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Counterpoise-corrected potential energy surfaces of simple H-bonded systems

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Abstract. Geometries and stabilization energies of various simple H-bonded complexes (water dimer, hydrogen fluoride dimer, formamide dimer, formic acid dimer) have been determined by a gradient optimization that eliminates the basis set superposition error (BSSE) by the counterpoise (CP) method in each gradient cycle as well as by the standard gradient optimization. Both optimization methods lead to different potential energy surfaces (PES). The difference depends on the theoretical level used and is larger if correlation energy is considered. Intermolecular distances from the CP-corrected PES are consistently longer, and this difference might be significant (~0.1 Å); also angular characteristics determined from both surfaces differ significantly. Different geometries were obtained even when passing to larger basis sets (aug-cc-pVDZ). The standard optimization procedure can result in a completely wrong structure. For example, the "quasi-linear" structure of the $(HF)_2$ (global minimum) does not exist at the standard MP2/6-31G** PES (where only cyclic structure was detected) and is found only at the CP-corrected PES. Stabilization energies obtained from the CP-corrected PES are always larger than these from the standard PES where the BSSE is added only a posteriori for the final optimized structure; both energies converge only when passing to a larger basis set (aug-cc-pVDZ).

Key words Counterpoise-corrected gradient optimization – H-bonded systems

1 Introduction

Molecular clusters can be studied theoretically using variational or perturbation methods. The former method determines the interaction energy as the difference between the energy of a supersystem and the sum of the energies of its subsystems. In the perturbation method the interaction energy is evaluated directly as the sum of various energy contributions (Coulombic, exchange-repulsion, induction, dispersion,...). All these terms have clear physical meaning, and, further, the computation time should be expected to be shorter than for the variational method. In fact, however, the opposite is true. The perturbation method is nowadays used only rarely, and the vast majority of complex calculations are done using the variational (supermolecular) method. This method is straightforward, but the respective interaction energy is affected by a serious obstacle – the fact that different basis sets are used for evaluation of the energies of the supersystem and its subsystems. The supersystem, having a larger basis set than the subsystems, undergoes an artificial stabilization that is commonly referred to as the basis set superposition error (BSSE). In 1970, Boys and Bernardi [1] introduced the function counterpoise (CP) method which eliminates the BSSE completely. The principle of the method is simple: subsystems are not treated in their own basis sets but in the basis sets of the whole complex. Much literature has been devoted to this subject and opinions about the applicability of the CP method have been varied. We believe, however, that convincing arguments collected in Warsaw and Utrecht laboratories [2, 3] give definitive arguments supporting the original procedure of Boys and Bernardi [1].

In the case of single-point calculations the situation is clear and the interaction energy is corrected for the BSSE. The structure of larger clusters cannot, however, be evaluated using a point-by-point method and, instead, gradient optimization is applied. Usually, the complex is optimized using standard supermolecular gradient optimization and only at the very end, a posteriori, the BSSE correction is added. This means that the structure of a complex is optimized on a standard potential energy surface (i.e. without the CP corrections) and not on the CP-corrected potential energy surface

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(PES). There is evidence that the geometry and vibrational frequencies of small complexes determined on these surfaces differ [4–6]. In the following, the expressions "standard PES" and "CP-corrected PES" will be used to mean that, for the first, geometry is optimized with standard (uncorrected) energies, and for the second, it is optimized with CP-corrected energies. The problem of gradient optimization was not solved by introduction of a "chemical Hamiltonian" [7] which eliminates the BSSE from the very beginning, since this method is impractical for beyond-Hartree-Fock gradient optimization. Simon et al. [8] recently offered a straightforward and elegant solution. Their method allows one to evaluate the gradient and the Hessian of a complex at any Hartree-Fock (HF) or correlated level using an arbitrary ab initio code. These authors applied the method to three H-bonded complexes ($HF \cdots HCN$, $HF \cdots H_2O$, $HCCH \cdots H_2O$) and demonstrated that various complex properties obtained from a CP-corrected PES differ from these obtained from a standard surface.

It is known that the BSSE depends also on the structure of a complex – more compact structures have larger BSSE than "loose" ones. The multi-minima PES determined by the standard and CP-corrected optimization can give different results. Relative stabilization energies of various stationary points are, for reactivity purposes, more important than the respective absolute values. Comparison of both kinds of multi-minima surfaces is thus of topical importance.

