Intermolecular potentials of the methane dimer calculated with Møller-Plesset perturbation theory and density functional theory

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We have calculated the intermolecular interaction potentials of the methane dimer at the minimum-energy D_{3d} conformation using the Hartree-Fock (HF) self-consistent theory, the correlation-corrected second-order Møller-Plesset (MP2) perturbation theory, and the density functional theory (DFT) with the Perdew-Wang (PW91) functional as the exchange or the correlation part. The HF calculations yield unbound potentials largely due to the exchange-repulsion interaction. In the MP2 calculations, the basis set effects on the repulsion exponent, the equilibrium bond length, the binding energy, and the asymptotic behavior of the calculated intermolecular potentials have been thoroughly studied. We have employed basis sets from the Slater-type orbitals fitted with Gaussian functions (STO-*n*G) ($n=3-6$) [*Quantum Theory of Molecular and Solids: The Self-Consistent Field for Molecular and Solids* (McGraw-Hill, New York, 1974), Vol. 4], Pople's medium size basis sets of Krishnan *et al.* [J. Chem. Phys. **72**, 650 (1980)] [up to 6-311++G($3df$,$3pd$)] to Dunning's correlation consistent basis sets [J. Chem. Phys. **90**, 1007 (1989)] (cc-pV*X*Z and aug-cc-pV*X*Z) (*X*=D, T, and Q). With increasing basis size, the repulsion exponent and the equilibrium bond length converge at the 6-31G** basis set and the 6-311++G($2d$,$2p$) basis set, respectively, while a large basis set (aug-cc-pVTZ) is required to converge the binding energy at a chemical accuracy (~0.01 kcal/mol). Up to the largest basis set used, the asymptotic dispersion coefficient has not converged to the destined C_6 value from molecular polarizability calculations. The slow convergence could indicate the inefficacy of using the MP2 calculations with Gaussian-type functions to model the asymptotic behavior. Both the basis set superposition error (BSSE) corrected and uncorrected results are presented to emphasize the importance of including such corrections. Only the BSSE corrected results systematically converge to the destined potential curve with increasing basis size. The DFT calculations generate a wide range of interaction patterns, from purely unbound to strongly bound, underestimating or overestimating the binding energy. The binding energy calculated using the PW91PW91 functional and the equilibrium bond length calculated using the PW91VP86 functional are close to the MP2 results at the basis set limit.
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I. INTRODUCTION

Intermolecular interaction potentials, or van der Waals interactions, or non-covalent-bonded interactions, play an essential role in condensed matter physics, materials chemistry, and structural biology. While these interactions are normally one or two orders of magnitude weaker than typical covalent bonds, they are crucial in determining the thermodynamic properties of molecular liquids and solids,[1] the energy transfers among molecular complexes,[2] and the conformational tertiary structures of macromolecules such as protein and DNA.[3] Unlike intramolecular covalent bonds, intermolecular bonds do not originate from sharing of electrons but rather arise from simultaneous electron correlation of the separated subsystems.[4] Different from stiff covalent bonds, they are relatively soft and nonrigid. Early studies of intermolecular interactions can be traced back to one century ago,[5] while measurements of these interactions are still challenging in the present time.[6] The main difficulty in determining intermolecular interactions experimentally resides at limited samplings of the potential energy surface. For example, experiments using the x-ray crystallography or the laser spectroscopy mainly explore the equilibrium regions of the potential, while thermodynamic measurements in the gas or liquid phase often yield isotropic potential data without the desired stereochemical responses. In addition, the measured potentials sensitively depend on the thermodynamic conditions. Usually two measurements carried out in different conditions cannot be compared directly but rely on auxiliary theoretical modeling.

Alternatively intermolecular potentials can be calculated in terms of correlation-corrected quantum chemistry methods[7–9] or density functional theory (DFT).[10,11] These quantum mechanics based potentials are requested by *ab initio* molecular dynamics simulations[12] and by classical molecular simulations using force field constructions.[13] Among the components of an intermolecular interaction, the London dispersion force is the most difficult to calculate. The reason is that dispersion interactions arise from the nonlocal "dynamic" correlations.[14] This nonlocality demands full explo-

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ration of the time-dependent perspective of quantum mechanics. Often an electron correlation-corrected method and a large basis set are required to obtain accurate dispersion forces.[15] Also a technical note is in order. Most present implementations of quantum chemistry programs utilize Gaussian-type functions to fasten the calculations of Coulomb repulsion integrals. Because Gaussian-type functions are local functions, a large basis set is indispensable to perform a correlation energy calculation. Moreover, these functions do not have the correct asymptotic behavior as the intermolecular separation becomes large. Therefore, the basis set limit of the calculated potential must be estimated so as to be consistent with the conventional perturbation theory.

