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Theoretical Investigation of the Dispersion Interaction in Argon Dimer and Trimer

Rifaat Hilal[a], Walid M. I. Hassan[b], Shabaan A. K. Elroby[a] and Saadullah G. Aziz[a] *

[a]King Abdulaziz University, P.O.Box 80203, Jeddah 21589, Saudi arabia
[b]Cairo University, Cairo 12613 Egypt

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 devised 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

* Corresponding author. Tel.: +966 2 6952293; fax: +966 2 6952292.
E-mail address: saziz@kau.edu.sa.

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

3.1.Computational methods and Basis set

Figure 1 depictss the potential energy surface for the Ar_2 dimer which was computed by using the CCSD(T) method at aug-cc-pVXZ (where X=2,3,4), CBS, 6-31++G** and 6-311++G** basis sets. For comparison, Figure 1(b) ashows the PES for Ar_2 trimer which was computed by using the CCSD(T) at different basis sets. It is clear that the vdW interaction of pure isotropic nature is very well accounted for. All basis sets investigated were able to describe,almost equally, t the dissociative arm of the PES. However, the well depth and the internuclear distance (R_e) were much more sensitive to the basis set quality. In general, R_e and well depth values tend to shift to shorter values as the zeta exponent of the aug-basis set increases. The results obtained with the Gaussian type function 6-31++G** were of slightly lower quality as compared to th of the aug-cc-pVDZ basis set. However, increasing the spatial extent of the Gaussian basis set by an extra *d* and *f* functions led to marked improvement in the predicted potential energy curve, yet this happened at the expense of tremendous increase in computational time. The aug-cc-pVTZ predicted a PES that is of comparable quality as that obtained at the basis set limit (CBS).
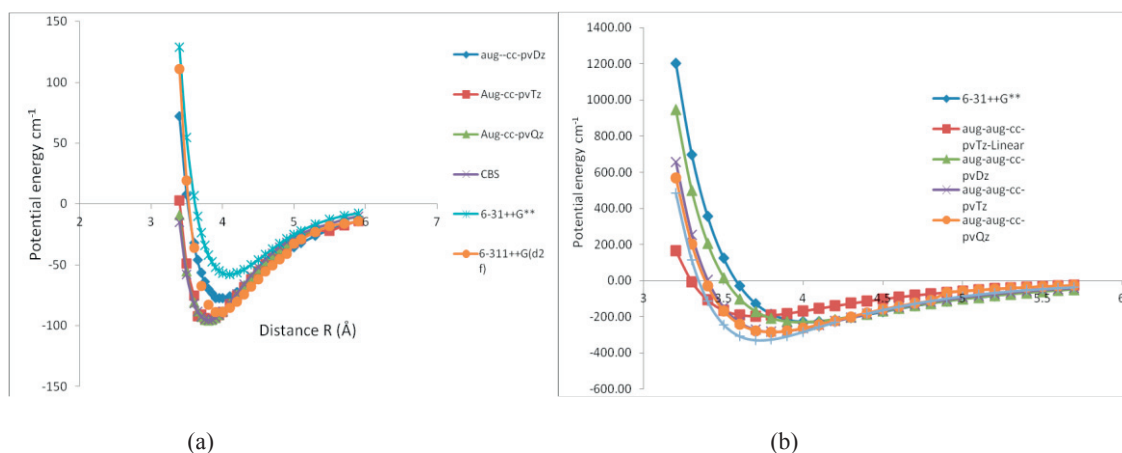

| (a)   (b) |

Figure 1: The potential energy surface for (a) the Ar_2 dimer and (b) the Ar_2 trimer computed at the CCSD(T) level using different basis sets.Table 1 lists the characteristic quantities which were computed for Ar_2 potential energy curves by using different levels of theory. Our computation was able to pick up about 96% of the correlation interaction energy at the CCSD(T)/aug-cc-pVTZ level of theory. Apparently, this has not been improved by basis set extrapolation to the CBS limit. The computed R_e value is comparable to the experimental and best benchmark value of 3.75 Å [29]. Meanwhile, the GT basis set (6-31++G**) was unable to pick up more than 58% of the well depth and it predicted a far too long R_e value. Improving its extension in space and its diffusion tendency have led to real improvements in its efficiency. As a result it picked up c.a. 91% of the well depth and the R_e value was . Table 2 depicts Ar_3 characteristic quantities which were computed at the same chemistry level.. The present computation showed clearly that the triangular Ar_3 is more stable than its linear counterpart. It is interesting to note that the equilibrium distance for linear Ar_3 is the same as that for Ar_2 but slightly longer than that for triangular Ar_3. The Ar_3 cluster well depths showed the same trend in line with basis set quality. This is exactly similar to that reported for the Ar_2 case. The well depth at the CBS limit of 285.866 cm^{-1} was of very good quality. The 6-31++G** basis set was able to recover up to 79% of the total correlation interaction energy. Furthermore, this basis set tends always to exaggerate well-positions.

