Theoret. Chim. Acta (Berl.) 36, 207—214 (1975)

Weak Intermolecular Interaction

III*. *Ab initio* SCF Calculation of Interaction Energy and its Components near the Van der Waals Minimum

Miroslav Urban
Department of Physical Chemistry, Komenský University, 801 00 Bratislava, Czechoslovakia

Pavel Hobza
Institute of Hygiene and Epidemiology, 100 42 Praha 10, Czechoslovakia

Received May 6, 1974/August 19, 1974

The SCF interaction energy (ΔE^{SCF}) between two hydrogen molecules was separated into (Coulomb + exchange) and (induction + charge-transfer) components. The effect of the basis set and orientation of the two molecules on the ΔE^{SCF} energy and its components are discussed.

Key word: Weak molecular interaction

1. Introduction

In the course of the last few years several papers were published in which interaction energy between extremely simple systems on the *ab initio* level was determinated (He–He [1, 2], Li–Li [3, 4], He–H, He–Li [5], H_2–H_2 [6, 7], Li^+–H_2 [8], He–HF, He–H_2O [9]). A common feature of all these papers was the inclusion of the configuration interaction, i.e. a partial or complete inclusion of the correlation energy (depending on the size of the CI basis set). It was shown that results were not considerably inferior if a truncated CI basis was used. However even such a treatment is limited to the simplest systems as the CI calculations on larger systems are practically not feasible. On the other hand, the SCF interaction energy (ΔE^{SCF}) formed [10–12] by ΔE^1 (Coloumb and exchange repulsion energies) and E^2 (induction and charge-transfer energies) is still accessible for moderately large systems. With noncharged nonpolar systems it was found that the intersystem correlation energy (forming the dominant part of the total correlation energy [4]) could be at a sufficiently large distance identified with the dispersion energy. If we were able to determine the dispersion energy with a sufficient accuracy (without using the CI method), we could thus determine the total interaction energy between larger systems, too. Perturbation calculation of dispersion energy [8] with the use of *ab initio* HF function of separate systems was performed by Kochanski [13, 14], who studied the interaction of two hydrogen molecules. Later the same author [15] also determined the total interaction energy as the sum of the SCF interaction energy and perturbation dispersion energy under assumption that the SCF interaction energy may be substituted by the

---

* Part II: Collection Czechoslov. Chem. Commun. 39, 2866 (1974).

ΔE^1 energy for any geometric configuration and any value of the exponent of the polarization function. The induction and charge-transfer energies were thus assumed to be negligible.

The aim of the present paper was to study the effect of the basis set used on the SCF interaction energy (ΔE^{SCF}) and both its components (ΔE^1 and E^2) in the interaction of two H_2 molecules. It is obvious that for sufficiently accurate calculation of this type it is necessary to use a large flexible basis set with polarization functions. These functions have to polarize both the individual systems and density in the long range interaction region. Up to now little is known about the size of the basis set, which is still able to provide a satisfactory account of the interaction energy. Knowledge of this, as well as of the rules of selection of the basis set for calculation of dispersion energy may be very useful in nonempirical calculation of interaction energies of larger systems.

2. Calculations

The SCF interaction energy was determined as the difference between energy of $(H_2)_2$ in particular configuration and the sum of energies of isolated H_2 molecules (with the H_2 internuclear distance fixed at 1.4 a.u.). In all calculations the Gaussian atomic functions were used. Table 1 gives the basis sets used. The basis set VI was recommended [14] for perturbation calculation of dispersion energy. The ΔE^1 component was obtained in a standard way, i.e. as the difference of the energy given by the first iteration of the SCF procedure, where starting vectors were Schmidt's orthogonalized vectors of separated systems, and the sum of ener-

Table 1. Basis set

Bases	Exponents of polarization functions	E_{SCF} (a.u.)
I [1*s*][a]		−1.0855075
II [1*s*][b]		−1.1220256
III [2*s*][c]		−1.1247602
IV [2*s*][d]		−1.1265894
V [2*s*1*p*][e]	1.0	−1.1311967
VI [2*s*1*p*][f]	0.2	−1.1273125
VII [4*s*2*p*][g]	2.0, 0.5	−1.1333010
VIII [4*s*3*p*][h]	1.5, 0.5, 0.15	−1.1330878
IX [4*s*3*p*][i]	1.5, 0.5, 0.15	−1.1333249

[a] (3*s*) basis [16] was contracted to [1*s*].