For general polar molecular systems, the relatively weak dispersion energy is masked by the competing electrostatic energies and hydrogen bond interactions. Nonpolar atomic and molecular dimers are usually taken as a prototype case to study the dispersion energy. Many previous studies on dispersion forces have focused on atomic inert gas dimers and several important conclusions have been drawn from the calculations.[16] There are, however, comparatively fewer detailed studies on whether similar conclusions can be applied to molecular dimers. Because of the extra degrees of freedom and the stereochemical responses, the conclusions about atomic dimers may need to be extended or modified in dealing with molecular dimers. Methane is a nonpolar molecule with vanishing dipole and quadrupole moments and the first nonvanishing electrostatic interaction is the octopole-octopole interaction. The higher order electrostatic interactions are rather weak and decay fast at large intermolecular separation. The dominant long-range attraction for the methane dimer is thus due to the London dispersion force. On the other hand, the strong repulsive force almost comes from the exchange-repulsion interaction due to the overlapping of electron clouds. Because the exchange-repulsion interactions have been incorporated in the Hatree-Fock (HF) self-consistent theory, post-HF methods such as the Møller-Plesset (MP) perturbation theory and the coupled cluster (CC) theory are often used to calculate the correlation effect. Contrasting both sets of calculation helps to delineate the relative importance of the dispersion energy in the overall intermolecular interaction. In addition, the interaction potentials of alkanes, among them methane being the smallest model, are very crucial in determining the packing morphology in solids and liquids and in lipid bilayers.[17–19] The potentials are also requested for mesoscale simulations for macromolecules[20] because many polymers contain alkyl groups as their backbone units or side chains. Therefore, the calculation of intermolecular interactions of the methane dimer is a "must" and serves as a prototype example to start to investigate the various factors affecting the calculations of these interactions.

There have been many quantum chemistry studies of intermolecular potentials of the methane dimer using correlation-corrected methods.[21–32] Szczesniak *et al.*[21] have used the MP2 method with the Sadlej basis to calculate the interaction energies for the six conformers of the methane dimer. They found that the minimum-energy conformation is the D_{3d} conformer and the dimer structure is determined by minimizing the steric repulsion between hydrogen atoms belonging to opposite subsystems. Tsuzuki and Tanabe[24] have studied the basis set effects using basis sets from 6-31G* to 6-311++G$(2d,2p)$ to calculate the interaction energies for two conformers of the methane dimer (but none of them is the D_{3d} conformer). They observed little basis set effect on the HF calculations as long as one uses a basis set larger than the 6-31G* one. The basis set effect is significant for the MP2 interaction energies and the basis set superposition error (BSSE). The dispersion energy can be seriously underestimated if a smaller (than 6-31G*) basis set has been used. They found that the BSSE uncorrected interaction energies do not systematically converge to a destined value, in contrast to those with BSSE corrections. Tsuzuki *et al.*[27,31] studied 12 conformers and verified that the D_{3d} conformer corresponds to the minimum-energy geometry. They observed that a large basis set with multiple polarization functions is necessary to evaluate the dispersion energy accurately. They found that augmentation of the diffuse d and p functions to the 6-311G** basis set more efficiently yields the dispersion energy. Tsuzuki and Luthi[28] and Tsuzuki *et al.*[31] explored the effect of the choice of the correlation-correction methods on the calculations of intermolecular interactions. They demonstrated that the MP2 and MP3 energies are not too far away from the higher level MP4(SDTQ) calculations, while the latter is not less expensive than the CCSD(T) calculation. They tested the DFT using the BLYP, BPW91, and B3LYP functionals but found unbound interactions while the PW91 functional underestimates only 8% of the potential well depth. They suggest that DFT with the PW91 functional could be an alternative to the *ab initio* methods. Recently, Tsuzuki *et al.*[32] have estimated the MP2 and CCSD(T) interaction energies of the *n*-alkane dimers at the basis set limit using Dunning's correlation consistent basis sets.

