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Intermolecular interaction potentials of methane–argon complex calculated using LDA approaches*

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The intermolecular interaction potential for methane–argon complex is calculated by local density approximation (LDA) approaches. The calculated potential has a minimum when the intermolecular distance of methane–argon complex is 6.75 a.u.; the corresponding depth of the potential is 0.0163eV which has good agreement with experimental data. We also have made a nonlinear fitting of our results for the Lennard-Jones (12-6) potential function and obtain that $V(R) = 143794365.332/R^{12} - 3032.093/R^6$ (R in a.u. and $V(R)$ in eV).

Keywords: intermolecular interaction potential, LDA, Methane-argon complex
PACC: 3420B, 3120J

1. Introduction

Analytical functions for describing the interaction between molecules are highly relevant to the theoretical study of several problems and cornerstone for simulations employing molecular dynamics and Monte Carlo methods. Methane's molecule is an interesting one for it is the smallest hydrocarbon molecule and has high symmetry (Td). When we study the intermolecular interactions for methane with Ar atom, the orientation of the dimer becomes inessential. Moreover, nonbonding interactions of organic molecules are important for understanding their structures and properties in condensed phase.[1] In addition, nonbonding interactions play an important role to determine three-dimensional structures of large molecules such as proteins, polymers and DNA chain etc.[2–4] Those who carry out simulations of organic molecules in condensed phase also request an accurate nonbonding interaction potential. However, it is difficult to confirm the details of the shape of the nonbonding interaction potential only from experimental measurements.[5] Another way to the obtain the nonbonding interaction potential is to carry out a quantum chemical calculation with a suitable approximation. The requirements of a large basis set and electron correlation correction are difficulties in using *ab initio* methods to determine the intermolecular interaction potentials.[6] A large flexible basis set and electron correlation correction are necessary to accurately evaluate the dispersion interaction,[7] which is one of the most important intermolecular interaction energy terms. The dispersion interaction is responsible for the heat of evaporation and the heat of sublimation of hydrocarbon molecules.[8] The basis set's effects on the calculated nonbonding interaction potentials of hydrocarbon molecules have been studied extensively.[9–12] But only a little has been reported about the effects of the choice of the electron correlation correction procedure. The Møller–Plesset perturbation method[13,14] has been used for the correction of electron correlation energies in these studies. However, Olsen *et al* have reported divergent behaviour in the Møller-Plesset series.[15]

In this paper we study the interaction energy for CH_4–Ar complex using the local density approximation (LDA) method in the frame of density functional theory (DFT).[16,17] The LDA calculations for interaction potentials of CH_4–Ar complex have not been

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reported so far. We have found that the intermolecular interaction potentials of CH_4–Ar complex obtained from the LDA method have a minimum. In order to evaluate the accuracy of the calculated interaction potentials from our LDA calculations, we have made a comparison between our calculated interaction potentials and the results obtained by others. In the next section, we a briefly outline our computational method. The results and discussion are presented in Sec.3.

2. Computational method

The LDA calculation has been performed within the DFT in the LDA using our program. For the exchange-correlation energy among electrons, we use a functional form fitted to the Monte Carlo results for the homogeneous electron gas.[18] The total energy for the interacting electron system is given by

$$E(n) = \int v_{\rm ext}(r)n(r)\mathrm{d}r + T_{\rm s}[n] + \frac{1}{2}\iint \frac{n(r)n(r')}{|r-r'|}\mathrm{d}r\mathrm{d}r' + E_{\rm xc}[n], \quad (1)$$

Instead of using the many-electron wavefunction, the ground-state total energy is expressed as a function of $n(r)$. Here, $v_{\rm ext}$ is the potential of nuclei, and $T_{\rm s}$ and $E_{\rm xc}$ are the kinetic energy and the exchange-correlation energy, respectively. The Kohn–Sham equation is obtained by minimizing the above total energy with respect to the single-electron density:

$$n(r) = \sum_i |\varphi_i(r)|^2, \quad (2)$$

$$\left[\frac{1}{2}\nabla^2 + v_{\rm exc} + \int \frac{n(r')}{|r-r'|}\mathrm{d}r' + \frac{\delta E_{\rm xc}[n]}{\delta n(r)}\right]\varphi_i(r) = \varepsilon_i\varphi_i(r). \quad (3)$$

