

Ab initio study of intermolecular potential of H₂O trimer

G. Chałasiński

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901
and Department of Chemistry, University of Warsaw, Pasteural, 02-093 Warsaw, Poland

M. M. Szczeniak

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

P. Cieplak

Department of Chemistry, University of Warsaw, Pasteural, 02-093 Warsaw, Poland

S. Scheiner

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

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Nonadditive contribution to the interaction energy in water trimer is analyzed in terms of Heitler–London exchange, SCF deformation, induction and dispersion nonadditivities. Nonadditivity originates mainly from the SCF deformation effect which is due to electric polarization. However, polarization does not serve as a universal mechanism for nonadditivity in water. In the double-donor configuration, for example, the Heitler–London exchange contribution is the most important and polarization yields the wrong sign. Correlation effects do not contribute significantly to the nonadditivity. A detailed analysis of the pair potential is also provided. The present two-body potential and its components are compared to the existing *ab initio* potentials (MCY) as well as to empirical ones (RWK2, TIP, SPC). The ways to improve these potentials are suggested.

I. INTRODUCTION

Owing to its ubiquitous presence on Earth and crucial role in most biological processes water has long been a favorite object of scientific research. Interpretation of unusual physical and chemical properties of water in terms of properties of the water molecule and its smallest aggregates the dimer and trimer has been particularly challenging. Unfortunately, our knowledge is still interpretative rather than predictive. For example, several empirical pair potentials have been proposed for water.^{1–5} These potentials, however, are often determined for a single phase and cannot be expected adequate for other phases. Description of the structure and properties of other phases requires considering also many-body potentials and nonadditive effects. Experimental determination of these effects is often quite impossible. In this context, *ab initio* methods should serve as a potentially ideal source of such information. However, quantum mechanical calculations even of a pair potential for water are far from routine.^{6–9} The three- and four-body effects were evaluated from first principles by Clementi *et al.*¹⁰ and by Koehler *et al.*¹¹ Unfortunately, the nonadditive contributions were not partitioned into components each with differing physical origin. In addition, the employed basis sets were relatively small. More extensive recent calculations by Clementi's group⁸ also focused only on the total interaction energy. MP4 calculations were performed for a large number of points to provide a new *ab initio* analytical potential. The nonadditive effect in this study was implicitly taken into account within the framework of the classic model of polarization effects derived from atomic charges and bond polarizabilities.⁸

The goal of the present paper is to apply state-of-the-art *ab initio* methodology to determine the origin and importance of the three-body effect in (H₂O)₃. Since such calculations

require also evaluation of all the two-body terms, a similar analysis will be carried out for the related two-body contributions. The paper will focus on the following topics: (i) the decomposition of two- and three-body effects into their components, such as exchange, induction–deformation, and dispersion, (ii) analysis of the anisotropy of the individual components, (iii) critical evaluation of the two- and three-body components of the empirical water potentials with the special emphasis on the RWK2 potential of Reimers, Watts, and Klein,² and its derivatives.⁵

By applying a newly proposed^{12–14} combination of Intermolecular Møller–Plesset Perturbation Theory (IMPPT)^{15,16} with the supermolecular Møller–Plesset Perturbation Theory (MPPT) the total interaction energy will be dissected into its different contributions and the properties of each will be analyzed on an individual basis.

II. INTERACTION ENERGY DECOMPOSITION

The total energy of cluster $ABC \cdots Z$ composed of monomers A, B, \dots, Z , under the assumption of no relaxation of monomer geometries in the complex, can be defined (cf. Ref. 14)

$$E_{AB \cdots Z}^{(i)} = \sum_X E_X^{(i)} + \sum_{X>Y} \Delta E_{XY}^{(i)} + \sum_{X>Y>W} \Delta E_{XYW}^{(i)} + \cdots + \Delta E_{AB \cdots Z}^{(i)}, \quad (1)$$

where $X, Y, W = A, B, \dots, Z$; and (i) denotes the particular order of MPPT. The terms in Eq. (1) have clear physical interpretation as the monomer energies, $E_X^{(i)}$, two-body energies $\Delta E_{XY}^{(i)}$, three-body energies, $\Delta E_{XYW}^{(i)}$, etc. The interpretation of individual many-body contributions in Eq. (1) in terms of

IMPPT is possible in light of the recent analysis by Chafasiński *et al.*¹⁴ Below the contents of the two- and three-body corrections through $i=3$ will be briefly summarized. It should be recalled that the intermolecular interaction corrections $\epsilon^{(ij)}$ are of the i th order with respect to the intermolecular interaction operator and of the j th order with respect to the sum of monomer correlation potentials.

A. SCF component

Two-body:

$$\Delta E_{AB}^{\text{SCF}} = \Delta E_{AB}^{\text{HL}} + \Delta E_{\text{def},AB}^{\text{SCF}}, \quad (2)$$

$$\Delta E_{AB}^{\text{HL}} = \epsilon_{\text{es},AB}^{(10)} + \Delta E_{\text{exch},AB}^{\text{HL}}, \quad (3)$$

where $\Delta E_{AB}^{\text{HL}}$ and $\Delta E_{\text{def},AB}^{\text{SCF}}$ are the Heitler–London and SCF deformation contributions, respectively. $\Delta E_{AB}^{\text{HL}}$ is further divided into the electrostatic, $\epsilon_{\text{es},AB}^{(10)}$, and exchange, $\Delta E_{\text{exch},AB}^{\text{HL}}$, components.

Three-body:

$$\Delta E_{ABC}^{\text{SCF}} = \Delta E_{\text{exch},ABC}^{\text{HL}} + \Delta E_{\text{def},ABC}^{\text{SCF}}. \quad (4)$$

The three-body term includes only the exchange and SCF deformation contributions.

The SCF deformation (two- and three-body) originates from mutual polarization restrained by the Pauli principle. The two second-order approximations in terms of IMPPT theory to the SCF deformation are also considered: the uncoupled and coupled Hartree–Fock induction contributions, $\epsilon_{\text{ind}}^{(20)}$ and $\epsilon_{\text{ind}}^{\text{CHF}}$.

B. $\Delta E^{(2)}$ component

Two-body:

$$\Delta E_{AB}^{(2)} = \epsilon_{\text{es-r},AB}^{(12)} + \epsilon_{\text{disp},AB}^{(20)} + \Delta E_{\text{def},AB}^{(2)} + \Delta E_{\text{exch},AB}^{(2)}. \quad (5)$$

$\epsilon_{\text{es-r},AB}^{(12)}$ denotes the second-order electrostatic correlation energy with orbital relaxation,¹⁷ and $\epsilon_{\text{disp},AB}^{(20)}$ the uncoupled Hartree–Fock dispersion energy. $\Delta E_{\text{def},AB}^{(2)}$ and $\Delta E_{\text{exch},AB}^{(2)}$ stand for the second-order deformation correlation correction to the SCF deformation and the second-order exchange correlation, respectively. The last two terms have not yet been rigorously defined and extracted from $\Delta E_{AB}^{(2)}$.

Three-body:

$$\Delta E_{ABC}^{(2)} = \Delta E_{\text{def},ABC}^{(2)} + \Delta E_{\text{exch},ABC}^{(2)}. \quad (6)$$

Only $\Delta E_{\text{def}}^{(2)}$ and $\Delta E_{\text{exch}}^{(2)}$ are nonadditive.

