



Molecular potential energies in dodecahedron cell of methane hydrate and dispersion correction for DFT

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ABSTRACT

The interaction potential energies of water–water and water–methane in structure-I unit cell of methane hydrate are calculated from 2.1 to 8.0 Å using density functional theory (DFT) B3LYP/TZVP. The curves of potential energies are corrected for basis set superposition error (BSSE) and dispersion interaction using a 4-term L–J (4,6–8,12) correction equation, which is derived from CCSD(T)/cc-pVTZ calculations of water–water and water–methane molecular pairs, using least squares curve-fitting. The methane hydrate unit cell is a regular water dodecahedron cell consisting of 20 water molecules with a methane molecule in the center. The geometries of water and methane are optimized at CCSD(T)/cc-pVTZ level. The BSSE-corrections are calculated for water–water and water–methane interaction energies as functions of the side length, *l*, of the dodecahedron cell at B3LYP/TZVP level in the range from 2.1 to 8.0 Å. The BSSE CP-corrected and dispersion-corrected potential energy surfaces (PES) of water–water and water–methane are useful for molecular dynamics simulation of gas clathrate-hydrates.

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1. Introduction

Natural gas clathrate-hydrates constitute the earth's largest energy resource, more than twice the amount of all other fossil energy, oil, natural gas and coal in the continents [1]. On the other hand, exploration of methane clathrate-hydrate is a major concern for global green house effects, because the green house effect of methane is 20 times stronger than the effect of carbon dioxide [1]. It follows that the kinetics studies of gas hydrate formation and dissociation are of great industrial and environmental interest and may be quite helpful in the exploration and transportation of natural gas hydrate, sequestration of CO₂ in the deep oceans, and storage of hydrogen as a clean fuel [2,3]. Computational chemistry and molecular modeling can make important contributions to the study of gas hydrates [4].

Natural gas hydrates are nonstoichiometric inclusion compounds consisting of a three-dimensional host lattice of water molecules, in which guest molecules, such as methane and/or

carbon dioxide, are encaged in polyhedral cells formed by hydrogen-bonded water molecules. Three distinctive structures [4] have been identified as structure-I, structure-II and structure-H. Each structure consists of at least two types of polyhedron structures. Fig. 1(A) is an empty dodecahedron cell and (B) is a cell with a guest methane molecule in the center. This is the basic building block for all hydrate structures. Having the ability to model and make quantitative predictions of methane hydrate behavior would be an important contribution to the safe and efficient production and transportation for natural gas hydrates.

Since the late 1950s, most modeling efforts have used a van der Waals and Platteeuw statistical mechanical model with the Lennard–Jones and Devonshire (LJD) spherical cell potential approximation [5,6]. The Lennard–Jones 6–12 and Kihara potentials are commonly chosen to represent average interactions between the lattice (water) and guest molecules (methane, ethane, etc.). The parameters in these potentials are often determined by mixing the potentials for pure component water and pure component guest molecules. Lennard–Jones parameters for liquid hydrocarbons have been optimized to reproduce experimental densities and heats of vaporization with an accuracy of approximately 5% in what is termed the OPLS model [7].

An alternative approach to fitting experimental data is to compute the potential directly from first-principles, or *ab initio*

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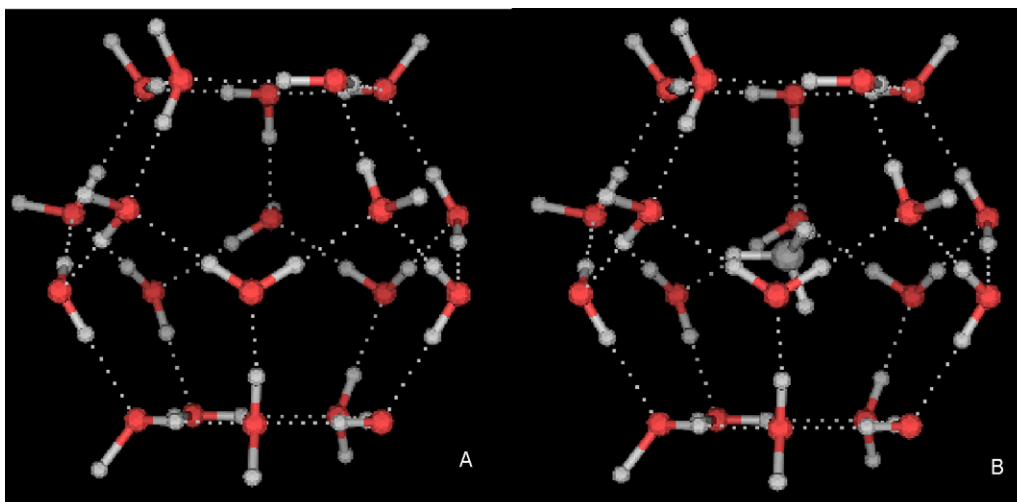


