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***Ab initio* calculations as a source of intermolecular potential functions. Ethanol–water with a minimal basis set**

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The potential energy surface of the (*trans*)ethanol–water dimer has been explored with *ab initio* quantum mechanical calculations employing a minimal basis set to obtain a potential function suitable to computer simulations of the relevant aqueous solution. In all, 410 interaction energy values has been calculated. A part of the complex geometries has been produced approaching the water molecule to the ethanol along 17 different axes, and a part with an iterative random procedure. On this data base a fit with the experimental geometry of the water molecule and one with the ST2 model have been performed, with standard deviations of 0.69 and 0.73 kcal/mole, respectively. A limited test concerning the role of the three body term in open chain trimers has also been carried out. Finally, these SCF calculations have been used to check the possibility of the electrostatic approximation and of the pair potential library given by Clementi, to provide reliable intermolecular potential energy values in this kind of systems.

I. INTRODUCTION

Hydrogen bonded systems have been the subject of an increasing number of studies in recent years. Among the many reviews published on this topic, that by Schuster, Zundel, and Sandorfy¹ extensively covers both experimental and theoretical aspects of this field of research, while the more recent by Schuster² presents a summary of the new computational results reported between 1976 and 1978.

A part of these studies has been conceived to provide analytical potential energy functions representative of *ab initio*^{3–9} quantum mechanical calculations of intermolecular interactions. This is one of the two main approaches to solve the problem of producing potential functions suitable for computer simulations of molecular fluids and solutions, the other one deriving such functions by a numerical fit of some model interactions (e.g., Lennard-Jones and Coulomb) to experimental data. The latter, however, are usually available for a small region of the potential energy surface of a small number of systems. Thus, they can be more useful as a standard to be compared with the results of quantum mechanical calculations than as a direct source of potential energy functions. This use of experimental data as a test is particularly important, since it has been shown¹⁰ that more sophisticated SCF calculations do not necessarily improve the quality of the results of the simulation. To summarize, a typical example of the so called theoretical or *ab initio* treatment of a molecular system in a condensed phase can be considered to be made of three steps. In the first, a number of dimer geometries are selected for each pair of molecular species in a way which ensures that the potential energy surface of the relevant complex has been extensively sampled, and their interaction energies are calculated with quantum mechanical techniques. Then an analytical function is fitted on this set of energy values (second step) to obtain an expression to be used in the third step, i.e., the computer simulation of the molecular assembly with Monte Carlo or molecular dynamics methods.

In this paper we report on the first two steps as ap-

plied to the water–ethanol dimer, for which *ab initio* computations as well as experimental data in gas phase are not available, to our knowledge. The dilute aqueous solution of ethanol, which on the contrary has been thoroughly studied, is presently being simulated in the third step of the above scheme and will be the subject of a forthcoming paper.

II. DETAILS OF CALCULATION

Two main methods have been used in literature to select dimer geometries: the grid search, in which a molecule is placed at the crossing points of a more or less regular grid that surrounds the other molecule, and the technique proposed by Harrison *et al.*⁵ The latter consists of an iterative procedure starting with the random generation of a number (~ 100) of geometries of the complex, whose interaction energies are quantum mechanically calculated. A model potential function is fitted to these points, allowing the dimerization energies of a new set of random geometries to be predicted. The statistical error of this estimate is determined by calculating the corresponding *ab initio* energy values and comparing them with the predicted ones. The process is then repeated until the errors on the predicted and calculated values match within a given tolerance.

The method we have used in this work can be considered a compromise between those sketched above, i.e., we let a water molecule approach the ethanol molecule along 17 directions, 13 of which are shown in Fig. 1. These directions have been chosen to ensure a good sampling of the more interesting regions of the potential surface, and to guarantee that the data for the fit enclose a sufficient number of low energy points, which, on the contrary, are rarely produced by a random generation of dimer geometries, as also pointed out by Jorgensen.⁸ For a given distance between oxygen of water and the origin of each axis, several different orientations of the water molecule have been considered. Points with predicted interaction energies above 10.0 kcal/mole have been rejected as they are sampled with negligible probability in the simulation. The range of separations explored is from 2.3 to 11.0 Å and 250

points have been collected this way. This set has been the data base for a first fit, which has been used to predict the interaction energies of a new set of complex configurations with random positions and orientations of the water molecule, whose only constraint was to be in the less explored regions of the potential surface. Three sets of 40 energy values were sufficient to reach convergence, in the meaning explained above. A fourth set was tested for safety and the total number of points at the end of the SCF calculations was 410. The geometries of the monomers were kept fixed throughout this work with experimental values of their internal coordinates. Those adopted for water¹¹ are 0.9572 Å and 104.52° for bond length and angle, respectively. The geometrical parameters of *trans*-ethanol¹² in its staggered conformation are collected in Table I. The energies of the isolated monomers are -75.733 06 a.u. for water and -153.464 897 a.u. for ethanol. The internal barrier found for a rotation around the C-O bond is 3.1 kcal/mole. The basis set used in this work is the van Dujneveldt's (7, 3, 3) minimal basis set contracted to (2, 1, 1). The exponents and contraction coefficients are given in Ref. 13. About 150 sec were required to generate each energy value with the GAUSSIAN/70 program¹⁴ on an IBM 370/168. The calculated interaction energies ranged from -9.5 to 9.8 kcal/mole.

