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LETTERS

New Medium-Size Basis Sets To Evaluate the Dispersion Interaction of Hydrocarbon Molecules

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Medium-size basis sets were proposed to evaluate efficiently the dispersion interactions of hydrocarbon molecules. The aug(d,p)-6-311G** basis set was prepared by the augmentation of the diffuse d and p functions ($\alpha_d(C) = 0.1565$ and $\alpha_p(H) = 0.1875$) to the 6-311G** basis set. The aug(df,pd)-6-311G** basis set was prepared by the further augmentation of the diffuse f and d functions ($\alpha_f(C) = 0.2$ and $\alpha_d(H) = 0.25$) to the aug(d,p)-6-311G** basis set. The calculated MP2 and CCSD(T) intermolecular interaction energies of methane, ethane, propane, ethylene, acetylene, and benzene dimers with these basis sets were compared with those calculated with Sadlej's basis set and Dunning's correlation-consistent basis sets. Although the aug(d,p)-6-311G** basis set was more compact than Sadlej's basis set, this basis set was more effective to evaluate the dispersion energy. The aug(df,pd)-6-311G** basis set was considerably smaller than Dunning's cc-pVQZ and cc-pV5Z basis sets. The calculated interaction energies with the aug(df,pd)-6-311G** basis set were close to those calculated with the nearly BSSE-free cc-pVQZ and cc-pV5Z basis sets.

Dispersion interaction is well-known as the weak attractive interaction between rare gas atoms.[1] The same interaction is one of the important interactions between organic molecules. The dispersion interaction is responsible for the heats of sublimation of hydrocarbon molecules and makes a significant contribution to the solvent properties of polar neutral compounds.[2,3] The detailed information on the dispersion interactions of organic molecules is important to understand their condensed-phase properties and to carry out molecular dynamics simulations.[4,5]

Ab initio molecular orbital calculation has been employed to study the intermolecular interactions of small molecules.[6−8] However, the evaluation of the dispersion interaction was not an easy task. The dispersion interaction has its origin in electron correlation and molecular polarization.[1,9] A large basis set and electron correlation correction are necessary to evaluate the dispersion interaction. Small basis sets underestimate molecular polarizability and dispersion interaction. A large flexible basis set, which has a lot of polarization functions, is necessary to evaluate the dispersion interaction accurately.[9−11] However, the use of such a basis set causes the technical difficulties associated with handling large numbers of basis functions.

An efficient medium-size basis set has been strongly requested to evaluate the dispersion interactions of large molecules.[9] In this paper we have proposed two medium-size basis sets (aug(d,p)-6-311G** and aug(df,pd)-6-311G**) to evaluate efficiently the dispersion interactions of hydrocarbon molecules. We have compared the performance of the basis sets for the calculations of the intermolecular interaction energies of methane, ethane, propane, ethylene, acetylene, and benzene dimers with Sadlej's basis set[12,13] and Dunning's correlation-consistent basis sets.[14−16]

The Gaussian 94 program[17] was used for ab initio molecular orbital calculations of the dimers. The electron correlation energies were corrected by the MP2 method[18,19] and by the coupled-cluster calculations with single and double excitations

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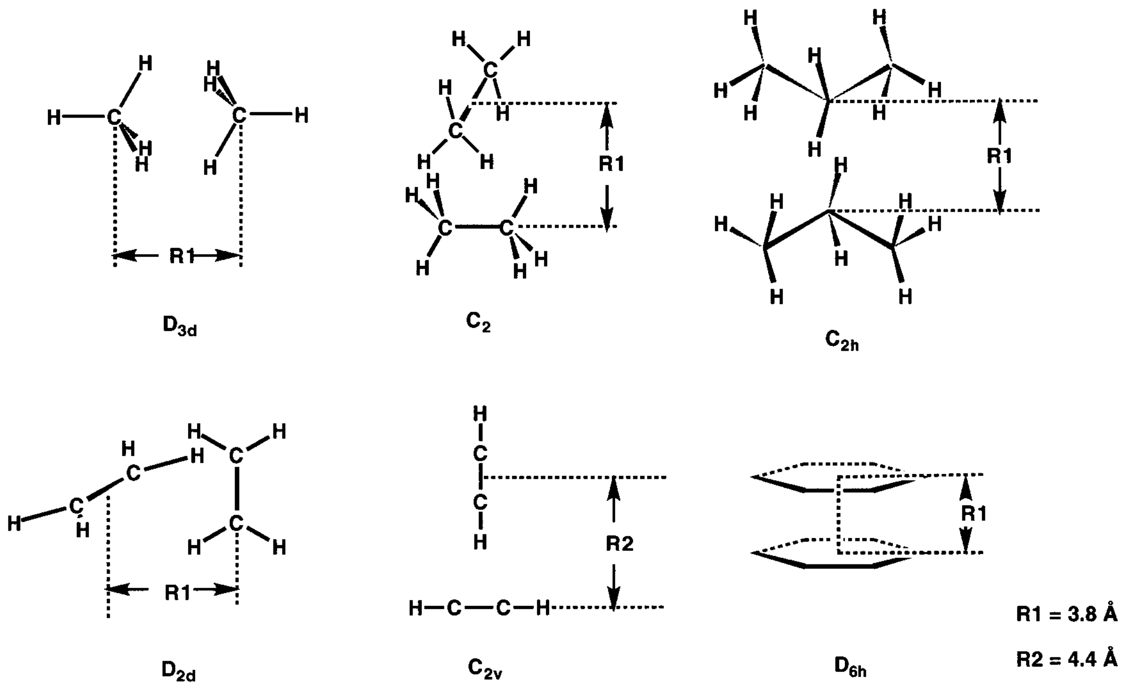

