

The role of mid-bond basis set functions on the interaction energy and equilibrium structure of He and Hg vdW dimers; A revised view

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Abstract

The ground state *ab initio* CCSD(T) potential curves with various basis sets (aug-cc-pVXZ-PP (X = D, T, Q, 5, 6)) are presented for dimers of helium and mercury. In this context, the effect of parameter variations of the mid-bond functions with respect to the interaction energy and the equilibrium distance are discussed. Our results show that the use of the new optimized set of mid-bond functions in the aug-cc-pVQZ calculation will lower the interaction energy of helium to $D_e = 33.21 \mu E_h$; closer to the experimental value of $34.68 \mu E_h$ (Aziz, McCourt and Wong; *Mol. Phys.* **61** (1987) 1487). For the pseudohelium – mercury dimer, the usage of previously optimized mid-bond functions connected with the aug-cc-pVQZ-PP basis set calculation leads to the interaction energy $D_e = 1713.15 \mu E_h$, which is in very good agreement with the experimental value of $1731.41 \mu E_h$ of Ceccherini and Moraldi (*Chem. Phys. Lett.* **337** (2001) 386) and Koperski *et al.* (*Chem. Phys. Lett.* **219** (1994) 161). The quality of these results obtained using mid-bond functions with respect to the computational requirements is quite encouraging.

Keywords: bond-functions, Complete Basis Set, van der Waals, weak interactions

Introduction

The investigation of van der Waals (vdW) complexes has been an issue of research for decades. Both experimental and theoretical approaches were applied in order to obtain deeper understanding of the physical origin of the system stability. The rare gases and the metals of the IIb group (Zn, Cd, and Hg) present a specific class of elements. They are especially

interesting due to their prospective use in excimer lasers, adsorption and catalytic processes and simulations of dynamics of planet atmospheres (Macrae *et al.* (2004)). In recent time, an intense effort has been directed into simulations (with various computational methods) of such complexes with respect to some of their physical and chemical properties. Molecular dynamic presents a perspective and effective method in property simulation (Grotendorst *et al.* (2000)) and a good pair potential is essential.

The intermolecular perturbation theory (I-PT) (Hirschfelder *et al.* (1967)) is an approach, where the interaction energy is computed directly as a sum of contributions of physically different origin.

$$\Delta E = \sum E_{\text{els}}^{(nij)} + \sum E_{\text{ind}}^{(nij)} + \sum E_{\text{disp}}^{(nij)} + \sum E_{\text{exch}}^{(nij)} + \sum E_{\text{other}}^{(nij)} \quad (1)$$

The terms in Eq. 1 have the following meaning: $E_{\text{els}}^{(nij)}$ is the electrostatic, $E_{\text{ind}}^{(nij)}$ the induction, $E_{\text{disp}}^{(nij)}$ the dispersive and $E_{\text{exch}}^{(nij)}$ the exchange contribution to the interaction energy. The superscript indices represent the order of the perturbation (n) and the order of the Møller-Plesset fluctuation potential (i,j) of the systems A,B, respectively. Further deeper discussions can be found in (Chalasinski *et al.* (1994), Jeziorski *et al.* (1978), Rybak *et al.* (1987), Jeziorski *et al.* (1993)).

Most theoretical studies apply the supermolecular approach (SM), where the interaction energy is obtained as a difference of the energies of the supersystem (AB) and the weakly bound subsystems (A and B) (Chalaśiński *et al.* (1994)).

$$\Delta E = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} \quad (2)$$

This SM procedure is relatively simple, however not drawback free. It offers no deeper insight into the forces contributing to the interaction force (or energy). The most significant disadvantage is the need to cope with the BSSE (Basis Set Superposition Error) (van Duijneveldt *et al.* (1994), Liu *et al.* (1973)). The counterpoise (CP) correction has been proposed by Boys and Bernardi (1970) and recently reviewed by Xantheas (1996). His method does converge to the 'true' interaction energy at infinite basis set (Complete Basis Set - CBS), which is not the case in the method of Boys and Bernardi (according to Xantheas). However, practical use of infinite basis is not realistic. By using a sufficiently large basis set, the energy converges to the CBS limit within acceptable accuracy. A better correspondence to the CBS energy can be achieved by extrapolating a series of energies computed in smaller basis sets (e.g. DZ, TZ, QZ, 5Z) to the limit of the infinite basis. To guarantee a convergence

to a realistic limit, the largest basis from the series should be of sufficient size. Dunning *et al.* (1994) and Peterson *et al.* (2005) proposed the use of correlation consistent basis sets (-cc-) which are designed for extrapolations to the CBS limit. Another set of *triple zeta* basis sets were proposed by Sadlej in cooperation with the theoretical chemistry group at Comenius University (Sadlej *et al.* (1991, 1992)). Of course, the computational costs rise dramatically with the growth of the basis set.