Fig. 1. The regular dodecahedron cell of clathrate-hydrate structure-I. (A) The empty dodecahedron cell of 20 hydrogen-bonded water molecules; (B) the dodecahedron cell of 20 hydrogen-bonded water molecules and an engaged methane molecule.

methods [8–14]. Such an approach would provide a direct route to determine the molecular interaction energy, which can then be validated independently using experimental data. The accuracy and efficiency of *ab initio* calculations for methane–water and water–water interactions have been studied by several research groups [15–18]. The intermolecular potential energy between methane and water used by Owichi and Scheraga [15] and Swaminathan [16] in Monte Carlo (MC) studies of methane in aqueous solutions were based on *ab initio* calculations. The calculated points on the potential energy surface (PES) were then used to obtain the best least squares fit by adjusting the parameters of an empirical distance-based potential function. In order to make more accurate evaluation for the $\text{H}_2\text{O}-\text{CH}_4$ contact interaction energy, Novoa et al. [17] and Szczesniak et al. [18] performed accurate *ab initio* calculations on methane–water pair. They suggested that the counterpoise (CP) method provides reasonable estimates of the interaction energy when the basis set is large enough. The basis sets found to be adequate from their study consist of near Hartree–Fock limit (NHFL) (4d3 f, 4p3d), 6-3111G (4d3 f, 4p3d) and cc-pVQZ. Cao et al. [3] performed systematic calculations, including 18,000 points on the six-dimensional potential energy hypersurface of $\text{CH}_4-\text{H}_2\text{O}$ molecular pair using the MP2/cc-pVQZ method.

In the previous *ab initio* studies of water–water and water–methane interaction energies for methane hydrate MD simulation, the potential energy curves were derived from water–water and water–methane pair calculations. In this study the potential energies of water–water and water–methane are calculated in dodecahedron cell and expressed as the functions of dodecahedron side length in the range from 2.1 to 8.0 Å. At the same time, corrections are made for dispersion interaction and basis set superposition error (BSSE) in the same range as for the curves of potential energies.

2. Method and scheme

The study of the potential hypersurface of methane hydrate structure-I is carried out in the following five steps: (1) B3LYP/TZVP calculations of molecular total energy $E_{\text{total}}^{\text{emp}}(l)$ and $E_{\text{total}}^{\text{mth}}(l)$ as a function of side length l of the empty dodecahedron cell consisting of 20 water molecules and the cell containing a methane molecule; (2) CP correction for BSSE in the two

dodecahedron cells; (3) calculation of the total molecular binding energy $E_{\text{bid}}^{20\text{w}}(l)$ in the empty cell and total binding energy $E_{\text{bid}}^{20\text{w}+\text{m}}(l)$ in the cell with a methane molecule present; (4) calculation of DFT van der Waals (vdw) energy between 20 water molecules and a methane molecule $E_{\text{vdw}}^{20\text{w}-\text{m}}(l)$; (5) dispersion corrections for water–water pair binding energy $E_{\text{bid}}^{\text{ww}}(l)$ and water–methane pair vdw energy $E_{\text{vdw}}^{\text{wm}}(l)$. In above notations the superscripts ‘emp’ and ‘mth’ refer to the empty cell and the cell containing the methane molecule, respectively, and ‘20w + m’ indicates the binding energy among the 21 molecules and ‘20w – m’ the binding energy between 20 water molecules and a methane molecule. As described above, the water–water pair binding energy $E_{\text{bid}}^{\text{ww}}(l)$ and the methane–water pair van der Waals energy $E_{\text{vdw}}^{\text{wm}}(l)$ of the cell is the energy differences between the two molecular clusters. The magnitudes of molecular interaction energies are much smaller than the electronic energies of the molecular cluster. Therefore, small irregular changes in molecular structure (bond lengths and angles) may cause large errors in molecular interaction energies. To make progress, we use “rigid monomer approximation” in all calculations, which may cause an error $-0.2 \pm 0.1 \text{ kJ mol}^{-1}$ in the water dimer [20], which is tolerable in this study. For this purpose, we optimize the geometries of water and methane molecules at CCSD(T)/cc-pVZT level, then keep the geometries of water and methane molecules constant in all cluster configurations.

The London dispersion [21] energy plays an important role in molecular interactions in molecular cluster, solution, solids, and biological macromolecules. However, density functional theory (DFT) in the Kohn–Sham formulation and with presently available exchange–correlation functionals does not describe the dispersion interaction correctly [22]. Considerable efforts [23,24] have been made by several authors to include the dispersion in DFT-based approaches using theoretical [25–28], semi-empirical [29–32], and empirical [33–38] methods. Because of the simplicity and high efficiency of empirical approaches, remarkable progress has been made in recent years [33,34]. Direct inclusion of London forces with an *a posteriori* function in the non-local part of the correlation potential [35] and in pseudopotentials [36] has been suggested recently by several authors [35,37,38].