[b] Analogous to I, exponents were scaled by 1.425 according to Ref. [17].

[c] (4*s*) basis [16] was contracted to [2*s*].

[d] Analogous to III, exponents were scaled by 1.44 according to Ref. [18].

[e] *s* part is the same as in IV.

[f] *s* part is the same as in IV, *p* function choosen from Ref. [14].

[g] *s* part is identical with (6*s*) basis [16] contracted to [4*s*], for three *s* functions with the greatest exponents (2.34648; 10.2465; 68.1600) contraction coefficients (0.07243; 0.01610; 0.002142) have been determined according to H_2 calculation in (6*s*) basis. *p* functions choosen from Ref. [19].

[h] Reference [20].

[i] *s* part comes from VII, *p* part from VIII.

Table 2. SCF interaction energy and its components for different configurations (Fig. 1) of dimer (energies in 10^{-4} a.u.)

Configuration		1			2			3			4		
Basis	d (a.u.)	ΔE^1	$-E^2$	ΔE^{SCF}	ΔE^1	$-E^2$	ΔE^{SCF}	ΔE^1	$-E^2$	ΔE^{SCF}	ΔE^1	$-E^2$	ΔE^{SCF}
I	5.5	3.929	0	3.929	3.602	0	3.602	1.867	0.005	1.862	2.922	0.620	2.302
	6.0	1.948	0	1.948	1.733	0	1.733	0.655	0.002	0.653	1.021	0.216	0.805
	6.5	1.045	0	1.045	0.898	0	0.898	0.322	0.014	0.308	0.736	0.055	0.681
	7.0	0.566	0	0.566	0.464	0	0.464	0.161	0.025	0.136	0.618	0.016	0.602
	7.5	0.302	0	0.302	0.229	0	0.229	0.053	0.027	0.026	0.470	0.019	0.451
	8.0	0.161	0	0.161	0.108	0	0.108	−0.010	0.023	−0.033	0.328	0.025	0.303
II	5.5	4.593	0	4.593	4.264	0	4.264	5.821	1.641	4.180	10.696	2.911	7.785
	6.0	1.655	0	1.655	1.452	0	1.452	1.867	0.801	1.066	4.385	1.560	2.825
	6.5	0.612	0	0.612	0.478	0	0.478	0.478	0.364	0.114	1.839	0.790	1.049
	7.0	0.252	0	0.252	0.161	0	0.161	0.040	0.152	−0.112	0.823	0.371	0.452
	7.5	0.126	0	0.126	0.062	0	0.062	−0.070	0.058	−0.128	0.414	0.159	0.255
	8.0	0.077	0	0.077	0.030	0	0.030	−0.082	0.020	−0.102	0.241	0.062	0.179
III	5.5	6.791	0.000	6.791	6.477	0.001	6.476	8.217	1.433	6.784	13.721	2.591	11.130
	6.0	2.788	0.007	2.781	2.594	0.008	2.586	3.048	0.659	2.389	5.643	0.800	4.843
	6.5	1.157	0.012	1.145	1.029	0.013	1.016	1.070	0.322	0.748	2.396	0.263	2.133
	7.0	0.494	0.015	0.479	0.406	0.015	0.391	0.329	0.166	0.163	1.086	0.107	0.979
