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Nonaddive effects are calculated for $(HF)_3$ and $(HCl)_3$ complexes and analyzed via the combination of perturbation theory of intermolecular forces with Møller–Plesset perturbation theory (MPPT). In both systems the nonadditivity is dominated by the self-consistent field (SCF) deformation effect, i.e., mutual polarization of the monomer wavefunctions. Heitler–London exchange and correlation effects are of secondary importance. Three-body terms exhibit much lesser basis set dependence than the two-body effects and even quite moderate basis sets which are not accurate enough for treatment of two-body forces can yield three-body effects of quantitative quality. This is due in large measure to the additivity of strongly basis set dependent components such as uncorrelated and correlated electrostatics and dispersion. Various approximate models for the three-body potentials and total interaction in the $(HF)_3$ cluster are analyzed from the point of view of their ability to predict the orientation dependence of interaction energy.

I. INTRODUCTION

Nonaddive effects in interactions of polar systems have been the subject of vigorous study in the last two decades (for a relatively recent review see Ref. 1). Water trimer is perhaps the most notorious of all. It was first found by Hankins *et al.*[2] that the interaction energy in $(H_2O)_3$ strongly departs from pairwise additivity and certain configurations are stabilized solely by three-body effects. Later investigation by Clementi *et al.*[3,4] into the nature of this nonadditivity at the self-consistent-field (SCF) level showed that it correlates well with the three-body induction effect. This conclusion was confirmed in the simultaneous study of Beyer *et al.*[5] on ion $\cdots (H_2O)_2$ and $(HF)_3$ systems through Morokuma-type partitioning[6] of the SCF interaction energy. This activity ultimately resulted in the derivation of the first *ab initio* three-body analytical potential for water trimer in the form of an induction-type expression involving adjustable parameters.[7] Other nonadditive potentials used for water were also constructed on the same assumption as to the nature of the nonadditive effect.[8,9]

However, the Morokuma method used in the only study of the nature of nonadditivity in polar systems by Beyer *et al.*[5] has several drawbacks which make it inherently unsuitable for such studies. To name a few (i) all the terms in this method are defined in monomer basis sets which leads to serious problems with definitions of the "exchange," "charge–transfer," and "polarization" terms,[10] (ii) the basis set superposition effect greatly exceeds the entire nonadditivity, (iii) the two-body "MIX" term reflecting all the residual errors of this decomposition may be an order of magnitude larger than the effect in question,[5] etc. Moreover, calculations for other trimers, e.g., of NH_3[11] and CH_4,[12] showed that the problem of finding a single origin for nonadditive effects is far from being resolved since the SCF nonadditivity did not correlate with the induction effect in these ostensibly similar systems.

Decomposition of the total nonadditive effect into rigorously defined and physically meaningful contributions is essential to understanding the origin and significance of the nonadditivity phenomenon, as well as to constructing approximate many-body potentials for use in solid and liquid state studies. Thus it seems that the problem of the interaction energy decomposition needs to be revisited. For this purpose we apply the perturbation theory of intermolecular forces[13] which, when combined with the supermolecular Møller–Plesset perturbation theory (MPPT), is very well suited for such a problem.[14] Not only does this approach properly define various contributions to SCF interaction energy but it also allows for a quantitative examination of the role of various intra- and intermolecular correlation effects in this phenomenon. In this paper such an analysis is performed for the two relatively simple trimers: $(HF)_3$ and its second row analog $(HCl)_3$.

II. NONADDITIVE EFFECTS IN VAN DER WAALS COMPLEXES

The total energy of a cluster $AB \cdots Z$ composed of the subsystems $A,B,...,Z$ can be defined as

$$E_{AB \cdots Z; G_{AB \cdots Z}}^{(i)} = \sum_X E_{X,G_X}^{(i)} + \sum_X \widetilde{\Delta E}_X^{(i)}$$
$$+ \sum_{X>Y} \widetilde{\Delta E}_{XY}^{(i)} + \sum_{X>Y>W} \widetilde{\Delta E}_{XYW}^{(i)}$$
$$+ \cdots \widetilde{\Delta E}_{AB \cdots Z}^{(i)}; \qquad (1)$$

where $X,Y,W = A,B,...,Z$; and (i) denotes some level of theory, e.g., a particular order of MPPT (but could also be SCF, CC, etc.). The terms in Eq. (1) have clear physical interpretation. The one-body term $\widetilde{\Delta E}_X^{(i)}$ represents the effect of the relaxation of geometry of subsystem X in the complex and is defined as

$$\widetilde{\Delta E}_X^{(i)} = E_{X;G_{AB \cdots Z}}^{(i)} - E_{X;G_X}^{(i)}; \qquad (2)$$

where $E_{X;G_{AB \cdots Z}}^{(i)}$ denotes the energy evaluated at the geometry which X assumes within complex $AB \cdots Z$ and $E_{X;G_X}^{(i)}$ at

the geometry optimized for the isolated monomer.

The two-body term $\tilde{\Delta}E_{CD}^{(i)}$ represents the pairwise interaction between two monomers C and D in the configuration that they assume within complex $AB \cdots Z$:

$$\tilde{\Delta}E_{CD}^{(i)} = E_{CD;G_{AB\cdots Z}}^{(i)} - \sum_{X=C,D} E_{X;G_{AB\cdots Z}}^{(i)}. \qquad (3)$$

Higher many-body terms are defined recursively; e.g.,

$$\tilde{\Delta}E_{CDF}^{(i)} = E_{CDF;G_{AB\cdots Z}}^{(i)} - \sum_{X=C,D,F} E_{X;G_{AB\cdots Z}}^{(i)}$$

$$- \sum_{X>Y,\overline{X}=C,D,F} \tilde{\Delta}E_{XY}^{(i)}, \qquad (4)$$

where $\tilde{\Delta}E_{CDF}^{(i)}$ is a three-body contribution arising between relaxed-geometry monomers arranged in the same configuration as in the complex. Besides the physical interpretation, the partitioning of Eq. (1) has a practical advantage. The absolute energies of the many-body subsystems which are subtracted in Eqs. (3) and (4) are orders of magnitude larger than the interaction energies. Since the basis set superposition error (BSSE) must be taken care of in all finite basis calculations, it is actually quite convenient (see below) to subtract the energies which are obtained at the same geometries. Moreover, the one-body term $\tilde{\Delta}E_X^{(i)}$ may be relatively large and obscure the role of many-body terms if not separated.