In this study we use a 4-term L–J (4,6–8,12) dispersion-correction equation for DFT, with two attractive terms with exponents 4 and 6 and two repulsive terms with exponents

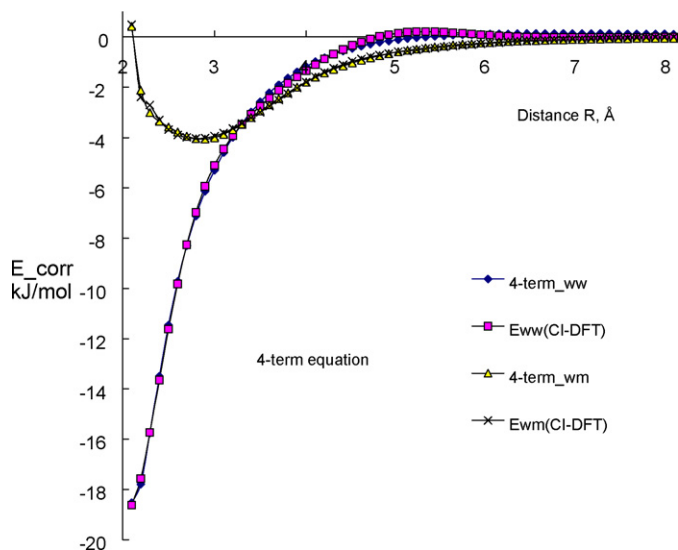


Fig. 2. The interaction energy differences $\Delta E(r) = E_{\text{CCSDT}}(r) - E_{\text{DFT}}(r)$ of water–water and water–methane pair between CCSD(T)/cc-pVTZ and B3LYP/TZVP calculations. The notations Eww (CI-DFT) and Ewm (CI-DFT) indicate the interaction energy difference of water dimer and water–methane pair, respectively. The energy corrections $E_{\text{corr}}(r)$ for DFT are obtained by curve-fitting technique to the energy differences $\Delta E(r)$ using a 4-term L–J (4,6–8,12) equation. The notations 4-term_ww and 4-term_wm indicate the energy correction curve of water dimer and water–methane pair, respectively.

8 and 12,

$$E_{\text{corr}}(r_l) = c_1 f_{\text{dmp}}(r_l; d) \left\{ d \left[-2 \frac{\sigma^4}{r_l} \right] \right\} + c_2 f_{\text{dmp}}(r_l; d) \left\{ d \left[-2 \left(\frac{\sigma}{r_l} \right)^6 \right] \right\} + c_3 f_{\text{dmp}}(r_l; d) \left\{ d \left[\left(\frac{\sigma}{r_l} \right)^8 \right] \right\} + c_4 f_{\text{dmp}}(r_l; d) \left\{ d \left[\left(\frac{\sigma}{r_l} \right)^{12} \right] \right\} \quad (1)$$

where the d and σ are van der Waals parameters. In Eq. (1) $f_{\text{dmp}}(r; d, d_0)$ is a damping function,

$$f_{\text{dmp}}(r; d) = 1.0 - e^{-(r-d-r_0)} \quad (2)$$

where r_0 is a constant. In this study $r_0 = 1.75$ is used. From short distance to long distance the damping function takes the values from 0 to 1. The damping function makes the van der Waals interaction softer in the short distance. The four coefficients (c_1 , c_2 , c_3 and c_4) in Eq. (1) are determined using least squares curve-fitting based on the energy differences between CCSD(T)/cc-pVTZ and B3LYP/TZVP calculations of water–water and water–methane molecular pairs. The detailed derivation of dispersion-correction equations can be found in our previous work [39]. The output of the dispersion-correction equations for water–water and water–methane molecular pairs are shown in Fig. 2. The coefficients of water–water and water–methane dispersion-correction equations and correlation coefficients (R) and standard estimated error (SEE) are listed in Table 1 using van der Waals parameters of Rappe [20].

Table 1

The coefficients in dispersion-correction equation using 4-term L–J (4,6–8,12) potential equations for water–water and water–methane interactions

Molecule	R	SEE	c_0	c_1 (attractive, 4)	c_2 (attractive, 6)	c_3 (repulsive, 8)	c_4 (repulsive, 12)
w–w	0.9999	0.1800	0.1637	7.3014	−0.0805	−0.1992	1.4917
w–m	0.9924	0.1814	0.3383	−4.5557	7.9977	0.0232	−1.4924

3. Calculation details

3.1. Total energy of the cell

The methane hydrate cell is a regular water dodecahedron consisting of 20 water molecules and a methane molecule in the center. The total energies of molecular clusters $E_{\text{total}}^{\text{emp}}(l)$ and $E_{\text{total}}^{\text{mth}}(l)$ are calculated as a function of side length l of dodecahedron using B3LYP/TZVP of deMon [19] from 2.1 to 8.0 Å with increments of 0.1 Å. Fig. 3(A) and (B) shows the total energy $E_{\text{total}}^{\text{emp}}(l)$ of the empty unit cell and total energy $E_{\text{total}}^{\text{mth}}(l)$ of the cell with a methane molecule, respectively. The total energies of unit cells, $E_{\text{total}}^{\text{emp}}(l)$ and $E_{\text{total}}^{\text{mth}}(l)$, contain BSSE and do not reflect contributions of dispersion interaction.

