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Comment on "Intermolecular interaction potentials of the methane dimer from the local density approximation"

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To verify the recently calculated intermolecular interaction potentials of the methane dimer within the density functional theory using the (Perdew) local density approximation (LDA) [Chen *et al.*, Phys. Rev. A **69**, 034701 (2004)], we have performed a parallel series of calculations using the LDA/6-311++G (3df, 3pd) level of theory with selected exchange functionals (B, G96, MPW, O, PBE, PW91, S, and XA). None of the above calculated intermolecular interaction potentials from the local density approximation reproduce the results reported in the commented paper. In addition, we point out the inappropriateness of using the Lennard-Jones function to model the long-range parts of the calculated intermolecular interaction potentials, as suggested positively by Chen *et al.*

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Chen *et al.* [1] recently reported the intermolecular interaction potentials of the methane dimer $(CH_4)_2$ within the standard density functional theory (DFT) scheme [2] using the (Perdew) local density approximation (LDA) [3], the pseudopotential [4,5], and the plane-wave expansion [6]. Their results agreed surprisingly well with those obtained by the correlation-corrected Møller-Plesset (MP2, MP3) [7] and coupled cluster [CCSD(T)] [8] methods using a large basis set [9]. Because it has been known for some time that the usual DFT based approaches, using either the LDA or the generalized gradient approximation (GGA), cannot calculate the intermolecular interaction potentials of molecular dimers to such a high level of accuracy [10–12], it is important to perform a parallel series of calculations using the available implementations of commonly used exchange-correlation functionals to verify the proposed results by Chen *et al.*

All the calculations were performed using the GAUSSIAN03 package suite [13] and followed a theoretical procedure similar to that employed by Tsuzuki *et al.* [9]. Figure 1 shows the calculated interaction potentials of $(CH_4)_2$ with a set of selected exchange functionals (B, G96, MPW, O, PBE, PW91, S, and XA) [14], together with the Perdew correlation functional dubbed as PL (Perdew local) [3]. Although we have used a pretty large basis set, 6-311++G (3df, 3pd), which has been shown to lead to convergent results for $(CH_4)_2$ at a chemical accuracy [15], none of the calculated intermolecular interaction potentials reproduce the results of Chen *et al.* A puzzling point in the commented paper is that there are two sets of data, one reported in their Fig. 1 and the other as numerical data in the text [1], while the latter is twice the former. Because there was no further clarification on this apparent inconsistency in the commented paper, we present both data for comparison in Fig. 1 (open symbol-lines). Restated, neither of them can be reproduced in the present calculations.

Chen *et al.* also concluded that through a nonlinear fitting their calculated intermolecular potentials can be well-described by the Lennard-Jones (LJ) potential function

$$V(R) = \frac{a}{R^{12}} - \frac{b}{R^6}. \tag{1}$$

Because this conclusion is contrary to what has been believed that results based on the LDA cannot be used to model the long-range dispersion interaction well [16–18], the determined accuracy from their calculations remains to be verified. For the sake of comparison, in Fig. 2 we present the calculated raw data and the claimed fitting curve by Chen *et al.* using their fitting values of a and b [1]. To our great surprise, the fitting curve is anything but like the calculated raw data. To clarify this point, we perform a nonlinear fitting of their calculated data to the LJ function and obtain $a = 2.09 \times 10^6$ Å^{12} kcal/mol, $b = 1.84 \times 10^3$ Å^6 kcal/mol, and the fitting is shown in Fig. 2. As expected, although the LJ function can model the strong repulsive part quite well, there is a significant discrepancy from the calculated data for the

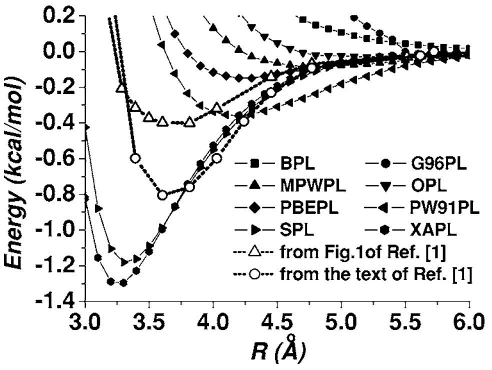

FIG. 1. The calculated intermolecular interaction potentials using a series of exchange-correlation functionals. The open symbol-lines are the two sets of data taken from Fig. 1 and the text of Ref. [1], respectively. The closed symbol-lines are calculated in the present work using a combination of the selected exchange functionals with the Perdew correlation functional.

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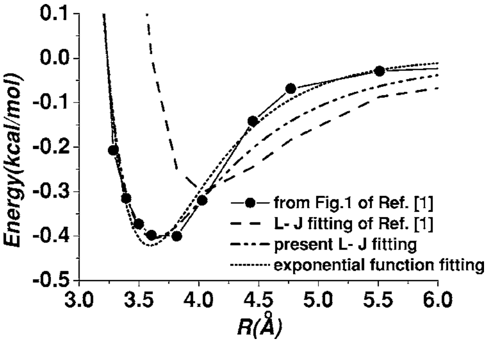

FIG. 2. Comparison of the calculated data in Ref. [1] with the fittings using the LJ function and the exponential function. The original fitting by Chen *et al.* is also presented for comparison.

long-range interaction part ($R > 4$Å). The calculated data using the LDA often decays faster than $-1/R^6$ for the long-range part, due to the local nature of the functionals used. To demonstrate this point, we perform another nonlinear fitting using the exponential function

$$V(R) = Ae^{-\alpha R} - Be^{-\beta R} \tag{2}$$

and obtain $A = 1.14 \times 10^6$ kcal/mol, α=4.23 Å^{-1}, B=3.33$\times 10^2$ kcal/mol, and β=1.71 Å^{-1}. As can be seen in Fig. 2, the long-range part of the calculated data is well-modeled by the fast-decaying exponential function, but not the LJ function.

To sum up this comment, the proposed calculated intermolecular interaction potentials of the methane dimer by Chen *et al.* cannot be reproduced using the available implementations of the LDA functionals. The calculated data cannot be used to model long-range dispersion interactions of the methane dimer either. We call for a careful examination and cautious usage of the calculated potentials by Chen *et al.*.

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