	7.5	0.225	0.016	0.209	0.163	0.016	0.147	0.063	0.093	−0.030	0.539	0.059	0.480
	8.0	0.114	0.014	0.100	0.070	0.015	0.055	−0.023	0.057	−0.080	0.297	0.042	0.255
IV	5.5	5.640	0.130	5.510	5.322	0.135	5.187	6.897	1.944	4.953	11.768	2.278	9.490
	6.0	2.147	0.222	1.925	1.951	0.226	1.725	2.427	1.323	1.104	4.874	1.284	3.590
	6.5	0.828	0.210	0.618	0.699	0.211	0.488	0.756	0.937	−0.181	2.087	0.956	1.131
	7.0	0.340	0.142	0.198	0.252	0.143	0.109	0.169	0.618	−0.449	0.945	0.740	0.205
	7.5	0.158	0.075	0.083	0.096	0.076	0.020	−0.014	0.362	−0.376	0.469	0.519	−0.050
	8.0	0.087	0.033	0.054	0.042	0.033	0.009	−0.058	0.184	−0.242	0.263	0.316	−0.053
V	5.5	5.970[a]	0.366	5.604	5.469	0.371	5.098	6.422	1.987	4.435	12.671	2.327	10.344
	6.0	2.364	0.318	2.046	2.046	0.321	1.725	2.133	1.352	0.781	5.416	1.269	4.147
	6.5	0.968[a]	0.240	0.728	0.757	0.243	0.514	0.568	0.954	−0.386	2.447	0.899	1.548
	7.0	0.436[a]	0.155	0.281	0.287	0.152	0.135	0.043	0.633	−0.590	1.200	0.691	0.509
	7.5	0.222	0.079	0.143	0.119	0.080	0.039	−0.102	0.376	−0.478	0.652	0.496	0.156
	8.0	0.132	0.034	0.098	0.057	0.034	0.023	−0.123	0.193	−0.316	0.396	0.312	0.084
VI	5.5	5.870[a]	1.886	3.984	5.314[a]	1.852	3.462	5.954	4.019	1.935	12.832	7.719	5.113
	6.0	2.329[a]	1.592	0.737	1.999	1.606	0.393	1.853	2.942	−1.089	5.434	5.549	−0.115
	6.5	0.964[a]	1.188	−0.224	0.724[a]	1.183	−0.459	0.404	2.085	−1.681	2.440	3.885	−1.445
	7.0	0.432[a]	0.741	−0.309	0.269[a]	0.743	−0.474	−0.051	1.385	−1.436	1.207	2.550	−1.343
	7.5	0.223[a]	0.387	−0.164	0.101[a]	0.383	−0.282	−0.156	0.839	−0.995	0.675	1.529	−0.854
	8.0	0.148	0.183	−0.035	0.062	0.183	−0.121	−0.154	0.451	−0.605	0.425	0.824	−0.399
VII	5.5				7.212	0.545	6.667				15.889	3.385	12.504
	6.0				2.956	0.171	2.785				6.952	1.434	5.518
	6.5				1.216	0.051	1.165						2.500
	7.0				0.512	0.016	0.496				1.573	0.371	1.202
	7.5						0.220				0.854	0.220	0.634
	8.0				0.109	0.003	0.106				0.513	0.134	0.379
IX	5.5										16.547	3.386	13.161
	6.0										7.388	1.322	6.066
	6.5										3.465	0.527	2.938
	7.0										1.747	0.214	1.533
	7.5										0.967	0.088	0.879