3.2. CP-correction for BSSE

BSSE [40–43] exist in all quantum chemical calculations that deal with molecular interactions using finite basis sets. In some cases the BSSE may be so large as to completely mask the true molecular interaction [43]. The CP [44,45] method is used to correct the BSSE of methane hydrate in this study. The BSSE of water and methane in the empty cell and in the cell with a methane molecule are calculated using the following equations for B3LYP/TZVP calculations:

$$\Delta E_{\text{w,emp}}^{\text{BSSE}}(l) = E_{\text{w}}(l; s_{\text{w}} + s_{19\text{gw}}) - E_{\text{w}}(s_{\text{w}}) \quad (3)$$

$$\Delta E_{\text{m,mth}}^{\text{BSSE}}(l) = E_{\text{m}}(l; s_{\text{m}} + s_{20\text{gw}}) - E_{\text{m}}(s_{\text{m}}) \quad (4)$$

$$\Delta E_{\text{w,mth}}^{\text{BSSE}}(l) = E_{\text{w}}(l; s_{\text{w}} + s_{19\text{gw}} + s_{\text{gm}}) - E_{\text{w}}(s_{\text{w}}) \quad (5)$$

In the above equations the notations s_{w} and s_{m} refer to sets of basis functions of a water molecule and a methane molecule, respectively. The notation $s_{19\text{gw}}$ refers to the set of basis functions of 19 ghost water molecules and s_{gm} refers to the set of basis functions of a ghost methane molecule. The BSSE curves of a methane molecule and five water molecules, which form a pentagon face of the dodecahedron cell, are shown in Fig. 4. In Fig. 4 we find that the five water molecules fall into two very different BSSE curve types because of their different orientations. The BSSE of a water molecule in dodecahedron cell is around 1.0–2.0 kJ mol^{−1} and the BSSE of a methane molecule is around 0.5 kJ mol^{−1} at equilibrium distance ($l_e \approx 2.8$ Å). However, at short distances BSSE are very large.

3.3. Total molecular binding energies in two cells

In Fig. 3(A) the total energy $E_{\text{total}}^{\text{emp}}(l)$ of the empty cell is the sum of the 20 water molecular energies and the total water–water binding energy between 20 water molecules, as shown in Eq. (6). In Fig. 3(B) the total energy $E_{\text{total}}^{\text{mth}}(l)$ of the cell containing a methane molecule is the sum of 20 water molecules, plus a methane molecule and the total interaction energy between water and methane molecules, as shown in Eq. (7).

$$E_{\text{total}}^{\text{emp}}(l) = 20E_{\text{w}} + E_{\text{bid}}^{20\text{w}}(l) \quad (6)$$

