate Simulation

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Abstract: A general and empirical method is proposed for correction of London dispersion and other deficiencies in density functional theory (DFT). This method is based on the existing Lennard-Jones (L-J) equation and van der Waals parameters. The benchmark of energy correction is set as the energy difference between DFT and more accurate methods, for example CCSD(T). The energy correction includes all differences between CCSD(T) and DFT, dispersion energy, configuration interaction, induction interaction, residual correlation, and other effects. The energy correction is expressed as a linear combination of van der Waals potentials of nonbonded atomic pairs. The combination coefficients are determined using a least-squares approach in a training set of molecular pairs. The coefficients then can be used for the energy corrections in DFT calculations in a molecular family. Three correction equations of molecular pair interaction energy, water–water, water–methane, and methane–methane, are derived for methane hydrate simulation. The correction equation of the water–water pair is applied in the DFT calculation of water pentamer, yielding good intermolecular potential energy surfaces (PES), very close to the results of CCSD(T) over the active interaction range from 2.1 Å to 8.0 Å.

1. Introduction

The London dispersion energy¹ plays an important role in molecular interactions in molecular clusters, solutions, solids, and biological macromolecules. Density functional theory (DFT) within the Kohn–Sham formulation and with presently available exchange-correlation functionals does not describe the dispersion interaction correctly.² The true correlation energy functional should include the van der Waals interaction,³ and future generations of optimized effective potentials^{4–7} may correct this deficiency of DFT. Since the pioneer work of Lein et al.² in 1999, considerable

progress has been achieved toward a better description for weak molecular interactions within DFT.^{8,9} The efforts for molecular dispersion correction in DFT approaches can be classified into three categories. (1) In the theoretical approaches, or nonempirical approaches, the molecular system is divided into two subsystems, and the dispersion interaction between them is calculated from intermolecular perturbation theory,^{10,11} or from the dynamic polarizabilities,^{12,13} or from ground state densities only.^{14–17} (2) Semiempirical approaches reparametrize the existing density functionals so that they describe dispersion properly. The mainstream in this category is represented by modification of the exchange functionals.^{18–21} (3) In empirical dispersion approaches²² empirical van der Waals potentials, in most cases using the $-c_6/R^6$ formula, are added to the DFT energy. The a posteriori empirical dispersion energy E_{dis} is calculated separately from the DFT calculation.

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Great efforts have been made for the correct description of weak molecular interaction energy in DFT. Several dispersion interaction correction methods are suggested.^{23–25} Some of them are effective in part interaction distance and may fail at other distances and are not proper to all types of molecular interactions. For example, the generalized-gradient approximation (GGA) DFT fails to handle the long-range part of the potential and is not appropriate in the simulation of physical sorption processes.^{23,24} There is still a long way to go for a comprehensive solution to this problem.¹⁷

Because of the simplicity and high efficiency of empirical approaches, some progress has been made in recent years.^{22,26} Direct inclusion of London forces with a posteriori functions into the nonlocal part of the correlation potential²⁷ and into pseudopotentials²⁸ has been suggested recently by several authors.^{27,29,30} Bordner et al. presented a method, which exploits the virtually unlimited number of ab initio calculations, as compared with experimental data to directly derive van der Waals parameters.²⁶ Zhechkov et al.²² use modified van der Waals potential, $U_0-U_1r^n-U_2r^{2n}$, for a better description at short distances. The results of DFT are basis set dependent. Therefore, it is difficult to find general a posteriori potential equations and van der Waals parameters, which are appropriate for all basis sets. In this study we suggest a general empirical method for a better description of the molecular dispersion interaction in DFT, using existing van der Waals parameters and L-J potential equations. It is effective over the active molecular interaction range, short distance, van der Waals equilibrium region, and long distance. This method is also efficient for other differences between DFT and higher level approaches, including dispersion energy, configuration interaction, induction interaction, residual correlation, and other effects.

2. Method and Scheme

In the derivation of the molecular pair interaction energy correction equation for DFT, the benchmark of energy correction is defined as the energy difference between DFT and the more accurate method. In this study we use CCSD(T) as the benchmark calculation, which stands for coupled-cluster (CC) theory with single, double, and part or full triple excitations

$$E_{\text{bench}}(r_i) = \Delta E(r_i) = E_{\text{CCSD-T}}(r_i) - E_{\text{DFT}}(r_i) \quad (i = 1, 2, \dots, n) \quad (1)$$

where r_i is the i th distance between two molecules, and n is the total number of distances. The energy correction is assumed to be a summation of van der Waals potentials over all nonbonded atomic pairs in the molecular cluster

$$E_{\text{corr}}(r_i) = \sum_{l=1}^m c_l U_l^{\text{vdw}}(r_i; d_l, \sigma_l) \quad (i = 1, 2, \dots, n) \quad (2)$$

where $U_l^{\text{vdw}}(r_i)$ is the van der Waals potential of the l th atomic pair at distance r_i , m is the number of van der Waals pairs, c_l is the coefficient for the van der Waals potential of the l th atomic pair, and d_l and σ_l are atomic van der Waals parameters. Because water and methane are small molecules, we use the distance r_i of the heavy atomic pair as the

distances of all atomic van der Waals pairs. The $U_l^{\text{vdw}}(r_i)$ could be any type of van der Waals potential, Lennard-Jones, Exp-6, or Morese potential. If the L-J (6-12) potential is used, then the van der Waals potential takes the form

$$U_l^{\text{vdw}}(r_i) = -2d_l \left(\frac{\sigma_l}{r_i} \right)^6 + d_l \left(\frac{\sigma_l}{r_i} \right)^{12} \quad (i = 1, 2, \dots, n; l = 1, 2, \dots, m) \quad (3)$$