For the exchange-correlation energy $E_{\rm xc}$, we use the LDA. In actual calculations we use norm-conserving pseudopotentials to simulate nuclei and core electrons, which are generated by using the Troullier–Martins scheme to describe the electron–ion interaction.[19−21] In constructing the pseudopotentials, core radii adopted are 1.50, 1.54, and 1.54a.u. for C 2s, 2p, and 3d states, respectively, 1.50, 1.60, and 2.00a.u. for H 1s, 2p and 3d states, respectively, and 1.65, 1.65, and 1.65a.u. for Ar 3s, 3p and 3d states, respectively. The valence wavefunctions are expanded by the planewave basis set with a cut-off energy of 25 Ry. Supposing the CH_4–Ar complex is in a large enough cubic box. We put the carbon atom of methane at the origin of coordinates and Ar atom is located on the bisector of the angle between the two H–C bonds in the H–C–H plane along x-axis for the initial geometry (for the coordinates of the complex see Fig.1(a)). Then, we fix the carbon atom of methane and the Ar atom and relax the hydrogen atom to obtain a stable complex geometry using the conjugate gradient (CG) minimization scheme to minimize the total energy regarding the electronic and ionic degrees of freedom.[22] We calculate the total energy in each geometry of the complex.

The interaction potential ΔE is calculated as a function of R, which defined as the distance (a.u.) between the centre of the CH_4 molecule and the Ar atom. To examine the interaction of the Ar atom and the methane molecule, we obtain the interaction potential ΔE from the expression

$$\Delta E = \frac{1}{2}(E_{AB} - E_A - E_B), \quad (4)$$

where E_{AB} is the potential of the complex, and E_A and E_B are the energies of monomers A and B, respectively.

The minimum of the interaction potential is determined as follows. First, the complex corresponding to the lowest computed interaction potential is found by shifting the intermolecular distance of CH_4–Ar. Next, additional calculations are performed in its vicinity to obtain the minimum potential.

3. Results and discussion

The optimized geometry of monomer methane and the orientation of the dimer are obtained using CG scheme. The C–H bond distance of the optimized methane is 0.1091nm. Changing the CH_4–Ar complex distance R from 5.0 to 10.0a.u. with a step of 0.5a.u., we obtain the minimum total energy (−789.17088eV) at R=6.5a.u.. At the minimum potential point (R=6.5a.u.), we additionally calculate the total energy from 6.2 to 6.9a.u. with a step of 0.1a.u. and obtain the minimum total energy (–789.17198eV) at R=6.8 a.u.. We also additionally calculate the total energy at R=6.75a.u. and 6.85a.u. and obtain the final minimum total energy (–789.17210 eV) at R=6.75a.u..