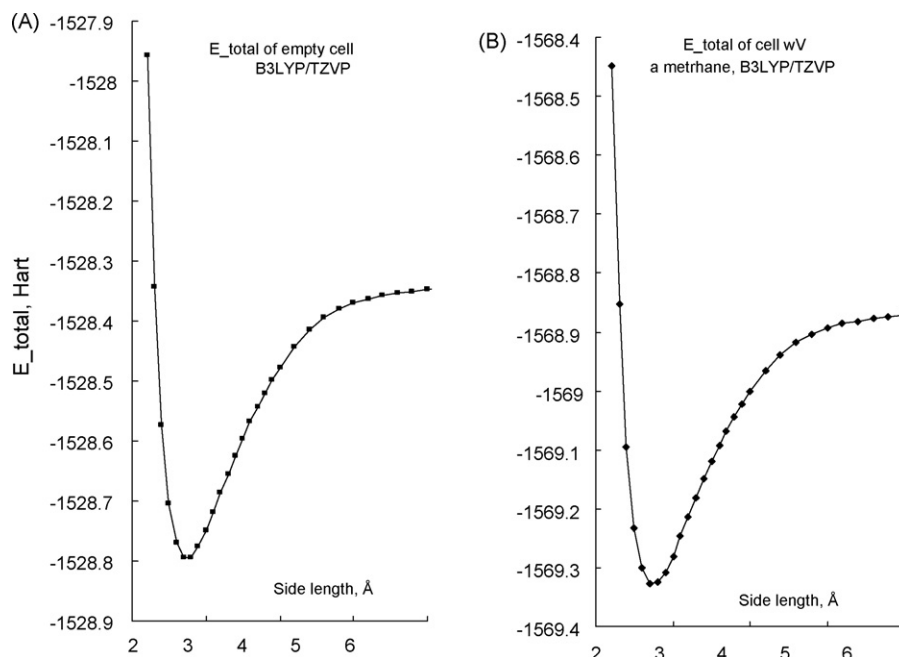


Fig. 3. (A) Total energy of the empty dodecahedron cell as a function of the side length, $E_{\text{total}}^{\text{emp}}(l)$, using B3LYP/TZVP of deMon. The empty cell consists of 20 hydrogen-bonded water molecules. (B) Total energy of the dodecahedron cell with a methane inside as a function of the side length, $E_{\text{total}}^{\text{mth}}(l)$, using B3LYP/TZVP of deMon.

$$E_{\text{total}}^{\text{mth}}(l) = 20E_w + E_m + E_{\text{bid}}^{20w+m}(l) \quad (7)$$

In Eqs. (6) and (7) the energies of water and methane molecules (E_w and E_m) contain the BSSE and have to be corrected by Eqs. (3)–(5). From Eqs. (6) and (7) we get the BSSE CP-corrected total binding energy $E_{\text{bid}}^{20w}(l)$ and $E_{\text{bid}}^{20w+m}(l)$ as follows:

$$E_{\text{bid}}^{20w}(l) = E_{\text{total}}^{\text{emp}}(l) - \sum_{i=1}^{20} E_{wi}(l; s_{wi} + s_{19gw}) \quad (8)$$

$$E_{\text{bid}}^{20w+m}(l) = E_{\text{total}}^{\text{mth}}(l) - \sum_{i=1}^{20} E_{wi}(l; s_{wi} + 19s_{19gw} + s_{gm}) - E_m(l; s_m + s_{20gw}) \quad (9)$$

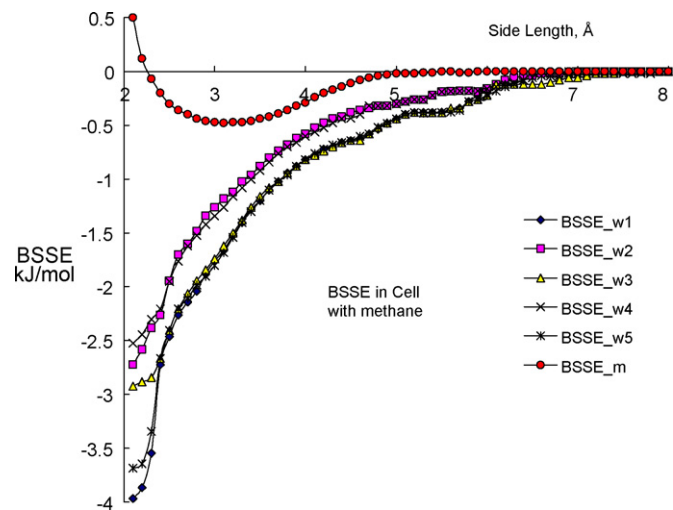


Fig. 4. The basis set superposition error (BSSE) of water and methane molecules in the dodecahedron unit cell with a methane molecule in B3LYP/TZVP calculation. The five water molecules form a regular pentagon, which is a face of the dodecahedron cell. The BSSE curves of five water molecules fall into two different types because of their different orientations.

Fig. 5 shows the BSSE CP-corrected total binding energy $E_{\text{bid}}^{20w}(l)$ of 20 water molecules in the empty unit cell as a function of side length l , and Fig. 6 is the BSSE CP-corrected total binding energy $E_{\text{bid}}^{20w+m}(l)$ between methane and 20 water molecules in the methane-containing cell.

3.4. Water–methane van der Waals energy

The binding energy $E_{\text{bid}}^{20w+m}(l)$ in the cell with a methane molecule consists of the binding energy between 20 water molecules $E_{\text{bid}}^{20w}(l)$ and the van der Waals energy between 20 water and a methane molecule $E_{\text{vdw}}^{20w-m}(l)$,

$$E_{\text{bid}}^{20w+m}(l) = E_{\text{bid}}^{20w}(l) + E_{\text{vdw}}^{20w-m}(l) \quad (10)$$