[a] Reference [15].

gies of isolated systems. This component is labeled as the first order term of the intermolecular interaction. The E^2 energy was defined as the difference between ΔE^{SCF} and ΔE^1 energies.

3. Results and Discussion

Table 2 gives the values of ΔE^{SCF}, ΔE^1, and E^2 energies for different configurations (Fig. 1). At the beginning of the present study no separation of the ΔE^{SCF} energy was performed. Therefore some values of the ΔE^1 energy in the Basis V and VI (indicated in Table 2 by a Type a) were those calculated already by Kochanski [15]. These values were systematically found more repulsive by about 2×10^{-6} a.u. in the Basis VI for Configurations 3 and 4. This kind of small discrepancies are generally due to a lack of accuracy in the calculations. We now comment in detail on the individual terms.

3.1. SCF *Interaction Energies*

The course of the dependence of ΔE^{SCF} on the distance is in various configurations qualitatively different. Whereas for Configurations 1 and 2 monotonic curves were obtained with all bases except for the Basis VI, with the Configuration 4 inflexions or even extremes were found (Fig. 2). Such extremes could be expected only in the Configuration 3. Reasons for the extraordinarity of the linear configuration will be discussed later. By comparison of ΔE^{SCF} values for scaled and unscaled [2*s*] basis sets it was found that ΔE^{SCF} was more repulsive with the unscaled basis set. This means that the unscaled basis set gives results closer to those obtained in a larger basis set. A similar comparison for the [1*s*] basis set was impossible owing to the unrealistic course of the dependence given by the unscaled basis set. On enlarging the basis set ΔE^{SCF} becomes more repulsive. The ΔE^{SCF} in Configurations 1 and 2 were correctly described by means of the basis set VII, further extension of the basis did not greatly change the results. The values of ΔE^{SCF} such as 0.0000193 and 0.0000096 a.u. obtained in Configuration 2 at 7.5 and 8.0 a.u. in the Basis VIII did not differ too much from the corresponding values

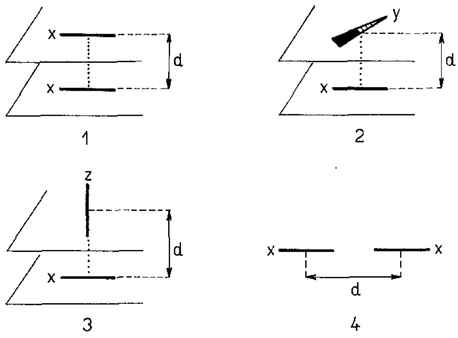

Fig. 1. Geometrical configurations

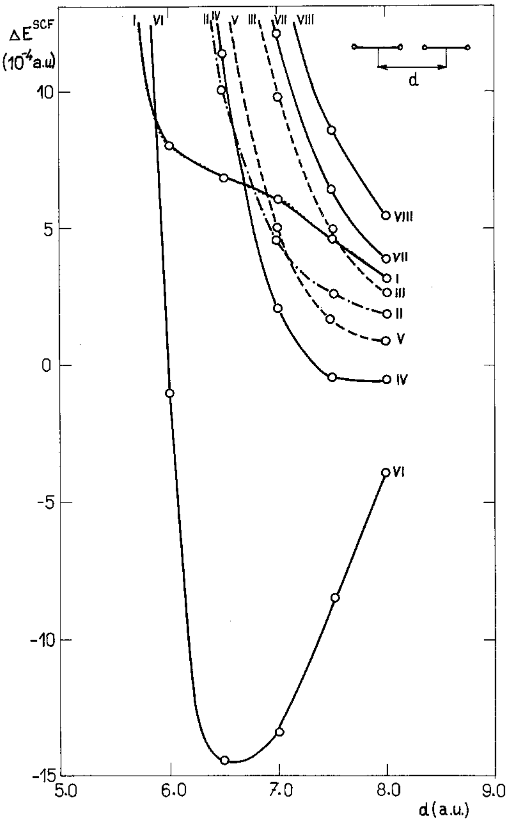

Fig. 2. Curves of the ΔE^{SCF} energy for linear configuration in different bases (see Table 1)

given by the Basis VII. On the other hand, ΔE^{SCF} in Configuration 4 was very sensitive to the basis size. Values of ΔE^{SCF} such as 0.0000855 and 0.0000535 a.u. at 7.5 and 8.0 a.u. in the Basis VIII and 0.0000879 a.u. at 7.5 a.u. in the Basis IX were significantly different from corresponding values given by the Basis VII.

3.2. ΔE^1 Energy

The course of the dependence of the ΔE^1 energy on the distance was again different in various configurations although the differences were lower than in the case of the ΔE^{SCF} values. It was again Configuration 4 that possessed a special position where in Basis I there existed an energy inflex on the ΔE^1 curve. Use of the unscaled [2*s*] basis gave slightly improved results in comparison with corresponding scaled ones. The ΔE^1 energy was sensitive to the extension of *s* set, becoming more repulsive with the increase of the number of those functions. That was in agreement with the Kochanski's [15] conclusion whose values of ΔE^1 (in all bases) were lower than ours, calculated in Bases VII and IX. The ΔE^1 energy was not too sensitive to changes of the exponent of the polarization functions. Remarkable was the difference of that energy in Bases VII and IX (differing only in the number of polarization functions) in the Configuration 4.