The total interaction energy in a two-body system AB may therefore be defined as

$$\Delta E_{AB}^{(i)} = \tilde{\Delta}E_A^{(i)} + \tilde{\Delta}E_B^{(i)} + \tilde{\Delta}E_{AB}^{(i)}, \qquad (5)$$

where the last term represents the interaction energy of monomers frozen in the geometries that they assume in the dimer. Likewise for the three-body system ABC,

$$\Delta E_{ABC}^{(i)} = \tilde{\Delta}E_A^{(i)} + \tilde{\Delta}E_B^{(i)} + \tilde{\Delta}E_C^{(i)} + \tilde{\Delta}E_{AB}^{(i)} + \tilde{\Delta}E_{BC}^{(i)}$$

$$+ \tilde{\Delta}E_{AC}^{(i)} + \tilde{\Delta}E_{ABC}^{(i)}. \qquad (6)$$

III. BASIS SET SUPERPOSITION ERROR DECOMPOSITION

As mentioned above, when the energies of supermolecule $AB \cdots Z$ and its components are computed with finite basis sets, the use of Eqs. (3) and (4) introduces BSSE. To evaluate the two-, three-, and many-body interaction energy terms, a generalization of the Boys and Bernardi counterpoise (CP) method[15] may be easily applied. Within this CP method all of the energies in Eqs. (3) and (4) are evaluated in the basis set of the whole complex $(\chi_A \cup \chi_B \cup \cdots \cup \chi_Z$, where χ_C denotes the basis set of C); see also Refs. 3 and 16. This approach ensures a basis-set-consistent calculation of all the terms entering Eqs. (3) and (4)[17,18] (although it does not remove the basis set extension effect on the interaction energy[18]).

IV. METHOD AND DEFINITIONS

The method of calculating the nonadditive effects by means of the supermolecular MPPT approach is currently being prepared in detail[14]; here we will briefly mention certain principal elements which are pertinent to the cases studied here.

A. The Hartree–Fock level

The perturbation theory of intermolecular forces interprets the SCF interaction energy as the sum of the following terms: electrostatic, exchange repulsion, and deformation energies.[14] Both the electrostatic and exchange energies are obtained with the Hartree–Fock wave functions for geometries relaxed as in the complex but electronically undeformed by the presence of the partner. The adjustment of monomer charge clouds is accounted for by the deformation energy. This deformation is primarily due to mutual electrostatic polarization of the charge distributions but it may be so strongly restrained by the Pauli exclusion principle acting between the monomers (and preventing the electrons of one subsystem from collapsing onto the occupied orbitals of the other) that it is highly disputable whether the classical induction energy can be sensibly extracted at finite intersystem distances.[19] Nevertheless, the deformation energy behaves asymptotically like the CHF induction energy.[20]

Nonadditive effects are absent in the electrostatic contribution but do arise in the exchange and deformation terms. In order to separate the exchange and deformation nonadditivity it is convenient to use the definition of the Heitler–London energy of the complex:

$$E_{AB\cdots Z}^{HL} = \frac{\langle \mathscr{A}\, AB \cdots Z | \mathscr{H} | \mathscr{A}\, AB \cdots Z\rangle}{\langle \mathscr{A}\, AB \cdots Z | AB \cdots Z\rangle} \qquad (7)$$

and for the monomer X

$$E_X^{HL} = \langle \mathscr{A} X | \mathscr{H}_X | \mathscr{A} X\rangle / \langle \mathscr{A} X | X\rangle \equiv E_X^{SCF},$$

where $A,B,\cdots,Z$ stand for the Hartree–Fock wave functions of the respective monomers unperturbed by the influence of each other, $\mathscr{A}$ symbolizes the antisymmetrizer, $\mathscr{H}$ the total Hamiltonian, and $\mathscr{H}_X$ the Hamiltonian of X. The Heitler–London energy and its components may now be defined with Eqs. (1)–(6) by replacing (i) by HL. This energy term describes the electrostatic and exchange interaction arising between unperturbed SCF monomers. Since the electrostatic term is additive, the Heitler–London three- and higher-body nonadditivities represent pure exchange contributions.

The SCF deformation term can then be defined as the difference between the SCF and HL interaction energies. Thus, for the three-body term we have:

$$\tilde{\Delta}E_{ABC}^{SCF-def} = \tilde{\Delta}E_{ABC}^{SCF} - \tilde{\Delta}E_{ABC}^{HL}. \qquad (8)$$

To do this subtraction properly, both SCF and HL interaction energies should be derived in a basis-set-consistent manner, i.e., in the basis set of the entire complex. Otherwise, the deformation term may have the wrong sign, as recently demonstrated by Gutowski *et al.* for the two-body term.[21] Such an unphysical characteristic was also observed in the Ar$_3$ study of Radzio and Andzelm.[22]

B. The MP2 level

The relationship between the perturbation theory of intermolecular forces and the supermolecular MPPT means of deriving the interaction energy was recently discussed by Chałasiński and Szczęśniak[23] and advanced to the three- and four-body case by Chałasiński *et al.*[14] To summarize the findings of Ref. 14, the second order of MPPT includes the

following intermolecular perturbation theoretical terms (with the first superscript corresponding to the intermolecular interaction operator and the second to the intrasystem correlation operator):

(a) $\epsilon_{elst}^{(12)}$—the second-order intrasystem correlation correction to the electrostatic effect, or in short, the second-order electrostatic correlation;

(b) $\epsilon_{disp}^{(20)}$—the second-order dispersion energy of the uncoupled Hartree–Fock (UCHF) type;

(c) exchange terms related to (a) and (b);

(d) the second-order deformation correlation terms (related to the induction energy coupled with exchange effects).

The electrostatic and dispersion energies are pairwise additive, thus, the nonadditive effects in the MP2 interaction energy originate solely from exchange and deformation effects.