C. $\Delta E^{(3)}$ component

Two-body:

$$\Delta E_{AB}^{(3)} = \epsilon_{\text{es-r},AB}^{(13)} + \epsilon_{\text{disp},AB}^{(21)} + \epsilon_{\text{disp},AB}^{(30)} + \Delta E_{\text{def},AB}^{(3)} + \Delta E_{\text{exch},AB}^{(3)}. \quad (7)$$

$\epsilon_{\text{es-r},AB}^{(13)}$ is the third-order electrostatic correlation energy, $\epsilon_{\text{disp},AB}^{(21)}$ the first-order intramonomer correlation correction to the dispersion energy, and $\epsilon_{\text{disp},AB}^{(30)}$ the Hartree–Fock third-order dispersion energy. Again, $\Delta E_{\text{def},AB}^{(3)}$ and $\Delta E_{\text{exch},AB}^{(3)}$ are not rigorously defined and represent, respectively, the deformation correlation and exchange correlation contributions in the third order.

Three-body:

$$\Delta E_{ABC}^{(3)} = \epsilon_{\text{disp},ABC}^{(30)} + \Delta E_{\text{def},ABC}^{(3)} + \Delta E_{\text{exch},ABC}^{(3)}. \quad (8)$$

The three-body term includes the third-order dispersion nonadditivity, as well as the deformation correlation and exchange correlation nonadditivities.

To assure consistency of evaluation of the MPPT and IMPPT corrections all the intermolecular perturbation terms $\epsilon^{(ij)}$ have to be derived within the basis set of the entire complex (i.e., trimer centered basis set, TCBS) and all the supermolecular quantities have to be evaluated via the Counterpoise Procedure,¹⁸ i.e., corrected for the basis set superposition error (BSSE).¹⁹ All the calculations were carried out using the GAUSSIAN 86 program²⁰ and the intermolecular perturbation theory package linked to GAUSSIAN 86.²¹

III. GEOMETRIES AND BASIS SETS

Two types of trimer configurations were considered in this study: the cyclic planar structure [Fig. 1(a)] and hydrogen-bonded configurations [Figs. 1(b)–1(d)]. The cyclic planar structure is especially convenient from the calculation point of view since the high C_{3h} symmetry requires only one, rather than three, TCBS calculation for monomer and dimer subunits in (H₂O)₃. By varying the α angle [see Fig. 1(a)] the anisotropy of the two- and three-body contributions to the trimer energy was investigated.

The H-bonded geometries included the donor–donor (d–d), donor–acceptor (d–a), and acceptor–acceptor (a–a) configurations. Such structures are important both in ice and liquid water. For each configuration the intersystem distance R [see Figs. 1(b)–1(d)] was also varied from 2.5 to 5 Å. The d–a structure was assumed in the form of the cyclic planar configuration with $\alpha = 75^\circ$ [see Figs. 1(a) and 1(b)].

The calculations were carried out in a basis set (10s,6p,2d/5s,2p) contracted to [5s,3p,1d/3s,1p]. The basis set was obtained by reducing the “medium-polarized” basis set of Sadlej,²² denoted S , used in our previous study of water dimer.²³ From the original [5s,3p,2d/3s,2p] set the less diffuse polarization CGTO at each nucleus was removed and the resultant basis set is termed RS . Such a modification was necessary since the full S basis seemed too large for trimer calculations at a large number of geometries. The values of monomer properties of H₂O obtained with our reduced basis RS are compared with the parent S basis in Table I. The performance of basis RS in the interaction energy calculations is analyzed in Table II.

IV. BASIS SET EFFECTS

As seen from Table I the RS basis overestimates the dipole moment at the SCF level, as well as its second-order correlation correction by 5% and 12%, respectively. The values of the SCF polarizabilities are slightly underestimated.

The calculated values of the two- and three-body interaction energy components in the minimum energy cyclic planar trimer ($R = 3.0$ Å, $\alpha = 75^\circ$) are reported in Table II.

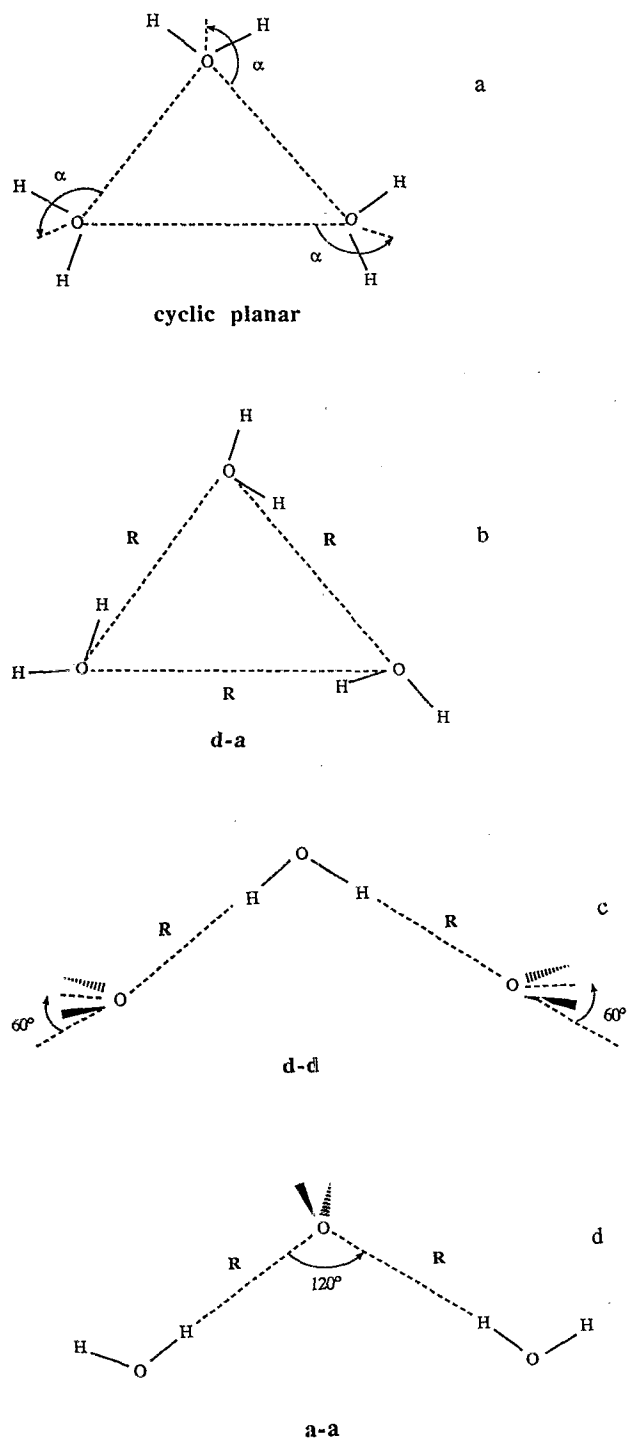


FIG. 1. Configurations of the H₂O trimer: (a) cyclic planar (belongs to C_{3h} group), (b) donor-acceptor (belongs to C_{3h} group), (c) donor-donor, (d) acceptor-acceptor.

The values are compared for S , RS , and $6-31G^{**}$ basis sets.

It was recently demonstrated that the full S basis set yields very reliable results for all the major interaction energy components.^{23,26} Furthermore, the contributions to the interaction energy may roughly be divided into two classes: weakly and strongly basis-set dependent.^{17(a)} The former

TABLE I. Dipole moment and polarizability of H₂O obtained with medium-polarized Sadlej (S) and reduced medium-polarized (RS) basis sets. All values in a.u.