The aim of the present paper is to compare geometries and interaction energies of simple H-bonded systems evaluated on CP-corrected and standard PES using small and medium basis sets. The way in which the complex geometries are determined by these two approaches differ. In the former case the CP-corrected energy is considered in each gradient optimization cycle while in the latter case the geometry is determined with uncorrected energies. The interaction energies determined from these two approaches also differ because CP corrections are applied in each gradient cycle (CP-corrected PES) or only at the end of optimization (standard PES). The aim of this paper is not to make benchmark calculations but rather to point out differences between standard and CP-corrected PES. It must be kept in mind that only small and medium basis sets are used and will be used in the near future for studies of extended molecular clusters such as, for example DNA base pairs. Benchmark calculations on CP-corrected PES of small H-bonded systems using extended basis sets with consideration of anharmonicity are in progress [9].

2 Computations

Interaction energy was evaluated at HF and second-order Møller-Plesset perturbational level (MP2). All the correlation calculations were performed with frozen-core approximations, i.e. the innermost electrons were not considered. Throughout the study various split-valence basis sets were used: 6-31G, 6-31G*, 6-31G** and 6-311G(2*d,p*). In some cases also a larger aug-cc-pVDZ basis set is used.

The computational method used follows closely the procedure of Simon et al. [8]. Our computation code constructs CP-corrected interaction energies and its derivatives with respect to all internal coordinates by consecutive calls of the Gaussian 94 program for supermolecule and subsystems with and without "ghost" functions (Ref. [8], Eqs. 4 and 5). This information is used for geometry optimization. We used a combined algorithm: steepest descent with linear scaling, if the gradient norm is large, followed by the direct inversion in the iterative subspace (DIIS) method of Pulay [10]. If the criteria of the optimization procedure are properly selected the convergence is relatively rapid. Typically, 10–15 gradient evaluations are needed to reach convergence criteria of 10^{-5} hartree/bohr or hartree/rad for the systems studied. Note that in each gradient cycle five gradients should be evaluated, which makes the total computational time about four times longer than for the case of standard optimization. The present version of the code does not allow us to use dummy atoms or to evaluate hessians and vibrational frequencies.

3 Complexes studied

Water dimer and hydrogen fluoride dimer are among the most frequently studied complexes. Both extensive theoretical and experimental data are available for analysis. Three stationary points exist on the PES of the water dimer (Fig. 1): the "quasi-linear" structure (a) represents the global minimum, while cyclic (b) and bifurcated (c) structures are saddle points. The PES of the hydrogen fluoride dimer (Fig. 2) is simpler and again the "quasi-linear" structure (a) corresponds to the minimum, while the cyclic structure (b) is a saddle point. The PES of the formamide dimer (Fig. 3) is more complex and consists of four stationary points. The cyclic structure of this dimer (a) possesses two H-bonds and has a pattern similar to that found in DNA base

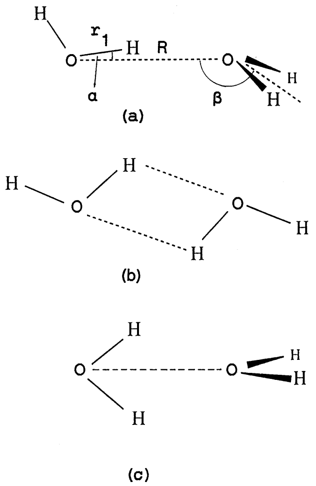

Fig. 1a–c. Structures of the water dimer: **a** quasi-linear; **b** cyclic; **c** bifurcated

pairs, which have been studied in our laboratory [11]. Finally, the PES of the formic acid dimer (Fig. 4) is characterized by two equivalent energy minima (a) separated by the symmetric transition structure (b).

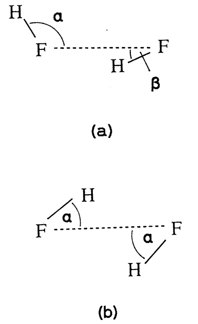

Fig. 2a, b. Structures of the hydrogen fluoride dimer: **a** quasi-linear; **b** cyclic