C. MP3 level

The third-order of MPPT is, according to Ref. 14, decomposed into the following terms:

(a) $\epsilon_{elst}^{(13)}$—the third-order electrostatic correlation correction;

(b) $\epsilon_{disp}^{(21)}$—dispersion correlation of "apparent" type; this is the first order intracorrelation correction to the second-order UCHF dispersion $\epsilon_{disp}^{(20)}$;

(c) $\epsilon_{disp}^{(30)}$—the third-order UCHF dispersion;

(d) exchange effects related to (a), (b), (c);

(e) third-order deformation correlation terms.

As in the second order MPPT interaction energy, the exchange and deformation effects are nonadditive. In addition, $\epsilon_{disp}^{(30)}$ is also nonadditive, asymptotically giving rise to the well-known Axilrod–Teller (AT) nonadditivity at the UCHF level. It is worthwhile to stress that in order to evaluate the AT nonadditivity it is unnecessary to allow for more than two-electron correlations.[14] Thus the inclusion of three-electron clusters is not required (as long as the internally uncorrelated AT term is desired) contrary to a suggestion by Habitz *et al.*[24]

As pointed out previously, the four-body dispersion terms do not appear in MP3. The four-body dispersion arises

TABLE I. Medium-polarized basis set (S) for the Cl atom.

Type	Exponent	Coefficient
1s	105 819.0	0.000 738
	15 872.0	0.005 718
	3 619.7	0.029 495
	1 030.8	0.117 241
	339.91	0.363 173
	124.538	0.583 958
2s	124.538	0.134 174
	49.514	0.624 271
	20.806	0.291 735
3s	6.5835	1.0
4s	2.5647	1.0
5s	0.5598	1.0
6s	0.1833	1.0
7s	0.059	1.0
1p	589.78	0.003 000
	139.85	0.023 296
	45.141	0.102 330
	16.873	0.279 094
	6.7411	0.448 283
	2.7715	0.331 500
2p	1.0239	1.0
3p	0.3814	1.0
4p	0.1094	1.0
5p	0.034	1.0
1d	1.0239	0.127 563
	0.3814	0.475 667
2d	0.1094	0.663 375
	0.034	0.113 090

in $\epsilon_{disp}^{(40)}$ and is expected to be present no earlier than at the MP4 level.

In summary, by carrying out the MPPT through the third order we can expect to extract nonadditivities in the following terms: $\widetilde{\Delta E}_{ABC}^{SCF}$ which can be further divided into Heitler–London exchange, $\widetilde{\Delta E}_{ABC}^{HL}$, and SCF deformation, $\widetilde{\Delta E}_{ABC}^{SCF\text{-}def}$, $\widetilde{\Delta E}_{ABC}^{(2)}$ which contains the nonadditive exchange and deformation terms, and $\widetilde{\Delta E}_{ABC}^{(3)}$ which contains nonadditive exchange, deformation, and AT-dispersion terms.

V. BASIS SETS

In the HF trimer calculations, two types of basis sets were used: the "medium-polarized" basis set recently pro-

TABLE II. Finite field calculations of electric properties of HF and HCl in medium-polarized basis sets (S). All values in a.u.

	HF $(r_{HF} = 0.917 \text{ Å})$[a]			HCl $(r_{HCl} = 1.275 \text{ Å})$[a]		
	μ	α_{zz}	α_{xx}	μ	α_{zz}	α_{xx}
SCF	0.757	5.732	4.446	0.482	17.768	15.981
(2)	− 0.048	0.661	0.846	− 0.028	0.548	0.680
(3)	0.005	− 0.203	− 0.293	− 0.006	− 0.077	− 0.063
(4)	− 0.016	0.322	0.370	− 0.010	0.166	0.165
MP4[e]	0.698	6.511	5.370	0.438	18.405	16.763
exp	0.707[b]	6.4[b]	5.08[b]	0.429[c]	21.1[d]	19.6[d]

[a] Reference 34.
[b] Reference 35.
[c] Reference 36.
[d] Reference 37.
[e] Sum of SCF + correlated terms up through the fourth order.

posed by Sadlej[25] (S) and the well-tempered basis set (WT) of Huzinaga and Klobukowski.[26] The S basis contains, apart from the atomic energy optimized part, also the electric-field derivatives thereof. Despite its moderate size, ($10s,6p,4d$ / $5s,4p$) contracted to [$5s,3p,2d$ /$3s,2p$], this basis set was designed to describe the electric properties and was shown to be very well suited for calculations of interaction energies.[27] Some calculations were also done in the S basis set augmented by a set of f functions on F with exponent 0.275 and d functions on H with exponent 0.075[28]; this set is denoted S(f,d). The WT basis sets were recently designed as an attractive alternative to the "geometrical" basis sets.[29] These high-quality basis sets are becoming increasingly popular in studies of intermolecular interactions when high accuracy is desired.[30] The WT set for F and $9s$ set of Huzinaga for H were augmented by the polarization functions from the S basis set. For selected points the WT basis set was further extended by the same f and d functions as in S(f,d) and is herein denoted as WT(f,d).

Since the S basis sets were only constructed for the first row atoms, Sadlej's procedure was followed to prepare the medium-polarized basis set for the Cl atom needed for our HCl trimer study. We began with the $12s,9p$ set for Cl$^-$ from McLean and Chandler.[32] This set was augmented by two diffuse functions s(0.059) and p(0.034).[33] The ($4d$) set contracted to [$2d$] was obtained in a manner identical to Ref. 25. The exponents and contraction coefficients are presented in Table I. The calculated electric properties of HF (see also Ref. 25) and HCl in medium-polarized (S) bases are shown in Table II.

