

Ab initio STUDY OF THE (BH)₂ DIMERMiroslav URBAN^a, Soňa HRIVNÁKOVÁ^a and Pavel HOBZA^b^a Department of Physical Chemistry, Comenius University, 816 31 Bratislava and^b Institute of Hygiene and Epidemiology,

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The total interaction energy between two BH molecules was calculated as a sum of the SCF and correlation interaction energies. The latter was obtained either semiempirically or by the 2nd and 3rd order perturbation theory. It appeared to be the main contribution to the total interaction energy with some geometries. Important differences in the SCF interaction energy of different geometrical configurations of the dimer were explained by the utilization of higher terms of the Coulomb energy multipole expansion. Unexpectedly the geometry of highest stability does not correspond to the linear arrangement of the dimer but rather to the T-shaped structure.

Ab initio calculations of interaction energies among atoms or molecules can give at least in principle results on two levels of sophistication. Ideally, we can obtain reliable quantitative information about the total interaction energy as well as about its physically interpretable components. However, this can be achieved only by the choice of an extended basis set and an adequate method of calculation. If one considers methods of the supermolecule type¹ in which the interaction energy between A and B systems is the difference between a total energy of the supersystem E_{AB} and those of subsystems $E_A + E_B$ it is necessary to know also an interaction correlation energy ΔE_{COR} in addition to the commonly used SCF interaction energy ΔE_{SCF} . Particularly, the exact calculation of ΔE_{COR} using a large basis set can be realized only in a limited number of cases covering interactions of light atoms and small molecules. Hence we are forced to perform calculations in most cases at lower levels. The SCF interaction energy is then calculated using a smaller basis set and the correlation energy is calculated either by less exact methods or even by a semiempirical way. Often it is neglected when dealing with polar systems or ions. Although the interaction energy obtained is only semiquantitative the results do not lose their interpretational significance.

The significance mentioned follows from the possibility of a comparison of the interaction energy obtained by the quantum chemical calculation from the wave functions of the supersystem AB and the parent subsystems A and B in the chosen basis set with the classical evaluation of interaction energy components, namely Coulomb, polarization, and dispersion ones which are eventually completed with the

semiempirical estimation of an exchange repulsion energy. The classical interaction energy components can be obtained using the multipole expansion of the interaction potential in reciprocal powers of the distance between interacting particles. In individual terms of the multipole expansion of the interaction energy observables of interacting molecules can be found: their multipole moments, polarizabilities, *etc.* Such an expansion can be utilized *e.g.*, in crystal theories as well as in theories of liquids and in those playing part in chemical reactivity and molecular biology.

It seems to be attractive to obtain information about intermolecular interaction energies knowing only properties of individual molecules. For a sake of a simplicity some terms of the interaction energy are often neglected and from those under consideration only the first term of the multipole expansion is often evaluated. This cannot be justified without a careful analysis². It is also necessary to pay great attention to the convergence of the multipole expansion^{3,4}. The fact cannot be ignored that this approximation is good only with large distances of subsystems. With distances which correspond to the supersystem minimal energy or shorter as well as in the cases where the charge penetration of both subsystems plays an important role the classical interaction energies can greatly differ from those calculated by the supermolecule method as has been demonstrated in several cases⁵⁻¹⁶ by direct calculations. One aim of this paper is to analyse such a difference in the Coulomb interaction energy in the BH...BH system. This system seems to be attractive as the BH molecule has not only a relatively large dipole moment but also unusually large quadrupole and octupole moments. We shall see later that these circumstances lead in the BH...BH system to a mutual compensation of individual positive and negative contributions to the multipole expansion of the Coulomb energy with some geometrical configurations. It leads also *a)* to the unusual order of stabilities of various geometrical structures and *b)* to the important role of ΔE_{COR} for some arrangements which is not common in interactions of polar systems. According to *b)* the correlation energy can no longer be neglected and a proper method should be chosen for its evaluation. The comparison of the effectiveness of the semiempirical Sinanoğlu-Pamuk method^{17,18} with the 2nd and 3rd order perturbation method^{19,20} for the calculation of a correlation energy is considered to be the other aim of this paper.

