

**Intermolecular interaction potentials of the methane dimer from the local density approximation**Xiang-Rong Chen,<sup>1,2,3</sup> Yu-Lin Bai,<sup>1,4</sup> Jun Zhu,<sup>1,\*</sup> and Xiang-Dong Yang<sup>1</sup><sup>1</sup>*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, People's Republic of China*<sup>2</sup>*International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, People's Republic of China*<sup>3</sup>*Institute of Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8571, Japan*<sup>4</sup>*Department of Science and Technology of Electronic Information, Yibin University, Yibin 644000, People's Republic of China*

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The intermolecular interaction potentials of methane (CH<sub>4</sub>) dimer are calculated within the density functional theory in the local density approximation (LDA). It is found that the calculated potentials have minima when the intermolecular distance of CH<sub>4</sub> dimer is about 7.0 a.u., which is in good agreement with the experiment. The depth of the potential is 0.017 eV. The results obtained by our LDA calculations seem to agree well with those obtained by MP2, MP3, and CCSD from the Møller-Plesset and coupled cluster methods by Tsuzuki *et al.* and with the experimental data.

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It is well known that properties of single molecule can be calculated more and more accurately with growing computer speed and refined algorithms from pure theory. To understand the structures and the properties of gases, liquids, solids, as well as any other matter in condensed phase, it is necessary to study the intermolecular interaction potentials, i.e., the nonbonding interaction potentials mainly resulting from van der Waals interactions [1]. The structures of numerous nonbonding interaction systems have been recently examined spectroscopically using experimental techniques [2–4]. Another effective way to obtain the information for nonbonding interaction systems is to carry out quantum chemical calculations with some suitable approximations [5–7], by which one can derive the detailed information about the interaction energies over a wide area of the potential surface. However, the requirements of a large basis set and the electron correlation correction are difficulties in using quantum chemical methods to determine intermolecular interaction energies [8].

Presently, the intermolecular interaction potentials for kinds of complexes, such as the rare-gas atom dimer (He-He, Ne-Ne, Ar-Ar, He-Ne, He-Ar, Ne-Ar) [9], C<sub>2</sub>H<sub>2</sub>-HCl [10], CO<sub>2</sub>-CO<sub>2</sub> [11], He-NH<sub>3</sub> [12], CH<sub>4</sub>-CH<sub>4</sub> [13] and so on, have been the focus of theoretical investigations using quantum chemical calculations. Here we only focus on methane dimer (CH<sub>4</sub>-CH<sub>4</sub>). The reason why we choose methane dimer is that methane is regarded as one of the origins of gases of the life on the earth or in the universe, and CH<sub>4</sub> molecule is a typical hydrocarbon molecule and the dispersion interaction is one of the major interactions in its hydrocarbon dimer. Tsuzuki *et al.* [13] have ever calculated the intermolecular interaction potentials of CH<sub>4</sub>-CH<sub>4</sub> methane dimer by the Hartree-Fock, Møller-Plesset, coupled cluster, and density functional (DF) methods [14,15] using GAUSSIAN 94 program. They have found that the calculated potentials do not have minima when the DF method with the BLYP [16,17], BPW91 [16,18], and B3LYP [17,19] functions is

applied. They have argued that the dispersion interaction is not covered by the density functional theory (DFT) using these functionals.

In this paper, we have also calculated the intermolecular interaction potentials of methane dimer within the frame of DFT in the local density approximation (LDA). The LDA calculations for methane dimer and other dimers have not been reported so far. Although it is well known that LDA calculation is not very accurate in describing the van der Waals-like interaction [20], it well describes the interlayer distance of graphite [21] and the intermolecular distance of face-centered cubic C<sub>60</sub> crystal [22]. Recently, we have reported rare-gas atoms adsorbed on graphite surfaces using LDA calculations [23]. The results obtained are in good agreement with experiments. Thus, we think that LDA calculation may well describe the nonbonding van der Waals interactions of carbon-related systems.

It is found in this work that LDA calculation is also suitable for describing the intermolecular interaction of methane dimer. We have found that the intermolecular interaction potentials of methane dimer obtained from the LDA method have minima. To evaluate the accuracy and validity, we have compared these calculated intermolecular interaction potentials with the experimental data, which are the spherically averaged intermolecular interaction potentials of methane dimer. It is shown that our calculated results agree well with experiments.

All the LDA calculations have been performed in the frame of the DFT. We suppose that the methane dimer is in a simple cubic box with an enough large side length. For the exchange-correlation potential among electrons, we use a functional form [24] fitted to the Monte Carlo results for the homogeneous electron gas [25]. Norm-conserving pseudopotentials generated by the Troullier-Martins scheme are adopted to describe the electron-ion interaction [26,27]. In constructing the pseudopotentials, core radii adopted are 1.50, 1.54, and 1.54 a.u. for C 2s, 2p, and 3d electronic states, respectively, and 1.50, 1.60, and 2.00 a.u. for H 1s, 2p, and 3d electronic states, respectively. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 50 Ry, which gives enough convergence of

