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Weak Intermolecular Interaction

IV. An Application of the Function Counterpoise Method to the Calculation of the Interaction Energy and its Components

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The function counterpoise method [1] was applied in the determination of the SCF interaction energy and its components between two molecules of hydrogen. Calculations were carried out for the rectangular and linear configurations of $(H_2)_2$ dimer.

Key word: Weak molecular interaction

1. Introduction

We have previously shown [2] that the SCF method is incapable of giving the correct interaction energies of the $(H_2)_2$ dimer, if the small or medium basis sets were used. This is caused by two facts:

1) The ΔE^1 energy becomes less repulsive when going from a large basis to a small one. At larger distances it is possible to identify this energy with the Coulomb one. In the case of $(H_2)_2$ dimer, the major contribution to the Coulomb energy arises from the quadrupole-quadrupole interaction. With small basis sets, however, the quadrupole is not satisfactorily represented.

2) The E^2 energy being of attractive nature, attains unrealistic values in smaller bases. Consequently, the SCF calculation with some bases gave spurious minima. This additional stabilization may be associated with the greater dimer basis set, as compared with the monomer basis set. Boys and Bernardi have noted [1] a considerable improvement may be achieved when the function counterpoise method is used. Recently, calculation of dimerization energies of polar systems (H_2O, HF, and HCN) were carried out with that method [3].

In the present paper the function counterpoise method was used for calculation of the interaction energy between two hydrogen molecules. We limited ourselves to rectangular (2) and linear (4) configurations only, having at our disposal results obtained from large bases [2]. Attention was paid not only to corrected SCF interaction energies ($\Delta E_c^{\mathrm{SCF}}$) but also to corrected ΔE^1 and E^2 energies (ΔE_c^1, E_c^2).

2. Method

Configurations and basis sets used were described in an earlier paper [2]. The $\Delta E_c^{\mathrm{SCF}}$ energy was determined as the difference between the energy of the supersystem (E_{AB}) and the sum of monomer energies (E_{A}, E_{B}). The E_{AB} energy was evaluated in the standard way, but the E_{A}, E_{B} energies were calculated by using the full set of expansion supersystem functions (for details see [3]). The ΔE_c^1 energy was defined as the difference between E_{AB}^1 and $E_{\mathrm{A}}+E_{\mathrm{B}}$. The E_{AB}^1 energy was obtained from the first iteration of the SCF procedure. Instead of the eigenfunctions of the isolated systems, however, Schmidt's orthogonalized eigenfunctions which correspond to eigenvalues of E_{A} and E_{B} energies were used. The E_c^2 energy was calculated as the difference between $\Delta E_c^{\mathrm{SCF}}$ and ΔE_c^1.

Let us now comment in detail on restrictions applied to the symmetry of wave functions. In the Configuration 2, symmetry restrictions were the same both in calculation of E_{AB}, E_{A}, and E_{B}. Symmetry orbitals in the Configuration 4 were formed as follows: $s_1 \pm s_4$, $s_2 \pm s_3$, $x_1 \mp x_4$, $x_2 \mp x_3$. Throughout the calculation of the E_{A} energy, that is when charges on the Molecule B (H_3, H_4) were equal to zero, the following symmetry orbitals were used: $s_1 \pm s_2$, $x_1 \mp x_2$, s_3, s_4, x_3, x_4. Though symmetry restrictions applied to functions localized on the Molecule A guarantee equivalent coefficients on Atoms 1 and 2, their different overlap with functions localized on the Molecule B results in a slight charge shift inside the Molecule A. The same situation applies to the calculation of the E_{B} energy.

3. Results and Discussion

Table 1 gives the values of $\Delta E_c^{\mathrm{SCF}}$, ΔE_c^1, and E_c^2 energies for rectangular and linear configurations. First let us consider in particular separate energy terms.

3.1. ΔE_c^1 Energy

Values of ΔE_c^1 and ΔE^1 (Table 2 in Ref. [2]) do not differ too much from each other. As to dependence of the ΔE_c^1 energy on the number of s function and the values of the exponent of polarization function, the same conclusions as for ΔE^1 energy are valid.