METHOD

SCF calculations were performed by the modified POLYATOM/2 program²¹ using the contracted Gaussian DZ basis set^{22,23}. The interaction energy ΔE_{SCF} for the BH...BH system was evaluated as the difference of (BH)₂ energy in the nuclear configuration chosen and the sum of energies of both subsystems BH. Five different geometries were assumed (Fig. 1) at several distances between the monomers. In all cases, the fixed distance $R(\text{B}-\text{H}) = 1.2362 \times 10^{-10}$ m was considered which is the experimental value for the BH molecule. Our choice of configurations I-V was not motivated by finding the absolute minimum on the dimer potential hypersurface but they are rather understood as typical model configurations which are suitable for an analysis of individual contributions to the interaction energy.

Components of the Interaction Energy

The Coulomb interaction energy E_C was calculated from a wave function $\psi_{AB}^0 = \psi_A^0 \psi_B^0$ which is assumed as a simple product of wave functions of the subsystems A and B. The following relationship⁶ holds for it using the nonexpanded interaction hamiltonian

$$E_C = -2 \sum_{a \in A} \sum_{b \in B} \left(\varphi_a(1) \frac{Z_b}{r_{1b}} \varphi_a(1) \right) - 2 \sum_{a \in A} \sum_{b \in B} \left(\varphi_b(1) \frac{Z_a}{r_{1a}} \varphi_b(1) \right) + 4 \sum_{a \in A} \sum_{b \in B} \left(\varphi_a(1) \varphi_a(1) \frac{1}{r_{12}} \varphi_b(2) \varphi_b(2) \right) + \sum_{a \in A} \sum_{b \in B} \frac{Z_a Z_b}{r_{ab}} \quad (1)$$

In Eq. (1) φ_a , φ_b stand for molecular orbitals of subsystems A and B, Z_a and Z_b are nuclear charges, r_{1a} , r_{12} , and r_{ab} stand for distances electron-nucleus, electron-electron, and nucleus-nucleus, respectively. In the Eq. (1) the charge distribution penetration is accounted for which comes from subsystems A and B and the energy E_C includes the multipole expansion of the Coulomb energy to all powers. We denote it as a nonexpanded Coulomb energy. It can be compared for various BH...BH configurations with the first several terms of the multipole expansion of the Coulomb energy, E_{MULT} , *i.e.* with the expanded Coulomb energy.

$$E_{MULT} = E(3) + E(4) + E(5) \quad (2)$$

Individual terms in Eq. (2) are proportional to R^{-3} , R^{-4} , and R^{-5} , where R is the intersystem distance defined in Fig. 1. $E(3)$ represents a dipole-dipole interaction E_{dd} , $E(4)$ does a dipole-quadrupole one E_{dQ} , $E(5)$ term includes quadrupole-quadrupole E_{QQ} and dipole-octupole E_{dO} interactions. Explicit formulas for individual structures I-V are as follows^{1,2}:

$$E_{MULT}^I = -\frac{2d^2}{R^3} + \frac{6Q^2}{R^5} - \frac{8dO}{R^5} \quad (3)$$

$$E_{MULT}^{II} = -\frac{d^2}{R^3} + \frac{9Q^2}{4R^5} + \frac{3dO}{R^5} \quad (4)$$

$$E_{MULT}^{III} = -\frac{3dQ}{2R^4} - \frac{3Q^2}{R^5} \quad (5)$$

$$E_{MULT}^{IV} = \frac{3dQ}{2R^4} - \frac{3Q^2}{R^5} \quad (6)$$

$$E_{MULT}^V = \frac{3Q^2}{4R^5} \quad (7)$$

The exchange repulsion energy E_{EX} can be calculated by the formula⁶

$$E_{EX} = \Delta E^{(1)} - E_C \quad (8)$$

where $\Delta E^{(1)}$ (first order interaction energy) is the difference between the energy of the first SCF

iteration of dimer and the sum of monomer SCF energies, the former being evaluated using the orthogonalized eigenvectors of separated systems as starting ones. The difference $\Delta E_{\text{SCF}} - \Delta E^{(1)}$ represents the delocalization interaction energy E_{DEL} . Its components can be further analysed²⁴ but it is not necessary for our aims.

