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Ab initio and DFT studies for accurate description of van der Waals interaction between He atoms

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Abstract

To evaluate the accuracy of density functional theory (DFT) for describing van der Waals interaction, we performed CCSD(T), MP4(SDTQ) and several DFT calculations for the He dimer. The results clarified that (1) CCSD(T) and MP4(SDTQ) with an 'adjusted' diffuse basis-set reproduce the experimental binding energy as well as the equilibrium distance, (2) MP3 and MP2 underestimate the binding energy, (3) B3LYP and B3PW91 completely fail to describe the binding, (4) Perdew–Wang exchange-correlation functional and its modified ones can provide a He–He binding state, although the calculated binding energies are largely overestimated. The basis-set dependence of the binding energy was also discussed. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Van der Waals interaction plays an important and fundamental role in the stability and conformation of biomolecules such as DNA, RNA, proteins and their complexes. For example, stacking interaction among nucleic acid bases is one of the main elements which determine the conformation of double-strand helical DNA structure. However, accurate description of the van der Waals interaction by molecular orbital (MO) calculations is a difficult and challenging task. It is thus necessary to develop an efficient MO method for evaluating stable structures and electronic properties of such large systems as biomolecules.

The MO methods based on the Kohn–Sham (KS) density functional theory (DFT) [1,2] has been proposed as a rather inexpensive alternative to the rigorous ab initio correlated methods [3]. The DFT method has been successfully applied for many atoms, molecules and solids to reproduce experimental results. However, currently there is no consensus on whether DFT can describe the weak and long-range interaction such as van der Waals [4]. Sponer et al. [5] calculated interaction energies of stacked cytosine dimer by the ab initio MP2 and DFT methods and concluded that none of the DFT methods is able to reproduce fully the ab initio MP2 data on the stacked cytosine dimer and that the DFT method needs further improvement to describe the base stacking energy

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satisfactorily. On the other hand, in our previous studies [6,7], we have confirmed the efficiency of the DFT method [8,9] using Slater-type basis-sets and non-local DFT functionals with generalized gradient approximation (GGA) by Perdew and Wang [10,11] for describing the DNA base stacking property.

In order to evaluate the accuracy of several DFT functionals for describing van der Waals interaction, several ab initio and DFT calculations have been performed [4,12–14] for rare-gas diatomic molecules, which are the simplest prototype molecule with van der Waals interaction. It was found very difficult to obtain a reliable He–He interaction potential, because the He atoms bind very weakly with each other, where the experimental binding energy is only 0.021 kcal/mol [15,16]. Currently no DFT calculation can reproduce the binding energy of He molecule.

The purpose of the present study is to obtain the accurate He–He interaction potential comparable to the experimental result [15,16] by using both the ab initio MO method and the adjusted diffuse basis-set. We furthermore investigate on which DFT functional can reproduce most accurately the potential. These results must be valuable in choosing DFT functional for performing MO calculations of large molecules with van der Waals interaction.

2. Method of MO calculations

Ab initio MO calculations, MP2, MP3, MP4 (SDTQ) (fourth-order perturbation theory including single, double, triple and quadruple substitutions) and CCSD(T) (coupled-cluster calculations with single and double substitutions and with noniterative triple corrections) were performed using the GAUSSIAN 98 (G98) program package [17]. In order to evaluate the accuracy of the exchange and correlation functionals, the DFT calculations implemented in G98 were carried out by using the six types of non-local DFT functionals: Becke's three-parameter functional with Lee, Yang and Parr's correlation functional (B3LYP) [18,19], the same three-parameter functional with Perdew–Wang91 correlation functional (B3PW91) [20], Perdew–Wang91 for exchange and correlation

functionals (PW91PW91) [21,22], the modified Perdew–Wang91 exchange by Adamo and Barone [23] plus Perdew–Wang91 correlation [21,22] functional (MPWPW91), Adamo and Barone's Becke-style one-parameter functional using the modified Perdew–Wang91 exchange [24] and Perdew–Wang91 correlation [21,22] (MPW1PW 91), and the 1996 exchange functional of Gill [25] plus Perdew–Wang91 correlation [21,22] (G96PW91). The interaction energy between He atoms was corrected for the basis-set superposition error (BSSE) [26,27], and the ultrafine grid was used for numerical integrations in the DFT calculations.