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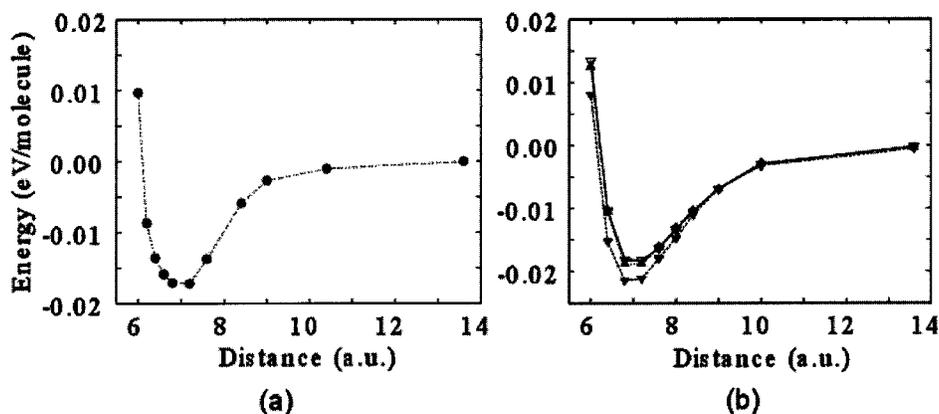


FIG. 1. The calculated intermolecular interaction potentials of methane dimer: (a) using LDA method; (b) using the MP2, MP3, and CCSD methods, where the solid triangle denotes the results from MP2, the open inverse triangle denotes those from MP3, the solid inverse triangle denotes those from CCSD.

relative total energies of carbon-related materials [26]. The conjugate-gradient (CG) minimization scheme is used both for the self-consistent electronic structure calculations and for the geometry optimization. The calculation method has been also seen elsewhere [23,28].

First, we have obtained the optimized geometry of methane molecule and the orientation of the methane dimer using CG minimization scheme. The C–H bond distance and the total energy of the optimized methane molecule are 1.093 Å and  $-215.860$  eV, respectively. In methane dimer, the orientation of each methane molecule is nearly the same. And then, the obtained optimized geometry of methane molecule and the orientation of the dimer are used for all our calculations. Changing the C–C distance of the dimer at 6.0, 6.4, 6.8, 7.2, 7.6, 8.0, 8.4, 9.0, 10.6, and 6.8 a.u., we have obtained the total energies of  $-431.711$ ,  $-431.758$ ,  $-431.767$ ,  $-431.765$ ,  $-431.758$ ,  $-431.749$ ,  $-431.742$ ,  $-431.736$ ,  $-431.733$ , and  $-431.732$  eV, respectively. This processing that the geometry and energy of methane molecule do not change corresponds to adiabatic approximation. In Fig. 1(a), we show the calculated intermolecular interaction potentials of methane dimer. It is found that the calculated potentials have minima when the intermolecular distance is about 7.0 a.u. The depth of the potential is about 0.017 eV.

To compare our LDA results with those obtained from other methods, we have performed the calculations for Møller–Plesset and coupled cluster calculations using GAUSSIAN 98 program [29]. Just as Tsuzuki *et al.* [13] did, we have also performed the following calculations. The geometry of monomer methane is optimized at the MP2/6-31G\* level. The C–H bond distance of the optimized methane is 1.090 Å. This geometry is used for all GAUSSIAN 98 calculations. The 6-311G\*\* basis set augmented with several diffuse polarization functions are used for the calculations. Diffuse *d* and *f* functions on carbon atoms and diffuse *p* and *d* functions on hydrogen atoms are added to the 6-311G\*\* basis set to prepare the aug(*df*,*pd*)-6-311G\*\* basis sets. Electron correlation energies are corrected by the Møller–Plesset perturbation methods MP2 and MP3 [30,31] and by the coupled

cluster methods CCSD [32] (the electron correlation energies are close to the MP4 ones [13], therefore, we do not perform the calculations by MP4).

The calculated intermolecular interaction potentials of the methane dimer by MP2, MP3, and CCSD using the 6-311G\*\* basis set are shown in Fig. 1(b), where the solid triangle represents the results from MP2, the open inverse triangle represents the results from MP3, the solid inverse triangle represents the results from CCSD. It is obvious that the calculated potentials with these different methods all have minima when the intermolecular distance is 7.0 a.u., which is consistent with that by our LDA calculations. The corresponding depths of the interaction potentials are about 0.019, 0.019, and 0.022 eV, respectively. All the results are in good agreement with those obtained by Tsuzuki *et al.* [13] using GAUSSIAN 94.

Spherically averaged potentials for methane have been reported from several experimental measurements in the gas phase. The carbon-carbon distances of the potential minima span in the range 7.26–8.07 a.u. The potential depths span in the range 0.014–0.020 eV [33–35]. All the calculated carbon-carbon distances of the potential minima are in agreement with experiment. Comparing with the potential depths obtained by MP2, MP3, and CCSD methods, the results by our LDA method seem to be better consistent with experimental data.

Finally, for our calculated results from LDA calculations, we have made a nonlinear fitting for the Lennard-Jones (12-6) potential function,

$$V(R) = \frac{a}{R^{12}} - \frac{b}{R^6} \quad (a > 0, b > 0). \quad (1)$$

We have obtained:  $a = 5.139\,085\,206\,149\,554 \times 10^8$ ,  $b = 5189.362\,652\,938\,745$ . It is demonstrated that the Lennard-Jones (12-6) potential function well describes the intermolecular interaction potentials of CH<sub>4</sub>-CH<sub>4</sub> complex.

In summary, intermolecular interaction potentials of methane dimer are calculated through the local density approxi-

mation in the frame of the density functional theory. The calculated potentials have minima when the intermolecular C-C distance is 7.0 a.u., which is in good agreement with experiment. The depth of the potential is about 0.017 eV. The calculated results are also in good agreement with those obtained from the Møller-Plesset and coupled cluster methods and with the experimental data.

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