The squared residues between benchmarks $E_{\text{bench}}(r_i)$ and corrected values $E_{\text{corr}}(r_i)$ by eq 2 are summed over the whole interaction range

$$Q = \sum_{i=1}^n \{ [E_{\text{bench}}(r_i) - E_{\text{corr}}(r_i)]^2 \} = \sum_{i=1}^n \{ [E_{\text{bench}}(r_i) - \sum_{l=1}^m c_l U_l^{\text{vdw}}(r_i)]^2 \} \quad (4)$$

A least-squares approach is used to find the best combination coefficients $\{c_l, l=1, \dots, m\}$. When the sum of squared residues takes its minimum value, the derivatives of Q to combination coefficients c_k are zero, $\partial Q / \partial c_k = 0$, leading to simultaneous linear equations

$$\text{for } \frac{\partial Q}{\partial c_k} = 0: \quad \sum_{l=1}^m c_l \sum_{i=1}^n U_l^{\text{vdw}}(r_i) U_k^{\text{vdw}}(r_i) = \sum_{i=1}^n E_{\text{bench}}(r_i) U_k^{\text{vdw}}(r_i) \quad (k = 1, \dots, m) \quad (5)$$

Equation 5 is $m \times m$ simultaneous linear equations and can be solved using a general inverse matrix to get the least-squares solution. The combination coefficients $\{c_l, l=1, \dots, m\}$ and eq 2 then can be used to correct other DFT calculations of molecular interaction energies in a molecular family. For the L-J (6-12) potentials the combination coefficients c_l also can be combined into the van der Waals parameters d_l . The molecular interaction energy correction method can be performed independently outside of the DFT software package.

A big difference in our interaction energy correction equation with other empirical methods is that we use both the attractive branch and the repulsive branch of the van der Waals potential. In other empirical dispersion correction equations²² based on the van der Waals potential only the attractive branch $-c_6/R^6$ is used, because the dispersion interaction is always attractive. The combination of two branches makes the correction equation easy to fit different molecular pair interaction energy, polar–polar, polar–nonpolar, and nonpolar–nonpolar.

3. Calculation Examples

In this section we derive the interaction energy correction equations of three molecular pairs: water–water, water–methane, and methane–methane, which will be used in methane hydrate simulation in our continuing study.

3.1. Benchmark for Corrections. In the benchmark calculations Xi'An-CI is used to compute the molecular interaction energies of three molecular pairs for future

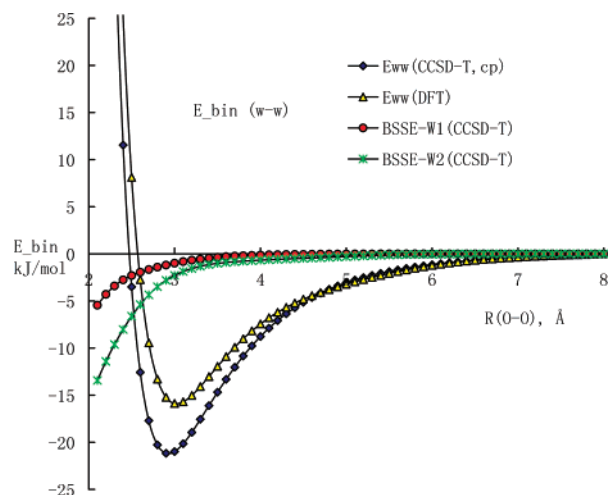


Figure 1. The molecular interaction energies of the water dimer calculated by CCSD(T)/TZVP of Xi'An-CI and BLYP/TZVP of DFT without dispersion correction. The CP-corrections for BSSE of two water molecules are performed in CCSD(T)/TZVP calculations.

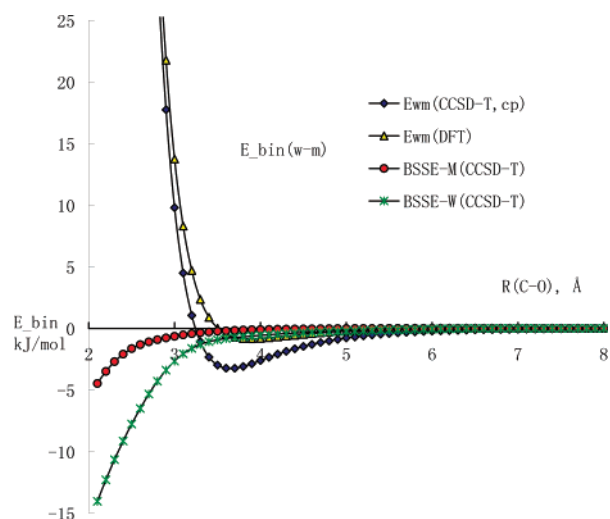


Figure 2. The molecular interaction energies of the water-methane calculated by CCSD(T)/TZVP of Xi'An-CI and BLYP/TZVP of DFT without dispersion correction. The CP-corrections for BSSE of water and methane molecules are performed in CCSD(T)/TZVP calculations.

