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Theoretical Investigations on the Solvation Process

I. A Simple Model for the Dimeric Water Associate*

ROSANNA BONACCORSI and CARLO PETRONGOLO
Laboratorio di Chimica Quantistica ed Energetica Molecolare del C.N.R.,
Via Risorgimento 35, 56100 Pisa, Italy

EOLO SCROCCO and JACOPO TOMASI
Istituto di Chimica Fisica dell'Università, Via Risorgimento 35, 56100 Pisa, Italy

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A model to facilitate the computation of the most stable conformer of associated $M \cdot H_2O$ (M being a polar molecule) which depends upon the electrostatic interaction energy between the two associated molecules is proposed and tested. SCF electrostatic potentials for the M molecule and a suitable point charge distribution for H_2O were employed in the model computations. Energies predicted by the model are found to be in good agreement with those resulting from an *ab initio* minimal STO basis SCF treatment of some conformations of the H_2O dimer.

Ein Modell zur Durchführung der Berechnung des stabilsten Konformeren eines Assoziationskomplexes $M \cdot H_2O$, wobei M ein polares Molekül ist, wird vorgeschlagen und untersucht. Es basiert auf der elektrostatischen Wechselwirkung zwischen beiden Partnern, und zwar wird für das Molekül M der elektrostatische Anteil seines SCF-Potentials und für H_2O eine angemessene Punktladungsverteilung zugrunde gelegt. Die resultierenden Energien sind in guter Übereinstimmung mit denen, die sich bei einer *ab initio* Rechnung mit minimaler STO Basis ergeben.

1. Introduction

In this paper an attempt will be made to find simple and computationally inexpensive procedures to be used as auxiliary tools for investigating the hydration process of molecules containing polar groups. More precisely, we want, in the present case, to demonstrate a method which allows one to forecast, with sufficient accuracy, the more stable conformation for a monohydrated associate, i.e. the angles which determine the position and the orientation of a water molecule with respect to the solvated molecule.

The search for the more stable conformations should replace a highly costly *ab initio* determination of the conformation energy hypersurface. The conformations thus determined will be used eventually as a starting point for more exact *ab initio* calculations on the overall associate.

2. The "Electrostatic Assumption"

The models proposed and tested in this paper relay on a sort of "electrostatic assumption". It will be provisionally assumed that the variations in the solvation energy due to changes in the orientation of the water molecule with respect to the

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solvated molecule are obtainable (within a sufficient good approximation) using only the electrostatic interaction among the interested molecules. As a consequence, it should be possible to obtain information sufficiently correct about the geometry of most stable conformations as well as approximate values for the interaction energy by using only the wavefunctions for each individual molecule in the associate (solute and water). Furthermore, the validity of the "electrostatic assumption" will enable us to use even more simplified models. (We have chosen models where the water molecule is described by suitable point charge distributions, while the solvated molecule is still represented by its SCF wavefunction).

The use of a point charge distribution to represent the electrostatic potential arising from a water molecule is not new having been first used by Bernard and Fowler [1] in 1933 and subsequently by several other workers [2–8] to calculate the intramolecular forces in liquid water and ice.

It is now possible to use more elaborate models, which employ descriptions of the electron distribution more accurate than a simple point charge model and it is especially possible to check the performance of a model by comparison with non empirical *ab initio* calculations.

For such a comparison we have selected the water dimer. The dimer will be considered as a particularly simple hydrated system; one of the two monomers will be considered as solvated molecule, the second as hydrating unit. By exchanging the rôle between the two monomers and varying the dimer geometry it will be possible to examine many particularly important solvation configurations.

The verification of the "electrostatic assumption" relies on a rather arbitrary partitioning of the overall energy of the associate. Here, Coulson's [9] definition of electrostatic interaction energy (ΔE_{ei}) will be adopted. In the case of dimeric association between molecules A and B, if one indicates with $\varrho_A(\boldsymbol{x}_1)$ the first order electron density function and with $\sum_{\alpha}^{\text{nucl}_A} Z_\alpha \delta(\boldsymbol{x}_1 - \boldsymbol{x}_\alpha)$ the nuclear charge distribution of the isolated molecule A (the subscripts B and β define the corresponding quantities for molecule B), according to Coulson one has:

$$\begin{aligned}\Delta E_{ei} = \int d\tau_1 \Big[\varrho_A(\boldsymbol{x}_1) - \sum_\alpha Z_\alpha \delta(\boldsymbol{x}_1 - \boldsymbol{x}_\alpha)\Big] \\ \cdot \int d\tau_2 \Big[\varrho_B(\boldsymbol{x}_2) - \sum_\alpha Z_\beta \delta(\boldsymbol{x}_2 - \boldsymbol{x}_\beta)\Big] \cdot \frac{1}{|\boldsymbol{x}_1 - \boldsymbol{x}_2|}\,.\end{aligned} \tag{1}$$

In other words, the electrostatic energy is the interaction energy between the two molecules placed in the appropriate position, without any deformations of the charge clouds or electron exchange.

The electrostatic interaction energy is related to an approximate expression for the wavefunction of the associate:

$$\Psi^0_{AB} = \Psi^0_A \cdot \Psi^0_B \tag{2}$$

namely, a simple product between the antisymmetrized wavefunctions of the isolated molecules A and B. The MO's belonging to A are not orthogonal to those belonging to B.

Eq. (1) is equivalent to the following definition:

$$\Delta E_{ei} = E^0_{AB} - E^{SCF}_A - E^{SCF}_B \,, \tag{3}$$

where E^{SCF}_A and E^{SCF}_B are the total energies for the isolated A and B molecules and

$$E^0_{AB} = \langle \Psi^0_{AB} | H_{AB} | \Psi^0_{AB} \rangle \,, \tag{4}$$

where H_{AB} is the dimer Hamiltonian.