Table 1: Characteristics of the potential energy function for Ar_2 which were computed   by using CCSD(T) method at different basis sets.

basis set	R_e (Å)	E_e (au)	R(Å)*	Binding energy

6-31++G**	4.0	-1053.93684	6.30	-56.778
6-311++G(d2f)	3.9	-1054.07360	6.30	-88.887
aug-cc-pVDZ	3.9	-1053.93972	6.70	-77.255
aug-cc-pVTZ	3.75	-1054.09794	6.70	-93.997
aug-cc-pVQZ	3.70	-1054.15053	6.70	-92.662
CBS	3.75	-1054.18062	6.70	-92.627

*   Dissociation limit.

Table 2: Characteristics of the potential energy function for Ar_3 which were computed   by using CCSD(T) method at different basis sets.

basis set	R_e (Å)	E_e (au)	$R(A^o)$*	Binding energy
6-31++G**	4.0	-1580.781316	5.3	-228.016
aug-cc-pVDZ	4.0	-1580.910109	5.1	-231.479
aug-cc-pVTZ	3.8	-1581.147566	5.0	-283.342
aug-cc-pVQZ	3.8	-1581.226468	4.9	-285.866
CBS	3.8	-1581.285850	4.9	-313.698

*   Dissociation limit.

It seems instructive to compare the behaviour of CCSD(T) method with those of the much less expensive MPx methods. Table 3   lists   the potential energy surface characteristics of Ar_2 which were computed at the MP2,MP4 and M06 methods at different basis sets. The augmented correlated basis functions were used in all these calculations. Initially it is worth mentioning that   the potential energy curves, in and around the minimum, were extremely shollwo, to the extent that they were almost being flat. This was true for all tested basis sets and particularly correct for both the MP2 and MP4 levels. Inspection of Table 3 reveals that the MP2/aug-cc-pVXZ (where X=3,4) levels reproduced remarkably the experimental R_e value. . However, their well depths were not as satisfactory as those of the CCDS(T) method using the same basis sets. This was also true for calculations using the other aug-cc-pVXZ basis sets. The well depths were much more sensitive to the method of computing the correlation energy. Furthermore, there was no real improvement on going from the MP2 to MP4 level. This can be explained by the basis set used, where electron-correlation in the case of vdW molecules result mainly from the fluctuation of the interacting dipoles. These fluctuations are either attractive or repulsive and thus, the true wave function has slightly higher amplitude at one point (attractive) and a lower one at another point (repulsive). The enhanced amplitude is expressed by a double excitation in the configuration interaction wave function in which an s orbital of one atom is replaced by a p orbital on the same atom. This is accounted for explicitly in the CCSD calculation. This leads to its ability in reproducing the correlation interaction energy. In Moller-Plesset perturbation theory this double excitation makes an important contribution to the first order wave function, and consequently to the second-order energy E(MP2). It is worth noting that the correlation energy picked up at the MP2 level represents 99.9 % of the total correlation that can be recovered at the MP4.