VI. RESULTS AND DISCUSSION

A. HF trimer

The geometry of (HF)$_3$ is illustrated in Fig. 1 where R is defined as the interfluorine distance and α the deviation angle between each hydrogen atom and the F–F axis. An SCF geometry optimization carried out by Karpfen et al.[38] yielded values of 2.73 Å for R(FF) and 26.9° for α. Also considered here are interfluorine distances of 2.0 and 2.5 Å with the same value of α. Based on their electrostatic considerations, Dykstra et al.[39] have calculated that angles of 37.0° and 40.6° are optimal for the longer distances of 4.0 and 5.0 Å, respec-
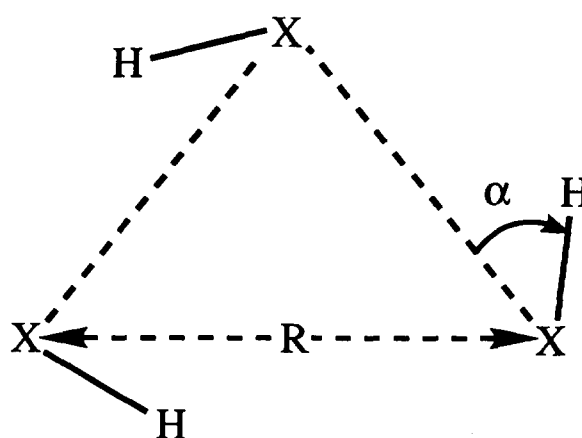

FIG. 1. Geometry of the HF ($X=F$) and HCl ($X=Cl$) trimers. Complexes belong to the C_{3h} point group.

tively; these geometries were also investigated. Additionally, for R(FF) = 2.73 Å the angle α was varied between $-30°$ and 150°.

The calculated two-body and three-body effects in the equilibrium trimer are reported in Tables III and IV, respectively. Considering first the two-body terms, the SCF interaction energies $\widetilde{\Delta E}_{AB}^{SCF}$ for the S and WT bases are very close and remain quite insensitive to the addition of the higher polarization functions f,d. The largest correlation contribution to the two-body interaction occurs at the $\widetilde{\Delta E}_{AB}^{(2)}$ level which amounts to only about 10% of $\widetilde{\Delta E}_{AB}^{SCF}$. $\widetilde{\Delta E}_{AB}^{(2)}$, however, nearly doubles upon addition of the (f,d) set, presumably due to improvement in the dispersion term. The higher-order terms tend to cancel one another, with $\widetilde{\Delta E}_{AB}^{(3)}$ being attractive and $\widetilde{\Delta E}_{AB}^{(4)}$ repulsive. Among the fourth-order terms, only the contribution from triple excitations seems to be very sensitive to the addition of the second polarization set (f,d).

The entries in parentheses correspond to BSSE-uncorrected treatment of the two-body term. It is evident that the BSSE correction should be applied in order to get meaningful interaction energy terms, particularly at the correlated levels.

As seen from the third column of Table V, correspond-

TABLE III. Basis set dependence of the two-body effects in equilibrium geometry of (HF)$_3$.[a] Entries in parentheses correspond to BSSE uncorrected values. All values in mH.

Basis	$\widetilde{\Delta E}_{AB}^{SCF}$	$\widetilde{\Delta E}_{AB}^{(2)}$	$\widetilde{\Delta E}_{AB}^{(3)}$	$\widetilde{E}_{AB}^{SDQ}$	$\widetilde{\Delta E}_{AB}^{(4)}$	$\widetilde{\Delta E}_{AB}^{b}(4)$
6-31G**	-6.491	-0.134	0.093	0.131	0.069	-6.462
	(-9.557)	(-1.715)	(0.578)		(-0.444)	(-11.138)
S	-5.102	-0.315	-0.115	0.232	0.140	-5.392
	(-5.664)	(-2.960)	(-0.144)		(0.012)	(-8.757)
WT	-5.157	-0.303	-0.174	0.249	0.179	-5.455
	(-5.353)	(-1.827)	(-0.215)		(0.019)	(-7.376)
S(f,d)	-5.189	-0.538	-0.145	0.213	0.082	-5.789
	(-6.097)	(-3.708)				
WT(f,d)	-5.220	-0.510				
	(-5.710)	(-2.518)				

[a] SCF optimized geometry of Karpfen et al. (Ref. 38): $R = 2.73$ Å, $\alpha = 26.9°$.
[b] Sum of $\widetilde{\Delta E}^{SCF} + \widetilde{\Delta E}^{(2)} + \widetilde{\Delta E}^{(3)} + \widetilde{\Delta E}^{(4)}$.

TABLE IV. Basis set dependence of the three-body effects in equilibrium structure of $(HF)_3$.[a] Entries in parentheses correspond to BSSE uncorrected values. All values in mH.

Basis	$\widetilde{\Delta E}^{SCF}_{ABC}$	$\widetilde{\Delta E}^{(2)}_{ABC}$	$\widetilde{\Delta E}^{(3)}_{ABC}$	$\widetilde{E}^{SDQ}_{ABC}$	$\widetilde{\Delta E}^{(4)}_{ABC}$	$\widetilde{\Delta E}^{b}_{ABC}(4)$
6-31G**	− 2.460	− 0.121	0.056	− 0.032	− 0.048	− 2.574
	(− 2.406)	(− 0.133)	(0.010)		(− 0.044)	(− 2.573)
S	− 2.540	− 0.118	0.074	− 0.030	− 0.060	− 2.636
	(− 2.542)	(0.829)	(0.102)		(0.051)	(− 1.658)
WT	− 2.550	− 0.104	0.080	− 0.032	− 0.063	− 2.636
	(− 2.660)	(0.205)	(0.097)		(− 0.029)	(− 2.331)
S(f,d)	− 2.591	− 0.110	0.081	− 0.028	− 0.057	− 2.681
	(− 2.446)	(1.102)				
WT(f,d)	− 2.590	− 0.103				
	(− 2.516)	(0.451)				

[a] SCF optimized geometry of Karpfen *et al.* (Ref. 38): $R = 2.73$ Å, $\alpha = 26.9°$.
[b] Sum of $\widetilde{\Delta E}^{SCF} + \widetilde{\Delta E}^{(2)} + \widetilde{\Delta E}^{(3)} + \widetilde{\Delta E}^{(4)}$.

ing to the SCF equilibrium geometry, the largest contribution to the two-body effect arises from the combination of the electrostatic and exchange repulsion as embodied by the Heitler–London two-body term which amounts to − 3.01 mH. However, the SCF deformation term is nearly as large: − 2.090 mH. As evident in the lower half of the table, the three-body effect is dominated by its SCF component $\widetilde{\Delta E}^{SCF}_{ABC}$ which is almost totally due to the three-body SCF-deformation term. The HL-exchange nonadditivity, as represented by $\widetilde{\Delta E}^{HL}_{ABC}$, amounts to only about 5% of $\widetilde{\Delta E}^{SCF}_{ABC}$ in the equilibrium geometry.

