

Hydrogen-bonded and van der Waals complexes studied by a Gaussian density functional method. The case of (HF)₂, ArHCl and Ar₂HCl systems

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Summary. Linear combination of Gaussian-type orbitals local spin density calculations (LCGTO-LSD) have been performed to further test the applicability to the method of hydrogen-bonded and van der Waals systems. The calculated minimum energy structures and binding energies for the (HF)₂, ArHCl and Ar₂HCl complexes are presented. In addition, the harmonic vibrational frequencies are reported for (HF)₂. The results show that by using nonlocal corrections and increasing the number of radial points in the grid, the calculated parameters are close to experimental ones and provide some encouraging evidence for the reliable use of density functional theory for these complex systems.

1. Introduction

The importance of hydrogen-bonded and van der Waals complexes in many fields of modern science is well known and largely documented in the current literature. Unfortunately these systems are difficult to study. Only 15 years ago the experimental information was obtained through indirect methods, such as pressure broadening of the gas phase spectra of monomers or measurements of gas phase transport properties. Recent theoretical and methodological developments in high resolution spectroscopies have allowed the possibility to investigate directly the intermolecular forces [1].

The difficulties in the study and characterization of these systems are also present for theoretical treatments. In fact, the weak intermolecular interaction between the monomers requires accurate computations that only highly correlated methods can give.

Reliable geometry optimizations, binding energies, vibrational frequencies and other spectroscopic constants have been obtained for small systems with accurate highly correlated methods (CI), but because of their computational expense, it is interesting to explore the applicability of density functional (DF) theory to the study of weakly bonded systems. DF methods have two main advantages with respect to the post-Hartree–Fock (HF-CI) ones. Firstly, their computational time grows as the third power of the number of basis functions N^3 while HF-CI grows as N^4 or more. Furthermore the DF scheme includes the treatment of electron correlation, as does CI. These advantages make the DF methods good candidates as practical tools to investigate hydrogen-bonded and van der Waals complexes in which the weak bonds are due to a delicate balance between several small effects.

To our knowledge, very few examples of the applicability of DF methods in these fields are present in the chemical literature [2, 3].

In order to verify the potentialities of DF methods, we have selected three complexes. The first one is the hydrogen fluoride dimer in which an intermolecular hydrogen bond is present. Many data from previous theoretical and experimental investigations [4–20] are available for this system, so accurate comparisons are possible. The other two complexes (ArHCl and Ar_2HCl) are typical van der Waals systems for which microwave and infrared spectroscopy studies [21–45] exist. Also in these cases, comparison between our results and experimental parameters can be made and discussed.

2. Computational details

The LCGTO-LSD method implemented in the deMon code [46] has been described in Refs. [47, 48]. Calculations have been performed by using a modified version of deMon that allows us to fix the internal coordinates in the z -matrix [49] and to use radial grid points of different amplitude [50]. In the calculation labelled LSD (local spin density), the Vosko, Wilk and Nusair parametrization [51] of the correlation energy of the homogeneous electron gas has been used, while in the case of that labelled NLSD (nonlocal spin density), nonlocal density gradient-type corrections have been included self-consistently, employing the functionals of Perdew and Wang [52] and Perdew [53] for exchange and correlation respectively. The orbital basis sets [54] for H, F Cl and Ar are (41/1*), (821/71/1*), (7321/621/1*) and (7321/621/1*), respectively. The auxiliary basis sets are (3,1;3,1) for F, (5,4;5,4) for Cl and Ar. The calculations have been performed using 194 angular grid points per atom and radial grids of 32, 64, and 96 points per atom. Full geometry optimization has been performed employing the Broyden–Fletcher–Goldfarb–Shanno method [55]. Binding energies have been obtained by subtracting the energies of the fragments from the energy of the complex.

3. Result and discussion

3.1 Hydrogen fluoride dimer

In tables 1 and 2 the results for the equilibrium geometry and harmonic vibrational frequencies of monomer and dimer obtained at different levels of theory are shown. Firstly, we discuss the calculated monomer properties because they are useful for quantitative accounting of changes that occur upon dimerization. Looking at the equilibrium geometry and harmonic vibrational frequencies we note that both LSD and NLSD computations give similar values that are in agreement with experimental and previous theoretical data. The greatest difference between our bond lengths and experimental ones is of only 0.026 Å. The error in the predicted vibrational frequency is of about 140 cm^{-1} with respect to the experimental value [10] and of about 10 cm^{-1} with respect to the other theoretical data [8, 9, 14].