Figure 1. Orientations of the dimers.

TABLE 1: Calculated MP2 Interaction Energies of Hydrocarbon Dimers Using Several Basis Sets[a]

basis set	BF[b]	PG[c]	methane[d]		ethane	propane	ethylene	acetylene	benzene
6-31G*	46	88	0.03	(0.02)	0.04	−0.32	−0.23	−1.14	0.06
6-311G**	84	126	−0.14	(−0.14)	−0.45	−1.01	−0.62	−1.08	−1.30
6-311++G**	100	142	−0.15	(−0.16)	−0.50	−1.11	−0.70	−1.07	−1.93
6-311G(2d,2p)	118	160	−0.30	(−0.31)	−0.85	−1.51	−1.09	−1.38	−2.13
Sadlej[e]	120	240	−0.37	(−0.40)	−0.90	−1.63	−1.15	−1.39	−2.97
aug(d,p)−6-311G**[f]	118	160	−0.40	(−0.43)	−0.99	−1.72	−1.23	−1.41	−2.85
aug(df,pd)−6-311G**[f]	172	214	−0.45	(−0.49)	−1.11	−1.85	−1.40	−1.53	−3.09

[a] Energies in kcal/mol. BSSE was corrected by the counterpoise method. [b] Number of basis functions used for the calculation of methane dimer. [c] Number of primitive Gaussians used for the calculation of methane dimer. [d] CCSD(T) interaction energies are in parentheses. [e] References 12 and 13. [f] See text.

TABLE 2: Calculated MP2 Correlation Interaction Energies of Hydrocarbon Dimers Using Several Basis Sets[a]

basis set	methane[b]		ethane	propane	ethylene	acetylene	benzene
6-31G*	−0.25	(−0.27)	−1.05	−1.68	−0.79	−0.38	−4.57
6-311G**	−0.42	(−0.42)	−1.54	−2.37	−1.17	−0.45	−5.76
6-311++G**	−0.43	(−0.44)	−1.61	−2.49	−1.28	−0.55	−6.30
6-311G(2d,2p)	−0.58	(−0.58)	−1.96	−2.90	−1.63	−0.72	−6.63
Sadlej[c]	−0.64	(−0.67)	−2.02	−3.04	−1.72	−0.80	−7.20
aug(d,p)−6-311G**[d]	−0.68	(−0.71)	−2.11	−3.12	−1.79	−0.82	−7.25
aug(df,pd)−6-311G**[d]	−0.72	(−0.77)	−2.23	−3.26	−1.96	−0.92	−7.37

[a] MP2 correlation interaction energy is the difference between the SCF and MP2 interaction energies. Energies in kcal/mol. BSSE was corrected by the counterpoise method. [b] CCSD(T) correlation interaction energies are in parentheses. [c] References 12 and 13. [d] See text.

with noniterative inclusion of triple excitation (CCSD(T)).[20,21] The geometries of single molecules were optimized at the MP2/6-31G* level.[22] These geometries were used for the calculations of the dimers shown in Figure 1. The selected intermolecular distances correspond to the minimum energy distances of these orientations of dimers.[11,23] The basis set superposition error (BSSE)[24] was corrected by the counterpoise method.[25]

The calculated intermolecular interaction energies of the six dimers are summarized in Table 1. The attractive interactions are underestimated by the 6-31G*[22] and 6-311G**[26] basis sets compared with the larger basis sets. The basis set effects on the HF interaction energies were small. On the other hand, the MP2 correlation interaction energies, corresponding to the difference between the MP2 and HF interaction energies, which would be essentially the attractive dispersion energies, were greatly dependent on the basis sets used as shown in Table 2. Similar basis set dependence has been observed in other calculations.[9−11]

Starting from Pople's 6-311G** basis set,[26] polarization functions were augmented to improve the basis set. At the first step, a set of d functions were added to carbon atoms and a set of p functions were added to hydrogen atoms. At the next step, a set of f functions were added to carbon atoms and a set of d functions were added to hydrogen atoms. At each step the effects of the choice of the Gaussian exponents of the polarization functions were examined. We have examined the three Gaussian exponents for the d functions on carbon atoms (α_d(C) = 0.313, 0.1565, and 0.078 25) and also three exponents for the p functions on hydrogen atoms (α_p(H) = 0.375, 0.1875, and 0.093 75). These Gaussian exponents were obtained by scaling the exponents of the polarization functions of Pople's standard 6-311G** basis set by the factors 0.5, 0.25, and 0.125.