	RS	S	Ref. ^a
μ^{SCF}	0.8164	0.7801	0.7801
$\mu^{(2)}$	-0.0558	-0.0497	-0.0631
α_{xx}^{SCF}	9.16	9.19	9.17
α_{yy}^{SCF}	7.64	7.83	7.91
α_{zz}^{SCF}	8.19	8.50	8.51

^aHigh-quality finite-field SCF or MP4 calculations with a large GTO basis (Refs. 24 and 25).

are exchange and deformation (induction), and the latter electrostatic and dispersion contributions. The behavior of supermolecular $\Delta E^{(i)}$ ($i = SCF, 2, 3, \dots$) terms with respect to basis set can be easily understood and interpreted in terms of basis set effects on the respective components, as shown in Ref. 17(a).

At the SCF level of theory the two-body exchange, induction and SCF deformation energies are fairly insensitive to the basis set details and even $6-31G^{**}$ seems satisfactory. The basis set dependence of the two-body ΔE_{AB}^{SCF} is largely determined by the SCF electrostatic energy, $\epsilon_{es}^{(10)}$. This term is poorly reproduced by the $6-31G^{**}$ basis but our RS basis gives a result fairly close to the S basis.

The SCF three-body terms, $\Delta E_{def,ABC}^{SCF}$ and $\Delta E_{exch,ABC}^{HL}$, are also fairly basis set independent. Only the value of $\Delta E_{exch,ABC}^{HL}$ for basis $6-31G^{**}$ is considerably overestimated. However, the exchange three-body term is very small for this geometry and relatively unimportant as the total nonaddi-

TABLE II. Basis set dependence of two- and three-body effects in the water trimer in cyclic configuration [Fig. 1(a)] $R = 3.0 \text{ \AA}$, $\alpha = 75^\circ$. All values (in kcal/mol) are BSSE corrected.

	$6-31G^{**}$	RS	S
Two-body			
$\Delta E_{ex,AB}^{SCF}$	-3.911	-3.344	-3.030
$\epsilon_{ex,AB}^{(10)}$	-5.865	-5.255	-4.864
$\Delta E_{exch,AB}^{HL}$	2.814	2.840	2.748
$\Delta E_{def,AB}^{SCF}$	-0.860	-0.929	-0.914
$\epsilon_{ind,AB}^{(20)}$	-0.876	-0.935	-0.934
$\Delta E_{AB}^{(2)}$	-0.290	-0.198	-0.563
$\epsilon_{disp,AB}^{(20)}$	-0.857	-1.092	-1.391
$\epsilon_{es-r,AB}^{(12)}$	0.059	0.320	0.300
$\Delta E_{exch,AB}^{(2)}$	0.507	0.574	0.526
$\Delta E_{AB}^{(3)}$	0.118	0.026	0.035
$\Delta E(3)_{AB}$	-4.083	-3.517	-3.558
Three-body			
ΔE_{ABC}^{SCF}	-1.059	-1.054	-1.034
$\Delta E_{exch,ABC}^{HL}$	-0.077	-0.055	-0.056
$\Delta E_{def,ABC}^{SCF}$	-0.982	-0.999	-0.978
$\epsilon_{ind,ABC}^{(20)}$	-0.565	-0.611	-0.591
$\Delta E_{ABC}^{(2)}$	-0.003	0.026	0.015
$\Delta E_{ABC}^{(3)}$	0.027	0.028	0.029
$\epsilon_{disp,ABC}^{(30)}$	0.004	0.016	0.023
$\Delta E(3)_{ABC}$	-1.035	-1.003	-0.990

vity is determined by the SCF deformation effects.

At the correlated level the basis set dependence of the two-body $\Delta E_{AB}^{(2)}$ is largely determined by the dispersion, $\epsilon_{\text{disp}}^{(20)}$, and electrostatic, $\epsilon_{\text{es-r}}^{(12)}$, components. The exchange residue, $\Delta E_{\text{exch},AB}^{(2)}$, is fairly insensitive to the variations in basis set. The dispersion term, as expected, varies strongly with the number and exponent values of polarization functions. For this reason 6-31G** basis gives such a poor result. The basis set *RS* is definitely better, but since it is short of one polarization function on each O and H compared with *S*, its value is underestimated by $\sim 30\%$. This error of about 0.3 kcal/mol makes the total $\Delta E_{AB}^{(2)}$ for the *RS* basis more than half of that for *S*.

The correlated three-body terms are very small and the results obtained with basis *RS* give reliable estimates.

Concluding, the *RS* basis set is expected to yield fairly accurate estimates of all the energy components except for the dispersion, and (less important) electrostatic correlation term. Consequently, the two-body $\Delta E_{AB}^{(2)}$ does not seem basis set saturated. It should be stressed, however, that this deficiency is not serious in the three-body case since both the electrostatics and second-order dispersion are additive.

V. ANISOTROPY OF TWO- AND THREE-BODY TERMS FOR THE CYCLIC TRIMER

A. Total interaction energy

$\Delta E(i)$ ($i = \text{SCF}, 2, 3$) as a function of the angle α are plotted in Fig. 2. The shape of the total interaction is determined by the SCF contribution. The second-order correlation effects lower the curve only slightly. The third-order correlation effects may be considered negligible. The global minimum for the cyclic trimer occurs at about $\alpha = 75^\circ$. There the water molecules assume the H-bond-type geometry [Fig. 1(b)]. The two barriers which occur at 20° and 150° correspond to the H-to-H and O-to-O orientations, respectively. The influence of three-body contributions on geometry is negligible, even for the largest of them, $\Delta E_{\text{def},ABC}^{\text{SCF}}$.

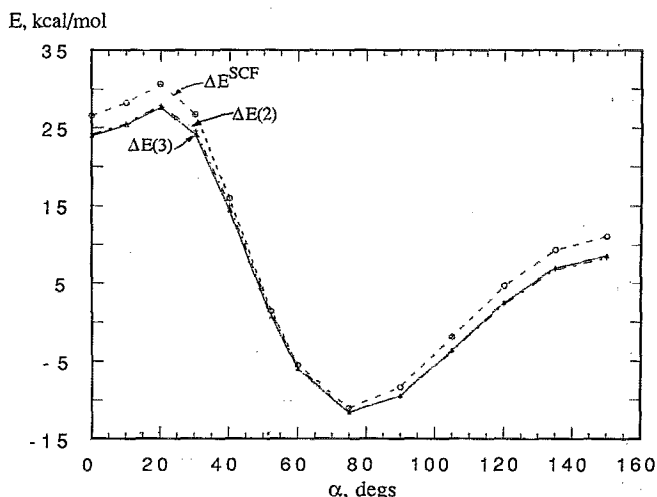


FIG. 2. α dependence of the total interaction energy in the cyclic planar H₂O trimer [see Fig. 1(a), *R* is kept fixed at 3.0 Å] at the SCF, MP2, and MP3 levels of theory (for definitions see the text).

Also, they contribute only a little to the depth of the minimum.

B. Anisotropy of SCF terms

1. Two-body terms

The components of the two-body SCF interaction energy are shown in Fig. 3 and Table III. It is seen that the anisotropy of the SCF interaction is determined by the electrostatic contribution $\epsilon_{\text{es},AB}^{(10)}$. This term generates both a minimum for the H-bond geometry and the barriers for the H-to-H and O-to-O geometries.

The exchange energy behaves differently. It has a maximum at the H-to-H structure from which it rolls down as α increases to reach a broad minimum in the region of O-to-O structure. The effect of the exchange term on the total SCF anisotropy is consequently small.