applications in methane hydrate study. Xi'An-CI is a configuration interaction (CI) software package based on the graphical unitary group approach (GUGA) developed by Prof. Wen's group.^{31–34} The molecular interaction range is from 2.1 Å to 8.0 Å with an increment of 0.1 Å. The CCSD(T) method and the basis sets TZVP and cc-pVTZ are used in the benchmark calculations. Figure 1 shows the molecular interaction energy of the water dimer obtained by using CCSD(T)/TZVP of Xi'An-CI and BLYP/TZVP of Gauss-03 DFT (no dispersion correction). Figure 2 shows the results of water-methane using the same methods. The geometries of water and methane molecules were optimized at the CCSD(T)/TZVP level and kept constant in all molecular configurations. The rigid monomer approximation may produce an error of -0.2 ± 0.1 kJ mol⁻¹ according to ref 38, which is tolerant in this study. In order to correct the

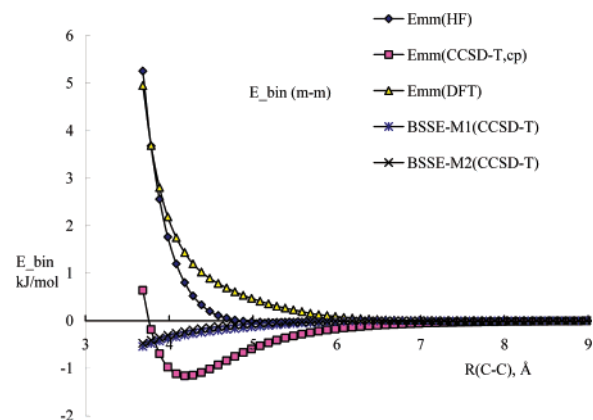


Figure 3. The molecular interaction energies of the methane-methane calculated by HF/cc-pVTZ and BLYP/TZVP of DFT without dispersion correction and CCSD(T)/cc-pVTZ of Xi'An-CI after CP-correction. According to the HF and DFT calculations, there is no attractive interaction between two methane molecules.

basis set superposition error (BSSE) caused by the basis set TZVP, we performed the counterpoise (CP) corrections for water and methane at all distances, and the BSSE CP-correction curves are shown in the figures. The CP-correction curves for BSSE of two water molecules in Figure 1 are quite different. The reason is that they have different orientations. The CP-corrected molecular interaction energy of CCSD(T)/TZVP is computed according to the following equation

$$E_{W-W}^{cp}(r) = E_{W-W}(r; s_{W1}, s_{W2}) - E_{W1}(r; s_{W1}, s_{gW2}) - E_{W2}(r; s_{gW1}, s_{W2}) \quad (6)$$

where s_{w1} and s_{w2} are basis functions of real water molecules 1 and 2, and s_{gw1} and s_{gw2} are basis functions of "ghost" water molecules 1 and 2, respectively.

As shown in Figure 1, after CP-correction the hydrogen bond energy of the water dimer ($E_{hb} = -21.17$ kJ/mol and $r_e = 2.90$ Å) calculated with CCSD(T)/TZVP of Xi'An CI is very close to the results of very accurate CCSD(T)(FULL)/IO249³⁹ calculations ($E_{hb} = -21.15$ kJ/mol and $r_e = 2.912$ Å). The notation "CCSD(T)(FULL)/IO249" stands for coupled-cluster (CC) with single, double, and full triple excitation configurations, and IO249 is a basis set for water with 249 basis functions. In Figure 1 the hydrogen bond energy calculated by DFT is much smaller than the results of CCSD(T). No CP-correction is made for DFT calculation. If CP-correction is performed for DFT, then the H-b energy will be even smaller.

In Figure 3 we show the calculation results of the molecular interaction energy between two methane molecules using CCSD(T)/cc-pVTZ of Xi'An-CI, BLYP/TZVP of DFT, and HF/cc-pVTZ. According to the calculation results of HF/cc-pVTZ and BLYP/TZVP without dispersion correction, there is no attractive interaction between two methane molecules. If CP-correction is performed for DFT and HF calculations, the interaction energies of the methane pair will be even positive. Because both HF and DFT cannot describe dispersion interaction.

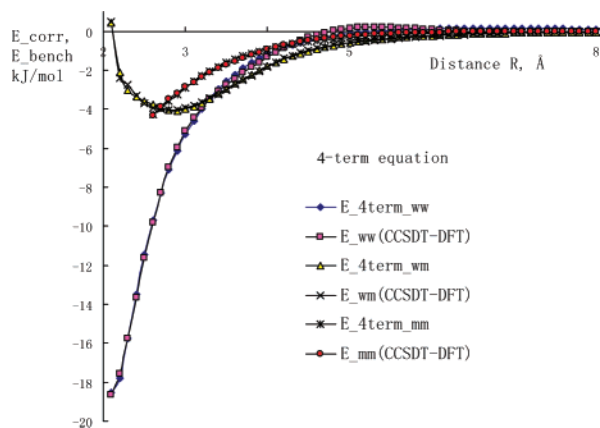


Figure 4. Comparison of the correction benchmark of interaction energy $E_{\text{bench}}(r) = E_{\text{CCSDT}}(r) - E_{\text{DFT}}(r)$ and the empirical correction of interaction energy $E_{\text{corr}}(r)$ of water–water, water–methane, and methane–methane pairs. The energy corrections $E_{\text{corr}}(r)$ are obtained by the curve fitting technique to the benchmark interaction energy $E_{\text{bench}}(r)$ using the L-J (4, 6-8,12) 4-term potential equation.