TABLE 3: Calculated Interaction Energies of Hydrocarbon Dimers at the MP2 Level Using Dunning's Correlation-Consistent Basis Sets[a]

			methane[d]			ethylene[d]			acetylene[d]		
basis set	BF[b]	PG[c]	E_{MP2}	E_{corr}	BSSE	E_{MP2}	E_{corr}	BSSE	E_{MP2}	E_{corr}	BSSE
aug(df,pd)−6-311G**[e]	172	214	−0.44	−0.72	0.33	−1.39	−1.96	1.35	−1.53	−0.92	1.00
cc-pVDZ[f]	68	142	−0.12	−0.40	0.19	−0.51	−1.13	0.97	−1.10	−0.45	0.60
cc-pVTZ[f]	172	264	−0.32	−0.60	0.09	−1.16	−1.73	0.41	−1.41	−0.80	0.24
cc-pVQZ[f]	350	464	−0.41	−0.69	0.03	−1.41	−1.97	0.18	−1.56	−0.96	0.12
cc-pV5Z[f]	622	772	−0.45	−0.73	0.02	−1.48	−2.05	0.07	−1.62	−1.03	0.05
basis set limit[g]			−0.48	−0.76		−1.54	−2.11		−1.68	−1.08	

[a] Energies in kcal/mol. BSSE was corrected by the counterpoise method. [b] Number of basis functions used for the calculation of methane dimer. [c] Number of primitive Gaussians used for the calculation of methane dimer. [d] E_{MP2} are the interaction energies calculated at the MP2 level. E_{corr} are the MP2 correlation interaction energies. BSSE are the differences between the calculated MP2 interaction energies with and without the counterpoise correction. [e] See text. [f] References 14−16. [g] Estimated values at the basis set limit. See text.

We have found that the $\alpha_d(C) = 0.1565$ and $\alpha_p(H) = 0.1875$ are the most effective to evaluate the attractive interactions. The aug(d,p)-6-311G** basis set is the 6-311G** basis set augmented with these diffuse d and p functions. The changes of the MP2 correlation interaction energies of the six dimers by the augmentation of the diffuse d and p functions are −0.26, −0.57, −0.75, −0.62, −0.37, and −1.49 kcal/mol, respectively. The MP2 correlation interaction energies calculated with the 6-311G** basis set are 21−45% smaller than those with the aug(d,p)-6-311G** basis set, which shows that the diffuse polarization functions are important to evaluate the attractive interactions of the hydrocarbon dimers. A similar magnitude of underestimation was observed in the CCSD(T) calculations of methane dimer.

The diffuse sp functions on carbon atoms and diffuse s functions on hydrogen atoms[27] are sometimes augmented to improve the basis set for the evaluations of the attractive interactions. But these diffuse functions are not so effective as the diffuse d and p functions of the aug(d,p)-6-311G** basis set. The changes of the calculated interaction energies by the augmentations of the diffuse sp and s functions are very small. The calculated interaction energies with the 6-311++G** basis set are close to those with the 6-311G** basis set as shown in Table 1.

The number of the polarization functions of the aug(d,p)-6-311G** basis set is the same as that of the 6-311G(2d,2p) basis set.[28] The 6-311G(2d,2p) basis set also underestimates the attractive interactions. The only difference between these two basis sets is the Gaussian exponents of the polarization functions. The Gaussian exponents of the polarization functions of the aug(d,p)-6-311G** basis set ($\alpha_d(C) = 0.626$ and 0.1565, $\alpha_p(H) = 0.75$ and 0.1875) are half of those of the 6-311G(2d,2p) basis set ($\alpha_d(C) = 1.252$ and 0.313, $\alpha_p(H) = 1.5$ and 0.375). This result shows the importance of the basis set flexibility in the tail region to evaluate the attractive interactions.