The $\Delta E_{\text{def},AB}^{\text{SCF}}$ term is relatively small but displays anisotropy reciprocal to $\Delta E_{\text{exch},AB}^{\text{HL}}$. This anisotropy is magnified in Fig. 4 where the induction terms $\epsilon_{\text{ind},AB}^{(20)}$ and $\epsilon_{\text{ind},AB}^{\text{CHF}}$ are also shown. All these terms have a minimum for H-to-H geometry and a flat maximum for O-to-O. It is worthwhile to note that $\epsilon_{\text{ind},AB}^{(20)}$ and $\epsilon_{\text{ind},AB}^{\text{CHF}}$ provide a fairly good approximation to $\Delta E_{\text{def},AB}^{\text{SCF}}$ except for H-to-H region. However, only the SCF deformation curve displays a very noticeable hump around the H-bond geometry. This hump most likely results from the charge-overlap and exchange effects.

2. Three-body terms

The SCF three-body term (see Fig. 5) encompasses the HL exchange and SCF deformation terms, $\Delta E_{\text{exch},ABC}^{\text{HL}}$ and $\Delta E_{\text{def},ABC}^{\text{SCF}}$. The SCF deformation dominates particularly around the H-bond geometry. The O-to-O and H-to-H geometries have also a significant HL exchange component. The anisotropy of the three-body SCF deformation, $\Delta E_{\text{def},ABC}^{\text{SCF}}$

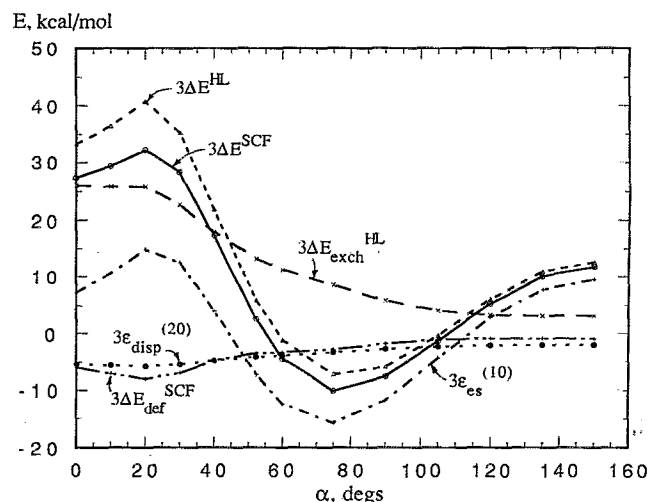


FIG. 3. α dependence of the two-body SCF interaction energy, its various components, and the dispersion component, in the cyclic planar H₂O trimer [see Fig. 1(a); *R* is kept fixed at 3.0 Å; for definitions see the text].

TABLE III. Two- and three-body contributions to the SCF interaction energy (in kcal/mol) in the cyclic H₂O trimer.

α	$\Sigma \Delta E_{AB}^{SCF}$	$\Sigma \epsilon_{ex,AB}^{(10)}$	Two-body			$\Sigma \epsilon_{ind,AB}^{(20)}$	$\Sigma \epsilon_{ind,AB}^{CHF}$
			$\Sigma \Delta E_{exch,AB}^{HL}$	$\Sigma \Delta E_{def,AB}^{SCF}$	$\epsilon_{ind,AB}^{(20)}$		
0.01	27.30	7.212	26.04	-5.953	-8.709	-10.92	
10.0	29.36	10.60	25.84	-7.085	-9.059	-11.46	
20.0	32.24	14.82	25.87	-8.023	-9.399	-11.93	
30.0	28.32	12.57	22.70	-6.952	-8.164	-10.26	
40.0	17.21	4.021	17.87	-4.683	-5.956	-7.299	
52.262	2.510	-7.275	13.21	-3.423	-4.238	-5.040	
60.0	-4.400	-12.38	11.29	-3.304	-3.683	-4.379	
75.0	-10.03	-15.76	8.518	-2.788	-2.804	-3.387	
90.0	-7.533	-11.72	5.901	-1.713	-1.917	-2.319	
105.0	-1.311	-4.326	4.028	-1.013	-1.369	-1.610	
120.0	5.298	2.861	3.254	-0.817	-1.174	-1.339	
135.0	10.07	7.805	3.106	-0.838	-1.145	-1.293	
150.0	11.78	9.542	3.102	-0.866	-1.144	-1.292	

α	ΔE_{ABC}^{SCF}	ΔE_{ABC}^{HL}	Three-body		ΔE_{tot}^{SCF}
			$\Delta E_{def,ABC}^{SCF}$	$\epsilon_{ind,ABC}^{(20)}$	
0.01	-0.764	0.278	-1.042	-1.694	26.54
10.0	-1.137	0.590	-1.727	-2.864	28.22
20.0	-1.565	0.809	-2.374	-3.710	30.67
30.0	-1.595	0.630	-2.225	-3.163	26.73
40.0	-1.244	0.294	-1.538	-1.822	15.97
52.262	-1.087	0.026	-1.113	-0.894	-1.418
60.0	-1.128	-0.033	-1.094	-0.722	-5.527
75.0	-1.054	-0.055	-0.991	-0.611	-11.09
90.0	-0.781	-0.055	-0.726	-0.512	-8.313
105.0	-0.603	-0.079	-0.524	-0.450	-1.914
120.0	-0.603	-0.129	-0.474	-0.457	4.695
135.0	-0.670	-0.179	-0.493	-0.487	9.401
150.0	-0.700	-0.196	-0.504	-0.499	11.08

parallels that of its two-body counterpart, $\Delta E_{def,AB}^{SCF}$. We note here that only for $\alpha > 100^\circ$ does the induction term $\epsilon_{ind,ABC}^{(20)}$ provide a fairly reasonable approximation to $\Delta E_{def,ABC}^{SCF}$. In the H-to-H region $\epsilon_{ind,ABC}^{(20)}$ is far too large in magnitude,

while in H-bond region far too small. As in the two-body case the three-body SCF deformation again displays a noticeable hump around the H-bond structure whereas the respective induction term does not.

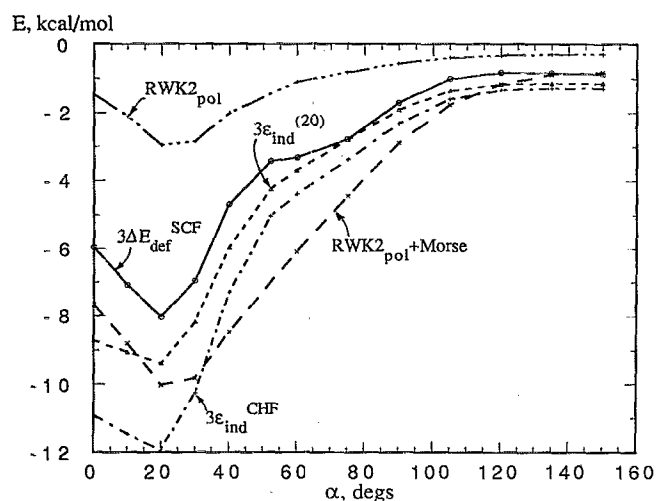


FIG. 4. α dependence of various *ab initio* and empirical approximations to the two-body SCF-deformation energy in the cyclic planar H₂O trimer [see Fig. 1(a); R is kept fixed at 3.0 Å]. RWK2_{pol} + Morse stands for the RWK2_{pol} contribution plus the Morse term of the RWK2-C potential. For other definitions see the text.