III. POTENTIAL FUNCTIONS AND RESULTS

Three different models for the ethanol monomer and two for water have been tested during the fitting step. First, hydrogens belonging to the hydrocarbon moiety of ethyl alcohol have been removed to reduce the number of distances to be evaluated at each step of the simulation.^{7,15} An obvious consequence of this exclusion is that conformational effects involving a methyl rotation around the C-C bond cannot be studied: however, the time saving was judged to compensate for this drawback. Two pseudoatomic centers were later substituted to the

TABLE I. Geometry of *trans*-ethanol in its staggered conformation (see Fig. 1).

Distances (Å)		Angles (deg)	
C1-C2	1.5115	C1C2O	107.77
C2-O	1.4310	C2OH	105.43
O-H	0.9710	C1C2H	110.72
C2-H	1.098	HC2H	107.97
C1-Hs	1.088	C2C1Hs	110.49
C1-Ha	1.091	C2C1Ha	110.13
		HsC1Ha	108.79
		HaC1Ha	108.45

hydrogens, one lying along the HC2H bisector and the other along the C-C bond, on the opposite side of C2, their distance from the closest carbon being an adjustable parameter. Introducing the latter point turned out to be convenient, while the former was discarded, so the model finally adopted contains four atoms C1, C2, O and H, plus a pseudoatomic center PSH, 0.5 Å far from C1. The water models mentioned above are the experimental molecule and the well-known ST2 water,¹⁸ which have been used for two separate fits (see below).

Many functional forms have been fitted to the first data base of 250 points, and finally the power series below has been selected:

$$V = \sum_i \sum_j a_{ij} r_{ij}^n, \quad (1)$$

with $i \in \text{C}_2\text{H}_5\text{OH}$, and $j \in \text{H}_2\text{O}$. The summations run over atomic and pseudoatomic centers of the molecules and the a 's are adjustable parameters. The exponents were allowed to assume the values 1, 3, 6, and 12 to take the Coulombic, dipole, and short range interactions into account. However, the expression above has been used only as a starting point, i.e., the multiple linear regression program¹⁷ was let free to enter or remove any term of Eq. (1), aiming only at a minimal standard deviation of the fit. On the other hand, a particular physical meaning cannot be given to fitting functions like these, since, as stressed by other authors^{7,18} they include parameters which are coupled and not unique. To enhance the quality of the fit in the low energy regions, point i was given a weight $w_i = 1 + \alpha \exp[(\Delta E_{\text{min}} - \Delta E_i)/RT]$, where ΔE_i is the interaction energy of point i and ΔE_{min} is the interaction energy of the absolute minimum. The α 's chosen were 30 in number for the experimental model and 40 for the ST2, with RT taken as 0.6 kcal/mole.

Table II collects the optimized values of the parameters in a way that also shows the functional form finally adopted. As can be seen, the total number of parameters is 18 in both cases, this value being a compromise between the opposite needs of accuracy and computational speed. The standard deviations of the fits are, in kcal/mole: $\sigma_{<10} = 0.69$, $\sigma_{<0} = 0.53$, $\sigma_{<-3} = 0.64$ for the experimental model and $\sigma_{<10} = 0.73$, $\sigma_{<0} = 0.63$, and $\sigma_{<-3} = 0.68$ for the ST2 one, where $\sigma_{<x}$ is the standard deviation for all points with interaction energy lower than X kcal/mole. The quality of the fits can also be appreciated from Fig. 2. Both of the fitting functions have

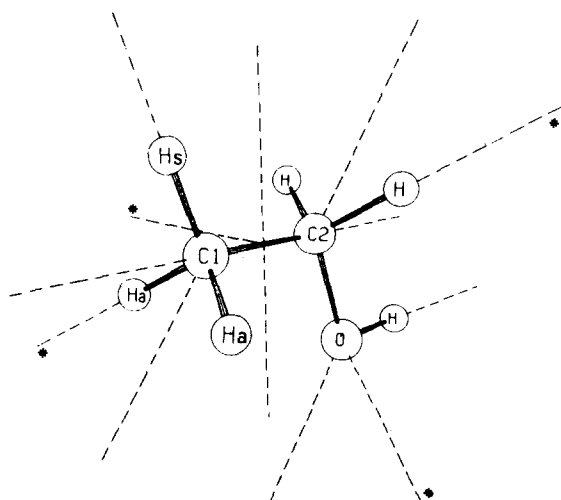


FIG. 1. Approach directions of the water oxygen toward the ethanol molecule. Each axis marked with an asterisk has its own symmetric, not shown for clarity, with respect to the C1C2O plane.

TABLE II. Optimized values of the parameters^a of the ethanol-water intermolecular potential energy functions. Upper part: fit for the experimental model of water molecule; lower part: fit for the ST2 model.

Center on EtOH (<i>i</i>)	Center on H ₂ O (<i>j</i>)	Inverse power of r_{ij}			
		6	12	3	1
C1	O				
	H	0.505 392 + 03		0.553 956 + 02	
PSH ^b	O		0.141 561 + 06		
	H			- 0.488 636 + 02	
C2	O		0.160 374 + 07	- 0.203 432 + 03	
	H	- 0.178 039 + 04	0.114 992 + 06	0.120 114 + 03	
O	O		0.333 185 + 06	0.279 466 + 03	
	H	0.322 725 + 03		- 0.182 549 + 03	
H	O	0.285 587 + 03		- 0.205 484 + 03	
	H	- 0.481 130 + 03	0.559 262 + 04	0.127 275 + 03	
C1	O		0.174 035 + 07		
	H				
	lp	- 0.694 199 + 03			
PSH ^b	O		- 0.942 213 + 05		
	H				
	lp	0.224 566 + 03			
C2	O	0.348 669 + 04			
	H				
	lp			- 0.500 927 + 02	
O	O		0.447 422 + 06		
	H	0.199 392 + 03		- 0.125 528 + 03	
	lp	- 0.531 897 + 03		0.123 721 + 03	
H	O	0.206 294 + 03		- 0.137 261 + 03	
	H			0.407 877 + 02	0.133 366 + 02
	lp	0.147 086 + 01	- 0.307 100 - 01		- 0.105 203 + 02

^aUnits consistent with distances in Å and energies in kcal/mole.^bPSH is the pseudoatomic center 0.5 Å far from C1 (see text).

been tested to exclude spurious minima which actually have not been found in the range of intermolecular separations occurring in a simulation with ~100 water molecules.

