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A density functional theory test study on the $N_2 \cdots He$ dimer

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Abstract. In the present contribution we report a study of the weakly bound van der Waals N_2–He molecule in the framework of the supermolecule approach by means of the PWPW and mPW1PW exchange–correlation functionals, using density functional theory local-spin-optimized atom-centered basis sets complemented with bond functions optimized at the mPW1PW level of theory. Calculations show that the mPW1PW functional using bond functions gives a realistic representation of the interaction-energy potentials for this van der Waals dimer, comparable to reference Møller–Plesset perturbation theory calculations. In contrast, the PWPW functional is unable to describe the bonding properties of this system and all values of the bonding properties obtained at different geometries with this functional are considered out-of-scale compared with the rest of the calculations presented in this study.

Key words: van der Waals – Energy surface – Density functional theory

1 Introduction

The study of weak molecular interactions is essential for the understanding of intermolecular forces in a variety of biological, chemical and physical phenomena. Supersonic expansions and static low temperature cells combined with high-resolution laser and Fourier transform IR spectroscopic techniques have been the main source of experimental information concerning the intermolecular potential-energy surfaces of van der Waals (vdW) molecules [1, 2, 3, 4]. Simultaneously, there has been an increase of interest among theoreticians to describe vdW interactions in molecular clusters [5, 6]. Absorption studies of homonuclear diatomic molecules interacting with rare gases have been limited mainly to studies of H_2 and O_2 [2, 3]. The IR spectrum of the N_2–Ar vdW complex has been obtained [4], but the rotational spacing is congested, making the interpretation difficult. The N_2–He system has been studied using molecular beams and its potential-energy surface has been derived [7]. N_2–He constitutes a good prototype for more complex molecular species interacting with rare gases. The surface derived for this complex has been used to predict correctly a variety of scattering and bulk data [7].

The availability of powerful computers and the development of efficient computational algorithms have made possible the quantum mechanical study of vdW interactions of small to medium-sized molecules [8, 9]. There are two main methods for the ab initio calculation of of vdW interactions. The first regards the interaction between the subsystems as a perturbation and partitions the energy into terms such as electrostatic, repulsion, polarization, induction, and dispersion. The second approach considers the interacting subsystems as a supermolecule [6, 10]. Since all the highly effective quantum chemistry methods developed for single-molecule calculations are, in principle, applicable without change, we use the supermolecule approach in the present study.

Density functional theory (DFT) calculations following the Kohn–Sham formalism are nowadays accepted as an alternative to conventional ab initio or semiempirical methods in describing accurately electronic, structural, and bonding properties in large molecules, bulk materials, interfaces, and surfaces. DFT includes electron correlation intrinsically, in a fashion that does not lead to the scaling problems of Hartree-Fock (HF) or post-HF methods; as a consequence, it has the potential to be applicable to fairly large systems [11]. DFT has also been successful in describing hydrogen bonds [12] and charge-transfer complexes [13]. The description of vdW interactions using approximate functionals within the Kohn–Sham approach to DFT encounters great challenges [14], even when encouraging results have been obtained recently for $(N_2)_2$ dimers [15] and complexes between N_2 and benzene [16]. The

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nitrogen dimers and nitrogen complexes have been studied using the PWPW exchange–correlation functional, which includes gradient corrections within the generalized gradient approximation, as proposed by Perdew and Wang [17]. Similar studies have been done for noncovalent interactions in noble gas dimers and for Cl_2–C_2H_2 and for water dimers by Adamo and Barone [18], using improved long-range-behavior exchange mPW1 functionals in conjunction with the PW correlation functional [17]. These systems represent an important frontier for DFT calculations.

Considering that the long-term goal of the present study corresponds to the study of the N_2–$(He)_n$ neutral and ionic clusters, we have tested the quality of the PWPW [17] and Adamo and Barone's mPW1PW [18] exchange–correlation functionals in predicting the electronic and bonding properties of the weakly interacting N_2–He vdW dimer, as compared to Møller–Plesset perturbation theory calculations at the MP2 and MP4 levels of approximation.

2 Theoretical method

The DFT calculations were performed in the framework of the supermolecule approach by applying the Kohn–Sham formalism [19]. The PWPW [17] and mPW1PW [18] exchange–correlation functionals were tested as implemented in the GAUSSIAN98 molecular package [20] for the total energy.