The interaction correlation energy ΔE_{COR} was calculated by two different methods as a difference between (BH)₂ and 2 BH energies similarly as with the evaluation of ΔE_{SCF} . With all dimer configurations the EPCE-F2 σ method by Sinanoğlu-Pamuk^{17,18} was used. This is a simple semiempirical method which is able, however, to give qualitatively correct interaction energies^{25,26} and which is applicable also for extended systems. For configuration III, results obtained by the EPCE-F2 σ method were compared with theoretically more substantiated but much more expensive ones in which the correlation energies of BH and (BH)₂ were calculated by the 2nd and 3rd order perturbation theory in^{19,20}. Roughly speaking such a correlation energy is comparable in many cases^{20,27,28} with that obtained by the configuration interaction method in which all configurations which are doubly excited with regard to the ground state SCF wave functions are considered. The program POLYCOR developed in our Laboratory²⁹ and compatible with the POLYATOM program was used for these calculations.

RESULTS AND DISCUSSION

The SCF energy and multipole moments of the BH molecule are presented in Table I. Calculated interaction energies ΔE_{SCF} and their components together with ΔE_{COR} are summarized in Table II for configurations I–V.

Before a deeper analysis is made of the results obtained, the reliability of the used DZ basis set should be estimated for the interaction energy calculations. First,

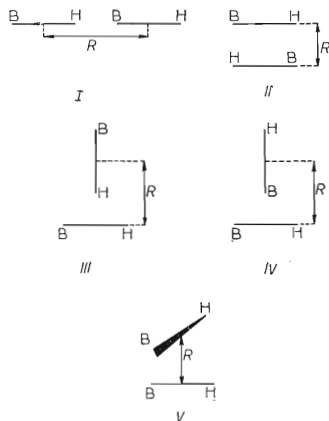


FIG. 1
Assumed Configurations of the (BH)₂ Dimer

it is important for the correct estimation of long range contributions to reproduce multipole moments which should be in the reasonable accord with the experimental values and eventually with those obtained by means of a more extended basis set. The dipole moment calculated by us (Table I) is somewhat larger than the value $5.78 \cdot 10^{-30}$ Cm computed with a very extensive basis set³⁰. Such a dipole moment overestimation is a typical feature of the DZ basis set. Our dipole moment is also substantially higher than both the value $4.44 \cdot 10^{-30}$ Cm obtained by the CEPA method with the very extensive basis set³¹ and the experimental value³¹ $4.24 \cdot 10^{-30}$ Cm. Correlation effects reduce strongly the BH dipole moment³¹. Authors of papers^{30,31} did not publish the moments of higher orders. The quadrupole moment can be found *e.g.*, in a paper by Blint and Goddard³² using the extended DZ basis set with polarization functions but it is calculated with an origin centered on the B atom. Using the SCF wave function it amounted³² to $-11.96 \cdot 10^{-40}$ Cm² and this value was reduced to $-9.76 \cdot 10^{-40}$ Cm² using the multiconfiguration wave function. We have calculated $Q = -12.15 \cdot 10^{-40}$ Cm² using the DZ basis set with the origin on the B atom. It seems to be reasonable that also the value calculated with the origin in the center of mass should be in accord with calculations using a larger basis set.

The second step needed for a proper estimation of the reliability of a chosen basis set is an estimation of so called counterpoise correction or superposition error^{1,33-35}. For this purpose, energies of both subsystems in the supersystem basis set are to be calculated for a given supersystem geometry. The corrected interaction energy can be obtained subtracting the sum of so obtained subsystem energies from the supersystem energy. The configurations *I* and *IV* with the intersystem separation corresponding to optimal ΔE_{SCF} values (Table II) were used as testing example at the SCF level. Noncorrected and corrected values -1.530 and -1.351 for the configuration *I* as well as values -76.66 and -67.44 for the configuration *IV* (all values in kJ/mol) differ relatively little, therefore the standard noncorrected interaction energies will be considered throughout this paper.