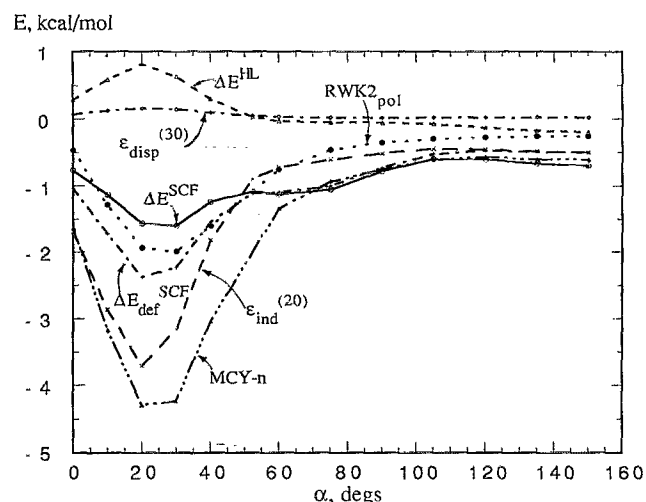


FIG. 5. α dependence of various *ab initio* and empirical three-body terms in the cyclic planar H₂O trimer [see Fig. 1(a); R is kept fixed at 3.0 Å; for definitions see the text].

The HL exchange term behaves in opposite fashion. It provides a maximal repulsion at the H-to-H geometry; then changes sign around H-bond geometry and finally gives a stabilizing contribution for O-to-O geometry. It acts to damp the larger $\Delta E_{\text{def}}^{\text{SCF}}$ effect.

Interestingly, the shapes of two-body and three-body SCF deformation curves are strikingly similar. This is no longer the case for either the analogous exchange terms or for dispersion terms (see below).

C. Anisotropy of correlation terms

1. Two-body terms

The correlation contributions $\Delta E_{AB}^{(2)}$, $\Delta E_{AB}^{(3)}$, $\epsilon_{\text{disp},AB}^{(20)}$, and $\epsilon_{\text{cs-r},AB}^{(12)}$ are presented in Figs. 3 and 6 and Table IV. One can see that the correlation contributions are quantitatively of secondary importance (note the expanded scale in Fig. 6). Although our correlated results are not as accurate as we would like (see discussion in Sec. IV), the following conclusions may be drawn safely.

The most anisotropic component of $\Delta E^{(2)}$ is $\epsilon_{\text{cs-r}}^{(12)}$. As seen from Fig. 6 the $\epsilon_{\text{cs-r}}^{(12)}$ term reveals a behavior roughly reciprocal to $\epsilon_{\text{es}}^{(10)}$ and apparently determines the anisotropy of $\Delta E^{(2)}$. Indeed, the shape of the $\Delta E^{(2)}$ curve is very similar to $\epsilon_{\text{cs-r}}^{(12)}$.

It is interesting to note that $\epsilon_{\text{cs-r}}^{(12)}$ and $\epsilon_{\text{disp}}^{(20)}$ nearly cancel each other in the H-bond region around $\alpha = 75^\circ$. This cancellation makes the total $\Delta E^{(2)}$ term small and extremely basis set dependent, as $\epsilon_{\text{cs-r}}^{(12)}$ and $\epsilon_{\text{disp}}^{(20)}$ are the most basis set dependent quantities.^{17(a)} This fact has previously been noticed in Ref. 23.

2. Three-body terms

Three-body correlation contributions $\Delta E_{ABC}^{(2)}$, $\Delta E_{ABC}^{(3)}$, and $\epsilon_{\text{disp},ABC}^{(30)}$ are shown in Fig. 7. All these terms are much smaller than the three-body SCF contribution. The anisotropy of $\Delta E_{ABC}^{(3)}$ resembles that of $\epsilon_{\text{disp},ABC}^{(30)}$ but one

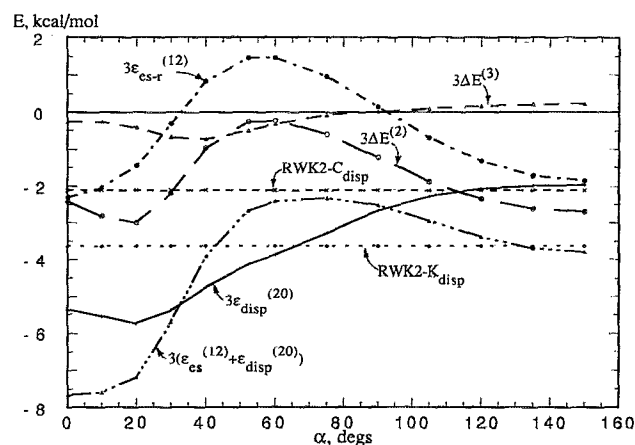


FIG. 6. α dependence of various two-body *ab initio* correlation components of the interaction energy as well as empirical RWK2 dispersion terms, in the cyclic planar H₂O trimer [see Fig. 1(a); R is kept fixed at 3.0 Å; for definitions see the text].

TABLE IV. Two- and three-body contributions to $\Delta E^{(2)}$ and $\Delta E^{(3)}$ terms in the cyclic H₂O trimer (in kcal/mol).

α	$\Sigma \Delta E_{AB}^{(2)}$	Two-body		$\Sigma \Delta E_{AB}^{(3)}$
		$\Sigma \epsilon_{\text{disp}}^{(20)}$	$\Sigma \epsilon_{\text{cs-r},AB}^{(12)}$	
0.01	-2.407	-5.367	-2.292	-0.256
10.0	-2.815	-5.544	-2.042	-0.268
20.0	-2.992	-5.766	-1.446	-0.424
30.0	-2.171	-5.390	-0.314	-0.671
40.0	-0.964	-4.736	0.828	-0.727
52.262	-0.260	-4.131	1.462	-0.498
60.0	-0.238	-3.863	1.461	-0.316
75.0	-0.595	-3.275	0.959	-0.077
90.0	-1.215	-2.667	1.471	0.017
105.0	-1.870	-2.263	-0.680	0.104
120.5	-2.345	-2.058	-1.322	0.167
135.0	-2.615	-1.976	-1.716	0.215
150.0	-2.700	-1.953	-1.844	0.233

α	Three-body		
	$\Delta E_{ABC}^{(2)}$	$\Delta E_{ABC}^{(3)}$	$\epsilon_{\text{disp},ABC}^{(30)}$
0.01	0.079	0.062	0.068
10.0	0.173	0.103	0.120
20.0	0.195	0.166	0.157
30.0	0.100	0.179	0.139
40.0	0.002	0.134	0.090
52.262	-0.026	0.084	0.045
60.0	-0.013	0.060	0.029
75.0	0.026	0.025	0.016
90.0	0.045	0.029	0.014
105.0	0.040	0.023	0.016
120.0	0.028	0.034	0.017
135.0	0.040	0.040	0.018
150.0	0.042	0.042	0.017

should expect that the exchange and deformation correlation ($\Delta E_{\text{exch},ABC}^{(3)}$ and $\Delta E_{\text{def},ABC}^{(3)}$) are also important. The behavior of $\Delta E_{ABC}^{(2)}$ is different and eludes interpretation since we do not know its components $\Delta E_{\text{exch},ABC}^{(2)}$ and $\Delta E_{\text{def},ABC}^{(2)}$. All of the above components are nearly negligible