In the MO calculations for long-range interaction, the choice of basis-set is essential. In particular, a diffuse basis-set is needed for describing delocalized electrons. As mentioned in our previous DFT studies [6,7] on the stacking interaction of cytosine dimer, the stacking properties cannot be described without diffuse functions. In the present calculations, we first used the following default basis-sets implemented in G98: (1) the standard split valence 6-31G, (2) the 6-311G augmented by a p-polarization function (6-311G(d)), (3) the 6-311G(d) augmented by a diffuse s-polarization function with a 0.086 exponent (6-311+G(d)), (4) Dunning's correlation consistent basis-sets (cc-pVXZ, X = D, T and Q). There is no default option for Dunning's correlation consistent basis-set augmented with diffuse polarization functions for He. After checking the incompleteness of these default basis-sets, we added some diffuse polarization functions to the default basis-sets and adjusted the exponents of the diffuse functions to reproduce the experimentally obtained binding energy and equilibrium distance of He dimer. From the results obtained by the above calculations, we elucidated the effect of basis-set on van der Waals interaction and proposed the efficient basis-set for describing the interaction.

3. Results and discussion

3.1. CCSD(T) results with various basis-sets

In order to obtain a reference potential curve for the He–He van der Waals interaction, which

provides the experimental binding energy and equilibrium distance [15,16], we first performed CCSD(T) calculations by using the several default basis-sets implemented in G98: 6-31G, 6-311G(d), 6-311+G(d) and cc-pVXZ (X = D, T and Q) basis-sets. Fig. 1a compares the potential energy curves in the range from 2.0 to 6.0 Å atomic distance. The experimentally obtained binding energy is 0.021 kcal/mol [15,16], so that all the calculations underestimate the binding energy with a large amount and fail to describe the van der Waals interaction. However, these results provide useful information on which type of basis-set is necessary for improving the result. From the comparison between the 6-31G and 6-311+G(d) results, it was found that the diffuse function is necessary for obtaining the He–He binding state. The

6-311+G(d) basis-set, which has only s-type diffuse function, is however not sufficient, because the obtained binding energy (0.002 kcal/mol) by 6-311+G(d) is only one-tenth of the experimental one. On the other hand, the cc-pVXZ basis-sets produce better results, although the obtained binding energies are still not comparable to the experiment. The calculation with the cc-pVQZ basis-set which has s- and p-type diffuse functions, provides the most reliable potential curve. From the above comparison, it was clarified that the diffuse functions are indispensable for improving the result. There are two choices for improving the basis-sets; the addition of diffuse functions to the 6-31G or the cc-pVQZ basis-set. We here choose the former, considering the computational efficiency in applying for large molecules like DNA.
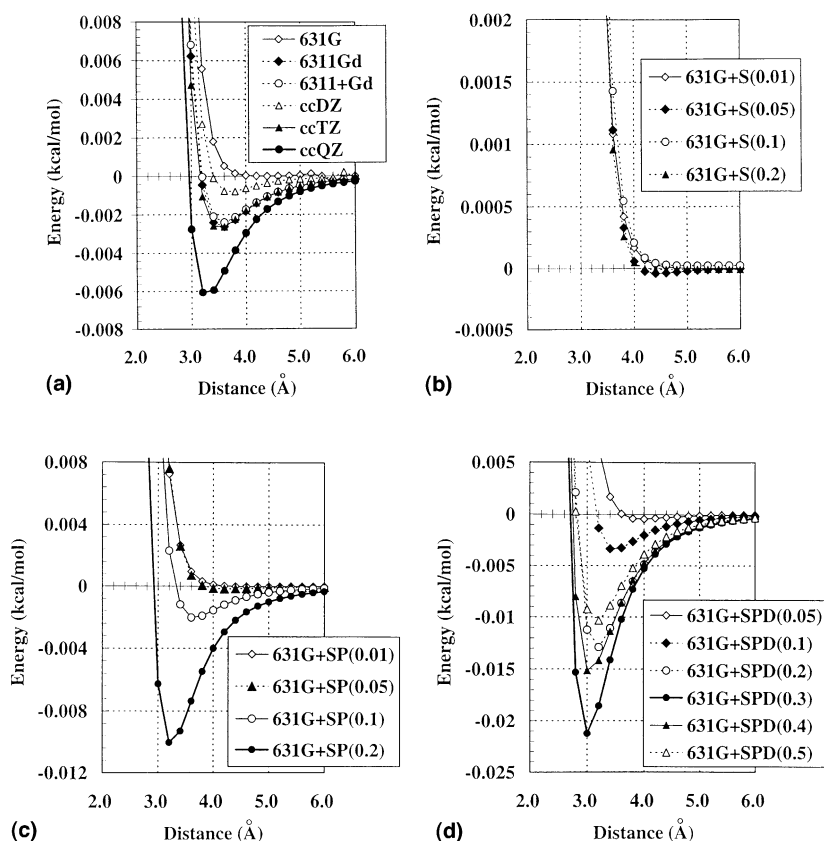