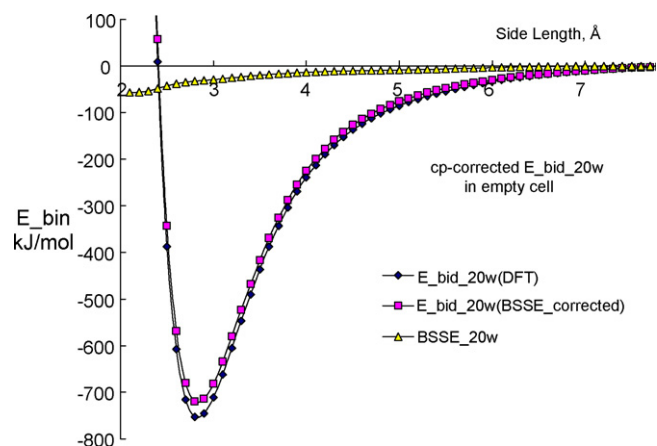


Fig. 5. The total binding energy $E_{\text{bid}}^{20w}(l)$ between 20 water molecules in the empty cell as a function of side length l of the dodecahedron after BSSE CP-correction. The notation $E_{\text{bid_20w}}(\text{DFT})$ is the total binding energy before BSSE CP-correction, $E_{\text{bid_20w}}(\text{BSSE_corrected})$ is the total binding energy after BSSE CP-correction, and BSSE_20w is the BSSE of 20 water molecules.

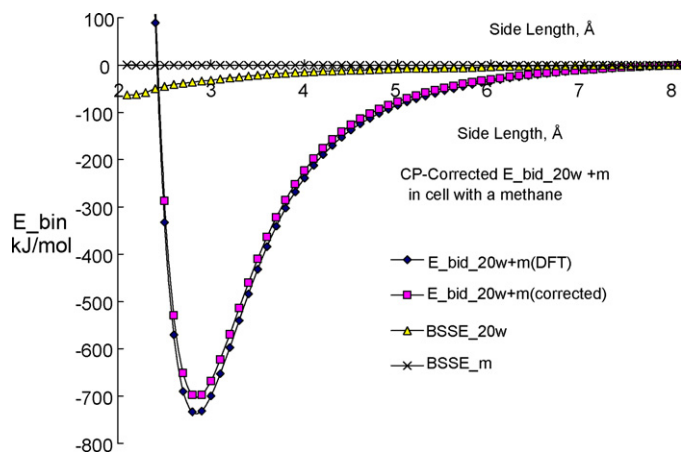


Fig. 6. The total binding energy $E_{\text{bid}}^{20\text{w}+\text{m}}(l)$ of 20 water molecules and a methane molecule in the dodecahedron cell as a function of side length l after BSSE CP-correction. The notation $E_{\text{bid}_20\text{w}+\text{m}}(\text{DFT})$ is the total binding energy before BSSE CP-correction, $E_{\text{bid}_20\text{w}+\text{m}}(\text{corrected})$ is the total binding energy after BSSE CP-correction, and $\text{BSSE}_{20\text{w}}$ and BSSE_m is the BSSE of 20 water molecules and a methane molecule, respectively.

From Eq. (10) we can attain the BSSE CP-corrected van der Waals energy between 20 water and a methane molecule,

$$E_{\text{vdw}}^{20\text{w}-\text{m}}(l) = E_{\text{bid}}^{20\text{w}+\text{m}}(l) - E_{\text{bid}}^{20\text{w}}(l) \quad (11)$$

The water–methane van der Waals energy $E_{\text{vdw}}^{20\text{w}-\text{m}}(l)$ obtained from Eq. (11) is shown in Fig. 8. Because $E_{\text{vdw}}^{20\text{w}-\text{m}}(l)$ is the difference of two energy differences and its value is much smaller than $E_{\text{bid}}^{20\text{w}}(l)$, the calculation error may be amplified by the energy difference calculations. Therefore, the calculation accuracy for the geometry of the molecular cluster is very important. As shown in Fig. 8, the van der Waals energy between methane and 20 water molecules $E_{\text{vdw}}^{20\text{w}-\text{m}}(l)$, obtained by B3LYP/TZVP, is very small, because no dispersion energy is described in DFT.

The orientation of the methane molecule has a big effect on the $\text{CH}_4\text{--H}_2\text{O}$ pair potential [3]. However, the orientation of methane is less important for the potential energy in the cell because of the higher symmetry of both the methane molecule and the dodecahedron cell. Our calculations show that the van der Waals energy differences are less than $\pm 2 \text{ kJ mol}^{-1}$ for 0° , 30° and 60° rotation of methane around Z-axis in dodecahedron cell. This corresponds to $\pm 0.1 \text{ kJ/mol}$ for each water–methane pair van der Waals energy. In this study we consider only one orientation of the methane molecule in the dodecahedron cell.