Table 1. Calculation Results of Water Dimer Using 4 Types of van der Waals Potential Equations

method	6-term	4-term	2-term	2-term+d
SEE	0.3913	0.3843	0.3776	0.2427
<i>R</i>	0.9967	0.9967	0.9967	0.9986
C_1 (OO_atr)	4.8236	2.0412	4.1205	6.0515
C_2 (OH_atr)	2.6249	-1.4331		
C_3 (HH_atr)	-1.5629	1.7016		
C_4 (OO_rpl)	-0.0537	0.2211	0.2211	-0.1110
C_5 (OH_rpl)	-2.6815			
C_6 (HH_rpl)	0.9131			

Figure 4 shows the energy differences of water–water, water–methane, and methane–methane interactions between CCSD(T) and DFT calculations

$$E_{\text{bench}}(r) = \Delta E(r) = E_{\text{CCSD-T}}(r) - E_{\text{DFT}}(r) \quad (7)$$

This energy difference is defined as the correction benchmark of the molecular interaction energy for DFT. The interactions of water–water, water–methane, and methane–methane represent the polar–polar, polar–nonpolar, and nonpolar–nonpolar molecular interactions, respectively. As shown in Figure 4, the energy correction benchmarks $E_{\text{bench}}(r)$ of three types of molecular interactions take very different forms. In the water dimer the energy correction is negative at all distances, which can be corrected by using only attractive branch $-2d(\sigma/r)^6$ of the L-J (6-12) potential. However, the energy correction benchmark $E_{\text{bench}}(r)$ of water–methane has a shallow and broad well, and it can be redressed by using both attractive and repulsive branches of the L-J (6-12) potential. The energy correction benchmark of methane–methane interaction for DFT is a negative upward flat slope. From the theoretical viewpoint, dispersion is attractive in all molecular interaction range. In this study the energy correction benchmark $E_{\text{bench}}(r)$ for DFT, defined by eq 1, actually includes all differences between advanced CCSD(T)

and DFT. Along with the dispersion, it may include configuration interaction, induction interaction, residual correlation, and other effects.

3.2. Correction Equation for Water Dimer. The correction method described in section 2 is applied to the water dimer. Four types of van der Waals potential equations are used in the energy corrections, and the results are summarized in Table 1. In the water dimer there are 9 atomic van der Waals pairs classified into 3 types, O–O, 4O–H, and 4H–H. The first energy correction is a 6-term equation, using L-J (6-12) potentials of three atomic pairs

$$E_{\text{corr}}(r_l) = c_1 \left[-2d_{\text{OO}} \left(\frac{\sigma_{\text{OO}}}{r_l} \right)^6 \right] + c_2 \left[-2d_{\text{HH}} \left(\frac{\sigma_{\text{HH}}}{r_l} \right)^6 \right] + c_3 \left[-2d_{\text{OH}} \left(\frac{\sigma_{\text{OH}}}{r_l} \right)^6 \right] + c_4 \left[d_{\text{OO}} \left(\frac{\sigma_{\text{OO}}}{r_l} \right)^{12} \right] + c_5 \left[d_{\text{HH}} \left(\frac{\sigma_{\text{HH}}}{r_l} \right)^{12} \right] + c_6 \left[d_{\text{OH}} \left(\frac{\sigma_{\text{OH}}}{r_l} \right)^{12} \right] \quad (8)$$

In eq 8 we separate the attractive branch and the repulsive branch in the L-J equation of each atomic pair and assign them different combination coefficients, because they may have different contributions to $E_{\text{corr}}(r)$. The standard estimated error (SEE) and correlation coefficient (*R*) are 0.3913 and 0.9967, respectively, as shown in Table 1. However, we find that some atomic van der Waals pairs have negative contributions to the molecular interaction energy. It is difficult to give a theoretical explanation for the “negative contributions”. In eq 8 the three attractive terms play the same role, and the role of the three repulsive terms is the same, too. In the next trial we use a 4-term equation, three attractive terms and one repulsive term

$$E_{\text{corr}}(r_l) = c_1 \left[-2d_{\text{OO}} \left(\frac{\sigma_{\text{OO}}}{r_l} \right)^6 \right] + c_2 \left[-2d_{\text{HH}} \left(\frac{\sigma_{\text{HH}}}{r_l} \right)^6 \right] + c_3 \left[-2d_{\text{OH}} \left(\frac{\sigma_{\text{OH}}}{r_l} \right)^6 \right] + c_4 d_{\text{OO}} \left[\left(\frac{\sigma_{\text{OO}}}{r_l} \right)^{12} \right] \quad (9)$$

As shown in Table 1, the 4-term eq 9 gives the results as good as the results of the 6-term eq 8, and the standard estimated error (SEE) of the 4-term eq 9 is even smaller than the SEE of the 6-term eq 8. Actually, the 4-term equation can be reduced to a 2-term equation, because the terms with the same exponent are one term after combination. In the next trial we use a 2-term equation, in which only the attractive term and the repulsive term of the heavy atomic pair O–O are used

$$E_{\text{corr}}(r_l) = c_1 \left[-2d_{\text{OO}} \left(\frac{\sigma_{\text{OO}}}{r_l} \right)^6 \right] + c_4 d_{\text{OO}} \left[\left(\frac{\sigma_{\text{OO}}}{r_l} \right)^{12} \right] \quad (10)$$

Surprisingly, the results of the 2-term eq 10 are better than that of both the 6-term and 4-term equations, as shown in Table 1.