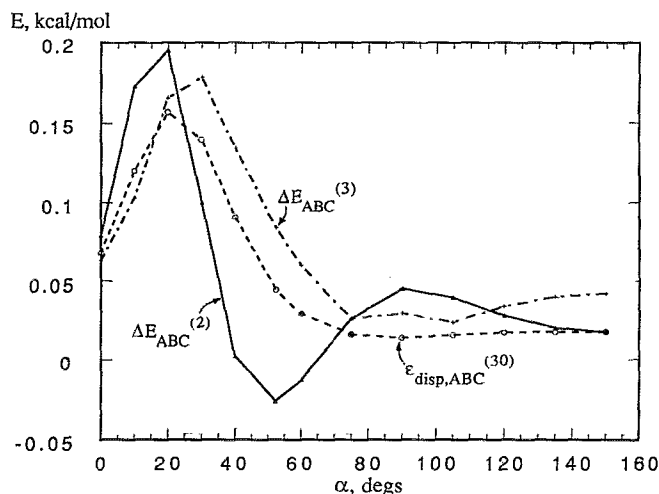


FIG. 7. α dependence of the three-body correlation components of the interaction energy, in the cyclic planar H₂O trimer [see Fig. 1(a); R is kept fixed at 3.0 Å; for definitions see the text].

in the cyclic trimer; their behavior is of interest in model considerations.

VI. *R* DEPENDENCE OF THREE-BODY TERMS IN d-a, d-d, AND a-a CONFIGURATIONS

The *R* dependence of the three-body contributions is reported in Table V.

A. d-a geometry

One can see from the first row of the table that the two-body SCF interaction has a minimum around $R = 3.0 \text{ \AA}$. At that distance $\Delta E_{ABC}^{\text{SCF}}$ and its components, $\Delta E_{\text{def},ABC}^{\text{SCF}}$ and $\Delta E_{ABC}^{\text{HL}}$, amount to 10.5, 10.0, and 0.5%, respectively, of the total SCF contribution. All of these three-body terms are attractive over the entire range of *R* considered; $\Delta E_{\text{def},ABC}^{\text{SCF}}$ provides the dominating contribution. $\epsilon_{\text{ind},ABC}^{(20)}$ provides only a crude approximation to $\Delta E_{\text{def},ABC}^{\text{SCF}}$ as it reproduces only 40% at $R = 2.5 \text{ \AA}$ and 80% at $R = 5.0 \text{ \AA}$. The dispersion nonadditivity $\epsilon_{\text{disp},ABC}^{(30)}$ is negligible at every *R*.

B. d-d geometry

The two-body SCF interaction reveals a minimum at around 3.5 \AA . As a percentage contribution of the total two-

body SCF interaction the $\Delta E_{ABC}^{\text{SCF}}$ term and its components, SCF deformation and HL exchange, constitute 3.1, 1.3, and 1.8%, respectively, in the minimum. All the terms are attractive over the entire range of *R* although much less so than in the d-a case. Unlike for the d-a structure, both $\Delta E_{\text{def},ABC}^{\text{SCF}}$ and $\Delta E_{ABC}^{\text{HL}}$ are *equally* important. Interestingly, $\epsilon_{\text{ind},ABC}^{(20)}$ is of opposite sign to $\Delta E_{\text{def},ABC}^{\text{SCF}}$ and, therefore, cannot be used to approximate it. $\epsilon_{\text{disp},ABC}^{(30)}$ is again quite negligible.

C. a-a geometry

The minimum for the two-body SCF interaction energy occurs around 3.0 \AA . The SCF three-body contribution is destabilizing over the entire range of *R* considered. In the minimum it amounts to -11.1% of the total SCF two-body term, with $\Delta E_{\text{def},ABC}^{\text{SCF}}$ and $\Delta E_{ABC}^{\text{HL}}$ (of opposite sign) contributing, respectively, -13.1 and $+2.0\%$. The induction nonadditivity $\epsilon_{\text{ind},ABC}^{(20)}$ approximates the SCF nonadditivity fairly well, as it yields between 81% (minimum) and 75% ($R = 5 \text{ \AA}$) of $\Delta E_{\text{def},ABC}^{\text{SCF}}$. The dispersion nonadditivity is again negligible.

In all the three configurations considered Table V lists also the correlated nonadditive components $\Delta E_{ABC}^{(2)}$ and $\Delta E_{ABC}^{(3)}$. In all the cases studied these components are truly negligible compared with the sum of the two-body SCF

TABLE V. Three-body contributions to the interaction energy for the d-a, d-d, and a-a geometries (in kcal/mol).

<i>R</i> , Å	2.5	2.75	3.0	3.5	4.0	5.0
d-a						
$\Sigma \Delta E_{AB}^{\text{SCF}}$	1.269	-8.376	-10.03	-7.645	-5.016	-2.334
$\Delta E_{ABC}^{\text{SCF}}$	-4.484	-2.085	-1.054	-0.332	-0.128	-0.028
$\Delta E_{ABC}^{\text{HL}}$	-0.683	-0.189	-0.055	-0.006	-0.001	0.0
$\Delta E_{\text{def},ABC}^{\text{SCF}}$	-3.801	-1.896	-0.999	-0.327	-0.127	-0.028
$\epsilon_{\text{ind},ABC}^{(20)}$	-1.557	-1.004	-0.611	-0.229	-0.094	-0.022
RWK2 _{pol}	-1.914	-0.905	-0.467	-0.153	-0.060	-0.013
$\epsilon_{\text{disp},ABC}^{(30)}$	0.077	0.034	0.016	0.004	0.001	0.0
$\Delta E_{ABC}^{(2)}$	0.334	0.103	0.026	-0.002	-0.002	-0.001
$\Delta E_{ABC}^{(3)}$	-0.028	0.034	0.026	0.011	0.005	0.001
d-d						
$\Sigma \Delta E_{AB}^{\text{SCF}}$	28.16	8.903	1.790	-0.976	-0.774	-0.257
$\Delta E_{ABC}^{\text{SCF}}$	-0.338	-0.246	-0.141	-0.031	-0.002	0.003
$\Delta E_{ABC}^{\text{HL}}$	-0.028	-0.170	-0.086	-0.018	-0.003	0.0
$\Delta E_{\text{def},ABC}^{\text{SCF}}$	-0.062	-0.076	-0.055	-0.014	0.001	0.003
$\epsilon_{\text{ind},ABC}^{(20)}$	0.419	0.119	0.030	0.003	0.004	0.002
RWK2 _{pol}	0.676	0.269	0.120	0.029	0.009	0.001
$\epsilon_{\text{disp},ABC}^{(30)}$	0.016	0.004	0.001	0.0	0.0	0.0
$\Delta E_{ABC}^{(2)}$	-0.102	-0.033	-0.032	-0.007	-0.004	-0.001
$\Delta E_{ABC}^{(3)}$	0.032	0.011	0.007	0.004	0.002	0.001
a-a						
$\Sigma \Delta E_{AB}^{\text{SCF}}$	8.555	-2.091	-4.763	-1.820	-2.564	-0.979
$\Delta E_{ABC}^{\text{SCF}}$	1.800	0.960	0.530	0.185	0.077	0.018
$\Delta E_{ABC}^{\text{HL}}$	-0.477	-0.210	-0.095	-0.019	-0.003	0.0
$\Delta E_{\text{def},ABC}^{\text{SCF}}$	2.278	1.170	0.625	0.204	0.080	0.018
$\epsilon_{\text{ind},ABC}^{(20)}$	1.176	0.740	0.427	0.147	0.058	0.013
RWK2 _{pol}	1.627	0.689	0.336	0.104	0.040	0.009
$\epsilon_{\text{disp},ABC}^{(30)}$	0.032	0.007	0.001	-0.0	0.0	0.0
$\Delta E_{ABC}^{(2)}$	0.076	0.056	0.044	0.025	0.012	0.003
$\Delta E_{ABC}^{(3)}$	0.013	-0.007	-0.011	-0.008	-0.004	-0.001

terms. Although we are at present unable to identify their origin, it may be noticed that they display a nonvanishing long-range behavior. On the other hand, both exchange–correlation and dispersion nonadditivities are fast-decaying functions of R . Therefore, it is justifiable to suspect that $\Delta E_{ABC}^{(2)}$ and $\Delta E_{ABC}^{(3)}$ are, at least for R larger than minimum, dominated by the deformation correlation effects.