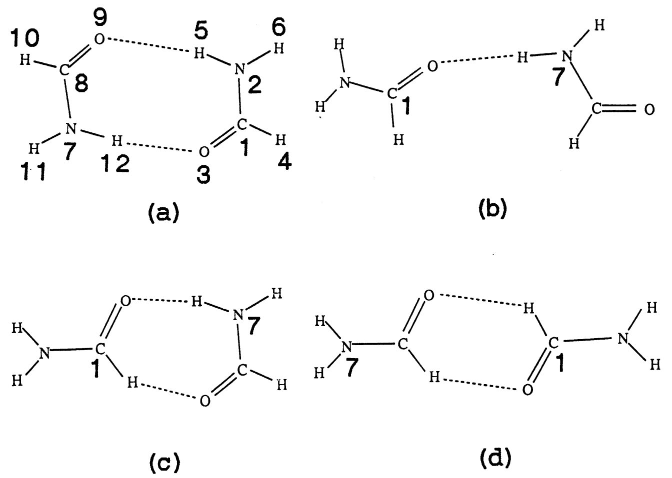

Fig. 3a–d. Structures of the formamide dimer

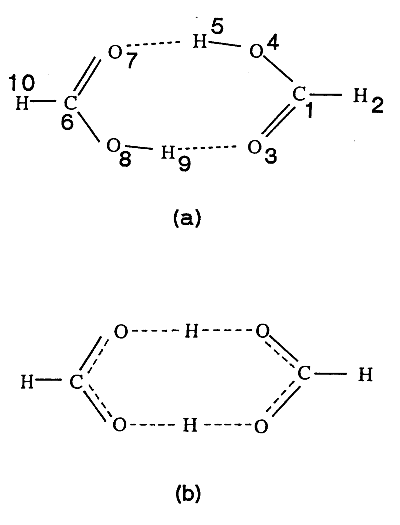

Fig. 4a, b. Structures of the formic acid dimer: **a** cyclic; **b** symmetric transition structure

4 Results and discussion

4.1 $(H_2O)_2$

Geometrical and energetical characteristics of all three stationary points of the water complex obtained from the CP-corrected and standard PES are shown in Table 1; all calculations were performed at the MP2/6-31G** level. Stabilization energies obtained from the CP-corrected PES are consistently larger than these obtained from the standard one; the largest difference was found for the global minimum "quasi-linear" structure. The stability order of various structures on both surfaces is the same, though the relative values of stabilization energy are larger on the CP-corrected PES. The intermolecular oxygen-oxygen distance obtained from the CP-corrected PES is again systematically longer than that from the standard PES. This difference is largest for the bifurcated (0.15 Å) and cyclic (0.1 Å) structures, both being less stable than the quasi-linear one.

The global minimum quasi-linear structure, was additionally studied at various levels of theory and the respective geometrical and energetical characteristics are summarized in Table 2. Stabilization energies obtained from the CP-corrected PES are again systematically larger than those from the standard PES; these differences are significantly larger at the MP2 level. Only for the largest basis set (aug-cc-pVDZ) do both stabilization energies converge. Also the intermolecular oxygen-oxygen distances from the CP-corrected surface are systematically longer than those from the standard PES. This difference is smallest (0.001 Å) for the HF/6-31G level and largest (0.129 Å) for the MP2/6-311G(2*d*,*p*) one. Even in the case of the aug-cc-pVDZ basis set containing diffuse *s*, *p*, and *d* functions this difference is not negligible (0.06 Å). Also the linearity of the H-bond (angle α) is affected by the inclusion of the BSSE; the CP-corrected surface is characterized by a considerably more linear H-bond. Differences in this angle are especially large at the correlated MP2 level when split-valence basis sets are used. The nonplanarity of the proton acceptor molecule (angle β) is even more sensitive to the quality of the PES, and the standard PES typically yields systematically smaller angles β. This difference is again larger for correlated calculations and remains large even at the MP2/aug-cc-pVDZ level.

The experimental intermolecular distance (2.946 Å, [12]) is shorter than our best CP-corrected estimates (MP2/aug-cc-pVDZ). The experimental oxygen-oxygen

Table 1. MP2/6-31G** optimized oxygen-oxygen distance (angstroms) and stabilization energy (kcal/mol) for various structures of the water dimer obtained from the CP-corrected and standard (in parantheses) PES

Dimer characteristics	Structure		
	linear	cyclic	bifurcated
r(O—O)	2.991 (2.913)	2.811 (2.714)	3.077 (2.926)
ΔE	5.07 (4.68)	3.67 (3.62)	3.34 (3.31)

distance is bracketed by MP2/aug-cc-pVDZ values from both surfaces and higher level calculations are required for a quantitative comparison with experiment [9]. From the data presented in the Table 2 it is, however, evident that the standard PES yields shorter intermolecular oxygen-oxygen distances, larger nonlinearity (angle α), and smaller angles that the proton accepting molecule is making with the O···O axis (angle β), than the CP-corrected PES.