Figures 3 and 4 show the effect of varying O-O separation and θ , respectively, on the interaction energy of the dimer with water as a proton acceptor (hereafter referred to as the EtW dimer). Similar comments can be made for Figs. 5 and 6, which relate to the complex with water as the proton donor molecule (WEt dimer). In Figs. 3 and 5 the distance has been varied choosing the significant angles (θ in Fig. 3, both α and ζ in Fig. 5) at their optimum values, while the variation of the angles (Figs. 4 and 6) has been carried out at the O-O distance of minimal energy. On the whole, the comparison between calculated and predicted energies, shown by these curves, confirms the goodness of the fits in these regions, by far the most extensively sampled in both Monte Carlo and molecular dynamics simulations.

The geometry of both open chain dimers EtW and WEt has been carefully optimized with the SCF calculations, and the results are given in Table III. As can be seen, the stronger hydrogen bond is associated with the shorter O-O separation in the dimer EtW. This is consistent

with the results by Del Bene¹⁹ for the analogous dimers between methanol and water at a STO-3G level, while the agreement breaks down if one considers the angles. The latter effect could originate from the fixed experimental geometries we have used for the monomers. Actually, the same basis set (STO-3G) produces different optimized geometries and binding energies for the

TABLE III. Optimized geometries^a and dimerization energies for the dimers EtW and WEt.

		SCF	Expt. model	ST2
EtW	R_{∞}^b	2.75	2.66	2.65
	θ^c	46.0	10.0	45.0
	$-\Delta E^d$	9.49	9.94	10.12
WEt	R_{∞}^b	2.84	2.76	2.75
	α^c	54.0	54.0	20.0
	$-\Delta E^d$	7.69	7.39	7.62

^aFor the definition of the geometrical variables see Figs. 4 and 6.^bAngstroms.^cDegrees.^dkcal/mole.

dimer methanol-methanol, according to whether optimized¹⁹ monomer geometries are used or not.²⁰ The agreement between the results of SCF computations and those predicted by the fitting potentials can be considered satisfactory, except for the angle θ of the EtW dimer and α of WEt, which are underestimated by the experimental and ST2 model, respectively. The former error is probably due to the use of a three point model for the water molecule (the experimental geometry in our case), as the same defect has been observed when the three point charges model of Matsuoka *et al.*¹⁴ has been used to fit the water dimer potential

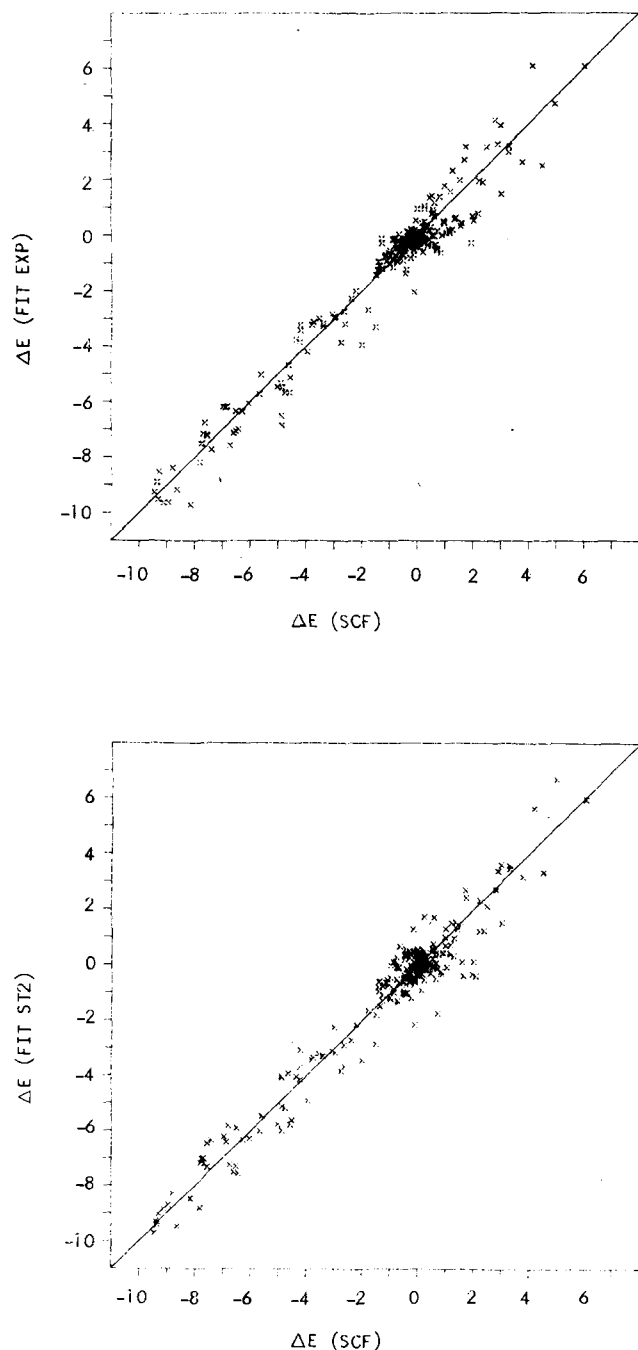


FIG. 2. Scatter diagrams of the SCF calculated and fitted interaction energies (kcal/mole). Upper part: fit with the experimental geometry of the water molecule, lower part: fit with the ST2 model.