Considering now the three-body effects displayed in Table IV, we note first that the SCF term is rather basis set insensitive. $\widetilde{\Delta E}^{SCF}_{ABC}$ is approximately half the magnitude of $\widetilde{\Delta E}^{SCF}_{AB}$. The contribution of correlation to nonadditivity is very small, less than 5% of the total. All the MPPT terms, i.e., second-, third-, and fourth-order, are quite similar in magnitude exhibiting a great deal of cancellation. Again $\widetilde{\Delta E}^{(2)}_{ABC}$ represents the largest correlation contribution. Unlike the analogous two-body term, $\widetilde{\Delta E}^{(2)}_{ABC}$ is quite insensitive to the presence of the (f,d) set, as well as to the choice of S or WT basis sets. It should be emphasized that the three-body effects show a remarkable basis set independence in contrast to the two-body terms (see Table III). Even the 6-31G**

TABLE V. Angular variations of two- and three-body effects in cyclic $(HF)_3$. $R = 2.73$ Å, all values in mH basis set S.

	α,(deg)					
	− 30.0	0.01	26.9	60.0	90.0	150.0
Two-body terms						
$\widetilde{\Delta E}^{SCF}_{AB}$	40.979	7.300	− 5.102	− 0.819	1.942	3.315
$\widetilde{\Delta E}^{HL}_{AB}$	49.104	11.283	− 3.014	− 0.383	2.187	3.525
$\epsilon^{(10)}_{elst}$	33.539	0.323	− 9.587	− 3.458	− 0.074	2.000
$\widetilde{\Delta E}^{exch^a}_{AB}$	15.565	10.960	6.573	3.074	2.113	1.525
$\widetilde{\Delta E}^{SCF\text{-}def}_{AB}$	− 8.125	− 3.983	− 2.088	− 0.436	− 0.245	− 0.210
$\epsilon^{(20)}_{disp}$	− 3.680	− 2.867	− 2.018	− 1.261	− 1.030	− 0.938
$\widetilde{\Delta E}^{(2)}_{AB}$	− 4.525	− 1.941	− 0.315	− 0.012	− 0.579	− 1.112
$\widetilde{\Delta E}^{(3)}_{AB}$	0.011	0.069	− 0.115	− 0.209	− 0.069	0.091
$\widetilde{\Delta E}^{b}_{AB}(3)$	36.465	5.428	− 5.532	− 1.041	1.297	2.206
Three-body terms						
$\widetilde{\Delta E}^{SCF}_{ABC}$	− 7.355	− 3.591	− 2.539	− 0.894	− 0.535	− 0.279
$\widetilde{\Delta E}^{HL}_{ABC}$	2.930	0.473	− 0.175	− 0.243	− 0.217	− 0.067
$\widetilde{\Delta E}^{SCF\text{-}def}_{ABC}$	− 10.285	− 4.064	− 2.364	− 0.651	− 0.318	− 0.212
$\widetilde{\Delta E}^{(2)}_{ABC}$	− 0.164	− 0.331	− 0.112	− 0.034	− 0.006	− 0.063
$\epsilon^{(30)}_{disp,ABC}$	0.264	0.091	0.015	0.014	0.019	0.026
$\widetilde{\Delta E}^{(3)}_{ABC}$	0.545	0.238	0.075	0.059	0.047	0.026
$\widetilde{\Delta E}^{(3)\,b}_{ABC}$	− 6.973	− 3.684	− 2.576	− 0.869	− 0.494	− 0.316
$\Delta E^{c}_{ABC}(3)$	102.42	12.60	− 19.17	− 3.99	3.40	6.67

[a] $\widetilde{\Delta E}^{exch}_{AB} = \widetilde{\Delta E}^{HL}_{AB} - \epsilon^{(10)}_{elst}$.
[b] Sum of $\widetilde{\Delta E}^{SCF} + \widetilde{\Delta E}^{(2)} + \widetilde{\Delta E}^{(3)}$.
[c] Total interaction energy of entire trimer [Eq. (6)] up through third-order MP theory.

basis set, included here (see Table IV) for comparison, which normally would not be considered very reliable for polar interactions, as evidenced by its very poor performance for two-body effects (Table III), yields very reliable values for three-body effects. This distinction can be easily explained by taking into account that the most basis-set dependent terms, i.e., electrostatic (uncorrelated or correlated), and the second-order dispersion, which are present implicitly in $\tilde{\Delta}E\,^{(i)}_{ABC}$ (see Ref. 40) are additive. Exchange and deformation effects, on the other hand, are not very susceptible to the changes in basis set. Interestingly, this stability with respect to basis set is lost when the values are not corrected for BSSE, which may serve as one more argument for such correction.

The dependence of the three-body effect upon geometrical configuration is presented in Tables V and VI. For all the configurations under consideration the total nonadditivity is determined for all intents and purposes by the SCF-deformation nonadditivity. The HL-exchange nonadditivity is of secondary importance and is pronounced only for smaller distances. The second and third orders of MPPT provide very small contributions at all the distances.

It is interesting to compare the size of two- and three-body contributions. As the separation of the three subsystems increases the relative ratio of the total three-body to total two-body term becomes progressively smaller. This is easy to understand considering that the two-body effects are asymptotically determined by the electrostatic dipole–dipole term which varies as R^{-3}, whereas the three-body effects are dominated by the SCF-deformation term which is asymptotically determined by the dipole–induced-dipole term of the order of R^{-6}.

It is worthwhile to comment on the relation between two- and three-body SCF-deformation contributions. Both

are of similar magnitude for each configuration and their ratio tends to a constant value as $R \to \infty$. The reason for this is that two- and three-body deformation terms are determined by the dipole–induced-dipole interaction, proportional to $(\mu_A)^2 \alpha_B$ in the former case and to $(\mu_A \mu_C) \alpha_B$ in the latter.