Recent theoretical studies on the water dimer [13, 14] estimate the stabilization energy to be around 5.0 kcal/mol and the intermolecular distance around 2.9 Å. Evidently, our best CP-corrected correlated stabilization energies are smaller while the CP-corrected distances are longer by about 0.1 Å.

4.2 $(HF)_2$

Two stationary points are known to exist on the PES of the HF dimer, a quasi-linear and a cyclic one (Fig. 2). The former structure corresponds to the energy minimum while the latter one is a transition structure separating two equivalent minima. For reactivity purposes, the energy difference between these two points reveals important information. As in the case of the previous complex we tried to determine the relative energies of these two structures first at the MP2/6-31G** level (Table 3). To our surprise two different stationary points exist only on the CP-corrected PES, on the standard PES only one stationary point exists that corresponds to the cyclic structure. This means that the optimization on the standard PES yields a structure that is qualitatively wrong. Geometrical characteristics and interaction energies obtained at HF and MP2 levels with various basis sets are summarized in Table 3. All structures obtained at the HF level are consistent with a quasi-linear structure, the linearity (angle β) being consistently smaller on the CP-corrected surface. The same is true for angle α, which is on the CP-corrected PES consistently larger by about 20°. Passing to the correlated levels (standard PES) reduces the differences between the two structures. At the MP2/6-31G** level the quasi-linear structure disappears. Enlarging the basis set leads to a slight improvement, but angle β is still too large and angle α too small. On the other hand, the CP-corrected angular geometrical characteristics obtained at correlated levels agree nicely with experimental values ($R = 2.72 \pm 0.03$ Å, $\alpha = 117 \pm 6°$, $\beta = 10 \pm 6°$ [15]). The intermolecular distance R on the CP-corrected PES is consistently larger than that on the standard surface. While the first value from MP2/6-311G(2*d*,*p*) calculations is larger than the experimental value, the second value is too short. Evidently, as in the previous case, the basis sets used are too small for making any reliable comparison with experiments. Further, in order to find a trend in the calculated results, the basis sets used should be improved systematically. Finally, the proton donor bond length (not shown) is longer on both surfaces than the proton acceptor bond lengths, and the differences at various levels of theory are similar for both surfaces. Stabilization energies obtained from the CP-corrected PES are, as in all previous cases, larger than those from the standard PES. Our best CP-corrected estimate from the MP2/6-311G(2*d*,*p*) calculations (4.4 kcal/mol) agrees well with the experimental value (4.6 ± 0.2 kcal/mol) taken from Ref. [16].

From the recent theoretical literature we will mention only the study by Peterson and Dunning [16] using MP2 and CCSD(T) methods with an extended aug-cc-pVQZ basis set. MP2 and CCSD(T) intermolecular distances R

Table 2. Geometrical (angstroms and degrees) and energetical (kcal/mol) characteristics of the quasi-linear structure of water dimer obtained from the CP-corrected and standard (in parentheses) PES at various levels of theory

	R	r_1	α	β	$-\Delta E$
HF/6-31G[a]	2.844 (2.843)	0.957 (0.957)	0.2 (0.3)	150.1 (142.4)	7.05 (7.05)
HF/6-31G*[a]	3.001 (2.971)	0.952 (0.952)	1.5 (5.2)	121.7 (115.9)	4.78 (4.70)
MP2/6-31G**[a]	2.991 (2.913)	0.967 (0.967)	2.7 (9.7)	129.5 (99.1)	5.07 (4.68)
MP2/6-311G(2d,p)[a]	3.025 (2.896)	0.965 (0.967)	2.0 (9.1)	110.7 (101.6)	4.61 (4.20)
MP2/aug-cc-pVDZ[a,b]	2.978 (2.917)	0.972 (0.973)	5.7 (5.8)	134.6 (122.4)	4.45 (4.43)

[a] Bond lengths and valence angle of the isolated water molecule calculated at sequence of used theoretical levels are: 0.950, 111.6; 0.947, 105.5; 0.992, 103.7; 0.961, 103.4; 0.966, 103.9, respectively.