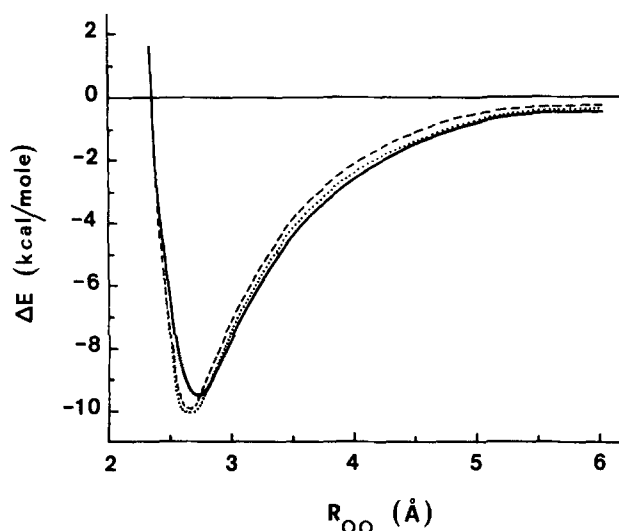


FIG. 3. Variation of the interaction energy of the dimer EtW with O-O separation. Full line: SCF calculations, dashed line: fit with the experimental geometry of the water molecule, dotted line: fit with the ST2 model.

surface explored at the CI^4 or SCF(STO-3G)⁸ level. Actually, the lack of points representative of the oxygen lone pairs prevents these models from being highly orientation dependent, as is also proved by the better reproduction of the θ value obtained by Jorgensen⁸ turning to the ST2 model. Furthermore, it can be noted that the curves of Figs. 4 and 6, for the experimental and ST2 model, respectively, are rather flat and close, on the whole, to the corresponding SCF ones, so that the errors on the angle value should not damage the results of a simulation employing these potentials. As to the values of the binding energies we have found for

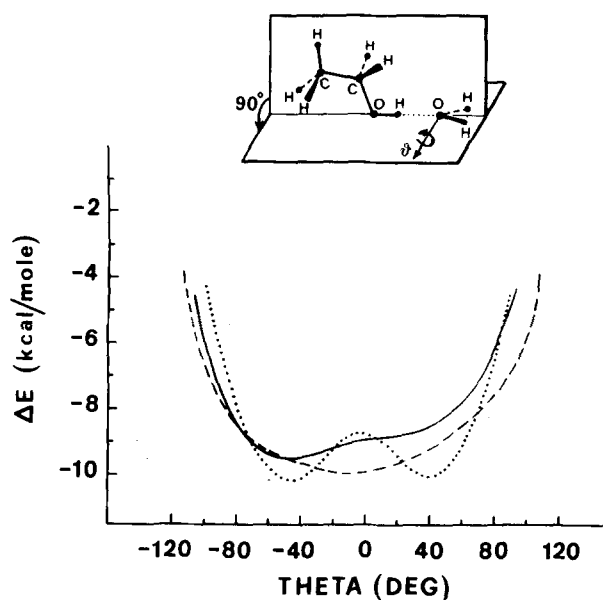


FIG. 4. Variation of the interaction energy of the dimer EtW with angle θ , at the O-O distance of the minimum. Full line: SCF calculations, dashed line: fit with the experimental geometry of the water molecule; dotted line: fit with the ST2 model.

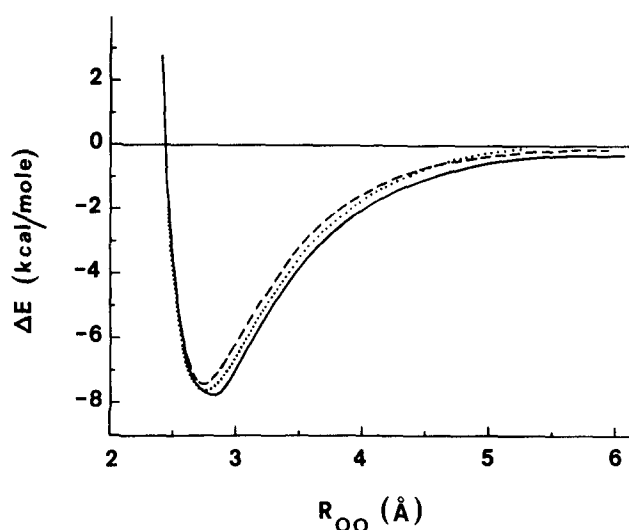


FIG. 5. Same as Fig. 3, for the dimer WEt.

both EtW and WEt dimers, maybe they are overestimated, as the following observations suggest:

(a) The corresponding results for the dimers between water and methanol obtained with the STO-3G basis set,¹⁹ are less negative [-6.26 vs -9.49 kcal/mole, for MeW (Me=methanol) and EtW, respectively, and -5.22 vs -7.69 kcal/mole for WMe and WEt].

(b) The STO-3G basis set yields results for the binding energy of the water dimer much closer to the experimental values²¹ and to the best theoretical estimates^{4,22} than the minimal basis set used in this work (-6.41⁸ vs -8.45 kcal/mole,²³ respectively).