Careful observation of Figure 4 reveals that the energy correction $E_{\text{corr}}(r)$ of the water dimer turns soft at short distances ~ 2.2 Å, and the largest errors are in the short

Table 2. Calculation Results of Water–Methane Using 4 Types of van der Waals Potential Equations

method	8_term	2_term	2_term+d	2-term+d*
SEE	1.0583	1.0020	0.6404	0.2405
R	0.8221	0.8221	0.9214	0.9836
C ₁ (CO_atr)	−0.4232	1.1849	2.5340	4.8243
C ₂ (OH_atr)	−0.5870			
C ₃ (CH_atr)	1.2659			
C ₄ (HH_atr)	0.8645			
C ₅ (CO_rpl)	−0.0007	0.0897	0.1982	0.9850
C ₆ (OH_rpl)	0.0191			
C ₇ (CH_rpl)	0.1422			
C ₈ (HH_rpl)	0.0513			

distance. For a better energy correction, we introduce a damping function⁴⁰ on the van der Waals potential

$$E_{\text{corr}}(r_i) = c_1 f_{\text{dmp}}(r_i; d_{\text{OO}}) \left[-2d_{\text{OO}} \left(\frac{\sigma_{\text{OO}}}{r_i} \right)^6 \right] + c_4 f_{\text{dmp}}(r_i; d_{\text{OO}}) d_{\text{OO}} \left[\left(\frac{\sigma_{\text{OO}}}{r_i} \right)^{12} \right] \quad (11)$$

The form of damping function $f_{\text{dmp}}(r; d_{\text{OO}})$ is as follows

$$f_{\text{dmp}}(r; d_{\text{OO}}) = 1.0 - e^{-(r-d_{\text{OO}}-r_0)} \quad (12)$$

In eq 12 r_0 is a constant, and for the water dimer we use $r_0 = 1.75$. As shown in Table 1 the calculation results of eq 11 are much better than the results of the other three equations. The damping function is a purely empirical one, which makes the van der Waals potential softer in the short distance and not much change in the other distances.

3.3. Correction Equation for Water–Methane. Following the same procedure used for the water dimer, we calculate the interaction energy correction functions for the water–methane. In the molecular pair $\text{H}_2\text{O}-\text{CH}_4$ there are 15 atomic vdW pairs (C–O, 4O–H, 2C–H, and 8H–H), which are classified into four types of van der Waals potentials. For the energy correction of the water–methane interaction we use four types of van der Waals potential equations. The first equation is 8-term L-J (6-12) potentials, including 4 attractive terms and 4 repulsive terms of the four types of atomic pairs. The second equation is a 2-term equation, only the L-J (6-12) potential of the heavy atomic pair (C–O) is used. In Table 2 we find that the results of the 2-term equation are better than the results of the 8-term equation. The third equation (2-term+d) is built by applying damping functions on the 2-term equation. The fourth equation (2-term+d*) uses the same equation as (2-term+d), but the two exponents in the L-J potential are optimized, 4 for the attractive branch and 8 for the repulsive branch.

In Table 2 we find that the damping functions improve the energy correction remarkably for the 2-term equation. The L-J (4-8) potential gives much better results ($R=0.9936$ and $\text{SEE}=0.2405$) than the L-J (6-12) potential does for the water–methane interaction. The optimization of exponents of the L-J potential in the 2-term equation is necessary for this polar–nonpolar molecular interaction pair.

Table 3. Calculation Results of Methane–Methane Using 4 Types of van der Waals Potential Equations

method	6_term	2_term	2_term+d	2-term+d ^a
SEE	0.0662	0.0667	0.0639	0.1442
R	0.9982	0.9981	0.9982	0.9906
C ₁ (CC_atr)	0.1814	6.0759	6.3352	2.6400
C ₂ (HH_atr)	1.4069			
C ₃ (CH_atr)	1.6612			
C ₄ (CC_rpl)	4.2606	3.3713	2.5648	−4.8178
C ₅ (HH_rpl)	5.4061			
C ₆ (CH_rpl)	−1.7799	--	--	--

^a Use the same potential equation as column 4 (2_term+d), the two exponents in L-J are 4 for the attractive branch and 8 for the repulsive branch.

Table 4. Four-Term L-J (4,6-8,12) Potential Equation for Water–Water, Water–Methane, and Methane–Methane Interactions

mol	R	SEE	C ₁ (atr, 4)	C ₂ (atr, 6)	C ₃ (rpl, 8)	C ₄ (rpl, 12)
w–w	0.9989	0.2244	−3.4933	11.9112	5.0585	−0.3427
w–m	0.9888	0.2127	2.7248	3.0574	0.0232	−0.0616
m–m	0.9997	0.0274	−4.1609	20.1582	24.5779	−2.6374