TABLE I

SCF Energy and Multipole Moments of the BH Molecule Using the DZ Basis Set

SCF energy, kJ mol ⁻¹	-65 937.287
Dipole moment, 10 ⁻³⁰ Cm	6.266
Quadrupole moment, 10 ⁻⁴⁰ Cm ²	-13.467 ^a , -19.891 ^b
Octupole moment, 10 ⁻⁵⁰ Cm ³	- 0.439 ^a , -48.255 ^b

^a Origin in the center of mass; ^b Origin in the geometrical center.

TABLE II
The Total Interaction Energy ΔE and Its Components ΔE_{SCF} , ΔE_{COR} , E_C , E_{EX} , E_{DEL} for Various Configurations of the (BH)₂ Dimer
Energies in kJ mol⁻¹, distances R in 10⁻¹⁰ m.

Structure ^a	R^a	ΔE	ΔE_{SCF}	ΔE_{COR}^b	E_C	E_{EX}	E_{DEL}
I	3.70	—	21.46	—	-17.54	48.48	— 9.480
	3.97	1.495	9.716	-8.221	-8.711	23.26	— 4.833
	4.76	-1.824	-0.878	-0.946	-2.081	2.358	— 1.152
	5.56	-1.675	-1.530	-0.145	-1.364	0.219	— 0.386
	6.35	-1.225	-1.167	-0.058	-1.071	0.018	— 0.117
	7.41	—	-0.802	—	-0.773	0.0	— 0.030
II	3.17	—	7.706	—	4.188	5.017	— 1.499
	4.23	—	0.683	—	0.935	0.137	— 0.389
	4.76	-0.010	0.077	-0.087	0.278	0.021	— 0.222
	5.29	-0.174	-0.145	-0.029	-0.031	0.0	— 0.114
	6.35	-0.270	-0.251	-0.019	-0.222	0.0	— 0.029
	7.94	-0.232	-0.222	-0.010	-0.215	0.0	— 0.007
III	2.65	-7.010	10.75	-17.76	-15.78	43.78	— 17.25
	2.91	-5.169	4.128	-9.387	-7.497	19.77	— 8.055
	3.17	-3.371	1.367	-4.738	-3.411	8.738	— 3.960
	3.44	-2.033	0.273	-1.434	-2.306	3.794	— 2.087
	3.70	-1.137	-0.056	-1.081	-0.499	1.622	— 1.179
	3.97	-0.587	-0.095	-0.492	-0.068	0.685	— 0.712
	4.23	-0.261	-0.039	-0.222	0.118	0.286	— 0.443
	7.94	—	0.095	—	0.095	0.0	— 0.0
	—	—	—	—	—	—	—
IV	1.85	—	72.75	—	-997.1	2 589.0	-1 519.0
	2.12	-89.10	-68.52	-20.57	-674.4	1 460.0	— 854.1
	2.22	-96.46	-76.66	-19.81	-560.4	1 148.0	— 664.3
	2.38	-86.91	-69.43	-17.47	-415.8	792.3	— 445.9
	3.17	—	-26.59	—	-79.34	104.7	— 51.95
	4.76	—	-6.711	—	-5.913	1.079	— 1.877
V	3.17	—	1.439	—	2.342	3.261	— 4.164
	4.23	0.289	0.386	-0.097	0.961	0.092	— 0.667
	5.29	0.193	0.203	-0.010	0.347	0.0	— 0.144
	6.35	0.116	0.116	0.0	0.144	0.0	— 0.028

^a For a definition see Fig. 1; ^b The EPCE—F2 σ correlation energy.

It is clear that quantitatively correct interaction energies cannot be obtained using a DZ basis set. Nevertheless, we can assume that our basis set gives us qualitatively correct information about relative values of the interaction energies and their components for individual dimer configurations.