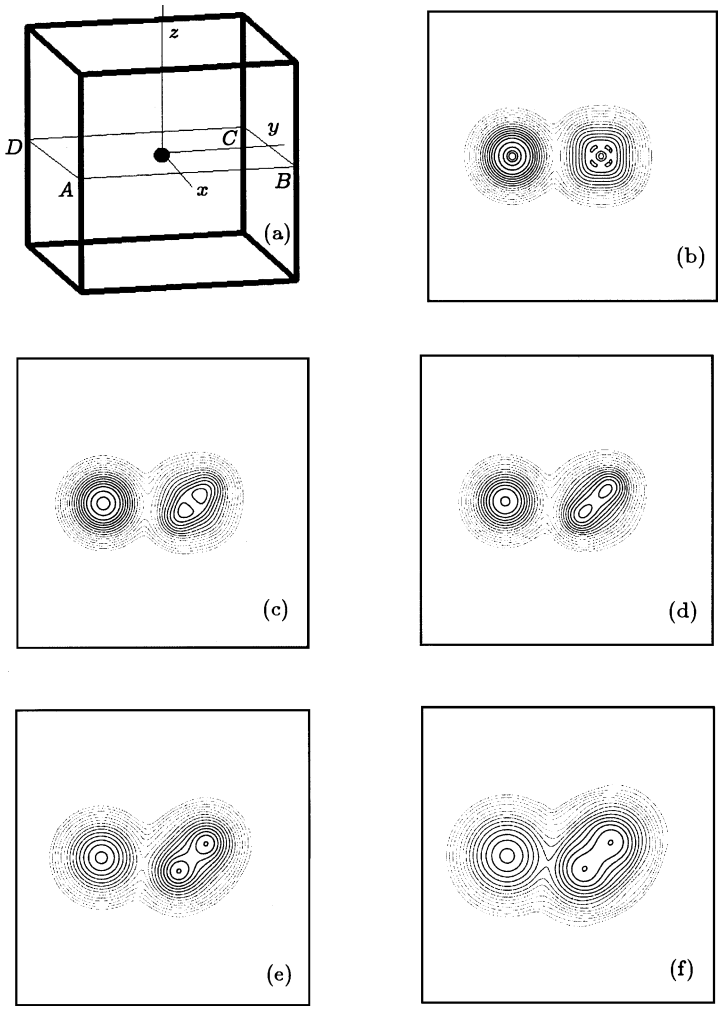


Fig.1. (a) We put the carbon atom of methane at the origin of coordinates and the Ar atom is located on the bisector of the angle between the two H–C bonds in the H–C–H plane along the x-axis; the x–y planar electronic structures of the CH_4–Ar complex at (b) z=0.0, (c) z=0.5a.u., (d) z=1.0a.u., (e) z=2.0a.u., and (f) z=3.0a.u. when R=6.75a.u.

Using Eq.(4), we find the interaction potential of the CH_4–Ar complex, ΔE=–0.0163eV. At this site (R=6.75a.u.), the x–y planar electronic structures (the z coordinates from 0.0 to 3.0a.u.) of the CH_4–Ar complex are shown in Fig.1 (b)–(f).

From the electronic structures, we can find that the C 2p electronic state (p-electronic states), H 1s electronic state and Ar 3p and 4s electronic states are mixed substantially in the potential region. This means that there is attractive interaction between the Ar atom and methane, resulting from the hybridization of C 2p electronic states (p-electronic states), H 1s electronic state and Ar 3p and 4s electronic states, which will strongly decrease the complex total potential, thus the interaction potential has a deeper potential well.

The solid triangles in Fig.2 show the calculated intermolecular interaction potential of the CH_4–Ar complex with our LDA calculation. It has a minimum when the intermolecular distance is 6.75a.u.. The depth of the potential is 0.0163 eV.

The quantum chemical calculation using MP/spd by Szczeniak *et al* obtained the depths ΔE=–0.014eV at R=7.5a.u.,[23] and using symmetry-adapted perturbation theory Heijmen *et al* obtained the depths ΔE=–0.018eV at R=7.0a.u.,[24] while the experimental depth of the potential is 0.014eV at R=7.33a.u. (0.388nm),[25] and 0.015eV at R=7.28a.u. (0.385nm).[26] From the above comparison, we conclude that the depths of our calculation has better agreement with experimental data than the quantum chemical calculation approach, while the position of minimum potential for our calculation is underestimated.