There are two intramolecular and four intermolecular parameters required to fully describe the geometry of $(\text{HF})_2$. These are shown in Fig. 1. As is clear from Table 1, the intramolecular parameters (r_1 and r_2) are not affected by different theoretical treatment and retain essentially the same value found in the free HF molecule. On the contrary, the intermolecular distance R changes significantly

Table 1. Geometrical equilibrium parameters of HF and (HF)₂ systems. The distances are in Å and the angles are in degrees

Method	<i>R</i>	<i>r</i> ₁	<i>r</i> ₂ (HF) ₂	α	β	<i>r</i> HF
LSD-32	1.611	0.945	0.955	111.1	168.3	0.940
NLSD-32	1.728	0.945	0.954	114.4	169.9	0.943
NLSD-64	1.754	0.947	0.953	114.0	169.2	0.943
NLSD-96	1.753	0.947	0.953	114.1	169.3	0.943
MP2 ^a	1.842	0.917	0.923	—	169.4	0.921
CISD ^b	1.807	0.934	0.935	109.9	165.9	0.933
ACCD ^c	1.848	0.924	0.926	120.1	170.3	0.922
EXP ^d	1.873	0.917	0.917	108.0	180.0	0.917
EXP ^e				117 ± 6	170 ± 6	

^a From Ref. [14]^b From Ref. [9]^c From Ref. [8]^d From Ref. [12]^e From Ref. [15]**Table 2.** Equilibrium vibrational frequencies (cm⁻¹) of HF and (HF)₂ systems

Method	<i>a'</i> (cm ⁻¹) (stretch)	<i>a'</i> (stretch)	<i>a'</i> (bend) (HF) ₂	<i>a''</i> (torsion)	<i>a'</i> (bend)	<i>a'</i> (bend)	stretch HF
LSD-32	3932 (3)	3691 (177)	750	598	296	212	4030
NLSD-32	3865 (-64)	3702 (166)	657	536	225	189	3980
NLSD-64	3864 (-65)	3710 (158)	637	510	257	190	3972
NLSD-96	3864 (-65)	3706 (162)	639	513	253	187	3970
MP2 ^a	4127 (198)	4057 (189)	582	516	231	163	4170
CISD ^b	4153 (224)	4095 (227)	607	486	218	156	4150
ACCD ^c	4103 (174)	4056 (188)	—	—	167	127	4167
EXP ^d	3929	3868	—	—	—	—	4138 (3962)

^a From Ref. [14]^b From Ref. [9]^c From Ref. [8]^d From Ref. [11]

in going from local to nonlocal computations. In fact, the LSD *R* value is too short with respect to the value obtained experimentally [12] (1.611 versus 1.873 Å).

The distance sensibly increases at the NLSD-32 level of theory and does not change significantly increasing the radial grid points. Our best value is 1.753 Å, that is 0.12 Å shorter with respect to the experimental and previous highly correlated theoretical predictions [8]. The NLSD-96 result appears to be of the same order as those obtained at the CISD level [9]. For the F–F distance we obtain 2.672, 2.696,

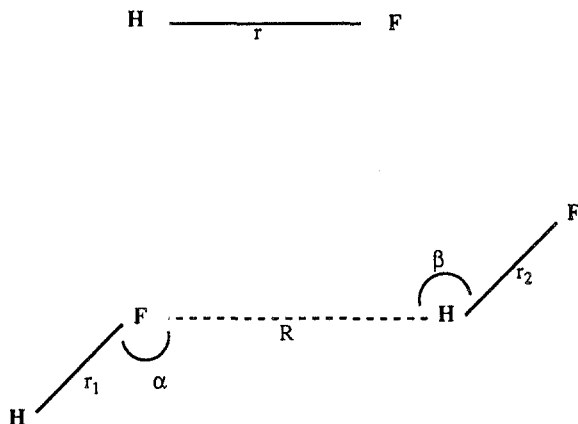


Fig. 1. Geometrical structures of HF and $(HF)_2$

and 2.695 Å at the NLS-D-32, NLS-D-64, and NLS-D-96 level of theory, respectively. Experiment yields 2.72 Å [15]. As previously found for the water dimer [2], the density functional methods tend to slightly underestimate the hydrogen bond distances. The inspection of Table 1 reveals that the agreement with the experiment is excellent for both α and β angles. The NLS-D values are about 114° and 169° for α and β , respectively. The experimental values are $117 \pm 6^\circ$ and $170 \pm 6^\circ$, respectively [15].