SCF Interaction Energies and the Multipole Expansion

Let us now turn our attention to the Table II. Comparing values of ΔE_{SCF} for various $(\text{BH})_2$ structures we can see that SCF interaction energies in minima on potential curves are similar for structures *I*, *II*, and *III* and they differ considerably from that of the structure *IV*. ΔE_{SCF} of the structure *V* is repulsive at all intersystem distances. The particular behaviour of the structure *IV* also follows from the inspection of the SCF interaction energy E_c components. It is seen that the large stabilization energy is characteristic for this structure, in addition to the E_{DEL} energy, the latter stabilizing all structures considered. Considering the first nonzero term of the multipole expansion, (which is the dipole-dipole interaction proportional to R^{-3}), we should expect the largest Coulomb stabilization with structure *I* rather than *IV* in which the dipole-dipole interaction vanishes. The next step in the interaction energy analysis is to look at higher terms in the multipole expansion (compare Eqs (2)–(7)). Results are presented in Table III for structure *I* and in Table IV for structures *II*–*V*. With all structures the contributions of Q and O were calculated using a geometrical center of BH molecules as the origin and the center of mass was used additionally with structure *I*. In the following discussion only configurations *I* and *IV*

TABLE III

The Coulomb Interaction Energy Multipole Expansion and Its Components for the Configuration *I* of the $(\text{BH})_2$ Dimer

Energy in kJ mol^{-1} , distance R in 10^{-10} m.

R^a	E_{dd}	E_{QQ}^b	E_{QQ}^c	E_{dO}^b	E_{dO}^c	E_{MULT}^b	E_{MULT}^c
3.70	−8.362	18.423	8.445	18.772	0.171	28.833	0.254
3.97	−6.798	13.048	5.981	13.295	0.121	19.545	−0.697
4.76	−3.934	5.244	2.404	5.343	0.049	6.652	−1.482
5.56	−2.478	2.426	1.112	2.472	0.022	2.421	−1.343
6.35	−1.660	1.244	0.570	1.268	0.012	0.852	−1.078
7.41	−1.045	0.576	0.264	0.587	0.005	0.117	−0.776
10.6	−0.359	0.097	0.044	0.099	0.001	−0.163	−0.313

^a For a definition see Fig. 1; ^b Origin in the geometrical center; ^c Origin in the center of mass.

TABLE IV

The Coulomb Interaction Energy Multipole Expansion and Its Components for Configurations II—V of the (BH)₂ DimerEnergies in kJ mol⁻¹, distances *R* in 10⁻¹⁰ m.

Configura- tion ^a	<i>R</i> ^a	<i>E</i> _{dd}	<i>E</i> _{dQ}	<i>E</i> _{QQ}	<i>E</i> _{dO}	<i>E</i> _{MULT}
II	3·17	-6·639	—	14·932	-15·215	— 6·922
	4·23	-2·801	—	3·543	— 3·611	— 2·868
	4·76	-1·967	—	1·966	— 2·004	— 2·004
	5·29	-1·434	—	1·161	— 1·183	— 1·456
	6·35	-0·830	—	0·467	— 0·475	— 0·839
	7·94	-0·425	—	0·153	— 0·156	— 0·428
	10·6	-0·179	—	0·036	— 0·037	— 0·180
III	2·65	—	20·646	— 49·541	—	— 28·895
	2·91	—	14·102	— 30·761	—	— 16·659
	3·17	—	9·957	— 19·909	—	— 9·953
	3·44	—	7·229	— 13·343	—	— 6·114
	3·70	—	5·374	— 9·211	—	— 3·837
	3·97	—	4·078	— 6·524	—	— 2·446
	4·23	—	3·150	— 4·725	—	— 1·574
	7·94	—	0·255	— 0·204	—	— 0·051
	10·6	—	0·081	— 0·048	—	— 0·032
IV	1·85	—	-85·990	-294·76	—	-380·75
	2·12	—	-50·406	-151·19	—	-201·59
	2·22	—	-41·469	-118·46	—	-159·93
	2·38	—	-31·468	-83·898	—	-115·37
	3·17	—	-9·957	-19·909	—	-29·866
	4·76	—	-1·967	-2·622	—	-4·589
	7·94	—	-0·255	-0·204	—	-0·459
	10·6	—	-0·081	-0·048	—	-0·129
V	3·17	—	—	4·977	—	4·977
	4·23	—	—	1·181	—	1·181
	5·29	—	—	0·387	—	0·387
	6·35	—	—	0·156	—	0·156
	7·94	—	—	0·051	—	0·051
	10·6	—	—	0·012	—	0·012

^a For definition see Fig. 1; distances are calculated towards the geometrical center of molecules.

will be analysed but the remaining three structures can be treated in a similar way using data in Tables I, II, and IV.