A method proposed by Tao and Pan (1992) enables the calculation of accurate interaction energies and equilibrium distances of dimers in a substantially smaller basis set by adding some functions between the subsystems (not centered at the atoms) where a higher electron density is expected. These functions are often denoted as mid-bond functions. The set of mid-bond functions used by Tao and Pan was optimized using MP4 calculations of the helium dimer. They preferred low angular momentum mid-bond functions combined with high angular momentum atom-centered functions. The obtained equilibrium interaction energy of helium was $D_e = 31.79 \mu E_h$ in agreement with the CBS limit.

The use of mid-bond functions usually leads to reasonable values of the interaction energy and equilibrium distance, however, their use should be considered carefully. The calculation of some physical quantities may lead to non-physical results since the electron density distribution in the supersystem might be affected by the presence of mid-bond functions. New problems may arise for hetero-atomic or hetero-molecular complexes but to our knowing a deeper study was not presented. The helium dimer represents very simple vdW complex, therefore it is very often used for testing novel computational methods or treatments.

With respect to the fact that the choice of mid-bond function exponents has not been neither discussed nor systematically studied, the aim of this work is to re-evaluate the applicability of this treatment. We will investigate the effect of mid-bond functions on the CCSD(T) interaction energies and equilibrium distances for the typical vdW dimer of helium. The mercury dimer is the next system under study which is built from huge atoms but its properties are comparable with He₂. Finally, we will develop a new alternative set of mid-bond functions suitable for the calculation of Potential Energy Surfaces (PES) of vdW complexes.

Method

In the optimization of the mid-bond function parameters we used quadruple-zeta basis set (aug-cc-pVQZ) (Peterson *et al.* (2005)) centered at helium atoms and bond functions centered in the centre of mass of the supersystem (at mid-bond). The optimization of the parameters of the mid-bond functions was performed for the interaction energy at the experimental equilibrium separation. The addition of mid-bond functions with a certain angular momentum continued until the effect of the next addition of function had no considerable effect on the interaction energy (change within some 5%). Then functions with higher angular momentum were added. Due to high computational costs only a direct optimization procedure was used where the functions were added subsequently and the previously optimized exponents were not changed. We did not limit ourselves to functions with low angular momentum but continued to functions with higher angular momentum until the effect was considerable.

Subsequently a series of SM potential curves was obtained for double-zeta (DZ) to six-zeta (6Z) calculations and fitted to the Murrell-Sorbie potential function (Murrell *et al.* (1974)).

$$\varphi(x) = -D_e e^{-a_1(x)} \sum_{i=0,1,2,\dots} a_i x^i, a_0 = 1, x \equiv r - r_e \quad (3)$$

The CBS limit values of D_e and r_e were obtained by extrapolating the values from this series.

The spectroscopic quantities ω_e and $\omega_e x_e$ were obtained from the Morse potential.

$$\varphi(x) = -D_e (1 - e^{-\alpha(x)})^2; x \equiv r - r_e \quad (4)$$

The CCSD(T) calculations of mercury were performed in a restricted active space in the aug-cc-pVQZ-PP (Peterson *et al.* (2005)) basis set with electron core potential (ECP) of Dolg (Figgen *et al.* (2005)). For metal atoms only 20 valence electrons have been used as active in CCSD(T). The effect of the remaining electrons was included in the ECP.

All calculations were performed using the Gaussian 03 package (Frisch *et al.* (2003))

Results

As described later, the mid-bond functions were successively optimized at one point of the PES until the effect of adding a next function was negligible. The rising computational cost was also monitored. Finally, we ended up with a basis set consisting of two *s* functions, three *p*, two *d*, two *f* and two *g* Gaussian basis functions. The exponents of these functions are collected in Table 1.