3.4. Correction Equation for Methane–Methane. The molecular pair methane–methane represents the nonpolar–nonpolar molecular interaction, in which dispersion makes the main contribution. The same correction procedure is applied to the methane–methane interaction energy correction for DFT calculations. Because the dispersion interaction is very weak in the nonpolar molecular pair, we use a higher basis set in the benchmark calculation, CCSD(T)/cc-pVTZ, and a lower basis set in the DFT calculation, BLYP/TZVP. Therefore, the correction for molecular interaction energy may reach the results of the larger basis set using only the smaller basis set in DFT calculations. The calculation results are summarized in Table 3. In Table 3 the 2-term+d L-J (6-12) potential equation gives the best correction for the methane–methane interaction. And the L-J (4-8) potential equation 2-term+d* does not give better results than the L-J (6-12) equation 2-term+d does for this molecular pair. It is best to use a 4-term L-J (4,6-8,12) potential equation for the methane hydrate simulation, two attractive terms with exponents 4 and 6 and two repulsive terms with exponents 8 and 12

$$E_{\text{corr}}(r_i) = c_1 f_{\text{dmp}}(r_i; d) \left[-d^2 \left(\frac{\sigma}{r_i} \right)^4 \right] + c_2 f_{\text{dmp}}(r_i; d) \left[-d^2 \left(\frac{\sigma}{r_i} \right)^6 \right] + c_3 f_{\text{dmp}}(r_i; d) \left[d \left(\frac{\sigma}{r_i} \right)^8 \right] + c_4 f_{\text{dmp}}(r_i; d) \left[d \left(\frac{\sigma}{r_i} \right)^{12} \right] \quad (13)$$

The 4-term equations give the best energy corrections for all three molecular pairs, water–water, water–methane, and methane–methane, as shown in Table 4 and Figure 4.

3.5. Check Correction Effect in Water Pentamer. The basics structural unit of methane hydrate is a dodecahedron cell consisting of 20 water molecules and a methane molecule in the center. Each face of the dodecahedron cell is a water

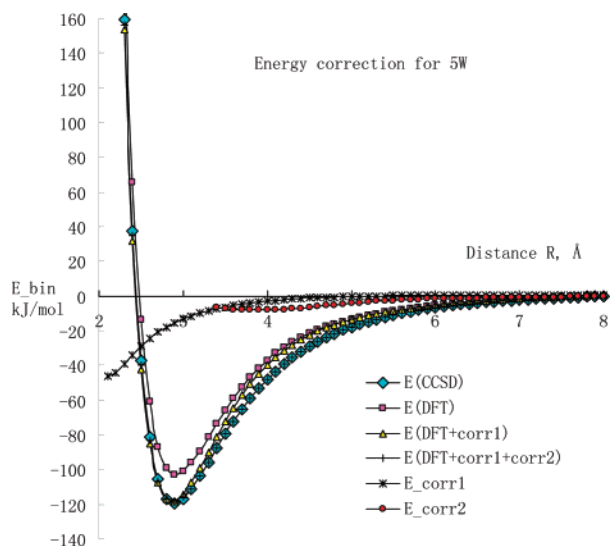


Figure 5. The dispersion-corrected water–water binding energy in the planar water pentamer for BLYP/TZVP calculations and comparison with CCSD(T)/TZVP. The 4-term dispersion-correction equation is used derived from the water dimer. E_{corr1} is the energy correction for hydrogen-bonded water pairs in pentamer, and E_{corr2} is the energy correction for non-hydrogen-bonded water pairs in pentamer, respectively.

pentamer, which is a regular pentagon of hydrogen-bonded five water molecules. In this example the molecular interaction energy correction equation $E_{\text{corr}}(r)$ obtained from the water dimer is applied to correct the DFT BLYP/TZVP calculation of the molecular interaction energy in water pentamer and compared with the CCSD(T)/TZVP calculation. The dispersion-corrected water–water binding energy in the water pentamer is expressed by the following two formulas

$$E_{\text{bin}}^{\text{5w}}(r) = E_{\text{bin}}^{\text{DFT}}(r) + \frac{5}{2} E_{\text{corr1}}^{\text{ww}}(r) \quad (14)$$

$$E_{\text{bin}}^{\text{5w}}(r) = E_{\text{bin}}^{\text{DFT}}(r) + \frac{5}{2} [E_{\text{corr1}}^{\text{ww}}(r) + E_{\text{corr2}}^{\text{ww}}(r)] \quad (15)$$

where $E_{\text{corr1}}^{\text{ww}}(r)$ is the energy correction for 5 hydrogen-bonded water pairs (w1–w2, w2–w3, w3–w4, w4–w5, and w5–w1) in the pentamer, and $E_{\text{corr2}}^{\text{ww}}(r)$ is the energy correction for 5 non-hydrogen-bonded water pairs (w1–w3, w1–w4, w2–w4, w2–w5, and w3–w5) in the pentamer, respectively. The energy corrections are calculated using the 4-term eq 13, and the coefficients listed in Table 4 are derived from the water dimer. In eqs 14 and 15 $E_{\text{bin}}^{\text{DFT}}(r)$ is the total binding energy in the water pentamer obtained by using the DFT calculation without dispersion

$$E_{\text{bin}}^{\text{DFT}}(r) = E_{\text{total}}^{\text{DFT}}(r) - E_{\text{total}}^{\text{DFT}}(\infty) \quad (16)$$

The dispersion-corrected total water binding energies in the water pentamer are shown in Figure 5. If we only use the energy correction $E_{\text{corr1}}^{\text{ww}}(r)$, which is the dispersion correction for hydrogen-bonded water pairs in the pentamer, there is a ~ 7 kJ mol^{−1} gap from 3.8 Å to 4.5 Å between the dispersion-corrected curve and the curve of CCSD(T)/TZVP,

because the energy correction $E_{\text{corr1}}^{\text{ww}}(r)$ does not include the dispersion compensation for cointeractions from non-hydrogen-bonded water molecules (w1–w3, w1–w4, w2–w4, w2–w5, and w3–w5). After further correction using $E_{\text{corr2}}^{\text{ww}}(r)$, which is the dispersion correction for non-hydrogen-bonded water pairs in the pentamer, the dispersion-corrected water–water binding energy curve of BLYP/TZVP fits the CCSD(T)/TZVP curve very well over the full interaction range.