Table 4 lists   the interaction energy for Ar_2 cluster which were computed by using the five DFT methods at the aug-correlated basis set (aug-cc-pVTZ). The corresponding potential energy functions were displayed in Figure

2. The results in Table 4 and Figure 2 indicate clearly that M06 and its long rang correlated version M06L seemed to over-estimate the correlation interaction energy. Furthermore, it predicted an Re value of 4.1 Å, which was much greater than the experimental value of 3.75 Å. However, it seems that the method was not quite reliable as it was claimed to be, the potential energy curve was not steady and smooth specially around the equilibrium separation and at the dissociative part of the curve. In contrast, the B97-D method was really improved compared to B97-2 functional and it was also much better than the PBEPBE method. The three functionals produced smooth potential energy curves that were consistent with that produced by the CCSD(T) method. The total correlation energy picked up by the B97-D method is about 93% of the experimental value. Furthermore, the Re value of 3.9 Å predicted by the B97-D method was in fair agreement with the experimental value[29]. In conclusion the B97-D-DFT level was very fast when compared with the CCSD(T) method. This advantage rendered it a good candidate for large molecular systems. Computation has been extended to the Ar_3 cluster. The DFT /aug-cc-pVTZ potential energy curves for both Ar_2 and Ar_3 are included in

In conclusion, we have used three computational methods to account for Ar_2 and Ar_3 cluster tcorrelation interaction energies; namely these were: CCDS(T), MPX and DFT methods. The CCSD(T) method was by far more accurate and consistent for the present computation. Although, it was more time consuming, yet through its stability, consistency and attained accuracy, it was by far much better than all other methods tested in this work. Of the DFT functionals we used in this work, the B97-D and the PBE0 funtionals were the most reliable ones. The basis set quality seemed also to be very important in accounting for Ar_2 very week interaction. The aug. correlated pVXZ (where X=2,3 and 4) basis sets have been used in the present work in addition to the popular Pople's 6-31++G** and the more extended 6-31++G(3df) basis sets. Very accurate well depths and well positions can be obtained by extrapolation of the aug-cc-pVXZ basis sets to the CBS limit. In general, a CCSD(T) computation at the aug-cc-pVTZ basis set acheived the minimum acceptable level of computation that can be applied for estimating correlation energies of large aromatic clusters.
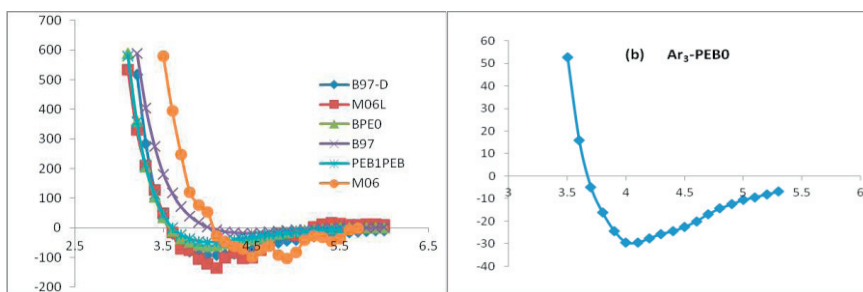

Figure 2: Potential energy functions for a) Ar_2 b) Ar_3 which were computed at different DFT methods using aug-cc-pVTZ basis set.

Table 3: The Ar_2 cluster well depths, equilibrium distances and BSSEs which were calculated at different levels of theory

Basis set	Energies/ cm^{-1}			BSSE,au
	M06	MP2	MP4	
6-31++G**	-117.6650(4.1)	-73.65946(4.1)	-73.70491(4.1)	63.35595
aug-cc-pVDZ	-130.34978	-88.52295(4.00)	-75.92045(4.0)	32.62978

aug-cc-pVTZ	-98.7825787	-108.72572(3.76)	-96.89125(3.82)	25.77171
aug-cc-pVQZ	-89.2540243	-112.79046(3.76)	-98.60226 (3.79)	12.81127
CBS	-80.389	-120.51882		2.189112

Table 4: Binding energies and equilibrium distances of the potential energy surfaces of Ar_2 cluster which were computed using different DFT functionals at aug-cc-pVTZ basis set..

DFT functional	Ar_2	
	R_e	E (cm^{-1})
M06L	4.1	-135.63532
B79-2	4.5	-16.89955
B97-D	4.0	-92.61828
PBEPBE	4.0	-62.11132

Table 3 lists the the well depths, equilibrium distances and basis set superposition errors (BSSE) obtained by the different basis sets used in the present study. For the corrected interaction energies, the basis sets used in this work showed repulsive interaction potential curves, except in the very small regions around the equilibrium separation which exhibited essentially large BSSE. It is clear that our results for Ar_2 cluster were consistent with those of Liedl [17] and indicated clearly that CCSD(T) potentials seemed to converge better with systematically increasing basis sets, if one was simply using uncorrected energies.