3.5. Dispersion corrections

As noted above, the water–water binding energy $E_{\text{bid}}^{20\text{w}}(l)$ and water–methane van der Waals energy $E_{\text{vdw}}^{20\text{w}-\text{m}}(l)$ obtained using DFT do not include the dispersion contributions. In this study, we use *a posteriori* empirical dispersion-correction equation defined by Eqs. (1) and (2) to correct the molecular interaction energy of B3LYP/TZVP calculations. The dispersion-correction equation $E_{\text{corr}}^{\text{ww}}(l)$ derived from water–water molecular pair is applied to the water–water pair binding energy in the empty dodecahedron cell,

$$E_{\text{bid}}^{\text{ww}}(l) = \frac{1}{30} \left[E_{\text{bid}}^{20\text{w}}(l) + \frac{20}{2} E_{\text{corr}}^{\text{ww}}(l) \right] \quad (12)$$

where $E_{\text{bid}}^{\text{ww}}(l)$ is the average water–water pair binding energy in the empty dodecahedron cell, in which there are total 30 water–water binding pairs. The factor $20/2$ before $E_{\text{corr}}^{\text{ww}}(l)$ in Eq. (12) indicates

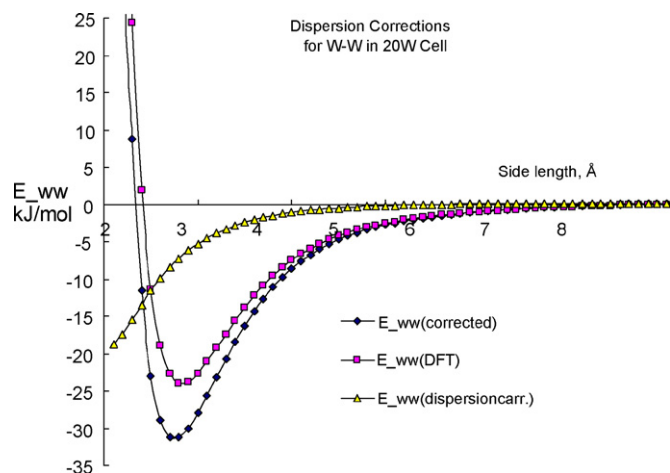


Fig. 7. The dispersion-corrected and BSSE CP-corrected water–water pair binding energy $E_{\text{bid}}^{\text{ww}}(l)$ as a function of side length of dodecahedron cell. The dispersion-corrected water–water pair binding energy includes the co-interaction energy from non-hydrogen-bonded water molecules in dodecahedron cell.

that the correction energy derived from water–water pair is assigned to each water molecule of the pair. The dispersion-correction equation $E_{\text{corr}}^{\text{wm}}(l)$ derived from water–methane molecular pair is applied to the water–methane pair van der Waals energy in the cell containing a methane molecule,

$$E_{\text{vdw}}^{\text{wm}}(l) = \frac{1}{20} E_{\text{bid}}^{\text{mth}}(l) + E_{\text{corr}}^{\text{wm}}(l) \quad (13)$$

where $E_{\text{vdw}}^{\text{wm}}(l)$ is the average water–methane pair van der Waals energy in the dodecahedron cell containing a methane molecule, in which there are total 20 water–methane interaction pairs. The dispersion-corrected $E_{\text{bid}}^{\text{ww}}(l)$ and $E_{\text{vdw}}^{\text{wm}}(l)$ are shown in Figs. 7 and 8. Some important results for water–water binding energy and water–methane van der Waals energy are summarized in Table 2. In Table 2 the water–water pair binding energy in the cell is $E_{\text{bid}}^{\text{ww}}(R_{\text{O-O}}) = -31.264 \text{ kJ mol}^{-1}$ at equilibrium distance of $R_{\text{O-O}} = 2.80 \text{ Å}$. This value is much larger than the hydrogen bond energy in water dimer [46,47], $E_{\text{hb}}^{\text{ww}}(l_{\text{min}}) = -22.6 \pm 2.9 \text{ kJ mol}^{-1}$.

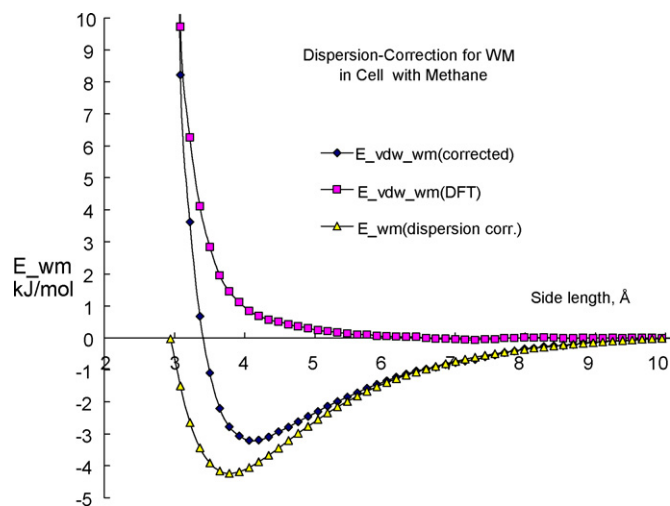


Fig. 8. The dispersion-corrected and BSSE CP-corrected water–methane pair van der Waals energy $E_{\text{vdw}}^{\text{wm}}(l) = E_{\text{bid}}^{\text{mth}}(l) + E_{\text{corr}}^{\text{wm}}(l)$ as a function of the side length of dodecahedron cell. If there is no dispersion correction the van der Waals energy between methane and water obtained with B3LYP/TZVP is very weak, because no dispersion energy is described by DFT.