(c) The binding energies for the dimers of methanol and ethanol at the STO-3G level^{7,20} are very similar (-6.15 and -6.00 kcal/mole, respectively), and, for (MeOH)₂, close to the value obtained correcting the experimental dimerization enthalpies^{24,25} in the gas phase, for the translational, rotational, and vibrational contributions ($\Delta E \approx -5.5$ kcal/mole).⁷ It is well known, however, that the results of a simulation reflect the accuracy of the whole potential energy surface, not only of the regions of the minima. For this reason we have chosen to include no correction for the dispersion energy to this potential, reserving to take it into account with the method exposed by Claverie,²⁶ and tested with encouraging results by Kolos,¹³ after having removed the

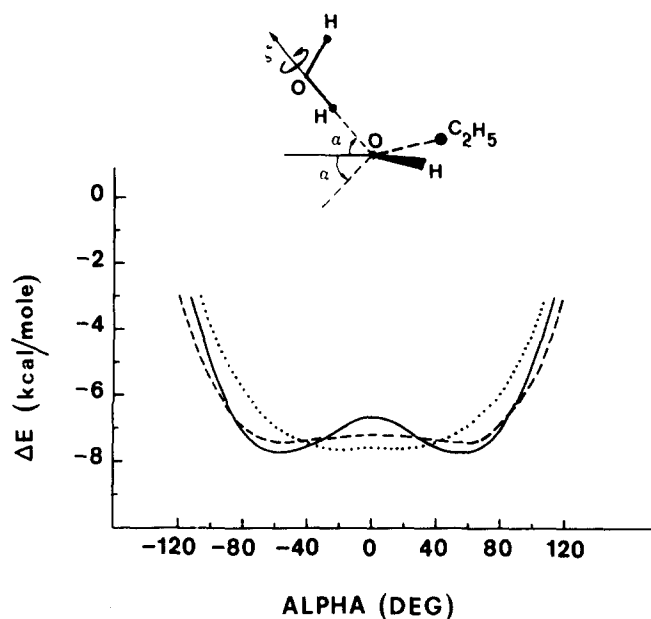


FIG. 6. Same as Fig. 4, for the dimer WEt.

basis set superposition error of the minimal basis set with the counterpoise method.²⁷ Both potentials will then be used in two parallel simulations of the dilute aqueous solution of ethanol, whose results will also help to assess their relative merits.

Finally, the role of the three body term, neglected in the simulations, in the potential energy has been examined taking into consideration a sample of five trimers which may occur in a simulation of a dilute aqueous solution of ethanol.

The three body nonadditive term for a complex ABC can be defined as follows:

$$\Delta E(\text{n. add.}) = E(ABC) - E(A) - E(B) - E(C) - \Delta E(AB) - \Delta E(AC) - \Delta E(BC), \quad (2)$$

where $E(ABC)$ is the SCF calculated energy of the trimer, $E(A)$, $E(B)$, and $E(C)$ are the energies of the monomers, and the last three terms on the right hand side of Eq. (2) are the interaction energies of all the molecular pairs involved in the complex. The results of our calculations, analyzed according to Eq. (2), are shown in Table IV. The first three trimers are labeled WWet, WEtW, and EtWW, adopting the nomenclature of Ref. 19. WEtW,

TABLE IV. Interaction energies (kcal/mole) of some trimers between water (W) and ethanol (Et). Total energy of monomers = -304.931 017 a.u.

Trimer	W _C W _A Et _B	W _A Et _B W _C	Et _B W _C W _A	Config. 4 ^a	Config. 20 ^a
$E(ABC)^b$	-304.960 196	-304.961 795	-304.963 924	-304.925 048	-304.949 844
$\Delta E(ABC)$	-18.31	-19.31	-20.65	3.75	-11.81
$\Delta E(AB)$	-7.69	-7.69	-0.64	3.61	-6.90
$\Delta E(BC)$	-0.56	-9.49	-9.49	0.19	0.65
$\Delta E(AC)$	-8.45	-0.65	-8.45	-0.15	-6.63
$\Delta E(\text{n. add.})$	-1.61	-1.48	-2.07	0.10	1.07

^aSee text for the definition of the geometry of these trimers.

^ba.u. of energy = 627.503 kcal/mole.

for example, is the trimer in which water acts as a proton donor to a central ethanol, which in turn donates a proton to another water. Each of these three trimers has been formed with the condition that the relative orientation of any two hydrogen bonded molecules be the same as in the corresponding dimers. The last two trimers of Table IV have been obtained substituting the ethanol molecule to the water labeled *B* in the configurations 4 and 20 of Ref. 28. This substitution has been carried out making to make coincide both the plane C2OH of ethanol with that of water *B*, and the coordinates of the two oxygens.

As can be seen from Table IV, the first three trimers examined are extra stabilized not negligibly, and this confirms that cooperative effects are very likely present in hydrogen bonded systems whenever chain structures such as O-H...O-H...O-H form. As to the order of trimer stability, we have found that EtWW and WWEt are the most and the least stable, respectively, in agreement with the results for the analogous trimers MeWW and WWMe.¹⁹ Also, the order of nonadditivities parallels in these two cases, increasing from WWEt (WWMe) to EtWW (MeWW). The numerical values of the three body terms are very close to the corresponding values for methanol-water trimers; however, their relative weight differs, ranging from ~7.6–10%, in our case, to be compared with ~12%–14% of Ref. 19.

14% is also the relative value of the three body term for the water open-chain trimer, in which the central water is both proton donor and acceptor, calculated with STO-3G¹⁹ and STO-4G²⁹ basis sets, which, however, are known to overestimate nonadditive terms.²⁹ Actually, calculations with extended basis sets³⁰ yield a stabilization close to 10%, due to the three body term in a water trimer built up with two dimers in a relative orientation close to that of their two body minima.