Many previous studies mainly focused on the equilibrium region of the potentials with relatively few discussions of the full potential curves. Nevertheless, to construct a reliable force field model for molecular simulations, the full intermolecular potential surfaces are required. In this paper we perform a comprehensive up-to-date study on interaction potentials of the prototype methane dimer in terms of the HF, MP2, and DFT methods to gain more understanding of this system. With current computational powers, a detailed editing of the potential database can be obtained for small size molecular clusters. It is thus so important to obtain general features of the calculations that we can follow to explore large scale molecular simulations via similar procedures. The purpose of this paper is twofold. First, we use the state-of-the-art methodology to obtain accurate potential energies for the methane dimer. We would like to verify or modify the previous conclusions about the basis set effects and the effect of including the BSSE on the calculation details of the intermolecular interactions. The basis set effects on repulsion exponents, equilibrium bond lengths, binding energies, and asymptotic coefficients of the calculated intermolecular potentials are thoroughly studied. This is achieved using basis sets from STO-3G (Ref. 35) to aug-cc-pVQZ.[37] The full potential curves are presented in order to see the overall scope of the potential. In particular, both the BSSE corrected and

uncorrected results are presented to emphasize the importance of these corrections. Second, this paper attempts to reassess the utilities of using the available implementation of the density functional theory in determining the intermolecular interactions. From the studies of atomic dimers, it has been found that conventional DFT based on the local density approximation (LDA) and generalized gradient approximation (GGA) cannot calculate the intermolecular interactions to a satisfying level of accuracy.[52] The popular BLYP and B3LYP functionals actually yield unbound potentials for the methane dimer.[28] It is thus desirable to investigate other possible combinations of available functionals to serve as alternatives for *ab initio* calculations.

The paper has been organized as follows. In Sec. II, we describe the details of these calculations. In Sec. III the results are presented and discussed. A summary and a brief perspective are given in Sec. IV.

II. METHODS AND CALCULATIONS

In the case of methane dimers, a large part of the exchange-repulsion interactions can be calculated by the HF method. The calculation of electron correlation energies depends on the level of the correlation-corrected method, the size of the basis set, and the correction of the BSSE. The state-of-the-art choice of the correlation-corrected method is either the Møller-Plesset (MPx,x=2,3,4) perturbation method[33] or the coupled cluster method with iterative single and double substitutions and with noniterative triple excitations [CCSD(T)] method.[34] It has been found that the MP2 results for the methane dimer are not too much different from those calculated by the much more expensive CCSD(T) as long as a large basis set has been used.[31] To study the basis set effects, we have employed comprehensive basis sets from the Slater-type orbitals fitted with Gaussian function (STO-nG) (n=3–6),[35] medium size basis sets of Krishnan *et al.* [up to 6-311++G(3df,3pd)] (Ref. 36) to Dunning's correlation consistent basis sets (aug-cc-pVXZ) (X=D, T, and Q).[37] The BSSE was corrected by the counterpoise (CP) method of Boys and Bernardi.[38] The MP2 interaction potentials at the basis set limit have been estimated using the methods of Helgaker *et al.*[39] and Feller[40] and a numerical extrapolation scheme based on the Lagrangian formula.[41]

All the HF, MP2, and DFT calculations are performed using the GAUSSIAN 03 program package[42] on a single node two-processor AMD 250 personal computer (PC) cluster with distributed memory. The equilibrium geometry of a single methane molecule was first optimized at the MP2/6-31G* level of theory. To obtain the most stable intermolecular geometry, the methane dimer has been modeled by first fixing the carbon-carbon (C–C) distance while letting the two monomers to rotate freely. By approaching the monomers from the far side with several initial choices of mutual orientation, we found the minimum-energy conformation corresponds to the D_{3d} symmetry conformer. This optimized conformer has been reached through the interplay of the steric stabilization of repulsive hydrogens in opposite monomers.[21] Subsequently the C–C distance was sampled in step 0.1 Å for a quite large range of intermolecular separation (normally 3–9 Å). During the scan we allow the individual methane molecule to be fully relaxed. This means that we do not fix the monomer geometry and the methane molecule is not assumed to be rigid. Although it is not expected to see much deviation from the rigid molecule approximation, in the real condensed phase environment, stretching, bending and torsional relaxations could be important for many subtle thermodynamic properties. The inclusion of intermolecular relaxation is especially relevant to the construction of force fields for use in molecular dynamics simulations where flexible models often work better than rigid models.[43]