3.2 Excited State and Ionized Ar Clusters

In ion-beam experiments and other high energy experiments involving argon matrices, usually allow the coexistence of not only ground state but also excited states clusters. In this section, we examine the low-lying singlet and triplet excited states of argon dimers and trimers. Figure 4 shows the PES for the low lying singlet Ar_2. On the one hand, ^1S state was a stable state whose configuration was almost similar to that of the ground state. The binding correlation energy of 93 cm^{-1} is indicative of its the stability. The well position of 3.8 Å was slightly greater than that of the ground state. The Σu symmetry of the ^1S state originated from a main configuration (37%) resulting from the highest occupied σu MO ($\phi_{18} \rightarrow \phi_{22}$) and a minor configuration involving MO($\phi_{13} \rightarrow \phi_{19}$) which contributed only 6% to this state. These MO's were nonbonding and thus don't affect the geometry or stability of Ar_2 cluster. The only bonding MO was ϕ_{13} which had the σ_g symmetry. The triplet state on the other hand, was repulsive at all inter-atomic separations. The CCSD(T) method, using the aug-cc-pVTZ basis set failed to locate a minimum on the potential energy curve. Ar_2^+ and Ar_3^+ are believed to exist in high energy experiments. These positive ions are expected to play a very important role also in large argon clusters. Thus, the stability of clusters of the form Ar_n^+(n=3,500) are believed to follow some magic numbers with a core where the positive charge will be concentrated. This core is believed to be Ar_2^+ or Ar_3^+. Figure 3 shows the potential energy surfaces for the Ar_2^+ and Ar_3^+ clusters which were computed at the CCSD(T)/pVTZ level of theory. It is noted that the well position in case of the Ar_2^+ was shifted considerably to shorter values. Thus, this ion was contracted and the positive charge wass concentrated to a much greater extent than in the case of the Ar_3^+ ion. The positive charge seemed to be delocalized and as a result had s slight effect on the optimum R_e .
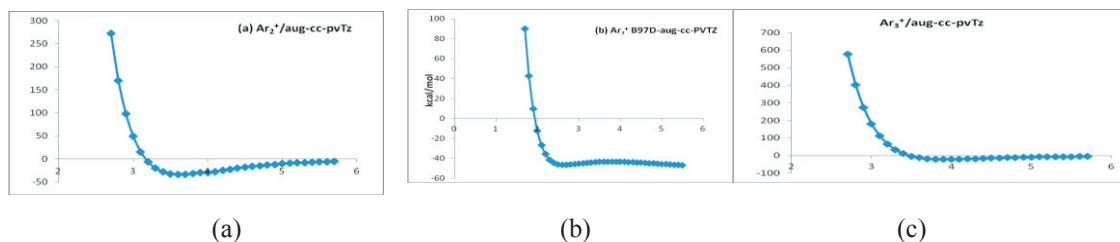
(a)   (b)   (c)

Figure 3: (a) The potential energy surfaces (kcal/mol) for (a) Ar_2^+ and (c) Ar_3^+ which were computed using CCSD(T) method and (b) the PES of Ar_2 cluster which was calculated using the B97-D functional. Both methods used the same basis set (aug-cc-pVTZ).

It should be noted that there were a convergence problem when modeling Ar_3^+ cluster by the B97-D DFT method. Furthermore, the PBE0 method showed also divergence from self-consistency with the increase of R_e and it failed to converge at R_e greater than 5.3 Å. Therefore, the stability and convergence behavior of these DFT methods need further investigation.

4.   Summary and Conclusions

The interatomic interaction energies for Ar_2 and Ar_3 clusters have been computed at the CCSD(T), MP2 and MP3 and five DFT methods using basis sets of different qualities. Extrapolation to the basis set limit (CBS) has been adopted. Results were compared to the theoretical benchmark and experimental data. The computations have been extended to the excited states of Ar_2 and Ar_3 and their ionic species (Ar_2^+ and Ar_3^+). Our results indicated clearly that the minimum acceptable level of theory to adequately compute weak non-bonded interactions will be the CCSD(T)/aug-cc-pVTZ level. The high speed and acceptable accuracy of the B97-D and the DFT-PBE0 functionals made them good candidates for modeling large vdWs clusters.

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