Table 2 shows the calculated harmonic vibrational frequencies together with the available experimental data and selected theoretical results obtained employing correlated methods. At the four levels of theory considered here, the agreement with the two available experimental frequencies [11] for $(HF)_2$ is very good, our values being higher than those obtained with the traditional highly correlated HF-based methods. There are no experimental values for the four vibrational frequencies of the HF dimer. Comparison can be made only with previous theoretical predictions [8, 9, 14]. The intermolecular stretching frequency is predicted to be 253 cm^{-1} , the HF-H bending occurs at 187 cm^{-1} , and the torsion at 513 cm^{-1} employing 96 grid points and nonlocal corrections. The increase of the number of radial grid points does not affect significantly the vibrational parameters. The agreement with previous theoretical data is good especially in the case of MP2 [14] and CISD [9] computations. We emphasize, however, that these predictions concern harmonic frequencies and should be used with caution because they characterize a region of the potential energy surface that is expected to be significantly anharmonic.

The energetic parameters are presented in Table 3. As expected the binding energy obtained employing the local approximation is too large (9.81 kcal/mol). When the nonlocal correction is taken into account we obtain a ΔE of 6.68 kcal/mol, by using 32 radial grid points per atom, and 6.60 kcal/mole with 64 and 96 points. Subtracting the relative zero point energy corrections (ZPE) we obtain a value of D^0 very close to the experimental determination (i.e. 4.9 versus 5.1 ± 1.0 kcal/mol) [10].

The binding energies obtained previously at MP2 [14], CISD [9] and approximate double substitution coupled cluster (ACCD) [8] levels of theory appear to be underestimated. No correction for basis set superposition error (BSSE) is included in these results. We think that the high quality of our basis sets and the extensive

Table 3. Energetic parameters of (HF)₂ dimer

Method	E (Hartree)	BE (kcal/mol) (HF) ₂	D_0 (kcal/mol)	ZPE (kcal/mol)
LSD-32	-199.69721	9.81	7.73	2.08
NLSD-32	-201.14916	6.68	4.94	1.74
NLSD-64	-201.15018	6.60	4.89	1.71
NLSD-96	-201.15019	6.60	4.85	1.75
MP2 ^a	—	5.00	3.10	1.90
DZ-PCl ^b	—	5.72	3.86	1.86
ACCD ^c	—	4.55	—	—
EXP ^d	—	—	5.1 ± 1.0	—

^a From Ref. [14]^b From Ref. [9]^c From Ref. [8]^d From Ref. [10]

grid used for the numerical integration of the exchange-correlation energy reduce the BSSE. On the other hand, a previous study on water dimer [2] shows that the inclusion of BSSE, calculated using the counterpoise method [56], produces a small decrease in the binding energy (about 0.4 kcal/mol). Considering this BSSE in our computation, the agreement between our D^0 value and the experimental one is excellent.

3.2 ArHCl and Ar₂HCl van der Waals complexes

Because of several studies, ArHCl represents a prototype for the study of van der Waals systems. Its ground state structure has been characterized by molecular beam electric resonance spectroscopy [27]. Experimental structural information is also available for Ar₂HCl [22, 23, 32–34]. *Ab initio* investigations have been made previously on both complexes [36–39].

As a first step of our work, we have performed calculations on the argon dimer to further test the reliability of the method previously used in the study of the CO₂H₂O complex [3]. From Table 4 it is evident that the agreement with experiment is good for all the computations. In particular NLSD-96 gives an equilibrium distance of 3.832 Å. The experimental value is 3.821 Å [40, 41]. The computed harmonic vibrational frequency for Ar₂ is 40 cm⁻¹ and compares well with two experimental values (25, 31.1 cm⁻¹) [42, 43]. Finally the computed binding energy (BE) is 0.21, 0.08 and 0.1 kcal/mol at NLSD-32, -64 and -96 levels, respectively. The experimental BE is 0.284 kcal/mol [44]. The calculated equilibrium geometries for HCl are close to experiment. In ArHCl and Ar₂HCl, the H–Cl distance retains the value of the isolated molecule. The value obtained at the NLSD-96 level for R (see Fig. 2 for the definition of geometrical parameters) is in good agreement with experimental data (4.017 versus 3.98 and 4.006 Å) [35, 45]. For the α angle our result is in disagreement with the experimental value (27.2 versus 41.7°) [35]. In the case of Ar₂HCl the agreement between our best calculations (NLSD-96) and