The role of the basis set in this kind of calculation has been tested in the above quoted study,²⁸ in which 29 configurations of the (H₂O)₃ complex have been examined with the minimal basis set employed in this work, as well as with an extended basis. The results shown in the last two columns of Table IV exhibit a close analogy with the corresponding results for the water trimers,²⁸ not restricted to the total interaction energy or to the non-additive term, but extended to all the pair contributions. As these configurations (4 and 20) have been selected at random, we believe that the conclusions reached in Ref. 28 can be transferred with enough confidence to mixed trimers containing one ethanol molecule and two water molecules. In particular, the three body term can be considered small, mainly with respect to the total interaction energy. Actually, the sum of all the 29 nonadditive contributions²⁸ is -1.04 kcal/mole vs a total interaction energy of -77.16 kcal/mole if calculated with the minimal basis set, and -1.02 vs +57.94 kcal/mole with the extended basis. All the numerical values of the three body term, however, are to be taken with caution, since, as pointed out by the same authors,²⁸ they are obtained as differences of differences between large numbers, so their accuracy may be questionable. On the other hand, the geometric

arrangements of the first three trimers of Table IV likely enhance the weight of the three body term, so that the ~10% estimate above quoted is rather to be considered as an upper bound. Thus, though attractive configurations similar to these are the most frequently sampled in every simulation, it seems reasonable to infer that a simulation assuming pairwise additivity of the potential should yield a total energy result not too affected by the neglect of three body terms, as they could cancel out to a large extent.

IV. COMPARISON OF APPROXIMATE METHODS TO OBTAIN INTERACTION POTENTIALS

The SCF calculations on ethanol-water complexes reported here have also been used to test how reliable potentials can be obtained with two approximate methods, i.e., the library of pair potentials given by Clementi and co-workers^{31–34} and the electrostatic potential method.³⁵

Clementi and co-workers have performed extensive SCF calculations, with the minimal basis set employed in this work, to explore the potential energy surface of water interacting with a molecule *M*, where *M* has been, in turn, each one of 21 amino acids,³¹ four DNA bases,³² and lysozyme.³⁴ To fit the interaction energies so obtained the following expression has been used:

$$V(M, W) = \sum_i \sum_j (-A_{ij}^{ab} / r_{ij}^6 + B_{ij}^{ab} / r_{ij}^{12} + C_{ij}^{ab} q_i q_j / r_{ij}), \quad (3)$$

where A_{ij}^{ab} , B_{ij}^{ab} , and C_{ij}^{ab} are fitting parameters, r_{ij} is the distance between atom *i* of molecule *M* and atom *j* of water, q_i and q_j are the Mulliken's gross atomic charges from the electron population analysis³⁶ for atoms *i* and *j*, *a* and *b* are indices that distinguish atoms not only for their atomic number, but according to their molecular environment too. The concept of the "class" of an atom has been so introduced, each class being characterized by its own set of parameters *A*, *B*, and *C*. According to the authors,^{31–34} this set of constants could also provide a tool to determine the interaction potentials between water and an organic molecule with a larger size than those explicitly taken into account, chiefly fragments of biopolymers. However, the ethanol-water complex seemed to us well suited to test the transferability of Eq. (3) to smaller size molecules, since ethanol can be considered as a part of threonine (namely, its side chain *R* in the general formula NH₂-CHR-COOH), plus a hydrogen atom. This made the choice of the appropriate "class" for each atom of ethanol straightforward. Actually, they all can be attributed from Fig. 4 and Table XVII of Ref. 31, with the exclusion of the missing hydrogen, which has been given the same class index as the other methylenic hydrogen. For the reader's convenience these data are collected in Table V. The gross charges of water oxygen and hydrogen are -0.6642 and 0.3321*e*, respectively.

In summary, in the electrostatic potential approximation,³⁵ the wave function of a complex *AB* is expressed by

$$\Psi_{AB}^0 = \Psi_A^0 \cdot \Psi_B^0, \quad (4)$$

where $\Psi_{A(B)}^0$ is the SCF wave function of the molecule

TABLE V. Class index, gross charge, and pairwise interaction constants^a for each atom of ethanol.

Atom EtOH	Class	Atom H ₂ O	A	B	C	Charge ^b
C1	6	O	0.102 073 144+02	0.294 559 020+06	0.999 955 520+00	-0.592
		H	0.356 004 411+01	0.389 186 260+05	0.100 027 880+01	
Hs	3	O	0.344 878 279+01	0.704 513 690+04	0.998 410 933+00	0.193
		H	0.130 720 375+01	0.280 374 992+03	0.998 704 314+00	
Ha	3	O	0.344 879 279+01	0.704 513 690+04	0.998 410 933+00	0.206
		H	0.130 720 375+01	0.280 374 992+03	0.998 704 314+00	
C2	17	O	0.102 073 144+02	0.102 467 840+06	0.993 570 738+00	-0.183
		H	0.356 004 411+01	0.121 598 151+06	0.992 949 978+00	
H	2	O	0.344 879 279+01	0.332 071 268+04	0.999 966 606+00	0.171
		H	0.824 252 534+01	0.145 269 011+04	0.100 000 000+01	
O	9	O	0.389 675 373+03	0.307 583 102+04	0.100 093 916+01	-0.521
		H	0.159 769 344+01	0.463 124 774+04	0.100 093 982+01	
H	4	O	0.389 675 373+03	0.307 583 102+04	0.100 093 016+01	0.349
		H	0.159 769 344+01	0.463 124 774+04	0.100 093 982+01	

^aTo obtain energies in kcal/mole, distances are to be expressed in Å.