Table 1: The optimized exponents of the Gaussian mid-bond basis functions.

Basis function	Exponent
2s	0.30, 0.45
3p	0.25, 0.30, 0.40
2d	0.25, 0.15
2f	0.30, 0.10
2g	0.25, 0.60

Next, the complete SM potential curve for the He...He dimer was obtained using the aug-cc-pVQZ+bf basis set (+bf denotes the use of the mid-bond functions from Table 1). A remarkable lowering of the well depth to $D_e = 33.21 \mu E_h$ can be seen when compared to the aug-cc-pVQZ calculation without mid-bond functions. The values of equilibrium interaction energy and equilibrium distances are summarized in Table 2 (quantities labeled with +bf correspond to aug-cc-pVQZ calculations with mid-bond functions included).

Table 2: Theoretical CCSD(T) and experimental spectroscopic properties of the He...He and Hg...Hg dimers. The CBS limit extrapolation is based on the sequence of the aVDZ to aV6Z calculations. In the aVQZ+bf results, the bond-functions were centered between the corresponding atoms.

Dimer	Calculation	$D_e / \mu E_h$	$r_e / \text{Å}$	$\omega_e / \text{cm}^{-1}$	$\omega_e \chi_e / \text{cm}^{-1}$
He...He	aVQZ	29.63	3.011	29.3	33.08
	aV5Z	31.24	2.993	31.3	35.61
	aV6Z	32.55	2.981	32.0	35.85
	aVQZ+bf	33.21	2.979	32.2	35.63
	CBS	34.87	2.966	32.4	35.85
	comp. ^{c)}	31.99	2.982	32.0	
	comp. ^{f)}	34.66			
	exp. ^{d)}	34.64	2.969		
	exp. ^{e)}	34.68	2.963		
Hg...Hg	aVQZ	1524.21	3.776	18.2	0.24
	aVQZ+bf	1713.15	3.722	19.4	0.25
	a) ^{a)}	1617.01 / 1580.26	3.769 / 3.63	19 / 18.5	
	b) ^{b)}	1731.41			

^{a)} the best result achieved in work Yu, Dolg (1997) / experimental value in Woon (1994)

^{b)} Ceccherini *et al.* (2001)

^{c)} Czajkowski *et al.* (1990)

^{d)} Liu *et al.* (1989)

^{e)} Aziz *et al.* (1993)

^{f)} Montgomery *et al.* (1989)

The value of the aug-cc-pVQZ+bf interaction energy is in very good agreement with the experimental value of Aziz, McCourt and Wong (1987) who obtained a value of

$D_e = 34.68 \mu E_h$. Compared to this value the relative error of our calculation is less than 5 %. Theoretical calculations come even closer to this experimental value, however, with much higher computational costs (usually Full CI or CASSCF calculations). The best agreement between theoretical and experimental values can be found in the works of Liu, Mclean (1989) and Montgomery *et al.* (1989) and recently by a QMC (Quantum Monte Carlo) computation of Anderson (1993). It seems that the suggested new mid-bond functions enabled us to calculate lower energetic minima in a QZ basis than the values for a 6Z without mid-bond functions (see Table 2 and Fig. 1).