Fig. 1. He–He binding energy curves obtained by CCSD(T) with various basis-sets: (a) the default basis-sets in G98; (b) the 6-31G basis-set augmented by a s-type diffuse function; (c) the 6-31G basis-set augmented by s- and p-type diffuse functions; (d) the 6-31G basis-set augmented by s-, p- and d-type diffuse functions. The value in a parenthesis indicates the exponent of the diffuse functions.

Starting from the 6-31G basis-set, we added diffuse functions to obtain appropriate basis-sets for describing van der Waals interaction of He–He. Fig. 1b shows the effect of s-type diffuse function added to the 6-31G basis-set. Even if the exponent of this function is changed from 0.01 to 0.2, there is almost no change in the potential energy curve. Then, we added both s- and p-type diffuse functions and adjusted their exponent. As shown in Fig. 1c, the result with the 0.2 exponent gives about 0.01 kcal/mol for the binding energy, indicating the effect of p-type diffuse function is rather important. Furthermore the d-type function was added and its exponent was adjusted in the range 0.05–0.5. As shown in Fig. 1d, the results with the 0.3 exponent reproduce the experimental binding energy, and the computed equilibrium distance (3.0 Å) is almost the same as that of the experiment (2.97 Å) [15,16]. Therefore, it is concluded that the basis-set 6-31G augmented by s-, p- and d-type diffuse functions with the 0.3 exponent is accurate enough for describing He–He van der Waals interaction.

We also checked the effect of the addition of f-type function and conclude that there is no remarkable improvement upon the addition. Furthermore, we used the 6-311G(d) basis-set, which includes polarization functions as a starting basis-set and made the same analysis as mentioned above. These results indicate that the effect of adding diffuse functions on the potential energy curve is almost the same as that for the 6-31G basis-set. The values of He–He binding energies obtained by the 6-31G plus s-, p- and d-type diffuse functions [6-31G+SPD(0.3)] and the 6-311G(d) plus s-, p-, d- and f-type diffuse functions [6-311G(d)+SPDF(0.3)] were compared in Table 1 with the experimental binding energy curve (LM2M2) [28] constructed from the ab initio calculations by Liu and McLean [29]. Although the deviation from LM2M2 is large in the repulsive region (from 3.0 to 4.8 Bohr distance), that is at most 0.003 kcal/mol in the equilibrium region (from 5.4 to 6.0 Bohr distance). In particular, the 6-31G+SPD(0.3) results are almost equal to those of LM2M2. Considering the accuracy and com-

Table 1
Values of He–He binding energies obtained by CCSD(T)/6-31G+SPD(0.3) and CCSD(T)/6-311G(d)+SPDF(0.3), and their deviations from the experimental binding energy LM2M2 [28]