3.2. E_c^2 Energy

Contrary to what was shown about the E^2 energy, with E_c^2 energy one always obtains monotonous curves i.e. without inflexes or extremes (Fig. 1). This indicates that all irregularities of the E^2 energy course which accompany the use of small or medium basis sets were removed when the function counterpoise method was applied. Moreover, the E_c^2 energy was almost insensitive to the size of the basis set and the value of the polarization function exponent. The absolute value was always greater in a linear configuration than in a rectangular one. If we compare the values of the E_c^2 with those of the E^2 determined in large bases, we can see that the former were slightly underestimated. This is contrary to the E^2 energy values that were strongly overestimated in some bases.

Table 1. Corrected SCF interaction energy ($\Delta E_c^{\mathrm{SCF}}$), its components ($\Delta E_c^1$, E_c^2) and basis function corrections ($\Delta\varepsilon$) in rectangular (2) and linear (4) configurations. Energies in 10^{-4} a.u.

Configuration[a]		2				4			
Basis	d(a.u.)	ΔE_c^1	$-E_c^2$	$\Delta E_c^{\mathrm{SCF}}$	$\Delta\varepsilon$	ΔE_c^1	$-E_c^2$	$\Delta E_c^{\mathrm{SCF}}$	$\Delta\varepsilon$
I	5.5			3.672	0.070	10.158	1.722	8.436	6.134
	6.0			1.735	0.002	3.427	0.556	2.871	2.066
	6.5			0.930	0.032	1.407	0.194	1.213	0.532
	7.0			0.508	0.044	0.774	0.078	0.696	0.094
	7.5			0.265	0.036	0.502	0.037	0.465	0.014
	8.0			0.130	0.022	0.335	0.020	0.315	0.012
II	5.5			5.426	1.162	10.753	1.920	8.833	1.048
	6.0			1.980	0.528	4.430	0.743	3.687	0.862
	6.5			0.688	0.210	1.889	0.288	1.601	0.552
	7.0			0.235	0.074	0.853	0.111	0.742	0.290
	7.5			0.086	0.024	0.430	0.043	0.387	0.132
	8.0			0.036	0.006	0.246	0.015	0.231	0.052
III	5.5	7.193	0.303	6.890	0.414	14.167	2.899	11.268	0.138
	6.0	2.922	0.105	2.817	0.231	5.904	1.007	4.897	0.054
	6.5	1.189	0.036	1.153	0.137	2.511	0.352	2.159	0.026
	7.0	0.485	0.012	0.473	0.082	1.125	0.126	0.999	0.020
	7.5	0.203	0.004	0.199	0.052	0.550	0.046	0.504	0.024
	8.0	0.088	0.001	0.087	0.032	0.299	0.018	0.281	0.026
IV	5.5	7.034	0.265	6.769	1.582	12.695	2.659	10.036	0.546
	6.0	2.835	0.078	2.757	1.032	5.178	0.936	4.242	0.652
	6.5	1.112	0.020	1.092	0.604	2.185	0.328	1.857	0.726
	7.0	0.427	0.006	0.421	0.312	0.978	0.115	0.863	0.658
	7.5	0.163	0.001	0.162	0.142	0.479	0.041	0.438	0.488
	8.0	0.065	0.000	0.065	0.056	0.264	0.015	0.249	0.302
V	5.5	7.041	0.359	6.682	1.584	13.618	2.764	10.854	0.510
	6.0	2.887	0.106	2.781	1.056	5.694	0.981	4.713	0.566
	6.5	1.167	0.029	1.138	0.624	2.526	0.348	2.178	0.630
	7.0	0.467	0.008	0.459	0.324	1.223	0.122	1.101	0.592
	7.5	0.190	0.002	0.188	0.149	0.661	0.045	0.616	0.460
	8.0	0.083	0.000	0.083	0.060	0.399	0.017	0.382	0.298
VI	5.5	6.471	0.449	6.022	2.560	13.715	3.382	10.333	5.220
	6.0	2.552	0.157	2.395	2.002	5.501	1.264	4.237	4.352
	6.5	0.986	0.055	0.931	1.390	2.327	0.425	1.902	3.348
	7.0	0.380	0.020	0.360	0.834	1.100	0.134	0.966	2.308
	7.5	0.154	0.008	0.146	0.428	0.606	0.046	0.560	1.414
	8.0	0.070	0.003	0.067	0.188	0.388	0.019	0.369	0.768

[a] Figure 1 in Ref. [2].