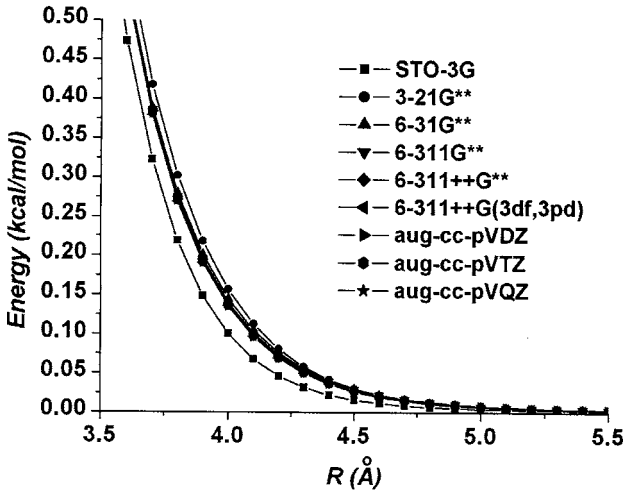

FIG. 1. The BSSE corrected HF interaction potentials of the methane dimer using several basis sets.

III. RESULTS AND DISCUSSIONS

The intermolecular interaction potentials of the D_{3d} conformer of the methane dimer have been calculated with the HF, the MP2, and the DFT methods. We present the respective results along with discussions and make comparisons among the results.

A. Hartree-Fock self-consistent field calculations

The BSSE corrected HF interaction potentials of the methane dimer using several basis sets are shown in Fig. 1. All the HF calculations yield purely repulsive potentials without minima for all the basis sets used. This can be attributed to the rather weak electrostatic interaction for the methane dimer. In the short range, the strong exchange-repulsion interaction dominates with little alternation from electrostatic and induction attractions. The HF potential is insensitive to the basis size as long as the 6-31G** basis set has been used. We can model the HF potential using the repulsive Buckingham function,[44]

$$V_{\mathrm{HF}}(R) = Ae^{-\alpha R},$$

where R is the C–C distance, A and α (the repulsion exponent) are the fitting parameters. The dependence of the repulsion exponent on the basis size is shown in Table I. It is seen that the repulsion exponent converges quickly after the 6-31G** basis set being used.

TABLE I. The basis set dependence of important potential parameters using the BSSE corrected HF and MP2 intermolecular potentials. R_0 is the distance at which the potential is zero and R_m is the equilibrium bond length. The CPU time of the MP2 calculation was recorded on a single node two-processor AMD 250 PC cluster with distributed memory.

	MP2		HF		MP2						
										two terms[c]	
Basis set	Number of basis function	CPU time (h)	A[a] (kcal/mol)	α[a] (Å^{-1})	R_0 (Å)	R_m (Å)	E_b (kcal/mol)	ω (cm^{-1})	one term[b] C_6	C_6	C_8
STO-3G	9	0.25	219 400	3.62	4.36	4.75	−0.009	42.99	189.03	136.04	1 596.61
3-21G	34	0.28	83 319	3.29	4.05	4.50	−0.047	78.39	641.57	419.58	6 477.70
6-31G	34	0.28	104 302	3.36	3.99	4.45	−0.053	73.33	676.57	438.12	6 957.93
6-311G	50	0.37	113 764	3.39	3.91	4.36	−0.064	83.45	747.23	486.94	8 437.88
3-21G**	58	0.38	83 602	3.30	3.85	4.31	−0.078	101.15	832.07	556.44	10 586.51
6-311G*	60	0.48	115 208	3.40	3.73	4.16	−0.104	108.73	951.51	454.57	8 356.77
cc-pVDZ	68	0.68	120 594	3.41	3.63	4.05	−0.150	130.17	1174.71	684.90	11 986.23
6-31G**	70	0.57	108 646	3.39	3.73	4.19	−0.101	108.73	941.68	544.89	11 028.72
6-311G**	84	1.17	115 208	3.40	3.59	4.02	−0.165	161.64	1207.04	640.12	14 790.89
6-311+G**	92	1.57	115 057	3.40	3.58	4.01	−0.174	159.31	1245.15	673.37	15 081.38
6-311++G**	100	2.42	115 298	3.40	3.57	4.01	−0.176	159.31	1259.19	671.72	15 584.98
aug-cc-pVDZ	118	3.22	123 739	3.42	3.35	3.78	−0.395	369.19	1995.05	764.34	22 587.36
6-311++G(2d,2p)	134	5.62	114 025	3.40	3.38	3.80	−0.315	217.47	1674.00	812.170	21 662.07
6-311++G(3d,3p)	168	12.22	112 605	3.40	3.33	3.75	−0.401	278.15	1964.62	1456.53	9 860.58
cc-pVTZ	172	13.35	113 006	3.40	3.37	3.80	−0.317	215.83	1880.25	1446.17	10 119.20
6-311++G(2df,2pd)	188	20.35	113 940	3.40	3.36	3.78	−0.331	209.88	1697.49	1437.55	10 518.06
6-311++G(3df,3pd)	222	22.63	112 373	3.40	3.30	3.73	−0.415	270.57	1979.52	1593.49	7 987.79
aug-cc-pVTZ	276	82.70	112 320	3.40	3.27	3.70	−0.453	260.45	2048.04	1442.32	11 755.28
aug-cc-pVQZ	528	941.83	111 828	3.40	3.26	3.68	−0.464	250.34	2029.20	1053.08	18 021.33
Basis set limit			113 458	3.40	3.25	3.66	−0.470	256.54	⋯	⋯	⋯