The orientation dependence of the two- and three-body effects is reported in Table V. The two-body SCF electrostatic term is the most orientation dependent. It reveals a sharp minimum at about 23° which determines the shape of the $(HF)_3$ cluster. The two other large two-body terms, HL exchange and SCF deformation, decrease monotonically from $\alpha = -30°$ to $\alpha = 150°$. Both have lesser influence on geometry shifting α towards larger values. The dispersion term is less angular dependent than is SCF deformation.

The two-body correlation terms, $\tilde{\Delta}E\,^{(2)}_{AB}$ and $\tilde{\Delta}E\,^{(3)}_{AB}$, are relatively smaller and show, respectively, a maximum and minimum at around 60°. These extrema may be attributed to the presence of the electrostatic components in these terms. According to Chałasiński and Szczęśniak[23] $\tilde{\Delta}E\,^{(2)}_{AB}$ and $\tilde{\Delta}E\,^{(3)}_{AB}$ are asymptotically proportional to $\mu_X^{(2)}\mu_Y^{SCF}/R^3$ and $\mu_X^{(3)}\mu_Y^{SCF}/R^3$, respectively. For the HF molecule the $\mu^{(2)}$ correction is negative and $\mu^{(3)}$ positive (see Table II). Thus, $\tilde{\Delta}E\,^{(2)}_{AB}$ behaves in a manner reciprocal to the SCF-electrostatic term, whereas $\tilde{\Delta}E\,^{(3)}_{AB}$ is parallel.

Explanation of the orientation dependence of the three-body terms is not immediately obvious. The three-body SCF-deformation effect behaves in a very similar manner to the two-body SCF deformation; namely, they are both negative and increase monotonically from $-30°$ to 150°. This is most likely due to the aforementioned close relationship between two- and three-body SCF-deformation terms.

The situation is quite different with the HL-exchange nonadditivity. This term is known to be strongly geometry-

TABLE VI. Two- and three-body contributions for different cyclic geometries of $(HF)_3$ obtained with basis set S. All values in mH.

R, (Å)	2.0	2.5	2.73	4.0	5.0
α, (deg)	26.9	26.9	26.9	37.0	40.6
Two-body terms					
$\tilde{\Delta}E^{SCF}_{AB}$	38.571	−2.952	−5.102	−2.052	−0.966
$\tilde{\Delta}E^{HL}_{AB}$	67.285	1.542	−3.014	−1.987	−0.954
$\tilde{\Delta}E^{SCF\text{-}def}_{AB}$	−28.714	−4.494	−2.090	−0.065	−0.012
$\tilde{\Delta}E^{(2)}_{AB}$	0.068	−0.381	−0.315	0.086	0.075
$\tilde{\Delta}E^{(3)}_{AB}$	−0.108	−0.162	−0.115	−0.017	−0.009
$\tilde{\Delta}E^{a}_{AB}(3)$	38.531	−3.495	−5.532	−1.982	−0.900
Three-body terms					
$\tilde{\Delta}E^{SCF}_{ABC}$	−31.690	−5.240	−2.540	−0.121	−0.027
$\tilde{\Delta}E^{HL}_{ABC}$	−9.935	−0.661	−0.175	0.000	0.000
$\tilde{\Delta}E^{SCF\text{-}def}_{ABC}$	−21.756	−4.579	−2.365	−0.121	−0.027
$\tilde{\Delta}E^{(2)}_{ABC}$	−0.040	−0.172	−0.118	−0.003	−0.000
$\tilde{\Delta}E^{(3)}_{ABC}$	0.222	0.122	0.074	0.004	0.001
$\tilde{\Delta}E^{a}_{ABC}(3)$	−31.510	−5.291	−2.576	−0.126	−0.026

^{a} Sum of $\tilde{\Delta}E^{SCF} + \tilde{\Delta}E^{(2)} + \tilde{\Delta}E^{(3)}$.

dependent. As demonstrated for rare-gas trimers,[41] while the two-body HL-exchange term is always positive, the three-body effect may be either positive or negative depending on geometry. In the case of $(HF)_3$ it shows a minimum at around 60° and changes its sign from negative to positive somewhere between 0° and 23°.

Finally, it is difficult to pinpoint the exact origin of $\widetilde{\Delta E}^{(2)}_{ABC}$ and $\widetilde{\Delta E}^{(3)}_{ABC}$ terms as they represent "unresolved mixtures" of exchange–dispersion, exchange–intramolecular correlation, deformation correlation, as well as, in the case of $\widetilde{\Delta E}^{(3)}_{ABC}$, AT nonadditivity. It can only be concluded that the latter term, represented in Table V by $\epsilon^{(30)}_{disp,ABC}$, does not dominate $\widetilde{\Delta E}^{(3)}_{ABC}$. This is not surprising since asymptotically $\epsilon^{(30)}_{disp,ABC}$ behaves as R^{-9} while the deformation–correlation term as R^{-6}.

The $\Delta E_{ABC}(3)$ values in the bottom row of Table V refer to the angular dependence of the total interaction energy of the entire trimer as a function of α(HFF) through the third order of MPPT. As is evident, the interaction energy has a deep minimum at around 26.9°. The question arises now as to what are the acceptable approximations to $\Delta E_{ABC}(3)$ which would be capable of reconstructing its orientation dependence. This problem is especially important in those areas of solid and liquid-state theory which make use of analytical pair- and more recently three-body potentials. The calculated individual contributions to interaction energy will allow for a construction of an *ordered set* of approximations leading to a reliable description of the cluster. Let us first begin from the detailed examination of the region of the minimum (Fig. 2) and then extend our conclusions to a wider range of angles (Fig. 3).