[b] Ref. [9]

Table 3. Structural (angstroms and degrees) and energetical (kcal/mol) characteristics of the quasi-linear (Fig. 2a) and cyclic (Fig. 2b) structures of the $(HF)_2$ dimer obtained from the CP-corrected and standard PES (in parentheses) at various levels of theory

Level	Quasi-linear				Cyclic		
	R	α	β	ΔE	R	α	ΔE
HF/6-31G	2.740 (2.706)	143.1 (125.1)	3.7 (8.5)	−6.26 (−6.26)	2.704 (2.571)	59.9 (55.9)	−3.86 (−3.56)
HF/6-31G*	2.798 (2.709)	117.7 (96.7)	6.9 (17.0)	−4.54 (−4.27)	2.738 (2.596)	55.3 (51.8)	−3.18 (−2.92)
MP2/6-31G**	2.800 (–)	115.4 (–)	6.5 (–)	−4.72 (–)	2.745 (2.539)	53.3 (48.3)	−3.09 (−2.49)
MP2/6-311G(2*d*,*p*)	2.820 (2.682)	116.3 (91.9)	6.6 (17.5)	−4.40 (−3.97)	2.741 (2.599)	52.9 (49.3)	−3.04 (−2.78)

[a] No quasi-linear structure obtained for the standard PES of the quasi-linear structure

were found to be 2.737 and 2.732 Å, respectively. After correcting for the BSSE, slightly larger values resulted: 2.753 and 2.745 Å, respectively. Because the BSSE corrections to the geometry were estimated by the point-by-point one-dimensional approach their values should be considered to be estimates. Corrected and standard (in parentheses) stabilization energies obtained at MP2 and CCSD(T) levels [16] amount to 4.63 (4.38) and 4.72 (4.48) kcal/mol, respectively. Evidently, our best stabilization energy obtained from the CP-corrected PES is close to both stabilization energies mentioned, while our CP-corrected intermolecular distance is longer.

At the highest theoretical level (MP2/6-311G(2*d*,*p*)) the energy difference between quasi-linear and cyclic structures is 1.36 kcal/mol (CP-corrected PES). Working at the same theoretical level but with the standard PES this energy difference becomes smaller (1.19 kcal/mol).

4.3 Formamide dimer

Four different structures localized on the PES [17] are shown in Fig. 3. These structures were studied at the HF/6-31G* level and their geometrical and energetical characteristics are summarized in Table 4. The stability order of the various structures is retained for both surfaces; structure (a) is by far the most stable one. If, however, the relative energies are considered we find some differences. First, the local minimum (c) is located 3.2 kcal/mol above the global minimum on the standard PES. This value increases to 4.4 kcal/mol for the CP-corrected PES; using larger basis sets and including the correlation energy increases this difference further. The most stable structure (a) was studied at three different levels and the results are given in Table 5. As with previous complexes, stabilization energies from the CP-corrected PES are systematically larger than those from the standard PES. Also, intermolecular distances are systematically longer for the former surface. The largest difference in stabilization energy and intermolecular distance was found at the MP2/6-31G** level.

Table 4. HF/6-31G* optimized C1-N7 distance (angstrom) and stabilization energy (kcal/mol) for various structures of the formamide dimer (Fig. 3a–d) obtained from the CP-corrected and standard (in parentheses) PES

	Structure			
	Fig. 3a	Fig. 3b	Fig. 3c	Fig. 3d
r(C1-N7)	3.774 (3.740)	4.209 (4.101)	3.551 (3.521)	4.892 (4.845)
ΔE	11.14 (11.10)	5.68 (5.63)	7.49 (7.46)	3.79 (3.76)

4.4 Formic acid dimer

The cyclic structure of this dimer (Fig. 4a) with two C═O···H─O H-bonds is very stable. By simultaneous transfer of two protons it passes through a transition structure (Fig. 4b) to the other energy minimum. The transition structure is characterized by the symmetrical distribution of both hydrogens between the respective oxygens. We tried to optimize both stationary points on the CP-corrected surface but we failed for the transition structure. The algorithm requires one to assign all the atoms to the first or second subsystem. During the subsequent optimization both protons migrate from the starting symmetrical position to the nonsymmetrical position characteristic for the energy minimum. Thus, this computational procedure does not allow us to investigate transition structures in which some atoms are symmetrically shared by both subsystems.