[a]Fit to the formula $V_{HF}(R)=Ae^{-\alpha R}$.
[b]Fit to the formula $V_{disp}(R)=-C_6/R^6$, C_6 in unit (kcal/mol Å^6), using data $R>5.0$ Å.
[c]Fit to the formula $V_{disp}(R)=(C_6/R^6)-(C_8/R^8)$, C_8 in unit (kcal/mol Å^8), using data $R>4.0$ Å.

B. MP2 calculations

Unlike the HF potentials, the MP2 potentials shown in Fig. 2 display clear minima and long-range attractive potential tails. Because the contributions from the octopole-octople interactions are small, the dispersion energy is mainly responsible for the attractions. Sharp differences between the HF calculations and the MP2 calculations indicate the importance of including the correlation corrections in the wave function calculations. The HF method in principle does not include the correlation effect so the attraction forces are due exclusively to the correlation effect.

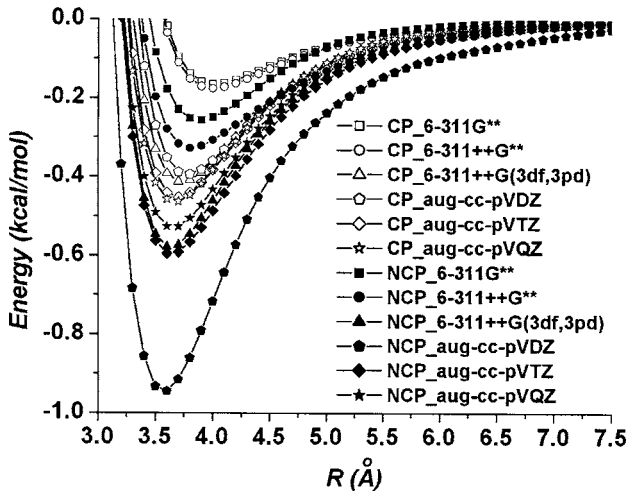

FIG. 2. The BSSE corrected (CP) and uncorrected (NCP) MP2 potentials of the methane dimer using a series of basis sets.

In Fig. 2, we compare the MP2 potentials with and without the BSSE corrections (denoted as CP and NCP, respectively). We see very strong dependence of the interaction potentials on the BSSE corrections. The potentials without the BSSE corrections fluctuate with increasing basis size and do not systematically converge to the destined curve at the basis set limit. On the contrary, the BSSE corrected potentials systematically approach to the destined curve with increasing basis size. Therefore, it is important to consider the BSSE correction in calculating the intermolecular interactions, in particular, for small basis sets.