| Distance	LM2M2	6-31G+SPD(0.3)	6-311G(d)+SPDF(0.3)	Deviations from LM2M2 (kcal/mol)	
(Bohr)	(kcal/mol)	(kcal/mol)	(kcal/mol)	6-31G+SPD(0.3)	6-311G(d)+PDF(0.3)
3.0	7.5347	8.3764	7.9142	0.8416	0.3795
3.5	2.2157	2.5276	2.3663	0.3118	0.1506
4.0	0.5821	0.6888	0.6379	0.1067	0.0558
4.3	0.2345	0.2863	0.2640	0.0518	0.0295
4.6	0.0774	0.1009	0.0926	0.0234	0.0152
4.8	0.0266	0.0398	0.0364	0.0132	0.0097
5.0	−0.0007	0.0063	0.0055	0.0069	0.0062
5.1	−0.0087	−0.0038	−0.0038	0.0049	0.0049
5.2	−0.0143	−0.0109	−0.0103	0.0034	0.0040
5.4	−0.0202	−0.0187	−0.0174	0.0015	0.0028
5.6	−0.0217	−0.0211	−0.0196	0.0006	0.0020
5.8	−0.0209	−0.0208	−0.0194	0.0001	0.0016
6.0	−0.0191	−0.0190	−0.0178	0.0000	0.0013
6.5	−0.0136	−0.0133	−0.0127	0.0004	0.0009
7.0	−0.0092	−0.0086	−0.0085	0.0006	0.0007
7.5	−0.0061	−0.0055	−0.0056	0.0005	0.0005
8.0	−0.0041	−0.0037	−0.0037	0.0004	0.0004
8.5	−0.0028	−0.0025	−0.0026	0.0003	0.0003
9.0	−0.0020	−0.0017	−0.0018	0.0002	0.0002
10.0	−0.0010	−0.0009	−0.0009	0.0001	0.0001
12.0	−0.0003	−0.0003	−0.0003	0.0000	0.0000
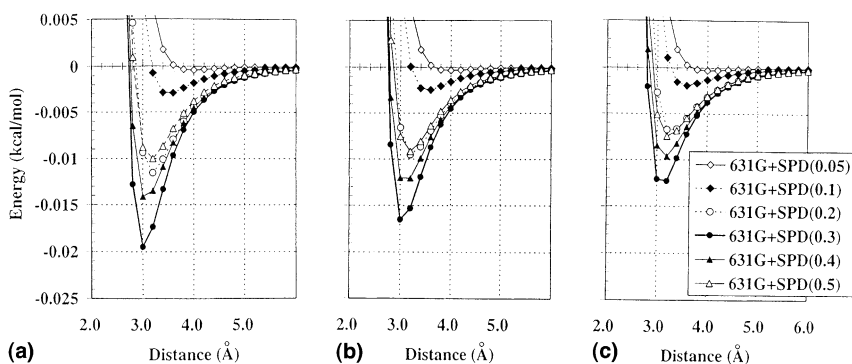
Fig. 2. He–He binding energy curves obtained by (a) MP4(SDTQ), (b) MP3 and (c) MP2 with the 6-31G basis-set augmented by s-, p- and d-type diffuse functions. The value in a parenthesis indicates the exponent of the diffuse functions.

putational efficiency, we conclude that the 6-31G+SPD(0.3) basis-set is the most adequate for the analysis of the van der Waals interaction between He atoms.

As for the effect of the BSSE, Dunning's group [30] investigated in detail its basis-set dependence by using the several types of augmented cc-pVXZ (X = D, T, Q, 5 and 6) basis-sets. They concluded that BSSE decreases with increasing the cc-pVXZ basis-set quality, but increases with increasing the number of augmented diffuse functions. In the present study, we choose rather small 6-31G or 6-311G(d) basis-set as a starting basis-set and augmented several types of diffuse functions to reproduce the experimental binding energy, because we attempt to propose an efficient basis-set for MO calculations of large molecules. These basis-sets contain a small core-part and a large diffused-part, so that their BSSE values were much larger than the binding energy of He dimer. These values were 0.13 for 6-31G+SPD(0.3) and 0.06 kcal/mol for 6-311G(d)+SPDF(0.3) at the equilibrium distance, indicating that these basis-sets are not complete. However, if the BSSE is cor-

rected, the CCSD(T) calculations with these basis-sets can provide a reasonable potential energy curve for He–He, as shown in Table 1. Therefore, we employed these basis-sets together with the BSSE in the following ab initio and DFT calculations.

3.2. MP4(SDTQ), MP3 and MP2 results

By using the 6-31G basis-set augmented by the s-, p- and d-type diffuse functions adjusted in the CCSD(T) calculation, the MP4(SDTQ) calculations were performed. The results of MP4(SDTQ), MP3 and MP2 are shown in Figs. 2a, b and c, respectively. The estimated binding energies and equilibrium distances obtained by these methods are listed in Table 2. The MP4(SDTQ) result is almost the same as that of CCSD(T), although the binding energy is slightly underestimated. On the other hand, the MP3 and MP2 results are remarkably different from that of CCSD(T), indicating that these methods are not sufficient for describing the He–He interaction. These findings indicate that the evaluation of the accuracy of

Table 2
Binding energies and equilibrium distances of He dimer

	Experiment [15,16]	CCSD(T)	MP4(SDTQ)	MP3	MP2	PW91PW91	MPWPW91	MPW1PW91
Binding energy (kcal/mol)	0.021	0.021	0.019	0.017	0.012	0.210	0.064	0.050
Equilibrium distance (Å)	2.97	3.0	3.0	3.0	3.2	2.7	3.2	3.0

DFT methods based on the MP2 data by Sponer et al. [5] has not much meaning and that more accurate ab initio method with higher correlation consideration than MP2 is indispensable for describing van der Waals interaction of He–He.