The interaction energy (IE) is defined as

$$\mathrm{IE}(\mathbf{R}) = E(N_2\cdots \mathrm{He};\mathbf{R}) - E(N_2\cdots \mathrm{X};\mathbf{R}) - E(\mathrm{X}\cdots \mathrm{He};\mathbf{R}), \qquad (1)$$

where, $E(N_2\cdots \mathrm{He};\mathbf{R})$ and $E(\mathrm{X}\cdots \mathrm{He};\mathbf{R})$ are used here to indicate that the monomer energies (He and N_2) are derived in the dimer-centered basis set. This amounts to applying the counterpoise procedure of Boys and Bernardi [21] to correct for the basis set superposition error at each molecular configuration, $\mathbf{R}$. Despite the long-lasting controversy on its credibility, the functional counterpoise method of Boys and Bernardi is well founded for HF and DFT approaches, while its application to post-HF approaches is more involved [22].

Møller–Plesset calculations at the MP2 and MP4 levels of theory for the total energy were also obtained in the framework of the supermolecule approach. The necessary energies were calculated using the GAUSSIAN98 molecular package [20]. Currently, going beyond the full MP4 treatment does not seem feasible. It has also been shown that in order to obtain quantitatively meaningful results incomplete higher-order MP calculations must be avoided [23], thus the complete MP4 approximation was adopted in the present study. With the linked cluster theorem automatically satisfied for each order of perturbation, this Møller–Plesset scheme is certainly size-consistent [24] and is one of the best and more economical methods available for a reliable calculation of interaction energies within the supermolecule approach. It also has several advantages compared to other methods owing to its uniform and systematic treatment of the electron correlation contributions [25]. The Møller–Plesset level of theory is accepted nowadays as a good starting point to account for the electronic correlation required to describe weak vdW interactions [26, 27, 28]. The MP2 and MP4 calculations stand as a reference for the discussion of the quality of the PWPW [17] and mPW1PW [18] exchange–correlation functionals.

In the DFT calculations, we used the TZVP [10.6.1/4.3.1] and the DZVP2 [6.1/2.1] Gaussian-type orbital one-particle atom-centered basis set of contracted Gaussian-type orbital functions for N and He atoms, respectively, which were optimized for local spin DFT calculations by Godbout et al. [29]. These DFT-optimized atom-centered functions are referred to here as TZVP(N) and DZVP2(He), respectively. These basis sets are comparable to the 6-31 + G** atomic set, which is standard in quantum chemistry. HF-optimized basis sets, such as 6-31 + G**, can be used in DFT calculations to give good geometries, but an accurate description of the bonding energies require the use of DFT-optimized basis sets [30]. They were complemented with a set taken from the standard bond functions (BFs) recommended by Tao and Pan [31], but were modified to increase the dispersion energy interaction among N_2 and He at the mPW1PW level of theory. These DFT-optimized BFs are referred to here as BF–DFT and they consist of three s functions (exponents 0.9, 0.3, and 0.1), three p functions (exponents 0.5, 0.3, 0.1), two d functions (exponents 0.4 and 0.2), one f function (0.4) and one g function (0.4). These BFs were placed at the midpoint of the vector $\mathbf{R}$, which joins He with the center of mass of N_2. For reasons that will be clear later, we did not attempt to find optimal BFs for the PWPW functional. A recent report on the use of BFs and related problems is offered by Tao [32].

The performance at the MPW1PW level of theory of the TZVP(N) and DZVP2(He) atom-centered basis sets complemented with the BF–DFT BFs can be judged by their predictions of the dipole polarizabilities of He(^{1}S) and $N_2(X^1\Sigma_g^{\,+})$, as shown in Table 1. As would be expected, the calculated polarizabilities showed a marked improvement by using the BFs, especially, for the perpendicular component of the polarizability of N_2 and for the He atom. The results are within 2–5% of the reference values obtained at the MP4 and CCSD(T) levels of theory, which in turns guaranties a fairly accurate dispersion interaction among the diatomic molecule and He.

3 Results and discussion

All counterpoise-corrected interaction energies were computed according to Eq. (1) for all possible configurations of N_2 and He. In the supermolecule calculations, N_2 was kept rigid at its experimental equilibrium bond length of $2.068a_o$. The dimer geometry is specified by $\mathbf{R}$, representing the distance between the center of mass of N_2 and He, and by the polar angle of orientation, β, of the vector along the N_2 bond with respect to the vector

Table 1. mPW1–PW91 dipole polarizabilities of $N_2(X^1\Sigma_g^{\,+})$ and He(^{1}S) using various basis sets (in atomic units). $\alpha_\perp$ and $\alpha_{||}$ correspond to the dipole polarizabilities along and perpendicular to the molecular axis, respectively, calculated relative to the center of mass, using the bond length of 2.068 au for N_2

System	Component	Basis set	This work	Reference results
N_2	$\alpha_\perp$	TZVP	6.596	9.9750[a], 10.1290[b]
		TZVP + BF-DFT	9.758	
	$\alpha_{\|\|}$	TZVP	14.378	14.4138[a], 14.9975[b]
		TZVP + BF-DFT	14.772	
He	α	DZVP2	0.388	1.3860 ± 0.0051[c]
		DZVP2 + BF-DFT	1.473	

[a] MP2

[b] CCSD(T) results in Ref. [33]

[c] Experimental result in Ref. [34]

along **R**. The equilibrium bond distance (R_e) and well depth (D_e) are obtained by fitting the calculated interaction-energy points to an eighth-order polynomial in the stretching coordinate, **R**.

