



On the performance of an complete basis set extrapolation scheme tailored for the equilibrium distance applied to the helium dimer potential energy surface



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ABSTRACT

Full configuration interaction calculations are performed for He_2 using various orbital basis sets of the aug-cc-pVXZ type, with the results being extrapolated to the one electron basis set limit both with counterpoise and without counterpoise correction. A two-point complete basis set extrapolation formula optimized for the equilibrium distance has been utilized for such a purpose. The results call into question the use of the extrapolation formula tailored for the equilibrium distance at other points on the potential surface.

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1. Introduction

Complete basis set (CBS) extrapolation techniques in conjunction with the correlation-consistent basis sets are among the most efficient procedures to account for the incompleteness of one-particle basis sets and reduce the error in standard *ab initio* electronic structure calculations [1,2]. Such techniques allow estimating the atomic and molecular properties with qualities approaching the complete basis set results [3,4]. However, the challenge still remains to develop property oriented extrapolation formulas that properly account for the convergence behavior of the desired property [5]. In order to address this challenge numerous approaches were proposed with the main focus directed toward accurate description of interaction energies of model systems where basis set effects play a crucial role [6–18].

To our knowledge, most of the previous work was focused on the extrapolation towards the complete basis set for the structures at equilibrium geometries. However, the effectiveness of the extrapolations, in general, depends on the inter-atomic separation R as shown by Jeziorska and Velilla [9,12]. Therefore, it is interesting to investigate the consequences of applying the extrapolation procedure developed for the equilibrium distance at other separation. The focus of the present paper is the exploration of those consequences.

In order to eliminate errors associated with the deficient treatment of electronic correlation we will employ the all-electron full configuration interaction (FCI) method in the non-relativistic

Born–Oppenheimer approximation. Such choice allows us to investigate one-electron basis set truncation errors independently of other factors. As a model system the helium dimer was chosen due to its simplicity and its paradigmatic role in investigations related to basis set artifacts. In addition, He_2 possessing only 4-electrons allows a FCI treatment even with the most extensive basis sets.

The article is organized as follows. In the next section, we explain the methodology and computational details, in Section 3 the results and discussions are presented and the conclusions are given in Section 4.

2. Methods and computational approach

The main body of this work consists of *ab initio* electronic structure computations of the interaction energies on a discrete grid of internuclear distances at the FCI level of theory, utilizing the series of correlation-consistent basis-sets. Those results are then subjected to the CBS extrapolation procedure to estimate the energies at the complete basis set limit.

The computations of FCI energies for He_2 have been carried out with the correlation-consistent, augmented basis sets (aug-cc-pVXZ, $X = \text{D, T, Q, 5}$) [19–24]. As it was indicated in our previous work [25] these basis sets are large enough for demonstrating the point of the current article. The calculations were performed for a set of 12 distinct He–He inter-atomic separations spanning the range from 3 to 9 bohr, covering the strongly repulsive region of the potential, the minimum well, and the attractive long-range region. GAMESS(US) package [26] was utilized for all calculations.

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In order to estimate the CBS values of the interaction energies at the FCI level, the well tested and extensively used two-point extrapolation function [12,27–30]

$$E_{\text{CBS}} = E_X + \frac{E_X - E_{X-1}}{[1 - (X - k)^{-1}]^{-3} - 1} \quad (1)$$

was used, where E_{X-1} and E_X are the energies obtained with basis sets of the cardinality $X - 1$ and X , respectively, k has been interpreted as an angular momentum offset number, which depends on the correlation level employed [27,12].

One of the arguable issues related to the complete basis set extrapolation techniques is whether the extrapolation should be performed employing the total interaction energies or alternatively that separate extrapolations should be performed for the Hartree-Fock (HF) level energy and correlation energy [12,27,32,33]. Eq. (1) was developed based on the partial wave expansion studies for ground state of He atom [28]. It was found that the second-order correlation energy has contributions from angular momentum l that goes asymptotically as powers of $(l + 1/2)^{-1}$. The leading terms in the error of a variational CI calculation in a truncated basis set at the angular quantum number l start in cubic terms of $(l + 1)^{-1}$. However, the higher angular momenta in the correlation consistent basis sets of Dunning et al. are added systematically to saturate the basis function space, both in radial and angular directions, simultaneously. The direct application of the partial wave expansion to the correlation energy in the correlation consistent basis set calculations may not be appropriate. Lee et al. have shown that the total energies rather than the correlation energies appear to be more suitable for extrapolation to the CBS when two-point extrapolation scheme with $(X + k)^{-3}$ function is employed [32]. This observation also has been confirmed in our recently published article [25]. Therefore, the total interaction energies will be extrapolated directly in the present paper.

It also has been the subject of some debate whether the counterpoise corrected [34] or uncorrected energies should be used in the extrapolation [10,16,35–38]. In order to address this concern, the energies with CP correction (CP) and without CP correction (NCP) will be included in the present analysis. Figs. 1 and 2 present the calculation results for the interaction energies with CP correction and without CP correction respectively.