3.3. Several DFT results

The accuracy of DFT methods is essentially due to the accuracy of the exchange and correlation functionals. Patton and Pederson [4] performed the PW91PW91 calculation with a large Gaussian-type basis-set constructed by contracting eight primitive Gaussian-functions. They found a binding state with the PW91PW91 functional but the calculated binding energy is about ten times as large as the experimental one [15,16]. We performed the same calculation with the adjusted basis-set. Fig. 3a shows the potential energy curve with the BSSE correction. The binding energy is estimated to be 0.21 kcal/mol, which is just ten times of the experimental one [15,16]. The PW91PW91 functional is found to largely overestimate the He–He binding energy with our basis-set too. Fig. 3a also clarifies that the dependence of exponent on the energy curve is much smaller than those in the ab initio calculations. This may indicate that DFT is relatively independent on the employed basis-set in comparison with the corresponding ab initio calculations, which is preferable characteristic for applications to large molecules such as DNA.

As for the other DFT functionals, Lacks and Gordon [13] carried out the Beck86 (B86), Perdew–Wang 86 (PW86) as well as PW91PW91 calculations by using the 10 s-type Gaussian basis-set of Huzinaga [31]. In the article we find that the B86 and PW86 exchange functionals are slightly more accurate than that of PW91PW91 for describing the van der Waals interactions between rare-gas atoms. The newer functional by Perdew, Burrke and Ernzerhof (PBE) [32] has the same form as the B86 exchange functional. They do not have s^4 term as in the PW91 exchange functional [21,22,33], where $s = |\nabla \rho| / 2\rho K_{\mathrm{F}}$ is the dimensionless density-gradient with the local Fermi vector $K_{\mathrm{F}} = (3\pi^2 \rho)^{1/3}$. The lack of this term may be responsible for the less enhanced contribution in the differential exchange energy ΔE_{exc}. The examination [13] on the power dependence in s^d indicates that the term with $d = 4$ is responsible for the overestimation of ΔE_{exc} in the PW91 exchange functional. We therefore used two other types of modified PW91 functionals; MPWPW91 [23] and MPW1PW91 [24], in which smaller value ($d = 3.73$) is employed. The latter is Becke-style one-parameter functional. The results for these two functionals are shown in Figs. 3b and c, respectively. The estimated binding energies and equilibrium distances are listed in Table 2. The results of these modified functionals are much better than that of PW91PW91. In particular, the binding energy (0.050 kcal/mol) and the equilibrium distance (3.0 Å) obtained by MPW1PW91 are comparable with the experimental results. The
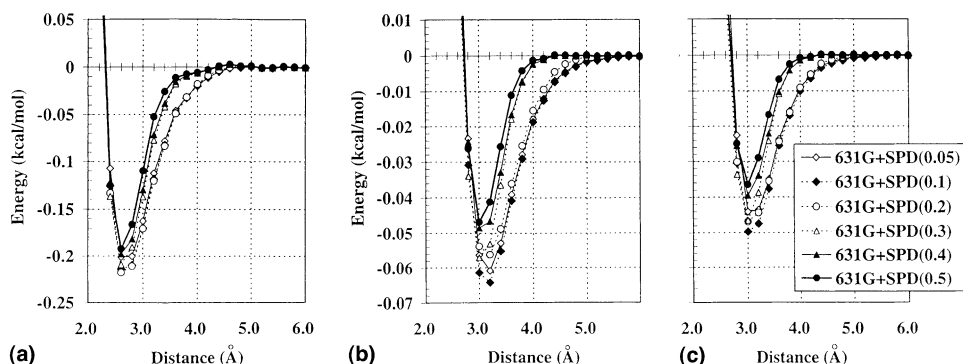