If we take the higher multipole moments contributions of structures *I* and *IV* into a consideration we can easily see that they influence considerably the relative stability of both configurations. *E.g.*, considering the structure *IV* at $R = 2.22 \cdot 10^{-10}$ m (the optimal distance on the SCF level) the contribution $E(5)$ is roughly three times larger than the $E(4)$ one and $E(5)$ is about two times as large as $E(3)$ with structure *I* at $R = 5.56 \cdot 10^{-10}$ m. Accounting the large quadrupole moment of the BH molecule (for sake of comparison let us mention that the HF molecule¹² has a dipole moment of $6.89 \cdot 10^{-30}$ Cm and a quadrupole one of $7.29 \cdot 10^{-40}$ Cm² towards the center of mass) the order of the relative stability is influenced by the fact that the quadrupole–quadrupole contribution proportional to R^{-5} bears a negative sign in the structure *IV*, *i.e.* it contributes to the system stabilization but the opposite is true with structure *I*. The latter contribution compensates the attractive dipole–dipole interaction in the linear dimer but it raises the stabilization given by the dipole–quadrupole interaction with configuration *IV* this being here the first term of the multipole expansion. Moreover, the term proportional to R^{-5} is also positive with configuration *I*. It takes its origin from the dipole–octupole interaction and as seen from Tables I and III it depends strongly on the choice of the coordinate system for the calculation of the octupole moment. If we place the coordinate origin at the geometrical center of a BH molecule this contribution destroys the convergency of the multipole expansion for all intersystem distances with the exception of the largest one. The placement of the origin at the center of mass improves the convergence considerably which is in accord with calculations on other systems (compare *e.g.*, the more detailed analysis by Lischka¹² or by Amos and Crispin³⁶). This naturally holds even for other configurations considered in which unfortunately SCF calculations were performed with the origin of coordinates at the geometrical centers of molecules. These were done before we intended to calculate the multipole expansion contributions. In no case are any qualitative conclusions influenced, namely, that with the exception of large distances the higher term contributions of the multipole expansion are comparable with the first term or they are even larger and they cannot be excluded from consideration. It should be noted that the necessity of higher term inclusion is well known with nonpolar molecules^{14–16,36} but it is rather exceptional with the interaction of two such polar molecules as BH systems.

To analyze the multipole expansion it is necessary to comment on the difference between E_{MULT} and the Coulomb energy E_C . This can be evaluated for all configurations by comparing the corresponding columns in Tables II, III, and IV. The data of the configuration *I* will be preferentially used in the discussion as calculations with the origin of the coordinate system lying in the center of mass are available. The pictorial representation, Fig. 2, is very instructive as it shows that E_{MULT} approaches E_C asymptotically only at large distances. With distances up to about

$3.7 \cdot 10^{-10}$ m the energies differ even in sign. The difference is remarkable also at distances where $|E(3)| < |E(5)|$ holds as the first two terms indicate multipole expansion convergence. This difference can be attributed to the influence of the

TABLE V

The Total Interaction Energy ΔE , SCF Interaction Energy ΔE_{SCF} and the Interaction Correlation Energy Contributions Taken from the Perturbation Treatment to the 2nd Order, (ΔE_{COR}^2), and up to the Third One, ($\Delta E_{\text{COR}}^{(2)+(3)}$) for the Configuration III of the (BH)₂ Dimer
Energies in kJ mol^{-1} , distances R in 10^{-10} m.

R^a	ΔE	ΔE_{SCF}	$\Delta E_{\text{COR}}^{(2)}$	$\Delta E_{\text{COR}}^{(2)+(3)}$
2.65	0.762	10.75	-9.076	-9.989
2.91	-2.473	4.218	-5.924	-6.691
3.17	-3.251	1.367	-3.993	-4.618
3.44	-2.989	0.273	-2.765	-3.262
3.70	-2.385	-0.056	-1.943	-2.329

^a For a definition see Fig. 1.