3.3. $\Delta E_c^{\mathrm{SCF}}$ Energy

The curve of dependence of $\Delta E_c^{\mathrm{SCF}}$ on the distance was found to be monotonous in both configurations and all bases used (Fig. 2). This dramatic change (in comparison with uncorrected values) was due to small sensitivity of the E_c^2 energy to the basis. The differences among $\Delta E_c^{\mathrm{SCF}}$ energies could be mainly attributed to differences in ΔE_c^1 energies. In all cases the $\Delta E_c^{\mathrm{SCF}}$ energy was more repulsive than the ΔE^{SCF} one. This shows that the first one was closer to the results obtained

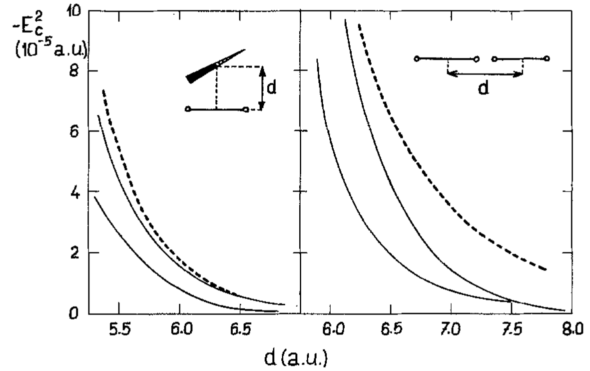

Fig. 1. E_c^2 energies in linear and rectangular configurations. Energy curves given by the basis sets I–VI fall into the region determined by full lines. Dashed line refers to uncorrected E^2 energy determined in the Basis VII

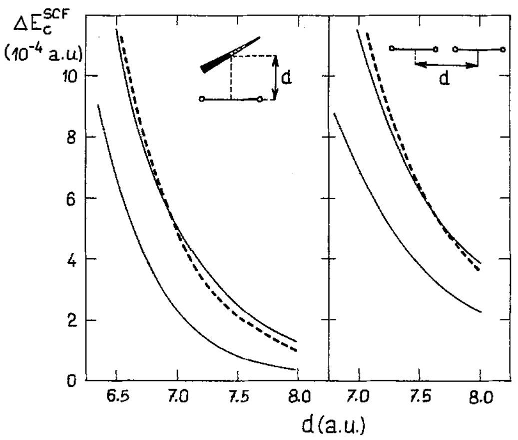

Fig. 2. ΔE_c^{SCF} energies in linear and rectangular configurations. Energy curves given by the basis sets I–VI fall into the region determined by full lines. Dashed line refers to ΔE^{SCF} energy determined in the Basis VII

with larger bases. As noted by Johansson *et al.* [3], the values of the interaction energy for polar systems were overcorrected. In order to remove this error the systematically selected correction factor was applied in order to make the results given by the minimal basis set comparable to those given by large bases and experiments. In our calculation we were not forced to use a similar factor. It should be pointed out that this might be due to compensation of errors, because the ΔE_c^1 and ΔE_c^2 energies are of opposite signs.

Table 1 shows the values of basis functions correction ($\Delta\varepsilon$) defined as the difference between values of corrected and uncorrected SCF interaction energies. As shown by Johansson *et al.* [3] the $\Delta\varepsilon$ values were significant only if a minimal basis set was used. In case of weak interactions, this correction was important even in the $DZ+P$ basis. Large values of the $\Delta\varepsilon$ in Basis VI may be attributed to the very diffuse polarization function which slightly polarizes the separated hydrogen molecules. Throughout the interaction this function strongly interferes

Table 2. Total interaction energy and its components determined in the Basis VI. The values of the dispersion energy (E^D) were taken from Ref. [4]. Energies in 10^{-4} a.u.