Table 4. Geometrical parameters of the minimum-energy structure of Ar_2 , HCl , ArHCl , and Ar_2HCl molecules. Distances are in Å and angles are in degrees. For the definition of geometrical parameters see Fig. 2

Parameter	NLSD-32	NLSD-64	NLSD-96	EXP
<i>Ar₂</i>				
<i>R</i>	3.791	3.892	3.832	3.821 ^a (3.759) ^b
<i>HCl</i>				
<i>R</i>	1.288	1.295	1.295	1.275 ^c
<i>ArHCl</i>				
<i>R</i>	3.712	4.058	4.017	3.98 ^e (4.006) ^d
<i>r</i>	1.291	1.297	1.297	1.274 ^e
α	33.0	28.3	27.2	41.7 ^e (45.) ^d
<i>Ar₂HCl</i>				
<i>R</i>	4.120	4.223	3.810	3.861 ^f
<i>r</i>	4.136	4.020	4.049	4.005 ^f
<i>r'</i>	1.291	1.298	1.297	1.275 ^f
α	54.3	57.9	58.4	58.1 ^f
β	55.4	46.5	35.3	30.4 ^f
γ	-1.4	0.0	30.3	28.4 ^f

^a From Ref. [40]

^b From Ref. [41]

^c From Ref. [23]

^d From Refs. [35, 45]

^e From Ref. [35]

^f From Ref. [23]

experiment [23] is very good for both distances and angles (see Table 4). It is important to note that in order to obtain the agreement for the torsional angle γ , the use of a radial grid with a large number of points is suggested.

Table 5 shows the total and binding energies. The experimental BE of ArHCl and Ar_2HCl are measured to be 0.33 and 0.91 kcal/mol, respectively [23, 24, 32–34]. Very good agreement is found with all our computations. Using the SCF energies, the BE becomes slightly dissociative (about -0.2 kcal/mol). On the other hand, previous works have shown that more accurate results are obtained when the exchange-correlation contribution to the energy gradient is integrated numerically using a grid with a large number of points [3, 57].

4. Conclusions

Both hydrogen-bonded and van der Waals systems have been studied employing grids with increasing numbers of points. On the basis of our studies and previous studies available in the literature we can outline some conclusions: (i) The intermolecular distances seem to be underestimated by about 0.1 Å for hydrogen-bonded systems, while they agree with experimental data for van der Waals complexes. (ii) The binding energies are well reproduced even with medium-sized

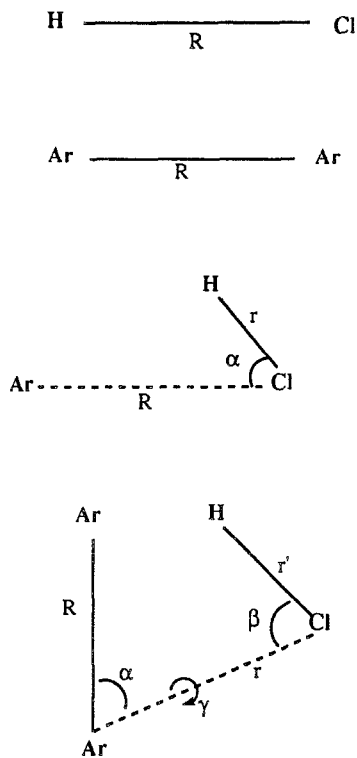


Fig. 2. Schematic drawing of HCl, Ar₂, ArHCl and Ar₂HCl

Table 5. Binding energy (kcal/mol) for Ar₂, HrHCl, and Ar₂HCl molecules

Molecules	BE (kcal/mol)
<i>Ar₂</i>	
NLSD-32	0.21
NLSD-64	0.08
NLSD-96	0.10
EXP ^a	0.28
<i>ArHCl</i>	
NLSD-32	0.33
NLSD-64	0.30
NLSD-96	0.38
EXP ^b	0.33
<i>Ar₂HCl</i>	
NLSD-32	0.59
NLSD-64	0.63
NLSD-96	0.96
EXP ^c	0.91

^a From Ref. [44]

^b From Ref. [24]

^c From Refs. [23, 32–34]

grids. (iii) The use of extensive grids gives results in better agreement with experiment and is mandatory to obtain accurate geometries in van der Waals systems with high amplitude motions.

Further work is required to see if it is possible to generalize these conclusions, to establish optimal grids and the methodological implementations that can improve the LCGTO-NLSD description of hydrogen-bonded systems.

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