3.3. E^2 Energy

Comparing the magnitude of the E^2 energy in different configurations we found this energy to be more attractive in the linear configuration than in the Configuration 3 and distinctly more attractive than in the Configurations 1 and 2. The dependence of the E^2 energy determined in small basis on the distances for different configurations showed an unrealistic course. Particular curves exhibited inflexes or even extremes. The correct course (i.e. monotonic increasing with the decrease of distance) were found in the largest bases only (Fig. 3). With regard to the values of the E^2 energy in different bases we may say that the separation of the ΔE^{SCF} energy makes sense in the largest bases only. The E^2 energy is very sensitive to the magnitude of the polarization function exponent, growing with its decreasing value. This growth was most expressively shown in Configurations 3 and 4 what may be explained by the fact that the distance between atoms of both molecules is the least in these configurations.

3.4. Total Interaction Energy

Kochanski [15] demonstrated that reasonable values of the total interaction energy might be obtained by using the Basis VI. The dispersion energy in that

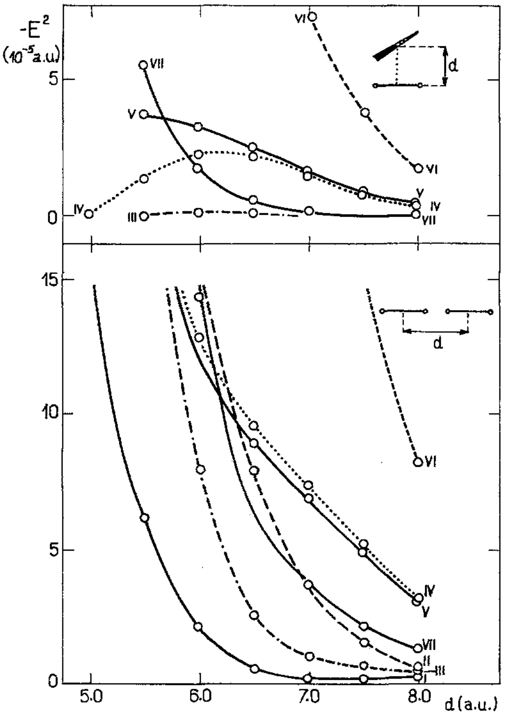

Fig. 3. Curves of the E^2 energy for linear and rectangular configurations in different bases (see Table 1)

study was determined by means of perturbation calculations using the HF wave functions of isolated systems, the ΔE^{SCF} energy being replaced by the ΔE^1 energy. Let us consider in detail whether this presumption is justified. When comparing the values of the ΔE^1 energy given by the Basis VI with the correct values of the ΔE^{SCF} energy (which may be expected in the Bases VII or IX), we note that these values do not differ too much. The values of the ΔE^1 energy are, however, less repulsive. Thus by neglecting the E^2 energy in the Basis VI (likewise in Bases I–V) we obtain the values near to correct ones and, on the contrary, application of the E^2 energy leads to unrealistic overestimation of the interaction. This is due to the fact that the ΔE^1 energy in Basis VI is less repulsive than in the larger bases. Neglect of the always attractive E^2 component thus leads to compensation of errors. Values of the E^2 energy given by Bases VII or IX which may be considered to be close to correct ones are in the region of Van der Waals minimum negligible for the Configuration 2, but not negligible for the Configuration 4. To estimate the total interaction energy, values of the dispersion energy in the Kochanski's $B3$ basis [15] [$2s3p$] may be used. In this basis the dispersion energy in the Configuration 2 at 6.5 and 7.0 a.u. equals to -1.475×10^{-4} and -0.945×10^{-4} a.u., at equal distances in Configuration 4 the dispersion energy equals to -3.270×10^{-4} and -2.015×10^{-4} a.u. If to these values of dispersion energy the relevant values of the ΔE^{SCF} energy determined in the Basis VII are added, for total interaction energy in the Configuration 2 at 6.5 and 7.0 a.u. the values of -0.310×10^{-4} and -0.449×10^{-4} a.u. are obtained. Values of the total interaction energy in the Configuration 2 are much higher than relevant values of the E^2 energy (in the Basis VII). For Configuration 4 when using the ΔE^{SCF} energies determined in the Basis IX in case of the total interaction energy at 6.5 and 7.0 a.u., the values of -0.332×10^{-4} and -0.482×10^{-4} a.u. are obtained. These energies are, however, comparable with E^2 energies given by the Basis IX. When using in the Configuration 4 in the Basis IX the ΔE^1 energy instead of the ΔE^{SCF} one, the total interaction energy even of repulsive character (0.195×10^{-4} a.u. at the distance 6.5 a.u.) was obtained.