^be units = 4.803 - 10 e. s. u.

$A(B)$, isolated. This means that only purely electrostatic interactions are taken into account, so that the interaction energy between A and B can be considered as the interaction energy of the potential field due to the charge distribution of A and the charge distribution of B . The charge distribution of A is defined as

$$\gamma_A(\mathbf{r}_1, \mathbf{R}) = -\rho_A(\mathbf{r}_1) + \sum_{\alpha} z_{\alpha} \delta(\mathbf{r}_1 - \mathbf{R}_{\alpha}), \quad (5)$$

where the first term on the right represents the electronic charge distribution and the second the nuclear one. So, the electrostatic potential at point \mathbf{r} due to A is

$$V_A(\mathbf{r}) = \int \frac{\gamma_A(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 \quad (6)$$

and the electrostatic interaction energy can be written as

$$\Delta E^{e1} = \int V_A(\mathbf{r}) \gamma_B(\mathbf{r}) d\mathbf{r}. \quad (7)$$

This expression can be more readily evaluated if the continuous charge distribution $\gamma_B(\mathbf{r})$ is substituted by a set of point charges q_j :

$$\gamma_B(\mathbf{r}_1) = \sum_j q_j \delta(\mathbf{r}_1 - \mathbf{r}_j). \quad (8)$$

Thus, ΔE^{e1} becomes

$$\Delta E^{e1} = \sum_j V_A(\mathbf{r}_j) q_j. \quad (9)$$

In a further approximation, another set of point charges models the charge distribution of A , yielding for ΔE^{e1}

$$\Delta E^{e1} = \sum_i \sum_j \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (10)$$

In this work we have substituted a set of 13 point charges³⁷ for the continuous charge distribution of water, adopting a method described elsewhere.³⁸ Thus, we have employed the intermediate level of approxi-

mation, expressed by Eq. (7), which obviously allows a remarkable reduction of computational time with respect to SCF calculations with the same basis (~1.5 vs ~150 sec each point, in our case). Of course, from this point of view, the "class" approximation is the best, its cost being practically zero.

Figures 7-10 show the results obtained with both "class" and electrostatic approximations for the physical situations described by Figs. 3-6, in the same order. As can be seen, in the region of dimer EtW (Figs. 7 and 8) each method reveals roughly the same amount of merits and defects. For example, the electrostatic potential curves of Fig. 7 shows the well-known collapse as the separation between charges of opposite sign decreases, while the "class" curve behaves very well in the repulsive region and reproduces the O-O separation and the binding energy within ~0.1 Å and ~1 kcal/mole, re-

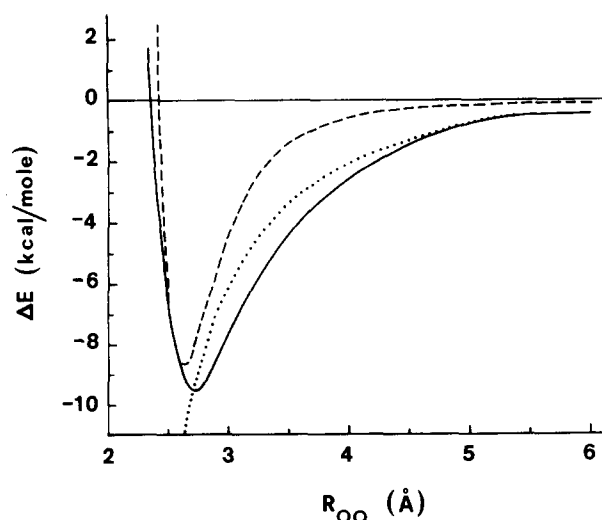


FIG. 7. Variation of the interaction energy of the dimer EtW with O-O separation. Full line: SCF calculations; dashed line: "class" approximation; dotted line: electrostatic model.

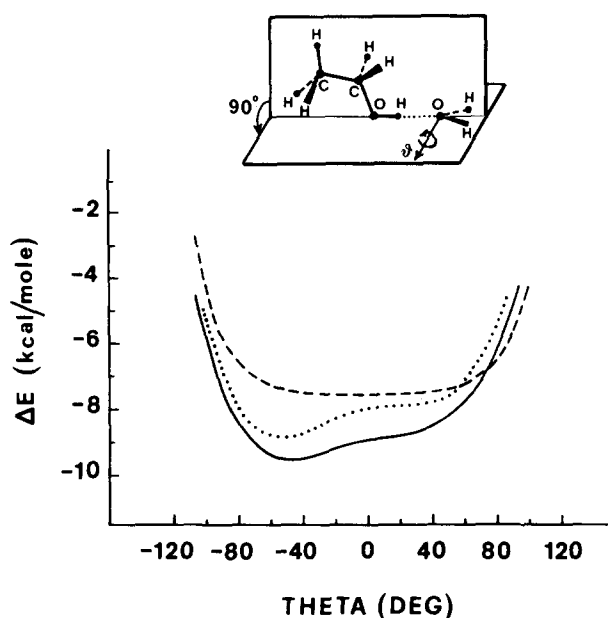


FIG. 8. Variation of the interaction energy of the dimer EtW with angle θ , at the O-O distance of the minimum. Full line: SCF calculations; dashed line: "class" approximation; dotted line: electrostatic model.

spectively. On the other hand, this curve shows a too narrow potential well, so that the electrostatic model yields potential energy values closer to the SCF ones for O-O distances greater than 3.0 Å. Also, the dependence of potential energy upon the angle is better reproduced by the electrostatic model. The situation changes if one considers the results of Figs. 9 and 10, i.e., while the electrostatic model maintains its known features, namely, short range collapse and good directionality; the "class" method reveals only a very weak attraction between water and ethanol.