Configuration[a]	1				2			
d(a.u.)	ΔE_c^1	$-E_c^2$	$-E^D$	E^{TOT}	ΔE_c^1	$-E_c^2$	$-E^D$	E^{TOT}
5.5	7.029	0.451	4.167	2.411	6.471	0.449	3.822	2.200
6.0	2.911	0.158	2.497	0.256	2.552	0.157	2.311	0.084
6.5	1.228	0.056	1.540	−0.368	0.986	0.055	1.436	−0.505
7.0	0.547	0.020	0.980	−0.453	0.380	0.020	0.919	−0.559
7.5	0.272	0.007	0.642	−0.376	0.154	0.008	0.605	−0.459
Configuration[a]	3				4			
5.5	7.111	1.448	5.651	0.012	13.715	3.382	8.760	1.573
6.0	2.309	0.508	3.364	−1.563	5.501	1.264	5.153	−0.916
6.5	0.562	0.175	2.051	−1.664	2.327	0.425	3.090	−1.188
7.0	−0.012	0.062	1.287	−1.361	1.100	0.134	1.905	−0.939
7.5	−0.157	0.023	0.832	−1.012	0.606	0.046	1.211	−0.651

[a] Figure 1 in Ref. [2].

with the internuclear regions of the neighbouring molecule. The values of the $\Delta\varepsilon$ were found to be always larger in the scaled than unscaled *DZ* basis set.

3.4. Total Energy

Utility of the mentioned corrections may be best judged on the basis of the calculated total interaction energies, that is on the basis of the sum of SCF interaction and dispersion energies. Table 2 shows values of the total interaction energy determined by means of Basis VI for Configurations 1–4 (cf. Fig. 1 in Ref. [2]). Such a basis was recommended by Kochanski [4] as the smallest one reasonably describing the dispersion energy. As far as numerical values are concerned the results for Configuration 2 were comparable with those obtained in larger bases. The interaction for Configuration 4 is, however, overestimated (cf. the discussion in Ref. [2]). This overestimation could be explained by small values of the ΔE_c^1 energy (in Configuration 2 the ΔE_c^1 energy was comparable with that calculated by using large bases). On the other hand, strong overestimation of the total (uncorrected) interaction energy was caused by unrealistic negative values of the E^2 energy.

The ΔE_c^1 energy was better described with an unscaled than scaled basis set; the former gave, moreover, smaller $\Delta\varepsilon$. Therefore, in addition to the mentioned bases, another basis was used, whose *s* part was taken from Basis III and the *p* part was formed by the polarization function with the exponent 0.2. Results for linear configuration are given in Table 3. Clearly the ΔE_c^{SCF} energies with this basis set are better described than with the Basis VI, and approximately as well as in the Basis V. The basis function corrections are significantly lower than in the Basis VI, so that the ΔE^{SCF} energies in this basis are also qualitatively correct and do not lead to spurious minima. In regard to the dispersion energy, it may be supposed that its magnitude does not change too much in comparison with the Basis VI, because the dispersion energy is not too sensitive to the quality of the *s* functions [4].

Table 3. Uncorrected SCF interaction energy, corrected SCF interaction energy and its components and basis function correction for a linear configuration in the *DZ* unscaled basis with polarization function with exponent 0.2. Energies in 10^{-4} a.u.

d(a.u.)	ΔE_c^1	$-E_c^2$	ΔE_c^{SCF}	ΔE^{SCF}	$\Delta\varepsilon$
5.5	14.779	3.653	11.126	10.456	0.670
6.0	6.162	1.438	4.724	3.992	0.732
6.5	2.693	0.558	2.135	1.551	0.584
7.0	1.287	0.215	1.072	0.656	0.416
7.5	0.686	0.081	0.605	0.313	0.292
8.0	0.406	0.031	0.375	0.183	0.192

4. Conclusion

To summarize, reasonable interaction energies may also be obtained by use of appropriate, carefully selected, small bases. This conclusion is hopeful with respect to calculations of the total interaction energy among larger molecules. Preference should be devoted to bases providing a correct characteristic of a single system for which the basis function correction is sufficiently small and which are able to correctly describe the dispersion energy. If a particular basis set possesses a large value of the $\Delta\varepsilon$, the use of the function counterpoise method is inevitable. Up to now little is known about the effect of the function counterpoise method on the value of the dispersion energy.

Finally let us comment the paper by Kochanski *et al.* [5] published recently. For a pair of H_2 molecules, these authors obtained greater interaction energy than we. A basis set comparable with our No. VII set has been used [5]. As only total SCF-CI interaction energies have been reported, it has not been possible to decide which contribution to the total energy is responsible for the discrepancy.

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