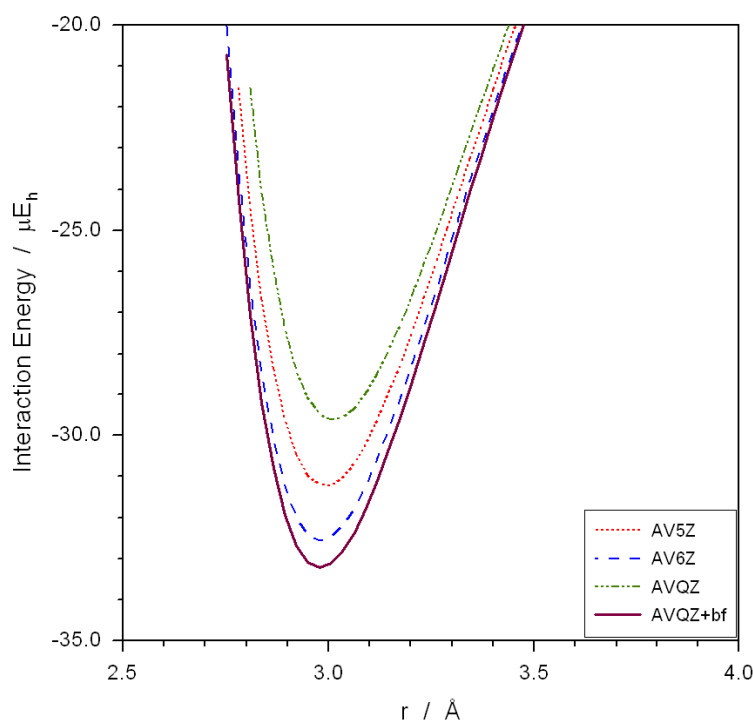


Fig. 1: The potential curves of He...He dimer for various basis sets.

In the next step, the applicability of the suggested scheme for the setting of mid-bond functions exponents was tested on Hg dimer with the same result. The potential curve of Hg₂ was computed using the aug-cc-pVQZ-PP+bf basis set. The obtained result is satisfactory with respect to the experiment. The equilibrium interaction energy $D_e = 1713.15 \mu E_h$ is in very good agreement with the experimental value of $1731.41 \mu E_h$ of Ceccherini *et al.* (2001) and Koperski *et al.* (1994). The relative error is about 1 %. The potential curves for aug-cc-pVQZ-PP+bf and aug-cc-pVQZ-PP calculations are depicted in Fig. 2.

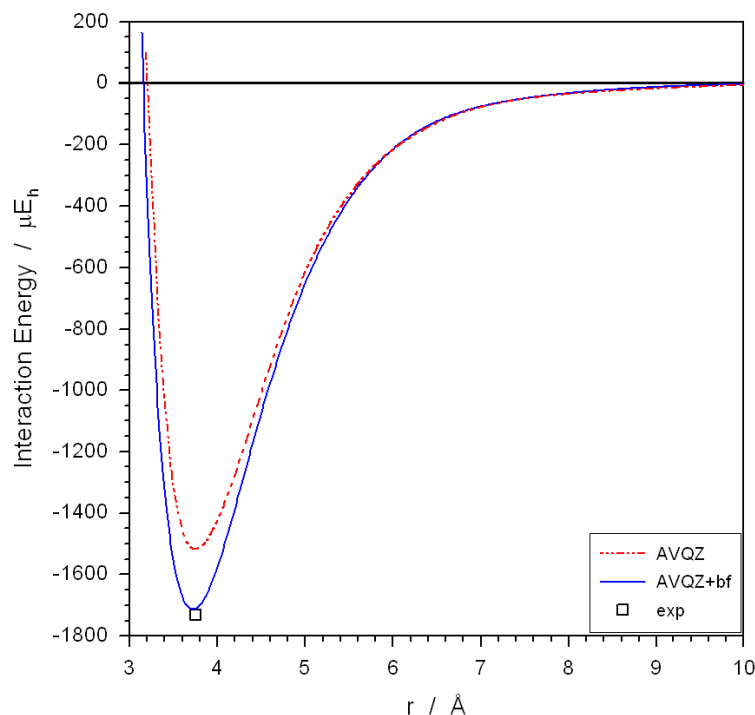


Fig. 2: The potential curves of Hg...Hg dimer for various basis sets. The experimental value is from Ceccherini *et al.* (2001).

Finally, it can be concluded that the newly developed mid-bond functions contribute strongly to the quality of potential curves. Their use with QZ basis sets resulted in the values of equilibrium interaction energy and equilibrium distance that are much closer to experimental values than those obtained from calculations in sizable basis sets that substantially prolong computational time and demand higher computational costs. In accordance with the results of Tao and Pan (1992) who tested the applicability of mid-bond functions in MP4 calculations, it was proved that also in CCSD(T) calculations the contribution of the high polarization functions to the interaction energy can be effectively recovered by the use of mid-bond functions. We have shown that the revised scheme of Tao and Pan with the new exponents is applicable to CC computations of homo-atomic dimers of various sizes. The application to hetero-atomic dimers remains a challenge. In this context we plan to investigate the effect of the position of the bond functions on the interaction energy in vdW systems.

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