Geometrical and energetical characteristics of the energy minimum (Fig. 4a) are summarized in Table 6; here we used only HF/6-31G** and MP2/6-31G** levels. From these values it is clear that also in this case intermolecular distances from the CP-corrected PES are systematically longer than those from the standard PES. The respective difference is larger (~0.08 Å) at the correlated level. Elongation of the O─H bond upon formation of the H-bond is shorter at both levels for the CP-corrected surface, the difference being larger at the correlated level. This conclusion might be of importance since the elongation of the X─H bond upon formation of the X─H···Y H-bond is proportional to the observable red shift of the X─H stretching frequency.

Table 5. Geometrical (angstroms and degrees) and energetical (kcal/mol) characteristics of the cyclic structure of the formamide dimer (Fig. 3a) obtained from the CP-corrected and standard (in parentheses) PES at various levels of theory

Level	R_{29}	r_{25}	r_{89}	α_{259}	α_{125}	ΔE
HF/6-31G	2.931 (2.911)	1.005 (1.007)	1.233 (1.234)	167.4 (168.0)	120.1 (120.2)	−14.03 (−14.01)
HF/6-31G*	3.016 (2.995)	1.005 (1.005)	1.204 (1.205)	170.5 (171.5)	125.4 (125.6)	−11.14 (−11.10)
MP2/6-31G**	2.972 (2.906)	1.018 (1.021)	1.235 (1.238)	173.6 (175.0)	120.3 (120.6)	−12.37 (−12.14)

Table 6. Geometrical (angstrom and degree) and energetical (kcal/mol) characteristics of the cyclic structure of the formic acid dimer (Fig. 4) obtained from the CP-corrected and standard (in parentheses) PES at various levels of theory

Level	R_{16}	r_{45}	α_{145}	ΔE
HF/-31G**	3.933 (3.900)	0.961 (0.963)	111.0 (111.3)	−13.05 (−13.02)
MP2/6-31G**	3.915 (3.833)	0.989 (0.995)	108.8 (109.5)	−13.21 (−12.92)

5 Conclusions

1. CP-corrected and standard PES of simple H-bonded complexes differ. The differences depend on the level of theory and the basis set used and they are larger at the correlated level. Intermolecular distances determined from the CP-corrected PES are systematically longer than those from a standard PES; the difference might be large (~0.1 Å). Also the intermolecular angles found from these surfaces differ considerably. Different geometrical characteristics remained even if larger basis sets were used. The stabilization energies determined from the CP-corrected PES are always larger than stabilization energies from the standard PES which are corrected for the BSSE only a posteriori.

2. The stability order of various isomers of a molecular complex determined for both surfaces is mostly similar but the relative energies are generally different.

3. Optimization on the standard PES using medium basis sets sometimes leads to a completely wrong geometric structure, while optimization on a CP-corrected PES yields the correct structure. This conclusion is a warning, and is clear evidence of the necessity to use only the CP-corrected gradient optimization.

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References

1. Boys SF, Bernardi F (1970) Mol Phys 19: 553
2. Chalasinski G, Szczesniak MM (1994) Chem Rev 94: 1873
3. van Duijneveldt FB, van Duijneveldt-van de Rijdt JGCM, van Lenthe JH (1994) Chem Rev 94: 1873
4. Bouteiller Y, Behrouz H (1992) J Phys Chem 96: 6033
5. Leclercq JM, Allavena M, Bouteiller Y (1983) J Chem Phys 78: 4606
6. Scheiner S (1997) Hydrogen bonding. A theoretical perspective. Oxford University Press, New York
7. Halasz G, Vibok A, Valiron P, Mayer I (1996) J Phys Chem 100: 6332
8. Simon S, Duran M, Dannenberg JJ (1996) J Chem Phys 105: 11024
9. Hobza P, Paizs B, Bludský O, Duran M, Suhai S (in preparation)
10. Pulay P (1982) J Comp Chem 3: 556
11. Šponer J, Leszczynski J, Hobza P (1996) J Biomol Struct Dyn 14: 117
12. Odutola JA, Dyke TR (1980) J Chem Phys 72: 5062
13. Feyereisen MW, Feller D, Dixon DA (1996) J Phys Chem 100: 2993
14. Halkier A, Koch H, Jørgensen P, Christiansen O, Nielsen IMB, Helgaker T (1997) Theor Chem Acc 97: 150
15. Howard BJ, Dyke TR, Klemperer W (1984) J Chem Phys 81: 5417
16. Peterson KA, Dunning TH Jr (1965) J Chem Phys 102: 2032
17. Neuheuser T, Hess BA, Reutel C, Weber E (1994) J Phys Chem 98: 6459