As shown in Table I, the basis set effect on the BSSE corrected interaction potentials is significant. The STO-3G basis set yields very small binding energy. The interaction energy becomes more accurate as one adds polarization functions and augments diffuse functions in Pople's basis sets. Small cc-pVDZ and cc-pVTZ basis sets lead to underestimated binding energies and it requires cc-pVQZ to saturate the result. Augmentation of the diffuse functions has significant effect on optimizing the binding energy. The cc-pVTZ basis set underestimates the energy by 30%, while the aug-cc-pVTZ basis set underestimates only 5% of the binding energy. Some subtle basis set features can also be observed. For small basis sets, adding polarization functions to the

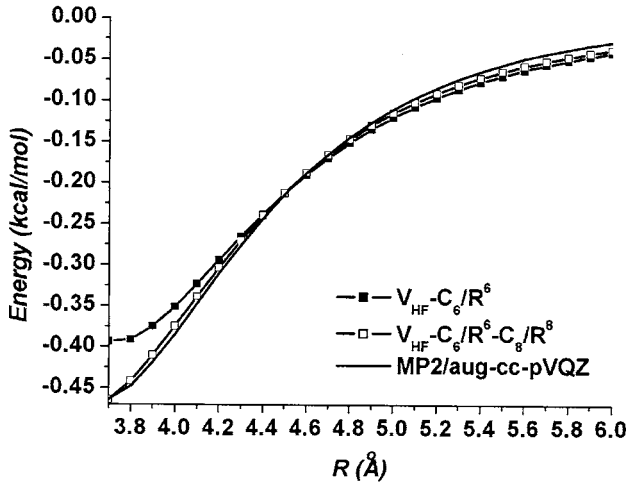

FIG. 3. Comparison of the BSSE corrected MP2 potential curve calculated at the aug-cc-pVQZ basis set and the sum of the HF potential and the long range dispersion potentials.

basis set does not significantly change the potential. On the other hand, augmentation of the diffuse functions has pretty significant effect. For example, the aug-cc-pVDZ energy is very close to the high level 6-311++G$(3df,3pd)$ and the cc-pVQZ results. These paraphrase Tsuzuki *et al.*[31] to construct a diffuse-function-augmented medium size 6-311G** basis set in their calculations. Together with diffuse functions, adding more polarization functions also improves the accuracy of the calculated potential. For example, the 6-311++G** underestimates the binding energy by 60%, while the 6-311++G$(3df,3pd)$ yields a binding energy by 12% lower than the MP2 energy at the basis set limit. It is understood that dispersion interactions arise from the nonlocal electron correlation effect so adding functions of extensive range help to optimize the potentials.

With the wide span of the basis sets used, the basis set dependence of important potential parameters can now be fully studied. In Table I we present the BSSE corrected data for the equilibrium bond length, the binding energy, and the asymptotic behavior. R_0 is the distance at which the potential is zero and can be obtained from a two point interpolation of the calculated data. The bond length R_m, the binding energy E_b, and the intermolecular vibration frequency ω can be obtained through a harmonic modeling of the three lowest potential data near the equilibrium regions. C_6 and C_8 are the dispersion coefficients and can be obtained through a nonlinear fitting of the long-range potential data. With increasing basis size, the equilibrium bond length converges at the 6-311++G$(2d,2p)$ basis set to a 0.1 Å accuracy, while a pretty large basis set (aug-cc-pVTZ) is required to converge the binding energy at a chemical accuracy ($\sim$0.01 kcal/mol). On the other hand, up to the largest basis set used, the asymptotic behavior has not yet converged to the destined C_6 value from the calculated monomer polarizability ($\sim$1784 kcal/mol Å^6).[45–47] Inclusion of the C_8 term is important if shorter range data were used for the modeling. As shown in Fig. 3, the long-range curve can be reproduced better when including the C_8 term. The slow convergence could be an indication of the inefficacy of using the MP2 method with Gaussian functions to calculate long-range interactions. Because Gaussian-type functions are local functions, a large basis set is required to obtain converged correlation energy calculations. Therefore, the basis set limit of the calculated potential must be estimated so as to be consistent with the conventional perturbation theory. Together with the nonlinear scaling of the computational cost with respect to the basis size, this is actually the main practical reason for the difficulty of obtaining dispersion interactions through *ab initio* molecular orbital methods.

The strong basis set dependence and the slow convergence on the dispersion coefficients call for an estimation of the important potential features at the basis set limit in a calculated potential. Basis set limit of the binding energy can be approached using Dunning's basis sets with an extrapolation scheme. We consider two analytical schemes[39,40] and a numerical scheme[41] while the results are similar. The binding energies obtained at the basis set limits (using Dunning's basis sets, aug-cc-pVXZ, X=D, T, and Q) are 0.472, 0.467, and 0.470 kcal/mol using the methods of Helgaker *et al.*,[39] Feller,[40] and the numerical method,[41] respectively. These values are very close to the results obtained by Tsuzuki *et al.*[32] For the other potential parameters, we used the numerical extrapolation based on the vanishing inverse of the number of basis function.[41] These results are shown in Table I for comparison.