The main result for the $N_2(X^1\Sigma_g^+)$ – $He(^1S)$ vdW complex is given by the computed minimum interaction-energy curves depicted in Fig. 1, which show how the D_e changes with β compared with the reference MP4 results of Salazar et al. [27]. This reference calculation made use of the POL1 basis set devised by Sadlej [35] and of the GLS basis of Garrison et al. [36], constructed to give accurate values for the electric moments and polarizabilities of N_2 and H_e, which were supplemented by Tao's BFs[31] to maximize their dispersion interaction. Figure 1 shows the T-shaped structure to be the most stable configuration, with a D_e of 19.57 cm^{-1} at an R_e of 3.69 Å at the MPW1PW level of theory, using the TZVP(N) and DZVP2(He) atom-centered basis sets complemented with the BF–DFT BFs. This is in agreement with the D_e value of 21.63 cm^{-1} at an R_e of 3.44 Å as found by Salazar et al. [27] and with the D_e of 20.82 cm^{-1} at an R_e of 3.43 Å as found by the MP4 results of Hu and Thakkar [28] for the same geometry. On the whole, the mPW1PW using the DFT-optimized atom-centered and bond-centered basis functions gives a realistic representation of the reference interaction-energy potential for N_2–He, although it still shows a less anisotropic behavior, which in turn produces a highly stable linear structure. The anisotropy in D_e, defined as $\Delta D_e = |D_e(L) - D_e(T)|$, where L and T denote the linear and the T-shaped structures, respectively, is found to be 2.59 using the mPW1PW functional, compared with a value of 3.91 found at the MP4 level of theory [27]. This also leads to the conclusion that the present DFT calculation provides a description of N_2–He that is more accurate for the linear geometry than for the T-shaped structure. Additionally, Fig. 1 shows a very flat minimum interaction-energy curve for the mPW1PW functional in the absence of BFs, with a even lower anisotropy value of $\Delta D_e = 1.66$. Although a T-shaped structure is also predicted as the most stable geometry at this level, its D_e value of 15.27 cm^{-1} at $R_e = 3.68$ Å is relatively too high.

The R_e and D_e values calculated at the three geometries represented by $\beta = 90°$, 45°, and 0° are presented in Table 2. Table 2 reveals that for all the approximations explored in the present study the T-shaped structure is the most stable conformation, followed by the structure with $\beta = 45°$, while the least stable geometry is represented by the linear conformation. It also shows that in the case of the PWPW functional in the absence of BFs, a T-shaped most-stable structure with a very large value of 80.81 cm^{-1} is predicted at an R_e of 3.31 Å. In fact, all the values obtained for the different geometries using the PWPW functional are considered out-of-scale compared with the rest of the calculations presented in Table 2; thus, no further steps were taken to improve these values using BFs. Table 2 also shows that the present mPW1PW val-

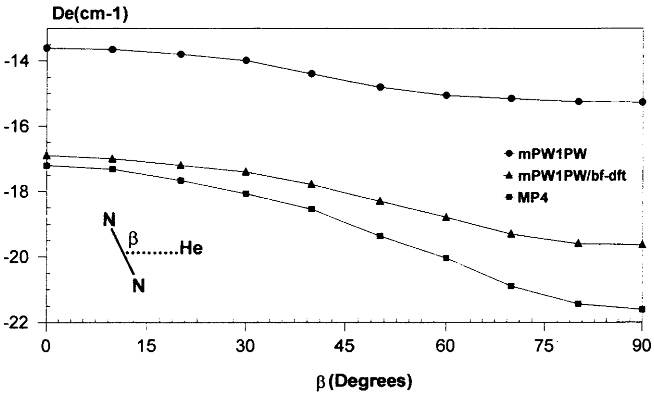

Fig. 1. Angular dependence of D_e for $N_2(X^1\Sigma_g^+)$ – $He(^1S)$

Table 2. Equilibrium bond distance (R_e) and well depth (D_e) for three β values using different methods and basis sets