4. Discussion and Conclusion

Because of the theoretical limitations, DFT in its usual local and gradient approximations fails to describe the molecular dispersion interaction correctly, and dispersion-correction is necessary. The empirical correction methods developed in the literature usually only uses the attractive branch of van der Waals equations and fail to correct the dispersion interaction at all interaction distances and for different molecular pairs. The empirical correction method proposed in this study uses both the attractive and repulsive branches of existing van der Waals potential equations and atomic parameters, which gives good energy corrections at all interaction distances. The molecular pairs water–water, water–methane, and methane–methane represent three types of molecular interactions: polar–polar, polar–nonpolar, and nonpolar–nonpolar interaction, respectively. Based on the calculation results of these three examples and the application to the water pentamer, we offer the following conclusions: (1) Because the dispersion behavior of the molecular interaction energy between polar–polar, polar–nonpolar, and nonpolar–nonpolar molecules is very different, it is not appropriate to use only the attractive branch of the L-J potential to redress the molecular dispersion interaction in DFT. Both attractive and repulsive branches are needed. (2) More potential terms of atomic vdW pairs do not certainly give better corrections for dispersion interactions. Use of only the vdW potential of a heavy atomic pair, for water–water it is the O–O pair, for water–methane it is the C–O pair, and for methane–methane it is the C–C pair, gives better results than the use of all the atomic vdW pairs. (3) For the polar–polar and nonpolar–nonpolar molecular interactions, the L-J (6-12) potential equation gives a good description for the molecular interaction energy correction; however, for the polar–nonpolar molecular interaction, the L-J (4-8) potential equation works better than the L-J (6-12) equation does. The 4-term L-J (4,6-8,12) potential equation, two attractive terms with the exponents 4 and 6 and two repulsive terms with the exponents 8 and 12, gives the best descriptions for all three types of molecular interactions. (4) A damping function is essential for a good correction to molecular dispersion interactions at a short distance.

The combination coefficients of vdW potential terms, optimized in a training set, can be used for the molecular interaction energy correction in a molecular family. This empirical and general correction method is efficient for dispersion interactions as well as configuration interaction, induction interaction, residual correlation, and other effects. It also can be used to reach the results of a larger basis set using only a smaller basis set. It can be performed independently outside the DFT software package.