C. Density functional theory

The density functionals used in the present work include two sets. The first set fixes the exchange functional as the PW91 and changes the correlation functionals. The correlation functionals include PL,[48] VWN5,[49] VWN,[49] TPSS,[50] PBE,[51] PW91,[52] VP86,[53] P86,[53] V5LYP,[54] LYP,[54] HCTH93, and HCTH407.[55–57] The second set fixes the correlation functional as the PW91 and changes the exchange functionals. The exchange functionals include HCTH93, HCTH147, HCTH407,[55–57] MPW,[58] MPW1,[58] OPTX or O,[59] B88 or B,[60] PBE,[51] Slater or S,[61] and Xα or XA.[61] The choice of these combinations is motivated by a recent suggestion that the PW91PW91 functional yield good binding energy of the methane dimer interaction.[28] However, the role of the PW91 as an exchange versus a correlation functional has not been systematically studied. Moreover, it is not clear if the functional is reliable for use in determining other potential parameters.

Figure 4 presents the calculated intermolecular potential curves using the PW91 as the exchange or the correlation functional. We see that the DFT calculations generally generate a diverse range of potential curves from purely unbound (BPW91) to strongly bound (XAPW91). In Table II we compare the bond lengths and the binding energies calculated using the several exchange-correlation functionals with the MP2 results. We see that the PW91PW91 combination produces reasonable potential well depth while the bond length is estimated too long. The PW91VP86 functional yields good bond length and captures the attraction effect quite well, although it overestimates the binding energy by

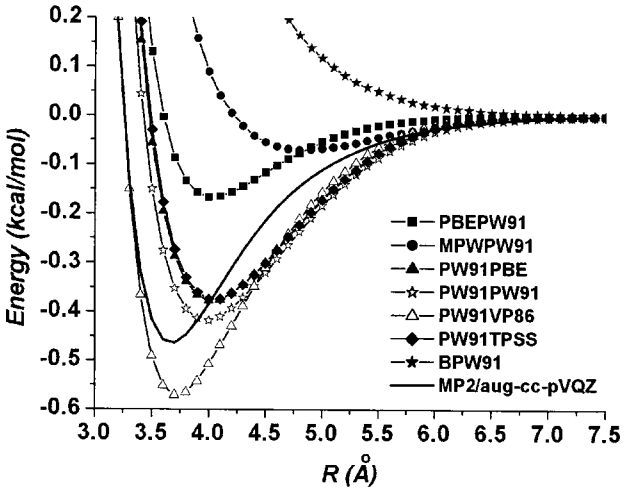

FIG. 4. The BSSE corrected DFT intermolecular potential curves using the PW91 as the exchange or correlation functional.

20%. It is promising that available functionals do capture partly the correlation effects which are essential in calculating the dispersion forces.

The results shown in Table II clearly demonstrate the relative roles played by the exchange and correlation functionals in the DFT calculations. By fixing the PW91 as the exchange functional, most correlation functionals yield bound potentials and the binding energies are around the MP2 result (except the HCTH correlation functionals, which yield seriously overbound potentials). On the other hand, by fixing the PW91 as the correlation functional, the varying exchange functionals either overestimate (S and XA) or underestimate (HCTH, MPW, O, B, and PBE) the binding energy. Previous studies on van der Waals systems[78,79] have shown that the exchange functional plays an essential role in determining the dispersion energy while the correlation part of a density functional does not significantly affect the DFT calculations. Our results are basically consistent with these observations, although we see appreciable effects due to the choice of the correlation functional. The performance of varying exchange functionals for a fixed correlation functional can be understood in terms of the behavior of the GGA enhancement factor $F(s)$ of the exchange functional at the large gradient-to-density ratio, denoted as s, region.[80] Following Lacks and Gordon,[81] we plot the $F(s)$ vs s curve in Fig. 5. We see in Fig. 5 that the order of the magnitude of $F(s)$ at large s is B88>HCTH>OPTX>PBE>MPW>PW91. This order is essentially the order of the binding energies calculated by the corresponding functionals in Table II. This correlation has been found in previous studies on van der Waals systems[78,79] and serves as a useful tool in analyzing the DFT calculations. Another criterion for $F(s)$ to be satisfied is the Lieb-Oxford condition[82] which requires that $F(s) \leqslant 2.273$. From Fig. 5 we see that the PBE, MPW, and PW91 exchange functionals obey this condition. The above analyses, together with Perdew's suggestion that the PW91 exchange functional should be used with the corresponding PW91 correlation functional,[83] explain why the PW91PW91 functional outperforms other combinations of the exchange and correlation functionals in the calculations of dispersion interactions.