VII. COMPARISON WITH OTHER POTENTIALS

Our total potential is compared with several others in Fig. 8 and in Table VI. The following empirical potentials are included: TIP3P,¹ TIP4P,¹ RWK2-K,^{27,28} RWK2-C,⁵ and SCP,^{4,29} as well as *ab initio*, old MCY (MCY-o)⁷ and the newly revised MCY-n⁸ (the last two are presented only in Table VI).

As seen from Table VI and Fig. 8 all the potentials except for ours yield very close results for the energy of the minimum H-bond structure. The reason is rather trivial, namely, all of them were adjusted to reproduce experimental well depth for the optimal dimer structure. On the other hand, even the most elaborate *ab initio* calculations which properly remove BSSE at both the SCF and correlated levels yield too small a well depth^{23,30,31} which may be attributed to extreme difficulties in basis set saturation of the dispersion term. (The MCY-n potential appears as deep as the empirical ones due to an incomplete removal of BSSE.)

The potentials differ markedly for the H-to-H repulsive structure around $\alpha = 20^\circ$. It is impossible at this point to indicate which one is the most reliable. However, we may expect that those which are considerably more repulsive than ours may be unreliable. This is particularly the case of RWK2-K and MCY-o. For the O-to-O structure near $\alpha = 150^\circ$ our potential is the least repulsive except for SPC (see Table VI). However, the difference is quite small.

As seen from the above discussion the differences among total potentials cannot be readily interpreted. It should be remembered that none of these potentials is claimed to be accurate over the entire range of intermolecu-

TABLE VI. Comparison of various *ab initio* and empirical potentials for water. All values in kcal/mol.

α , degs	20.	75.	150.
$\epsilon_{es}^{(10)}$	Electrostatic		
	14.82	-15.76	0.946
$\epsilon_{es-r}^{(12)}$	-0.482	0.319	-0.615
RWK2-K	23.87	-13.50	8.852
MCY-o	33.67	-18.72	12.15
MCY-n	27.01	-15.55	10.30
	Exchange		
ΔE_{exch}^{HL}	25.87	8.518	3.102
RWK2-K	28.19	4.886	4.111
RWK2-C	6.723	6.723	6.723
MCY-o ^a	66.70	11.97	1.545
	Polarization (2-body)		
ΔE_{def}^{SCF}	-10.40	-3.790	-13.70
RWK2 _{not}	-4.883	-1.286	-0.555
RWK2-K ^b	-5.095	-1.465	-0.555
RWK2-C ^b	-10.03	-4.448	-0.813
MCY-n ^c	-4.621	-1.503	-0.632
	Polarization (3-body)		
ΔE_{def}^{SCF}	-2.374	-0.999	-0.504
RWK2-C	-1.938	-0.467	-0.259
MCY-n	-4.293	-0.936	-0.609
	Dispersion		
$\Delta E^{(2)}$	-2.993	-0.595	-2.700
$\epsilon_{disp}^{(20)}$	-5.736	-3.275	-1.953
RWK2-K	-3.626	-3.626	-3.626
RWK2-C	-2.101	-2.101	-2.101
	Total		
$\Delta E^{SCF} + \Delta E^{(2)}$	27.68	-11.68	8.377
$\Delta E^{SCF} + \epsilon_{disp}^{(20)}$	24.93	-14.36	9.124
ΔE^{SCF}	30.67	-11.09	11.08
RWK2-K	43.34	-13.70	8.781
RWK2-C	18.47	-13.32	12.66
MCY-o	87.32	-14.79	12.32
MCY-n	30.86	-14.99	9.675
TIP3P	17.07	-14.54	13.82
TIP4P	22.04	-14.16	11.99
SPC	19.88	-15.45	7.122

^a Exchange repulsion cannot be uniquely extracted from MCY-o potential.

^b The Morse term included.

^c Polarization cannot be extracted from the MCY-o potential.

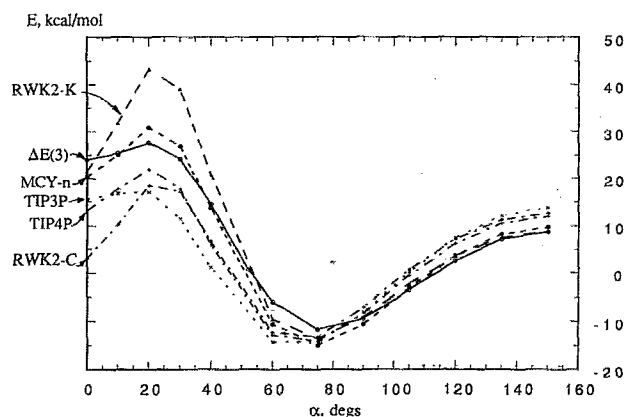


FIG. 8. α dependence of different *ab initio* and empirical potentials for the cyclic planar H₂O trimer [see Fig. 1 (a)]; R is kept fixed at 3.0 Å; for definitions see the text].

lar geometries. The quality of a potential is usually verified indirectly, i.e., through computer simulations. Furthermore, its functional form and parameters do not necessarily reflect the physical origin of various contributions to the interaction energy. In addition, it is possible to obtain two similar total potentials as a balance of completely different constituent terms. Therefore, the recent trend is to construct a total potential from well defined and physically meaningful contributions which can be derived, at least to some extent, separately. Such a philosophy has been adopted very successfully in the case of atom–atom³² and atom–diatom potentials.^{33,34} This trend is also represented by the RWK2 family of potentials for water² (see also Ref. 9). In the latter, the form as well as the parameters are designed to reflect the state-of-the-art knowledge of the contributions which enter the interaction energy. Consequently, the RWK2 potential

accounts for the electrostatic, exchange, polarization, and dispersion contributions as separate terms. Let us discuss in more details the RWK2-C⁵ and RWK2-K^{27,28} potentials and their respective components (Fig. 4 and Table VI). Whenever possible the *ab initio* potentials by Clementi's group, MCY-o (Ref. 7) and MCY-n (Ref. 8) will also be considered.

Both the RWK2 potentials employ the same four-point model to describe electrostatic energy and the related polarization contribution. They differ in the exchange, dispersion, and Morse terms. RWK2-K accounts for the exchange term by allowing for the O-O and H-H repulsions, whereas RWK2-C retains only O-O, differently parametrized. The dispersion component in RWK2-K includes C_6/R^6 , C_8/R^8 , and C_{10}/R^{10} van der Waals terms, while RWK2-C retains only C_6/R^6 . The Morse term is also parametrized differently in both potentials. Although originally designed to account for the so-called charge-transfer effects, the Morse term seems to make up for deficiencies of the other terms.