Method/basis set and geometry (β,degrees)	R_e (Å)	D_e (cm^{-1})
MP4/POL1 + GLS + BF[a]		
90	3.44	21.63
45	3.70	18.44
0	3.97	17.72
MP2/POL1 + GLS + BF[a]		
90	3.68	19.54
45	3.78	15.74
0	4.05	13.80
mPW1PW/TZVP + DZVP2 + BF–DFT		
90	3.69	19.57
45	3.97	17.94
0	4.23	16.98
mPW1PW/TZVP + DZVP2		
90	3.68	15.27
45	3.92	14.78
0	4.20	13.61
PWPW/TZVP + DZVP2		
90	3.31	80.81
45	3.57	78.48
0	3.70	76.09

[a] Reference [27], using the POL1 basis set for N [35] and the GLS basis set for He [36]

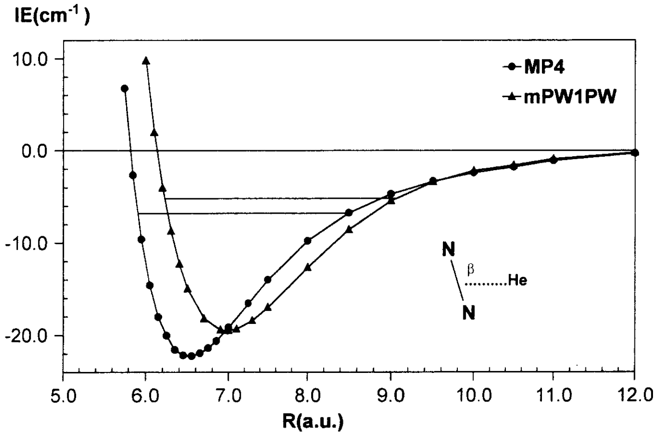

Fig. 2. Interaction-energy curves along the intermolecular coordinate for the most-stable T-shaped conformation of $N_2(X^1\Sigma_g^+)$ – $He(^1S)$

ues using DFT-optimized BFs are relatively close to the MP4 calculations used as a reference [27], except for the value of $D_e = 19.54\ \text{cm}^{-1}$ at $\beta = 90°$, which is equivalent to the value obtained for the same geometry at the MP2 level of theory. Moreover, It can be seen that R_e is systematically larger when using the mPW1PW functional than in the MP2 and MP4 calculations.

The interaction-energy curves obtained using the ab initio MP4/POL1 + GLS + BF level of theory and the mPW1PW exchange–correlation functional using the TZVP + DZVP2 + BF–DFT basis sets are depicted in Fig. 2 for the most-stable T-shaped conformation. The dissociation energy (D_o) of each interaction was obtained by fitting the calculated interaction-energy points to an eighth-order polynomial in the stretching coordinate, **R**, analytically continued with a seventh-order polynomial in $1/\mathbf{R}$ (from $1/\mathbf{R}^6$ to $1/\mathbf{R}^{12}$) in the asymptotic $\mathbf{R}\rightarrow\infty$ region. Vibrational energies were calculated from the fitted potential curves using the numerical Numerov–Cooley procedure [37] by treating N_2–He as a diatomic system with only one degree of freedom, **R**. This procedure shows that the calculated dissociation energy corresponded to a D_o of $6.02\ \text{cm}^{-1}$, with at least one vibrational state supported by this conformation using the mPW1PW functional, which is to be compared with $D_o = 7.07\ \text{cm}^{-1}$ obtained in the MP4 reference calculation [27].

4 Final remarks

In the present contribution, we have reported a study of the structure and bonding properties of the weakly interacting N_2–He vdW dimer by means of the PWPW and mPW1PW exchange–correlation functionals using DFT-optimized atom-centered basis sets complemented with BFs optimized at the mPW1PW level of theory and compared to ab initio reference calculations at the MP2 and MP4 levels of approximation.

On the whole, the mPW1PW exchange–correlation functional using DFT-optimized functions gives a realistic representation of the reference interaction-energy potential for N_2–He, although it still shows a less anisotropic behavior, which in turn produces a highly stable linear structure. In contrast, the PWPW functional is unable to describe bonding properties of these systems and all values obtained for different geometries with this functional are considered out-of-scale compared with the rest of the calculations presented.

Since DFT has the potential to be applicable to fairly large systems, mainly because it includes electron correlation intrinsically, in a fashion that does not lead to the scaling problems of the post-HF method, it seems reasonable to extend the use of the less demanding (in computation time and storage) mPW1PW exchange–correlation functional approximation, as described in the present contribution, to the challenging task of studying the N_2–$(He)_n$ neutral and ionic clusters, which represent the long-term goal of the present study.

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