Shown in Fig. 2 as the solid curve is $\Delta E_{ABC}(3)$, which will be treated as our reference, and several approximations to it. Starting from the simplest, the two-body electrostatic term (ES) shows the largest variations with angle. Indeed,
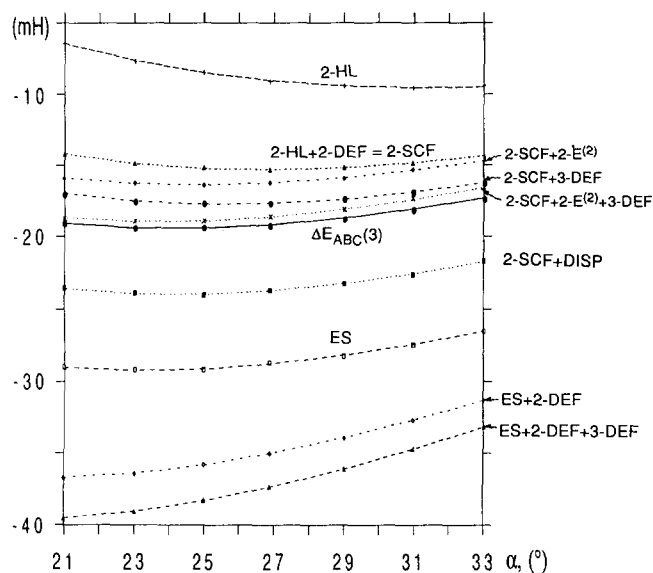

FIG. 2. Various approximations to the total interaction energy $\Delta E_{ABC}(3)$ of the cyclic $(HF)_3$ around minimum. "2-" and "3-" before a symbol denote the two-body and/or three-body contribution, respectively. The following symbols are used: "ES"—$\epsilon^{(10)}_{elst}$, "HL"—ΔE^{HL}, "DEF"—$\Delta E^{SCF-def}$, "SCF"—$\widetilde{\Delta E}^{SCF}$, "$E^{(2)}$"—$\widetilde{\Delta E}^{(2)}$. See Sec. IV for more details.
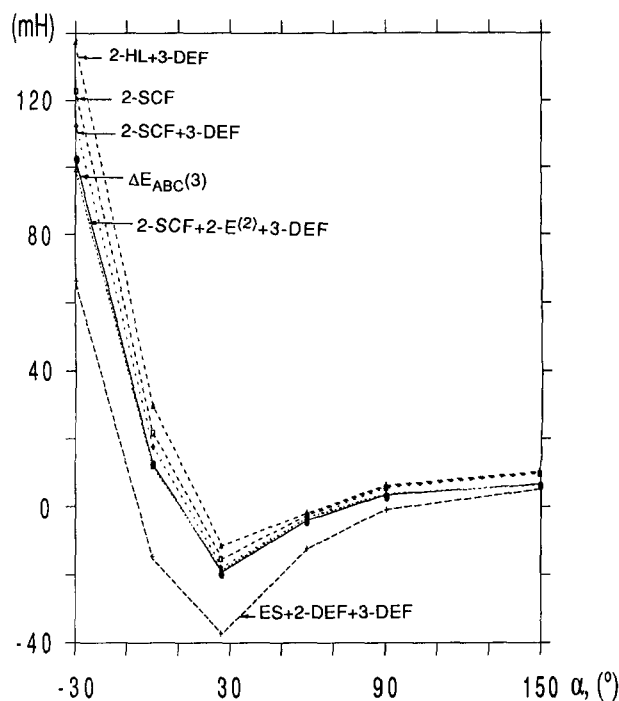

FIG. 3. Various approximations to the total interaction energy $\Delta E_{ABC}(3)$ of cyclic $(HF)_3$ in the wider range of α(HFF). See caption of Fig. 2 for explanation of the symbols.

this term, which exhibits a minimum at about 23°, determines the structure of the cluster [at a given R(FF) distance]. However, the minimum is too deep by some 10 mH. Addition of the two-body SCF-deformation term makes its angular dependence worse, i.e., the curve shifts downwards by another 7–8 mH and the minimum is shifted towards too small angles. A further worsening occurs upon the addition of the three-body SCF-deformation term. Thus, the model which includes only classical "electric interactions"[39] is inherently incapable of quantitatively describing the region of the minimum. Moreover, we tacitly assumed that R(FF) is constant; if, however, R is allowed to shorten, this model will cause the cluster to collapse.

To properly account for repulsion the electrostatic effect should be accompanied by two-body HL exchange which adds up to the full two-body HL term. Exchange repulsion disfavors small α angles as they lead to larger overlap; thus the curve corresponding to the two-body HL term has its minimum shifted to about 30° and lies too high on the energy scale by 10–15 mH. Allowing for addition of two-body SCF deformations to two-body HL makes for the two-body SCF curve, which now begins to resemble the reference curve, with its minimum at 27° but still some 3–5 mH too high in energy. A considerable reduction in this energy gap is obtained upon the further addition of the three-body SCF-deformation term. The α angle is now 26°.

Instead of adding three-body terms we may further improve the two-body interaction which so far lacks correlation effects. Addition of the two-body dispersion to $\widetilde{\Delta E}^{SCF}_{AB}$ predicts the minimum at 25°; however, the curve is now shifted downward by some 4 mH with respect to the reference. A more complete account of two-body correlation effects can be obtained at the MP2 level. The pairwise $\widetilde{\Delta E}(2)$ term com-

bining $\widetilde{\Delta E}\,^{\text{SCF}}_{AB}$ with $\widetilde{\Delta E}\,^{(2)}_{AB}$ is now located above the reference curve; their difference being almost exactly equal to the three-body deformation term. This results from the small magnitude of $\widetilde{\Delta E}\,^{(3)}_{AB}$ and the cancellation between three-body $\widetilde{\Delta E}\,^{(2)}_{ABC}$ and $\widetilde{\Delta E}\,^{(3)}_{ABC}$ terms.

These conclusions may be verified over the broader range of angles ($-30°$–$150°$) shown in Fig. 3. The electric interaction model combining SCF electrostatics with two- and three-body SCF-deformation terms again performs quite badly for both small and large α, evidently lacking the proper description of repulsion effects. The two-body HL accompanied by three-body SCF-deformation term shows some improvement. Both pairwise SCF and SCF augmented by three-body deformation models reproduce quite well the angular dependence of the interaction energy of the trimer except for large values of α ($>60°$) where all three curves depart from $\Delta E_{ABC}(3)$. This disparity is almost totally due to correlation effects, as evidenced by a considerable improvement upon the addition of two-body $\Delta E^{(2)}$ term to the model involving two-body SCF + three-body SCF deformation.