A. Electrostatic energy

The anisotropy of electrostatic energy predicted by potentials RWK2-K and RWK2-C is qualitatively similar to the one in the present *ab initio* potential. Quantitatively, the present *ab initio* curve lies slightly lower, except for the O-to-O configuration. This is due to the fact that the RWK2 electrostatic was fitted so as to reproduce the multipole expanded electrostatic interaction through the quadrupole-quadrupole term at the SCF level. The difference is largely due to interactions of higher moments, as well as to charge-overlap effects. This difference is quite substantial at smaller R . Therefore, one may question the adequacy of such an approach.

The *ab initio* MCY-o potential has too large an electrostatic contribution everywhere. The MCY-n, on the other hand, is still too large for H-to-H but approaches our result for H-bond and O-to-O configuration. This fact should be considered as a definite improvement in the new MCY potential.

B. Exchange energy

As pointed out above, the exchange terms in the RWK2-K and RWK2-C potentials are essentially different. The RWK2-C potential involves only the isotropic exchange contribution which describes the O-O repulsion. For this reason it is particularly inaccurate in the H-to-H region. RWK2-K has additional H-H terms. This fact ensures that the exchange anisotropy is qualitatively similar to ours. Quantitatively, RWK2-K_{exch} is reasonable for H-to-H, much too small for H-bond, and somewhat too large for O-to-O (see Table VI).

It should be stressed at this point that our electrostatic and exchange terms are accurate enough at the SCF level so that they could serve as reliable reference.

C. Polarization contribution

Polarization component of the RWK2-K and RWK2-C potentials has a "classic" form involving polarizabilities lo-

cated at different centers in one water molecule interacting with the field created by point charges of the other water molecules. The polarization term so defined accounts for both two- and three-body polarization contributions.

The two-body polarization contribution is shown in Fig. 4 and Table VI. It is seen that it yields a substantially smaller polarization effect than our SCF deformation term. Moreover, due to a simple 3-point electrostatic model in RWK2, the curve is perfectly smooth in the H-bond region in contrast to the irregularities observed in the *ab initio* result. It is worthwhile to note that the RWK2 polarization term is also close to that of the MCY-n potential. Although the polarization component is identical in both RWK2-C and RWK2-K the Morse terms are completely different. The Morse term is quite large in the RWK2-C potential, but nearly negligible in RWK2-K. Due to the fact that the Morse term may be viewed as accounting for "charge-transfer" effects it should be considered together with polarization contribution; their sum may be comparable with the $\Delta E_{\text{def}}^{\text{SCF}}$ *ab initio* term. Interestingly, in the RWK2-C case the Morse term makes up fairly well for the difference between our $\Delta E_{\text{def}}^{\text{SCF}}$ and the RWK2 polarization (see Fig. 4 and Table VI).

The three-body polarization contribution is shown in Fig. 5 and Table VI. It is much smaller than our three-body SCF deformation energy. The three-body term of the MCY-n potential is close to our result except for the H-to-H configuration (cf. Table VI).

D. Dispersion term

Dispersion terms of the RWK2-C and RWK2-K potentials are presented in Fig. 6 and Table VI. Both represent dispersion as isotropic and it is pointless to discuss which one is better. It should be mentioned that for the H-bond geometry the RWK2-C dispersion is not attractive enough, presumably due to the fact that the sum of all the other terms already provides a sufficient stabilization.

E. R dependence of three-body contributions.

Structures: d-a, d-d, a-a

The R dependence of the three-body contribution RWK2_{pol} is reported in Table V for the H-bonded structures d-a, d-d, and a-a.

For d-a geometry the RWK2's three-body term yields uniformly some 50% of $\Delta E_{\text{def}}^{\text{SCF}}$.

For d-d geometry the RWK2's three-body term, similarly as $\epsilon_{\text{ind}}^{(20)}$, is of opposite sign to $\Delta E_{\text{def}}^{\text{SCF}}$ and thus cannot be used as an approximation to it.

For a-a geometry the RWK2's three-body term amounts to 90% of $\Delta E_{\text{def}}^{\text{SCF}}$ at $R = 2.5 \text{ \AA}$ but it vanishes more quickly and at $R = 5 \text{ \AA}$ $\Delta E_{\text{def}}^{\text{SCF}}$ is twice as large as RWK2_{pol} .

VIII. SUMMARY AND CONCLUSIONS

Since the pioneering work of Clementi *et al.*¹⁰ is has been known that the nonadditive effects in water, although fairly small, cannot be neglected in computer simulations of

liquid water^{35,36} as well as in rationalization of the structure of ice.³⁷ On the basis of indirect evidence Clementi *et al.*¹⁰ postulated that the major component of the nonadditivity of interaction in water trimer originates from the electric polarization and hence can be reproduced at the SCF level.

To unambiguously identify the nature of nonadditive effect it is necessary to dissect this effect into its constituting fragments and analyze their properties on an individual basis. Such strategy was employed in the present work where the total nonadditivity was evaluated along with its components for several representative geometries of (H₂O)₃.

It has been shown that the total nonadditive effect is dominated by the SCF deformation nonadditivity for the cyclic planar, a–a and d–a geometries. $\Delta E_{\text{def}}^{\text{SCF}}$ indeed arises from the electric polarization. However, this polarization is severely constrained by the Pauli exclusion principle applied to intermolecular electron exchanges. This effect, sometimes misleadingly attributed to “charge transfer” effect, is by no means negligible. Due to its quantum nature the commonly used classic models of polarization may fail to reproduce $\Delta E_{\text{def},ABC}^{\text{SCF}}$. Such failure usually happens in regions of high overlap where the exchange effects are important.^{38,39} Furthermore, in such areas the leading exchange nonadditivity $\Delta E_{\text{exch},ABC}^{\text{HL}}$ may compete with $\Delta E_{\text{def},ABC}^{\text{SCF}}$. The d–d configuration serves as a good example of such a situation. As demonstrated here the $\Delta E_{\text{exch},ABC}^{\text{HL}}$ exceeds $\Delta E_{\text{def},ABC}^{\text{SCF}}$ in this structure. Furthermore, the classic polarization model predicts the wrong sign of the latter.

In agreement with the previous findings by Koehler *et al.*¹¹ and Habitz *et al.*⁴⁰ the contribution from correlation effects to nonadditivity is negligible. With regard to these effects it seems that the deformation correlation seems no less important than the third-order dispersion.

The above facts shed new light on the possible functional form and parametrization of the intermolecular water potential. In particular, it seems that classic polarization is too poor a model. The exchange effect allowed for in $\Delta E_{\text{def},ABC}^{\text{SCF}}$ must not be neglected. Due to the fact that its asymptotic behavior should be the same as for $\Delta E_{\text{exch},ABC}^{\text{HL}}$, these two terms may safely be combined together in the same functional form. It should be mentioned that the explicit three-body exchange term has been included in potentials for ion–water simulations.^{27,41}

In conclusion, we point out the necessity of a critical reevaluation of the two-body potentials. It appears that the open-ended models such as RWK2 which rely to a large extent on the physical origin of the interaction phenomenon are the most promising. In such models, for example, a reexamination of one term, say dispersion, does not necessarily require extensive reparametrization of the entire potential.

It may be pointed out at this juncture that the use of a truncated multipole expansion to describe electrostatic,^{27,28,42} and dispersion² terms may lead to a serious overestimation of these terms. The charge-overlap effects are usually significant around the minimum. Furthermore, it is expected that this problem worsens for terms which are of higher order with respect to intermolecular perturbation. The means of damping such terms as dispersion are to a large degree arbitrary.

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