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Theoretical Investigation of the Dispersion Interaction in Argon Dimer and Trimer

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Abstract

The present work attempts to assess and evaluate the performance of some new DFT methods in describing van der Waals (vdW) complexes that are characterized by the dominance of pure dispersion interactions. To achieve this goal, Argon dimers (Ar_2) and trimers (Ar_3) were investigated. As a reference calculation, the correlation interaction energy have been computed at the CCSD(T) level using the aug-correlated family of basis sets pVXZ (where X=2,3,4). Extrapolation to the CBS limit has been carried out and the behavior of the potential energy function has been analyzed and discussed. Correlation interaction energy has been computed at the MP2 and MP4 levels and compared to those calculated at the CCSD(T) method. Five new correlated DFT functionals, namely M06 and its long rang extension M06L, the B97-2 and its modified version B97-D which was deviseded for the dispersion interaction, and the PBEPBE and its correlated extension PBE0 methods have been used to compute the interaction energy in Ar_2 and Ar_3. The present work results indicate clearly that M06 and M06L did not only overestimate the equilibrium distance and depth but they also showed fluctuations in the potential energy curve near the minimum and along the dissociative arm. The B97-D and the PBE0 methods are much more reliable. However, these two later methods showed convergence problems when used to treat Ar_3^+; in addition to being extremely fast when compared to the CCSD(T) method extremely fast as compared to the CCSD(T). These features make them good candidate for investigating large vdW clusters. The BSSE has been estimated, analyzed and discussed. The relative stabilities of the excited states of Ar_2 and Ar_3 clusters together with those of the ionic species (Ar_2^+ and Ar_3^+)have been computed and analyzed.

Key Words: VdW clusters**;** dispersion interaction; Argon dimer and trimer; Ab initio computation; DFT funct

1. Introduction

The present research project has been launched aiming to theoretically assess and evaluate the cabilities of

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some new correlated DFT methods in reproducing cluster pure dispersion van der Waals interactions . These clusters are of great interest because the underlying type of interactions playkey roles in molecular recognition [1] protein folding [2] stacking of DNA bases [3] and intercalation of drugs into DNA [4]. Although non-bonded interactions have been studied extensively both experimentally [5] and theoretically [6] the features of the potential energy surface (PES) and the nature of these interactions are still far from being completely understood. The difficulties arise from the relative weakness of the interaction and the shallowness of PES. Because argon and aromatic hydrocarbon clusters lack permanent dipole moments, the major part of the binding force comes from the dispersion interactions, which require expensive calculations at a correlated level of theory.

Dispersion interactions are either isotropic, as in the case of rare-gases, or anisotropic in nature, as in the case of HF, CO, and methane. Theoretical efforts concentrate on rare gas interactions

because their results can be compared with experiments to evaluate the level of theoretical model employed. Thereafter the appropriate theoretical model can be extended to molecules.

The literature contains several theoretical calculations along these lines [7-12]. However, the need for tailoring the appropriate method to evaluate vdW interactions, still exists. The difficulty of resolving this issue lies inthree main reasons that emanate from the size and flexibility of the basis set, the inclusion of electron-correlation and the minimization of basis set superposition error. Thus, their extension to relatively large molecular systems, similar to the one studied in this laboratory, is governed by basis set limitations at the expense of computational demands.

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In most casesclusters are not expected to reside in their ground state only. Being highly energetic, clusters also exist in excited states or as ionized species. Thus, in the present work, the potential energy surface for Ar_2 and Ar_3 clusters will be fully explored at high level of theory. The stability of low-lying singlet and triplet states of Ar_2 and Ar_3 clusters will be investigated and the corresponding PES will be explored. The Ar_2^+ and Ar_3^+ ions will also be investigated and their binding energies will be computed at high level of theory. Computational challenge such as, basis set effect, and basis set superposition error will be addressed.

The ultimate aim of the present work is, thus, to establish an acceptable level of computation for predicting the behavior of vdW complexes. A level of theory that is able of picking up appreciable amount of correlation interaction energy, reproducing the equilibrium separation within the acceptable limits and at the same time being cost and time effective.

2. Computational methods

Ab intio calculations were performed using the Gaussian 09W program [13]. The coupled cluster method with singles, doubles, and noniterative triples [CCSD(T)] has been used throughout this work.The aug-cc-pVXZ basis sets (where X=2,3,and4) have been applied. Extrapolation to the basis set limit (CBS) has been carried out using the extrapolation formula:

$$E(x) = E_{CBS} + a\, e^{-(x-1)} + be^{-(x-1)2}$$

where, E_{CBS} is the energy at the complete basis set limit, x is the zeta exponent and a, b are arbitrary constants. This formula has been reported to give reliable and accurate results in a comprehensive study published recently by Feller et al [14]. BSSE was estimated by the function counterpoise method Proposed by Boys and Bernadi [15]. Five DFT methods [16-21] has been tested and evaluated in this work namely, M06, M06l [22-26] B97-D[27], and PBEPBE and its correlated extension PBE0 methods[28].

3. Results and Discussion