Several medium-size basis sets have been proposed to evaluate the dispersion energy efficiently.[12,13,29−35] Sadlej's basis set[12,13] is a commonly used medium-size basis set for this purpose. This basis set was not energy-optimized, but optimized to reproduce experimental dipole moments and polarizabilities. Recently Chalasinski and Szczesniak reported in their review that this basis set offered the best choice among these basis sets.[9] The calculated MP2 interaction energies of the methane, ethane, propane, ethylene, acetylene, and benzene dimers with Sadlej's basis set are −0.37, −0.90, −1.63, −1.15, −1.39, and −2.97 kcal/mol, respectively. Although the aug(d,p)-6-311G** basis set (118 basis functions and 160 primitive Gaussians for a methane dimer) is more compact and requires less CPU time than Sadlej's basis set (120 basis functions and 240 primitive Gaussians), the aug(d,p)-6-311G** basis set is better to evaluate the attractive interactions.

The main difference between the two basis sets is the number of the primitive Gaussians of polarization functions. Two sets of d functions on carbon atoms and two sets of p functions on hydrogen atoms are used in the aug(d,p)-6-311G** basis set. These polarization functions are not contracted. In Sadlej's basis set four sets of primitive Gaussians are used as the polarization functions. The four sets of the primitive Gaussians are contracted to the two sets of basis functions. Although the Sadlej's basis set employs larger numbers of the primitive Gaussians as the polarization functions, the performance of Sadlej's basis set was not better than the aug(d,p)-6-311G** basis set. This result shows that the larger numbers of primitive Gaussians used in Sadlej's basis set were not effective to improve the calculations of the attractive interactions.

We have examined four Gaussian exponents for the f functions on carbon atoms ($\alpha_f(C) = 0.8$, 0.4, 0.2, and 0.1) and also four exponents for the d functions on hydrogen atoms ($\alpha_d(H) = 1.0$, 0.5, 0.25, and 0.125). We have found that the $\alpha_f(C) = 0.2$ and $\alpha_d(H) = 0.25$ are the most effective. The aug(df,pd)-6-311G** basis set is the aug(d,p)-6-311G** basis set augmented with these diffuse f and d functions. The augmentations of these diffuse f and d functions further increased the correlation interaction energies. The MP2 correlation interaction energies of the dimers with the aug(df,pd)-6-311G** basis set are 2−12% larger than those with the aug(d,p)-6-311G** basis set. Additional polarization functions were augmented to the aug(df,pd)-6-311G** basis set to improve the basis set quality. However, the further augmentations affect little the calculated interaction energies, suggesting that the aug(df,pd)-6-311G** basis set is nearly saturated for the calculations of dispersion interactions.

The calculated MP2 interaction energies of the methane, ethylene, and acetylene dimers with the large correlation-consistent basis sets of Dunning are shown in Table 3. The interaction energies at the basis set limit were estimated by the extrapolations to the basis set limit with the fitting of the form $a + b\ \exp(-cX)$ (where X is 2 for cc-pVDZ, 3 for cc-pVTZ, etc).[36] The calculated interaction energies with the aug(df,pd)-6-311G** basis set are close to the estimated interaction energies at the basis set limit. Although the aug(df,pd)-6-311G** basis set is substantially smaller than Dunning's cc-pVQZ and cc-pV5Z basis sets,[14−16] the calculated intermolecular interaction energies of the three dimers with the aug(df,pd)-6-311G** basis set are close to those calculated with the nearly BSSE free cc-pVQZ and cc-pV5Z basis sets. The MP2 interaction energies of the methane dimer calculated with the aug-cc-pVDZ and aug-cc-pVTZ basis sets are −0.39 and −0.45 kcal/mol, respectively.

Although the aug-cc-pVDZ basis set (118 basis sets and 192 primitive Gaussians for a methane dimer) is larger than the aug-(d,p)-6-311G** basis set, the performance of these two basis sets are close. Similarly the performance of the aug-cc-pVTZ basis set (276 basis functions and 368 primitive Gaussians) is close to that of the considerably compact aug(df,pd)-6-311G** basis set.

Recently reported ab initio calculations show that the D_{3d} methane dimer (Figure 1) has the largest bonding energy.[23,37] The calculated MP2 and CCSD(T) interaction energies of the methane dimer using the aug(df,pd)-6-311G** basis set are −0.45 and −0.49 kcal/mol, respectively. The carbon−carbon separation of this dimer is 3.8 Å. The MP3/6-311G(3d,3p) level potential of this dimer has a minimum at this separation.[22] Several experimentally determined spherically averaged intermolecular interaction potentials of methane dimer have been reported.[38−43] The carbon−carbon distance of the potential minimum scatters in the range of 3.84−4.27 Å. The depth of the potential scatters in the range of 0.33−0.46 kcal/mol. Our calculated interaction energies cannot be directly compared with these spherically averaged potentials. However, the calculated interaction energies are not largely different from the depths of these experimentally determined potentials.

In summary, we have proposed new medium-size basis sets to evaluate the dispersion interactions of hydrocarbon molecules. Although these basis sets are compact, they can efficiently evaluate the dispersion interactions. The improvement of the basis set flexibility of the tail region by the augmentations of the diffuse polarization functions is important to evaluate the dispersion interactions.

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