Table 2

The summary of water–water pair binding energy, water–methane pair van der Waals energy, and structure parameters in dodecahedron cell

B3LYP/TZVP	$E_{\text{bid}}^{\text{ww}}(l_{\text{min}})$ (kJ/mol)	$R_{\text{O-O}}$ (Å)	$E_{\text{vdw}}^{\text{wm}}(l_{\text{min}})$ (kJ/mol)	$R_{\text{C-O}}$
No dispersion correction	−23.989	2.80	0.844 ^a	–
Dispersion correction	−31.264 ^b	2.80	−3.213	4.06
E_{corr}	−7.275	–	−4.057	–
Experimental	−22.6 ± 2.9 ^c	2.82 ^d	–	3.95 ^e

^a If no dispersion correction is used, the water–methane van der Waals energy is positive in DFT calculation.^b The dispersion-corrected water–water binding energy includes the co-interaction energy from non-hydrogen-bonded waters.^c The hydrogen bond energy of dimer (H₂O)₂, Refs. [46,47].^d Computed from the experimental value $R_{\text{C-O}} = 3.95$ Å.^e Ref. [4].

The reason is that in the water dodecahedron cell there are co-interactions from non-hydrogen-bonded water molecules, mainly contributed by dispersion interaction. The total van der Waals energy between 20 water and a methane in unit cell is $-64.26 \text{ kJ mol}^{-1}$ at an equilibrium distance of $R_{\text{C-O}} = 4.06$ Å, and the average van der Waals energy $E_{\text{vdw}}^{\text{wm}}(R_{\text{C-O}})$ of water–methane pair is $-3.213 \text{ kJ mol}^{-1}$ at the same equilibrium distance, in which the greatest contribution comes from dispersion interactions.

4. Discussion and conclusion

Ab initio quantum chemical calculations of molecular interaction potentials provide an alternative approach for force field parameter derivation, which is indispensable to molecular dynamics simulations for gas hydrates. Dispersion energy plays an important role in molecular weak interaction, especially in long distance interaction of non-polar molecules. The empirical correction method for dispersion interaction in DFT, used in this study, is an effective and robust approach for dealing with interactions in the range of 2.1–8.0 Å. In this study, the energy correction $E_{\text{corr}}(r)$ for DFT, defined as the difference between CCSDT and DFT, includes all differences between CCSDT and DFT. Along with the dispersion correction, it may include the corrections for configuration interaction, induction interaction, residual correlation, and other effects. The molecular water–water and water–methane pairs represent the polar–polar and polar–non-polar interaction, respectively. In this study the 4-term L–J (4,6–8,12) dispersion-correction equations are derived from CCSD(T)/cc-pVTZ calculations. On the other hand in the calculations of water dodecahedron cell the DFT B3LYP/TZVP method is used. Therefore, the molecular interaction energy correction includes a basis set upgrade, which is intended to achieve the more accurate results of a larger basis set while using only a smaller basis set, coupled with the interaction energy correction equation.

The CP-corrected and dispersion-corrected PES of average water–water pair binding energy and average water–methane pair van der Waals energy, provided in this study, may help in the derivation of force field parameters in molecular simulation for gas hydrates. The strategy developed in this investigation for the PES calculations of water–water binding energy $E_{\text{bid}}^{\text{ww}}(l)$ and water–methane van der Waals energy $E_{\text{vdw}}^{\text{wm}}(l)$ can be easily applied to other studies of gas hydrates, such as hydrogen, nitrogen and carbon dioxide.

Of even more general notice is the fact that in the quantum chemical calculations for molecular interactions in large molecular cluster, two problems have to be solved. The first problem is the BSSE. As shown in Fig. 4, BSSE completely blurs the real molecular interactions. Although BSSE can be corrected for by using CP correction, as shown in this study, it is a time-consuming procedure. The BSSE represents a strong disadvantage of the Gaussian basis set and a strong argument in favor of the plane wave basis set [48], especially for simulations of large systems with

many electronic structure calculations. On the other hand, the BSSE problem can be solved by using plane waves. Since plane waves are not atom centered functions, the BSSE does not appear in calculations employing plane waves.

The second problem in molecular cluster calculations that has to be solved is the dispersion interaction, which cannot be described correctly in the ordinary DFT and HF calculations. In this study, the dispersion interaction energy in water dodecahedron cell was corrected by using empirical pair correction equation derived from higher CCSDT calculations. However, this approach may not work well in larger molecular cluster because of many-body interactions. The empirical correction for dispersion interaction energy suggested in this study is not a comprehensive solution for the problem of many-body interactions. The DFT code using new functionals describing dispersion interaction is needed for truly large molecular cluster calculations.

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