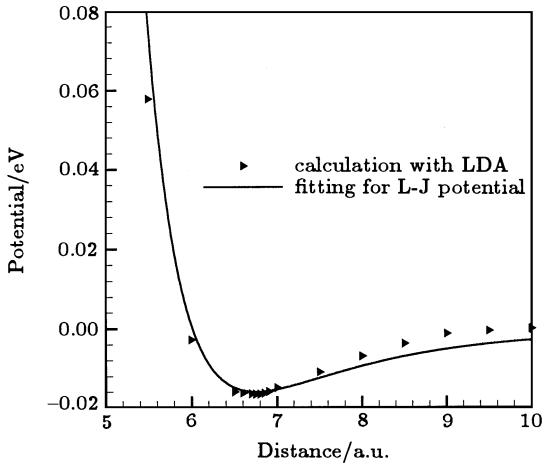


Fig.2. Calculated intermolecular interaction potential of CH_4–Ar complex using the LDA method. The solid triangles are intermolecular interaction potential of the CH_4–Ar complex with LDA calculation, and the solid lines are fitting for the L-J potential.

Finally, for our calculated results from LDA calculations, we have made a nonlinear-fitting for the Lennard-Jones (12-6) potential function (the solid lines in Fig.2),

$$V(R) = \frac{a}{R^{12}} - \frac{b}{R^6} \qquad (a > 0, b > 0). \qquad (5)$$

We obtain a=143794365.332, b=3032.093 (R in a.u. and $V(R)$ in eV). We find that the Lennard-Jones (12-6) potential function describes the intermolecular interaction potentials of the CH_4–Ar complex well.

4. Conclusion

The intermolecular interaction potential for CH_4–Ar complex is calculated with local density approximation (LDA) methods. The calculated potential has a minimum when the intermolecular distance is 6.75a.u. for the CH_4–Ar complex. The depth of the potential is 0.0163 eV which is in good agreement with experimental data.

References

[1] Jorgensen W L *et al* 1984 *J. Am. Chem. Soc.* **106** 6638
[2] Burkert U and Allinger N L 1982 *Molecular Mechanics* (Washington DC: ACS Monographs)
[3] Li W, Wang P Y, Dou S X and Tong P Q 2003 *Chin. Phys.* **12** 226
[4] Xue J M and Nobutsugu I 2002 *Chin. Phys.* **11** 1267
[5] Tsuzuki S *et al* 1996 *J. Phys. Chem.* **100** 4400
[6] Buckingham A D, Fowler P W and Hutson J M 1988 *Chem. Rev.* **88** 963
[7] Tsuzuki S, Uchimaru T, Tanabe K and Kuwajima S 1994 *J. Phys. Chem.* **98** 1830
[8] Kitaigorodsky A I 1973 *Molecular Crystals and Molecules* (New York: Academic)
[9] Tsuzuki S and Tanabe K 1991 *J. Phys. Chem.* **95** 2272
[10] Tsuzuki S, Uchimaru T and Tanabe K 1994 *J. Mol. Struct. Theochem.* **307** 107
[11] Tsuzuki S, Uchimaru T, Mikami M and Tanabe K 1996 *Chem. Phys. Lett.* **252** 206
[12] Jaffe R L and Smith G D 1996 *J. Chem. Phys.* **105** 2780
[13] Møller C and Plesset M S 1934 *Phys. Rev.* **46** 618
[14] Krishnan R and Pople J A 1978 *Int. J. Quant. Chem.* **14** 91
[15] Olsen J, Christiansen O, Koch H and Jørgensen P 1996 *J. Chem. Phys.* **105** 5082
[16] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
[17] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[18] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[19] Chen X R, Oshiyama A and Okada S 2003 *Phys. Rev.* B **67** 033408
[20] Troullier N and Martins J L 1991 *Phys. Rev.* B **43** 1993
[21] Kleinman L and Bylander D M 1982 *Phys. Rev. Lett.* **48** 1425
[22] Okada S *et al* 2002 *Phys. Rev.* B **65** 165410
[23] Szczeniak M *et al* 1992 *J. Chem. Phys.* **96** 463
[24] Heijmen T G A *et al* 1997 *J. Chem. Phys.* **107** 902
[25] Liuti G *et al* 1988 *Chem. Phys.* **126** 1
[26] Buck U *et al* 1981 *J. Chem. Phys.* **74** 1707