4. Conclusion

The results obtained indicate that only large basis sets give a true picture of both the SCF interaction energy and the perturbation dispersion energy. The Bases I–VI may give even an incorrect trend of the SCF interaction energy, mainly owing to an unrealistic E^2 energy. As the interaction energies between larger systems are hardly accessible by making use of larger basis sets, it is in our opinion necessary to look for a way how to arrive at meaningful SCF interaction energies by means of smaller basis sets. Of topical importance seems the basis [$2s\,1p$] recommended by Kochanski [14] as "the smallest basis set that can provide significant results for the HF dispersion contribution". To describe correctly the dispersion energy it is necessary to make use [13–15] of the polarization function exponent 0.2. As we have already demonstrated such polarization functions are not suitable for calculation of the SCF interaction energy. We tried therefore to correct the SCF interaction energy by means of the method suggested by Johansson *et al.* [21], for calculation of the interaction energy between two molecules of H_2O, NH_3, and HF using the minimal basis set. Application of these corrections to interaction of two molecules of hydrogen is to be the subject of a further communication.

References

1. Schaefer III, H. F., McLaughlin, D. R., Harris, F. E., Alder, B. J.: Phys. Rev. Letters **25**, 988 (1970)
2. Bertoncini, P., Wahl, A. C.: Phys. Rev. Letters **25**, 991 (1970)
3. Kutzelnigg, W., Gelus, M.: Chem. Phys. Letters **7**, 296 (1970)
4. Kutzelnigg, W., Staemmler, V., Gelus, M.: Chem. Phys. Letters **13**, 496 (1972)
5. Das, G., Wahl, A. C.: Phys. Rev. A **4**, 825 (1971)
6. Tapia, O., Bessis, G.: Theoret. Chim. Acta (Berl.) **25**, 130 (1972)
7. Bender, C. F., Schaefer III, H. F.: J. Chem. Phys. **57**, 217 (1972)
8. Kutzelnigg, W., Staemmler, V., Hoheisel, C.: Chem. Phys. **1**, 27 (1973)
9. Lischka, H.: Chem. Phys. Letters **20**, 448 (1973)
10. Morokuma, K.: J. Chem. Phys. **55**, 1236 (1971)
11. Dreyfus, M., Pullman, A.: Theoret. Chim. Acta (Berl.) **19**, 20 (1970)
12. Kollman, P. A., Allen, L. C.: Theoret. Chim. Acta (Berl.) **18**, 399 (1970)
13. Kochanski, E.: Chem. Phys. Letters **10**, 543 (1971)
14. Kochanski, E.: Chem. Phys. Letters **15**, 254 (1972)
15. Kochanski, E.: J. Chem. Phys. **58**, 5823 (1973)
16. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)
17. David, D. J.: Theoret. Chim. Acta (Berl.) **19**, 203 (1970)
18. Basch, H., Robin, M. B., Kuebler, N. A.: J. Chem. Phys. **47**, 1201 (1967)
19. Csizmadia, I. G., Kari, R. E., Polanyi, J. C., Roach, A. C., Robb, M. A.: J. Chem. Phys. **52**, 6205 (1970)
20. Bender, C. F., Schaefer, H. F., Kollman, P. A.: Mol. Phys. **24**, 235 (1972)
21. Johansson, A., Kollman, P., Rothenberg, S.: Theoret. Chim. Acta (Berl.) **29**, 167 (1973)

Dr. M. Urban
Department of Physical Chemistry
Komenský University
2 Šmeralova
80100 Bratislava
Czechoslovakia

Dr. P. Hobza
Institute of Hygiene and
Epidemiology
48 Šrobárova
10042 Praha 10
Czechoslovakia