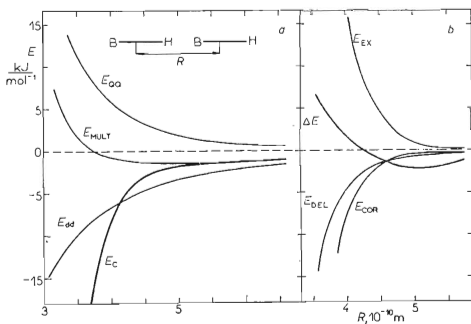


FIG. 2

A Comparison of Interaction Energy Contributions in the Linear Configuration of the (BH)₂ System

a Coulomb energy E_C and multipole expansions terms calculated toward the center of mass.
b Total interaction energy and its components.

charge density penetration of both subsystems^{5-7,15}, which plays a role in a decision about multipole expansion truncation. It should be noted that the multipole expansion convergence can be improved by procedures which utilize the molecular charge density separation in small volumes of space and the treatment of such interactions as a sum of pairing interactions between such local charges^{36,37}.

The above mentioned comments on the comparison of E_C and E_{MULT} show that the multipole expansion is intrinsically incapable to give quantitative information about the Coulomb interaction energy for medium (*i.e.* in the region of ΔE energy minima) or smaller distances. However, its role in the interpretation of interaction energies should not be underestimated.

The total interaction energy as a sum of all contributions namely E_C from Fig. 2a and E_{EX} , E_{DEL} , and E_{COR} from Fig. 2b is grafically depicted for the structure *I* by the solid line in Fig. 2b. This figure manifests relative values of all interaction energy components as a function of the intersystem separation. The total energy minimum can be found only at larger distance which is not typical of polar molecule interactions. This also corresponds to the extremely low SCF interaction energy which resembles values which are common with Van der Walls interaction but exceptional with those of polar systems. With the exception of the configuration *IV* this holds also for all other structures mentioned. It seems also unevitable to study interaction contributions in more detail.

Interaction Correlation Energy

Correlation contributions to the BH...BH interaction energy obtained by the EPCE-F2 σ method are presented in the 5th column of Table II. Their values are comparable with ΔE_{SCF} for the configurations *I* and *III*. At a BH...BH distance $4.76 \cdot 10^{-10}$ m, which corresponds to the ΔE energy minimum the contribution of ΔE_{COR} amounts to more than 50% of the total bonding energy with configuration *I*. With configuration *IV* ΔE_{COR} contributes to the dimer stabilization considerably less than do E_C and E_{DEL} together but because of a rather positive value of the exchange repulsion energy it amounts to not less than 20% of the total bonding energy. The correlation contributions of structures *II* and *V* are considerably less important than those of the SCF interaction energy. With configuration *V* correlation energy does not compensate for repulsion energy contributions, particularly those given by Coulomb forces, the total interaction energy being repulsive.

The interaction energies of configuration *III* seem to be physically incorrect when the correlation terms are calculated by the EPCE-F2 σ method as the total interaction energy decreases monotonically with the decrease of the intersystem separation. Perturbation calculations to the 2nd and 3rd order presented in Table V show that the EPCE-F2 σ interaction correlation energies given in Table II are overestimated at shorter distances to such a degree that they cannot be compensated

for the exchange repulsion energy. On the contrary they are unrealistically low at longer distances. Such a behaviour of the EPCE-F2 σ correlation energy was also found by Čársky and coworkers²⁶ with the H₂...H₂ interaction. The coincidence between the perturbation correlation energy and the EPCE-F2 σ one seems to be remarkably good at minimal energy distance of the configuration *III* which is in agreement with similar observation of other systems²⁵. Such a coincidence indicates that at minimal energy distances the EPCE-F2 σ correlation energy contributions are reliable and they can be used in the determination of the order of stabilities of respective configurations. This order is changed if the correlation energy contributions are considered: The (BH)₂ dimer *IV* is the most stable one at the SCF level and is followed in energy by structures *I*, *II*, and *III*. With inclusion of E_{COR} dimer *IV* is still the most stable but is followed by configuration *III*, *I*, and *II*. Configuration *V* is purely repulsive in all cases. The optimal intersystem distance was shortened considerably after the correlation energy was included.

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