The present study requires an exact extrapolation scheme at equilibrium distance. Therefore, we will determine k using the following equation:

$$E_{\text{CBS}}(R_e) = E_{\text{exact}}(R_e). \quad (2)$$

With this equation k can be calculated with the following formula:

$$k = X - 1 / \left[1 - \left(\frac{E_{\text{exact}}(R_e) - E_X}{E_{\text{exact}}(R_e) - E_{X-1}} \right)^{1/3} \right]. \quad (3)$$

For convenience, the k determined with Eq. (3) will be labeled by k_{eq} . Here the $E_{\text{exact}}(R_e) = -3.484669 \times 10^{-5}$ a.u. represents the exact interaction energy at the equilibrium distance. The non-relativistic Born-Oppenheimer energies computed using Gaussian-type geminals (E_{GTG}) [31] are taken as benchmark values. The resulting, extrapolated values will be labeled by $(X - 1, X)$ signifying their origin.

3. Results and discussion

3.1. Complete basis set extrapolation of the counterpoise corrected interaction energies

Fig. 1(a) shows the percentage errors, calculated as,

$$P_{\text{GTG}}^X = 100|(E_X - E_{\text{GTG}})/E_{\text{GTG}}| \quad (4)$$

of a given value E_X with respect to the GTG benchmark results. Here $X = \text{CBS}, \text{FCI}$ denote the either the complete basis set extrapolated energies (CBS) or FCI energies (FCI) in a given basis. As shown in Fig. 1(a) the extrapolation scheme using k_{eq} (optimal for the equilibrium distance) also improves the potential quality at most of the other distances. The improvement is particularly impressive at larger distances. For $(X - 1, X) = (2, 3)$, the $P_{\text{GTG}}^{\text{CBS}}$ are less than 2% for the internuclear separation $R > 5.6$ a.u. For the aug-cc-pVTZ basis set, the $P_{\text{GTG}}^{\text{FCI}}$ are larger than 4% at this range and the $P_{\text{GTG}}^{\text{FCI}}$ is almost 15% at 6.0 bohr. However applying Eq. (1) with $k = k_{\text{eq}}$ at the short range is not very useful for improving the potential quality. An obvious improvement is only observed for $(X - 1, X) = (2, 3)$. For $(X - 1, X) = (3, 4)$, $P_{\text{GTG}}^{\text{CBS}}$ is even larger than $P_{\text{GTG}}^{\text{FCI}}$ with aug-cc-pVQZ basis for R between 3.0 and 4.0 a.u. It should be mentioned that the very large percentage errors around 5.0 a.u. are caused by the interaction energies in those distances being very close to zero.

It is interesting to note that the most accurate potential energies are the results of $(X - 1, X) = (3, 4)$ not $(X - 1, X) = (4, 5)$ for the internuclear separation $R > 5.6$ a.u. In order to rationalize this observation let us inspect the R dependence of k in Eq. (1). Fig. 1(b) displays the values of the offset number k for various internuclear distances. Here k was obtained for different R by solving the following equation $E_{\text{CBS}}(R) = E_{\text{exact}}(R)$. As one can see, the value of k depends on the internuclear separation R . This might be expected since the main contributions to the total interaction energy differ depending on the distance. For the short range, the exchange energy is the main contribution to the total interaction energy. At large separations the dispersion energy becomes to be the most important term. This observation shows that the offset number not only depends on the correlation level but also the correlation type. The dispersion energy may have a much smaller offset number compared to exchange energy which is consistent with the findings of Jeziorska et al. [9]. However, k shows a different behavior for different X with increasing internuclear separation. The RMSE deviation of k corresponding to the values at the equilibrium distance for $(X - 1, X) = (2, 3)$, $(X - 1, X) = (3, 4)$ and $(X - 1, X) = (4, 5)$ are 0.4, 1.7 and 2.0 respectively. Therefore, the value of k at the equilibrium distance applied to the other distances is a better approximation in the cases of $(X - 1, X) = (2, 3)$ and $(X - 1, X) = (3, 4)$ compared to $(X - 1, X) = (4, 5)$. This may be the reason behind the $(X - 1, X) = (2, 3)$ and $(X - 1, X) = (3, 4)$ producing better results than $(X - 1, X) = (4, 5)$ for some distances. With this observation it might be possible to improve the accuracy of the interaction potential energies based on the calculations with small basis sets.

3.2. Complete basis set extrapolation on the interaction energies without CP correction

Fig. 2(a) shows that the complete basis extrapolation scheme with k_{eq} applied to the interaction energies without the CP correction does not substantially improve the quality of the potential at other distances. The FCI energies are better in general than the corresponding extrapolated results. For aug-cc-pV5Z basis set, $P_{\text{GTG}}^{\text{FCI}}$ is less than 2.5% for the internuclear separation $R > 5.6$ a.u. However, $P_{\text{GTG}}^{\text{CBS}}$ is larger than 2.5% at this range and the largest percentage error is almost 10% at 8.0 a.u. for $(X - 1, X) = (4, 5)$.

These results can also be rationalized based on Fig.2(b). It is clearly shown that the value of k is very sensitive to the internuclear separation. In addition the changes of k with increasing R are not monotonic. The optimal value of k at the equilibrium distance can be significantly different from the optimal values of k at other distances, therefore the potential energies cannot be

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