To broaden the scope of this test, the sample of SCF calculated energies has been divided into various sub-

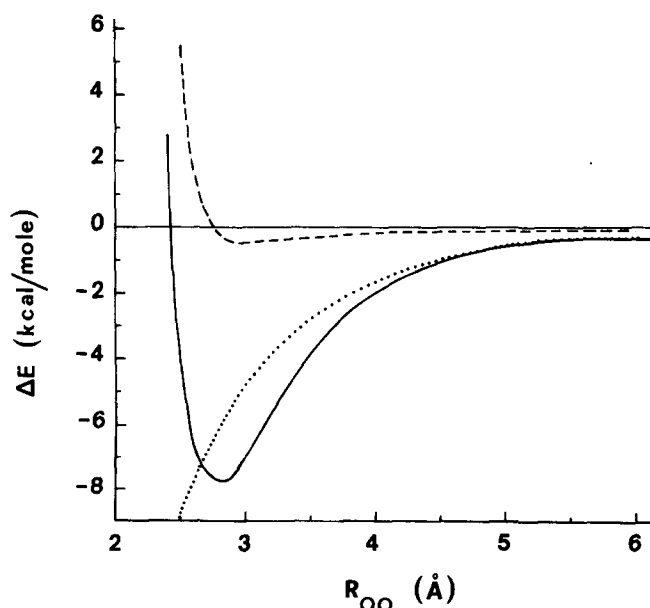


FIG. 9. Same as Fig. 7, for the dimer WEt.

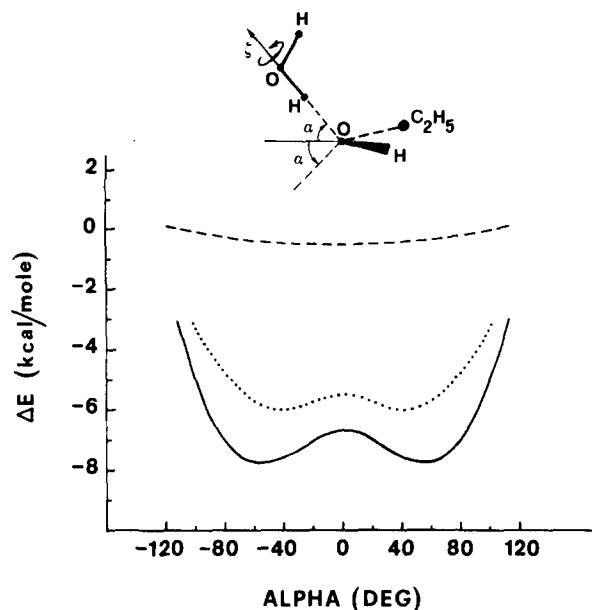


FIG. 10. Same as Fig. 8, for the dimer WEt.

sets, according to geometric or energetic criteria, as shown in Table VI, which collects the standard deviations of the points of each subset, obtained with the four potential functions examined in this paper. A threshold has been imposed on R_{\min} , i.e., the shortest separation O-X, where O is water oxygen and X is the closest atom among C1, C2, O, and H of ethanol, to prevent collapse between opposite charges. Table VI shows that both approximations give satisfactory results for the first subset, while the fit on the more attractive regions of the potential surface is not so good, mainly for the function obtained with the "class" method. The latter fact is likely to be ascribed to an insufficient number of points representative of the attractive region of the dimer WEt (see Figs. 9 and 10), in the sample which determined the values of the fitting parameters A , B , and C of Eq. (3).

It is worthwhile to stress at this point that the results of the above test have to be considered by no means as a general rule, because they have been obtained with a particular sampling of the potential surface of a par-

TABLE VI. Standard deviations (σ in kcal/mole) of the energies calculated with different potential functions, with respect to the relevant SCF values, for three subsets of the data base.

Features of the sample	No. points	σ of potential function ^a			
		A	B	C	D
$R_{\min} > 3^b$	293	0.48	0.55	0.69	1.67
$\Delta E_i < 0^c$	258	0.54	0.63	1.85	3.48
$\Delta E_i < -3$	75	0.64	0.68	1.67	5.85

^a A = fitting with the expt. model; B = fitting with ST2 model; C = electrostatic approximation; D = "class" approximation.

^b R_{\min} is the shortest distance (Å) between the oxygen of water and the closest atom among C1, C2, O, and H (alcoholic) of the ethanol molecule.

^c ΔE_i is the SCF interaction energy of point i (kcal/mole).

ticular molecular complex. Nevertheless, we think that, insofar as the interacting molecules have permanent electric multipole moments of considerable value, and provided that short range interactions are taken into account with different methods, the electrostatic potential can be used with confidence to explore large regions of the potential surface.³⁵ One could, for instance, carry out some preliminary SCF calculations around the minima and in the repulsive regions and then complete the data base for the fit with electrostatic interaction energies. Such an approach could allow a remarkable time saving, or, alternatively, the use of more accurate SCF calculations at the same total cost. A possible concern on this procedure is that the error inherent in the electrostatic approximation plus that of the fit could result in a larger final error. To avoid this circumstance we are presently testing the possibility of including the direct calculation of interaction energies with the electrostatic model in the simulation program, whenever the relevant intermolecular separation goes beyond the threshold imposed on the preliminary SCF calculations.

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