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References

- (1) London, F. Theory and systematic of molecular forces. *Phys. Z.* **1930**, *63*, 245–267.
- (2) Lein, M.; Dobson, J. F.; Gross, E. K. U. Towards the description of van der Waals interactions within density-functional theory. *J. Comput. Chem.* **1999**, *20*, 12–22.
- (3) Dobson, J. F.; Das, M. P. *Topics in Condensed Matter Physics*; Nova: New York, 1994; pp 121–142.
- (4) Grimme, S. Accurate description of van der Waals complexes by density functional theory including empirical corrections. *J. Comput. Chem.* **2004**, *25*, 1463–1473.
- (5) Chakarova, S. D.; Schröder, E. van der Waals interactions of polycyclic aromatic hydrocarbon dimers. *J. Chem. Phys.* **2005**, *122*, 054102.
- (6) Cybulski, S. M.; Seversen, C. E. Critical examination of the supermolecule density functional theory calculations of intermolecular interactions. *J. Chem. Phys.* **2005**, *122*, 014117.
- (7) Xu, X.; Goddard, W. A. The extended Perdew-Burke-Ernzerhof functional with improved accuracy for thermodynamic and electronic properties of molecular systems. *J. Chem. Phys.* **2004**, *121*, 4068–4082.
- (8) Tao, J.; Perdew, P.; Staroverov, S.; Scuseria, G. Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.
- (9) Tao, J.; Perdew, P. Test of a nonempirical density functional: Short-range part of the van der Waals interaction in rare-gas dimers. *J. Chem. Phys.* **2005**, *122*, 114102.
- (10) Hesselmann, A.; Jansen, G. Intermolecular dispersion energies from time-dependent density functional theory. *Chem. Phys. Lett.* **2003**, *367*, 778–784.
- (11) Misqitta, A. J.; Jeziorski, B.; Szalewicz, K. Dispersion Energy from Density-Functional Theory Description of Monomers. *Phys. Rev. Lett.* **2003**, *91*, 033201.
- (12) Osinga, V. P.; van Gisbergen, S. J. A.; Snijders, J. G.; Baerends, E. J. Density functional results for isotropic and anisotropic multipole polarizabilities and C_6 , C_7 , and C_8 Van der Waals dispersion coefficients for molecules. *J. Chem. Phys.* **1997**, *106*, 5091–5101.
- (13) Adamovic, I.; Gordon, M. S. Dynamic polarizability, dispersion coefficient C_6 , and dispersion energy in the effective fragment potential method. *Mol. Phys.* **2005**, *103*, 379–387.
- (14) Andersson, Y.; Langreth, D. C.; Lundqvist, B. I. van der Waals Interactions in Density-Functional Theory. *Phys. Rev. Lett.* **1996**, *76*, 102–105.
- (15) Dobson, J. F. Prospects for a van der Waals density functional. *Int. J. Quantum Chem.* **1998**, *69*, 615–618.
- (16) Sato, T.; Tsuneda, T.; Hirao, K. A density-functional study on π -aromatic interaction: Benzene dimer and naphthalene dimer. *J. Chem. Phys.* **2005**, *123*, 104307.
- (17) Ortmann, F. F.; Bechstedt, F. Semiempirical van der Waals correction to the density functional description of solids and molecular structures. *Phys. Rev. B* **2006**, *73*, 205101.
- (18) Lacks, D. J.; Gordon, R. G. Pair interactions of rare-gas atoms as a test of exchange-energy-density functionals in regions of large density gradients. *Phys. Rev. A* **1993**, *47*, 4681–4690.
- (19) Adamo, C.; Barone, V. Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The *mPW* and *mPW1PW* models. *J. Chem. Phys.* **1998**, *108*, 664–675.
- (20) Xin, X.; Goddard, W. A., III The X3LYP extended density functional for accurate descriptions of nonbond interactions, spin states, and thermochemical properties. *PNAS* **2004**, *101*, 2673–2677.
- (21) Kurita, N.; Inoue, H.; Sekino, H. Adjustment of Perdew-Wang exchange functional for describing van der Waals and DNA base-stacking interactions. *Chem. Phys. Lett.* **2003**, *370*, 161–169.
- (22) Zhechkov, L.; Heine, T.; Patchkovskii, S.; Seifert, G.; Duarte, H. A. An efficient *a posteriori* treatment for dispersion interaction in density-functional-based tight binding. *J. Chem. Theory Comput.* **2005**, *1*, 841–848.
- (23) Valdes, H.; Sordo, J. A. Ab initio and DFT studies on van der Waals trimers: The $\text{OCS} \cdot (\text{CO}_2)_2$ complexes. *J. Comput. Chem.* **2002**, *23*, 444–455.
- (24) Jensen, F. *Introduction to Computational Chemistry*; Odense University: Odense, Denmark, 1999.
- (25) Tran, F.; Weber, J.; Wesolowski, T. A.; Cheikh, F.; Ellinger, Y.; Pauzat, F. Physisorption of molecular hydrogen on polycyclic aromatic hydrocarbons: a theoretical study. *J. Phys. Chem. B* **2002**, *106*, 8689–8696.
- (26) Bordner, A. J.; Cavasotto, C. N.; Abagyan, R. A. Direct derivation of van der Waals force field parameters from quantum mechanical interaction energies. *J. Phys. Chem. B* **2003**, *107*, 9601–9609.
- (27) Dion, M.; Rydberg, H.; Schröder, E.; Landreth, D. C.; Lundqvist, B. I. Van der Waals Density Functional for General Geometries. *Phys. Rev. Lett.* **2004**, *92*, 246401.
- (28) von Lilienfeld, O. A.; Tavernelli, I.; Röhrlisberger, U.; Sebastiani, D. Optimization of Effective Atom Centered Potentials for London Dispersion Forces in Density Functional Theory. *Phys. Rev. Lett.* **2004**, *93*, 153004.
- (29) Elstner, M.; Hobza, P.; Frauenheim, T.; Suhai, S.; Kaxiras, E. Hydrogen bonding and stacking interactions of nucleic acid base pairs: A density-functional-theory based treatment. *J. Chem. Phys.* **2001**, *114*, 5149–5155.
- (30) Rappé, A. K.; Goddard, W. A., III A new model for charge distributions in molecular systems. *J. Phys. Chem.* **1991**, *95*, 3358–3363.
- (31) Wang, Y. B.; Zhai, G. H.; Suo, B.; Gan, Z. T.; Wen, Z. Y. Hole-particle correspondence in CI calculations. *Chem. Phys. Lett.* **2003**, *375*, 134–140.
- (32) Wang, Y. B.; Wen, Z. Y.; Zhang, Z. Y.; Du, Q. S. New realization of loop driving CI. *J. Comput. Chem.* **1992**, *13*, 187–198.
- (33) Gan, Z. T.; Su, K. H.; Wang, Y. B.; Wen, Z. Y. CI Benchmark Calculations on PC. *J. Comput. Chem.* **2001**, *22*, 560–563.

- (34) Suo, B.; Zhai, G. H.; Wang, Y. B.; Wen, Z. Y.; Hu, X. Q.; Li, L. M. Parallelization of MRCI based on hole-particle symmetry. *J. Comput. Chem.* **2005**, *26*, 88–96.
- (35) Kvenvolden, K. A. Gas hydrates-geological perspective and global change. *Rev. Geophys.* **1993**, *31*, 173–188.
- (36) Cao, Z.; Tester, J. W.; Trout, B. L. Computation of the methane–water potential energy hypersurface via *ab initio* methods. *J. Chem. Phys.* **2001**, *115*, 2550–2559.
- (37) Sloan, E. D. Introductory overview: hydrate knowledge development. *Am. Mineral.* **2004**, *89*, 1155–1161.
- (38) Klopper, W.; vanDuijneveldt-van de Rijdt, J. G. C. M.; vanDuijneveldt, F. B. Computational determination of equilibrium geometry and dissociation energy of the water dimer. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2227–2234.
- (39) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.
- (40) Zimmerli, U.; Parrinello, M.; Koumoutsakos, P. Dispersion corrections to density functionals for water aromatic interactions. *J. Chem. Phys.* **2004**, *120*, 2693–2699.

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