The simplest and quite successful means of probing the orientation dependence of the two-body Heitler–London interaction may be via the model of Buckingham and Fowler.[42] The analytical representation of this term can be accomplished, e.g., by the method proposed by Ahlrichs.[43] As for the three-body SCF-deformation term it is believed that asymptotically it can be approximated by the classical three-body induction term. Kollman and co-workers[8,9] described this effect in terms of the self-consistent polarization treatment for H_2O trimer. Alternatively, the multipole approximation utilizing atomic charges and bond polarizabilities can be applied as in the study by Clementi, Kołos, and others[3] for the same system. The latter treatment was somewhat modified[7] by treating charges and bond polarizabilities as adjustable parameters in the fit of three-body induction expression to the entire SCF nonadditivity. As mentioned earlier, due to the strong coupling between induction and exchange effects,[19] it is unclear as yet whether the SCF-deformation effect can be approximated by the induction term.

B. HCl trimer

The geometrical structure of $(HCl)_3$ was recently optimized by Latajka and Scheiner[44] using the 6-31G** basis set modified by adding diffuse functions, as well as reoptimization of the valence region. Their equilibrium structure was found to be the C_{3h} trimer with $R(ClCl) = 4.135$ Å and $r(HCl) = 1.271$ Å. The angle $\alpha(HClCl)$ between each H–Cl bond and the corresponding Cl–Cl axis was found to be 24.3°. Our calculations were performed here for two geometries: the latter equilibrium structure of Latajka and Scheiner, and a geometry in which all three $R(ClCl)$ distances were stretched to 5.0 Å keeping all other parameters unchanged.

The two-body and three-body terms, along with their decompositions, are presented in Table VII. In the two-body interaction, the SCF component is closely followed in magnitude by the second-order MPPT correlation contribution, $\widetilde{\Delta E}\,^{(2)}_{AB}$. The three-body term, on the other hand, is fully

TABLE VII. Two-body and three-body effects in cyclic $(HCl)_3$ ($\alpha = 24.3°$). All values in mH.

R, (Å)	4.135	5.0
Two-body terms		
$\widetilde{\Delta E}\,^{\text{SCF}}_{AB}$	-1.121	-0.799
$\widetilde{\Delta E}\,^{\text{HL}}_{AB}$	-0.660	-0.729
$\epsilon^{(10)}_{\text{elst}}$	-1.976	-0.795
$\widetilde{\Delta E}\,^{\text{SCF-def}}_{AB}$	-0.461	-0.070
$\widetilde{\Delta E}\,^{(2)}_{AB}$	-1.058	-0.292
$\epsilon^{(20)}_{\text{disp}}$	-1.346	-0.354
$\widetilde{\Delta E}\,^{(3)}_{AB}$	0.272	0.087
$\widetilde{\Delta E}_{AB}(3)$	-1.907	-1.003
Three-body terms		
$\widetilde{\Delta E}\,^{\text{SCF}}_{ABC}$	-0.393	-0.088
$\widetilde{\Delta E}\,^{\text{HL}}_{ABC}$	-0.004	0.000
$\widetilde{\Delta E}\,^{\text{SCF-def}}_{ABC}$	-0.389	-0.088
$\widetilde{\Delta E}\,^{(2)}_{ABC}$	0.006	0.001
$\epsilon^{(30)}_{\text{disp},ABC}$	0.019	0.003
$\widetilde{\Delta E}\,^{(3)}_{ABC}$	0.025	0.006
$\widetilde{\Delta E}_{ABC}(3)$	-0.363	-0.081

dominated by the SCF part with the correlated terms being quite negligible and $\widetilde{\Delta E}\,^{(3)}_{ABC}$ much larger than $\widetilde{\Delta E}\,^{(2)}_{ABC}$. In other words, the relative ratio of correlation vs SCF two-body effects differs considerably from that for the corresponding three-body effects. This conclusion may be rationalized as follows. In terms of perturbation theory the two- and three-body SCF deformation and two-body dispersion are all of the *second* order with respect to the intermolecular interaction operator whereas the three-body dispersion is of the *third* order.

As in the case of $(HF)_3$, the three-body deformation is fully responsible for the SCF and total nonadditive effect. Although the charge distribution in HCl is expected to be much more diffuse than in HF the role of exchange nonadditivity in the HCl trimer is even smaller in magnitude than in $(HF)_3$ when equilibrium structures are compared. The three-body second-order correlation term is here positive, in contrast to the $(HF)_3$ situation. This nonadditivity is most likely due to exchange correlation.

VII. CONCLUSIONS

The nonadditive effect in both trimers is totally dominated by the SCF-deformation term. Although of considerable magnitude, it has rather a small effect on the geometry of $(HF)_3$ which is determined by the two-body HL energy. In particular, it is the SCF-electrostatic term which for a given $R(FF)$ determines the value of $\alpha(HFF)$. Correlation effects have a small impact on the three-body potential.

Another very important conclusion of this paper is that the three-body potentials in the systems under consideration are found to be much less basis set demanding than the two-body potential and the former can be derived with reasona-

ble accuracy in quite modest basis sets at the SCF and even post-SCF levels. This is due to the fact that the dominant three-body effects, SCF deformation and HL exchange, only moderately depend upon the basis set. On the other hand, the terms which dominate the two-body potential, SCF electrostatic and dispersion, are strongly basis set dependent. In particular, since the electrostatic component is absent in three-body terms in every order of MPPT and dispersion appears beginning with the third order, the $\tilde{\Delta} E^{(2)}_{ABC}$ and $\tilde{\Delta} E^{(3)}_{ABC}$ [40] terms are less basis set dependent than their two-body counterparts $\tilde{\Delta} E^{(2)}_{AB}$ and $\tilde{\Delta} E^{(3)}_{AB}$. In comparison to the dimer calculation, that of a three-body system involves the much larger dimension of the SCF problem, as well as the larger number of degrees of freedom on the potential energy surface. Therefore, this finding should be encouraging for those interested in development of three-body potentials from first principles.

ACKNOWLEDGMENTS

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