TABLE II. Comparison of the bond lengths and the binding energies calculated using the several exchange-correlation functionals with the MP2 results using the 6-311++G($3df$,$3pd$) basis set.

	6-311++G($3df$,$3pd$)	
Functional	Bond length (Å)	Binding energy (kcal/mol)
PW91PL	4.19	−0.360
PW91VWN5	4.19	−0.358
PW91VWN	4.14	−0.387
PW91TPSS	4.05	−0.376
PW91PBE	4.04	−0.379
PW91PW91	3.99	−0.418
PW91VP86	3.73	−0.572
PW91P86	3.72	−0.577
PW91V5LYP	3.80	−0.669
PW91LYP	3.80	−0.669
PW91HCTH93	3.56	−1.444
PW91HCTH407	3.52	−3.367
HCTH93PW91	5.93	−0.003
HCTH147PW91	5.82	−0.006
HCTH407PW91	5.93	−0.004
MPWPW91	4.83	−0.071
MPW1PW91	4.80	−0.050
OPW91	5.23	−0.021
BPW91	Unbound	···
PBEPW91	4.04	−0.167
SPW91	3.08	−2.483
XAPW91	2.97	−2.671
MP2	3.73	−0.415

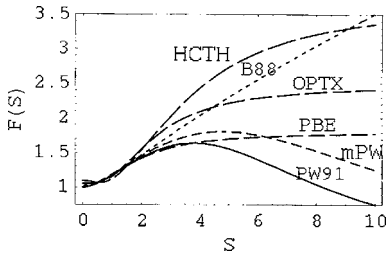

FIG. 5. The GGA enhancement factor as a function of s for the HCTH, B88, OPTX, mPW, PBE, and PW91 exchange functionals.

IV. CONCLUSION

In this paper we have systematically studied the calculated intermolecular potentials of the methane dimer at the most stable D_{3d} conformation using the HF, MP2, and DFT methods. A wide selection of basis sets has been employed in order to determine the basis set effects on the repulsion exponent, the binding energy, the equilibrium bond length, and the asymptotic behavior of the intermolecular potentials. BSSE corrections are considered as an important factor affecting the quality of the calculated potentials.

From this study we can draw several important conclusions about using the current theoretical methods to generate

the intermolecular potentials. Although only the methane dimer has been studied, these conclusions should also be useful to other molecular dimers.

(1) The HF calculations yield purely repulsive potentials for nonpolar molecular dimers. The basis size effect of the HF calculations is very small as long as the 6 -31G** basis set has been used.
(2) The van der Waals bond of the methane dimer is well produced using the MP2 method. BSSE corrections must be considered to yield systematic results. Basis set effects are significant for many important parameters such as bond lengths, binding energies, and dispersion coefficients. Small basis sets, especially without the augmentation of diffuse functions, could produce severe underestimation of the binding energy and overestimation of the bond length. Addition of diffuse functions and polarization functions leads to reliable binding curves.
(3) The DFT potentials display a wide range of patterns of binding curves, underestimating or overestimating the binding energy. The binding energy calculated using the PW91PW91 functional and the equilibrium bond length calculated using the PW91VP86 functional are close to the MP2 results.

From the present study we see very clearly that the HF method captures the exchange-repulsion interaction and saturates the potential curves at small basis set. Inclusion of the correlation corrections using *ab initio* molecular orbital methods makes the calculations computationally demanding (CPU time $\sim N^4$, where N is the number of basis function). The DFT calculations are comparatively cheaper but the results are not systematic. Some functionals do capture partly the correlation effects. These observations justify the recent efforts in improving the calculations of the intermolecular interactions using the HF or the DFT method by including explicit empirical or nonempirical dispersion energy corrections.[62–78] More works are definitely required to make the two ends (accuracy versus efficiency) meet.

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