Fig. 3. He–He binding energy curves obtained by (a) PW91PW91, (b) MPWPW91 and (c) MPW1PW91 with the 6-31G basis-set augmented by s-, p- and d-type diffuse functions. The value in a parenthesis indicates the exponent of the diffuse functions.
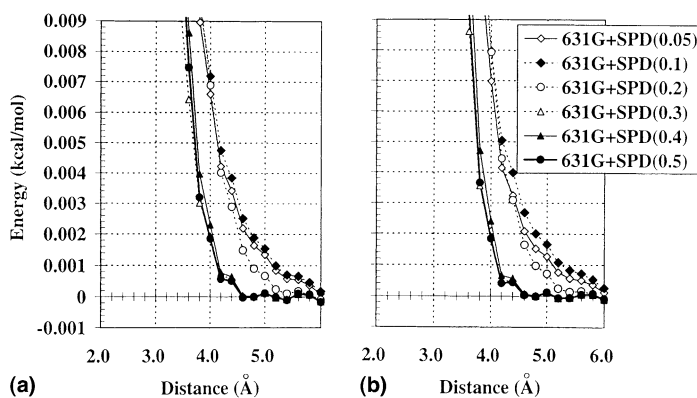
Fig. 4. He–He binding energy curves obtained by (a) B3LYP and (b) B3PW91 with the 6-31G basis-set augmented by s-, p- and d-type diffuse functions. The value in a parenthesis indicates the exponent of the diffuse functions.

DFT functionals with Becke's exchange functional, the B3LYP [18,19] and B3PW91 [20] calculations were also performed. Both the results completely fail to describe the He–He binding state, showing no minimal in the potential energy curves in Figs. 4a and b. These results are consistent with that by Adamo and Barone [23] and are comparable to the previous study [12] for Ne and Ar dimers. Finally, we checked the performance of the exchange functional by Gill [25]. In the G96PW91 calculation, the convergence for KS self-consistent field (SCF) is not easily obtained, so that the KS-SCF calculation stopped in halfway.

We see that DFT calculations with modified Perdew–Wang exchange functional have potential to describe the He–He van der Waals interaction quite accurately, although this binding property may be a result from fortuitous cancellations of inadequacies in the exchange-correlation functional. While we need further analysis on the long-range behavior of the functional, it is clear from the present DFT calculations that the Perdew–Wang-type exchange functional provides sufficient binding property, whereas the Becke-type one fails to do. It is also noted that the potential energy curves obtained by the DFT methods with the Perdew–Wang-type exchange functional are more reliable for describing the He–He interaction than other functionals such as Beck-type exchange functionals, so that these methods are recommended to use for analysis of stable structures of biomolecules. In order to clarify the deficiency of the exchange-correlation functionals in DFT methods for describing long-range behavior of electrons, we are investigating the long-range potential energy curve by several functionals with a long-range correction [34,35]. It is not entirely obvious that the wrong asymptotic behavior of Gaussian-type basis-sets has no significant contribution on such delicate and long-range properties of van der Waals interaction. The basis-set effect on van der Waals interaction is also under investigation by using our developed DFT code [8,9] based on Slater-type basis-set.

4. Conclusion

To propose an efficient method for describing van der Waals interaction, which plays an important and fundamental role in the stability and conformation of biomolecules, we performed CCSD(T), MP4(SDTQ) and several DFT calculations to evaluate the interatomic interaction between He atoms. Although the He dimer is very weakly bonded (its binding energy is only 0.021 kcal/mol) and therefore theoretical prediction is difficult, the CCSD(T) and MP4(SDTQ) methods using an 'adjusted' diffuse basis-set reproduce the experimental binding energy as well as the equilibrium distance. On the other hand, the MP3 and MP2 methods underestimate the binding energy.

Several DFT methods provide erroneous information. Especially the DFT methods with Becke-type exchange functional constantly predict the He dimer as unbounded. The DFT methods with the Perdew–Wang-type exchange functional can provide a He–He binding state, so that they are more accurate than those with the Becke-type exchange functional. However, the original PW91 exchange-correlation functional [33] overestimates the binding energy about ten times as the experimental value, which is probably because the PW91 exchange functional has the fourth-order term of electron-density-gradient and this term gives a wrong contribution to the differential exchange-energy ΔE_{exc} at the small-density-large-gradient regions between the He atoms. The modified Perdew–Wang exchange functional [23] improves this term, resulting in that the DFT methods with this exchange functional provide the comparable binding energies with the experimental one. Therefore, we conclude that the modification of the PW91 exchange functional is a promising way to produce the DFT functional applicable for investigating stable structures of biomolecules. The evaluation of other DFT functionals with and without a long-range correction and the analysis of other rare-gas dimers are in progress. The results will be published elsewhere.

Acknowledgements

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