The calculation of ΔE_{ei} according to Eq. (1) in the MO LCAO scheme is decidedly simpler than a complete calculation of the stabilization energy of the dimer, because $\varrho_A(x_1)$ and $\varrho_B(x_2)$ are expanded in different functional subspaces related to the atomic basis orbitals belonging to molecule A or B, respectively, and the form of simple product (Eq. (2)) does not require the calculation of the exchange integrals.

If one releases in (2) the constraint of simple product and allows the mutual deformation of the MO's of A and B, one introduces into the expression for the stabilization energy two further terms which, according to Coulson's terminology, may be related to "delocalization effects" and to "overlap repulsive forces". For distances equal or greater than the equilibrium one, these two terms cancel mutually to a great extent; the "electrostatic assumption" corresponds to considering their sum as nearly constant for changes in the conformation of the dimer.

3. Verification of the Electrostatic Assumption

The validity of the electrostatic assumption may be tested by a comparison of the values of the stabilization energy calculated according to Eq. (1) and according to the more complete expression, including the "delocalization effects" and the "overlap repulsive forces" (i.e. according to the SCF value: $\Delta E_{SCF} = E^{SCF}(AB) - E^{SCF}(A) - E^{SCF}(B)$).

The SCF values were obtained by LCAO MO calculations with a minimal basis set of Slater-type orbitals. The orbital exponents adopted were taken from Aung, Pitzer, and Chang [10] who optimized them on the monomer at the experimental geometry ($E^{SCF}(H_2O) = -75.70340$ a.u.).

Fig. 1 reports the geometrical configuration of the dimer chosen as reference. All the *ab initio* calculations [11–16] thus far performed on the water dimer con-

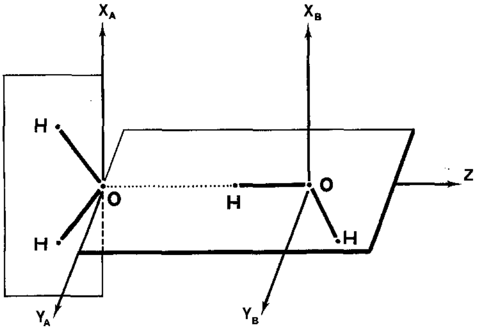

Fig. 1. Reference conformation of the dimer

Table 1. SCF *energies for some configurations of dimeric water*

R_{O-O} (Å)		E (a.u.)	R_{O-O} (Å)		E (a.u.)
2.61		-151.41545	2.76	$x_B = 127°46'30''$	-151.40017
2.61	$\hat{x}_A = 310°$	-151.41693	2.76	$x_B = 307°46'30''$	-151.41273
			2.76	$y_B = 250°$	-151.40257
2.68		-151.41596	2.76	$y_B = 180°$	-151.40310
2.68	$\hat{x}_A = 310°$	-151.41730	2.76	$x_A = 310°, x_B = 127°46'30''$	-151.40085
			2.76	$x_A = 310°, x_B = 307°46'30''$	-151.41155
2.76		-151.41598			
2.76	$\hat{x}_A = 30°$	-151.41599	2.96		-151.41467
2.76	$\hat{x}_A = 40°$	-151.41537	2.96	$x_A = 310°$	-151.41552
2.76	$\hat{x}_A = 130°$	-151.39643			
2.76	$\hat{x}_A = 180°$	-151.38065			
2.76	$\hat{x}_A = 290°$	-151.41663			
2.76	$\hat{x}_A = 310°$	151.41717	∞		-151.40680
2.76	$\hat{x}_A = 320°$	151.41705			

firm the most stable configuration to be near to the "linear" one of Fig. 1. In our calculations we have kept fixed the internal geometry of each monomer and considered as variable the O–O distance. In addition, for each O–O distance, we have considered several conformations differing among themselves by at least a rotation around one axis of the two cartesian systems indicated in Fig. 1. As an example, the most stable configuration corresponds to a counterclockwise rotation of the A molecule around the X_A axis of $-50°$, the O–O distance being equal to 2.705 Å; the corresponding energy is -151.4173 a.u. and the stabilization energy is 6.62 Kcal/mole (see Table 1). Morokuma and Winick [16], which adopt a basis set very near to the present one, obtain an angle $\hat{x}_A = -53.8°$, and a stabilization energy of 6.55 Kcal/mole.

Table 1 summarizes a selection of the SCF results on the dimer treated in the present paper. More detailed information may be obtained upon request to the authors.

It is commonly accepted that the electrostatic interaction energy becomes more important (for polar molecules) when the distance between the monomers increase. For the dimeric water only at distances R_{O-O} larger than 2.9–3 Å does the bond become almost completely electrostatic, while at the equilibrium distance a significant portion of the stabilization energy is not of electrostatic character. These conclusions may be drawn from the graph shown in Fig. 2. The dotted lines refer to SCF calculations for configurations hawing $\hat{x}_A = 0°$ (as in Fig. 1); the solid lines refer to ΔE_{ei} values calculated according to Eq. (1).

It is clear that the "electrostatic assumption" is not valid for variation in the distance between the monomers and that the ΔE_{ei} value at the more stable configuration is not equal to the SCF stabilization energy.

More important, for our purposes, are the comparisons displayed in Fig. 3. In this case the R_{O-O} distance is kept fixed ($R_{O-O} = 2.74$ Å, very near to the best value) and the orientation of the A molecule is changed by rotation around the x_A axis. Among the conformations considered is the most stable one which corresponds almost exactly to a rotation bringing an oxygen lone pair of A along

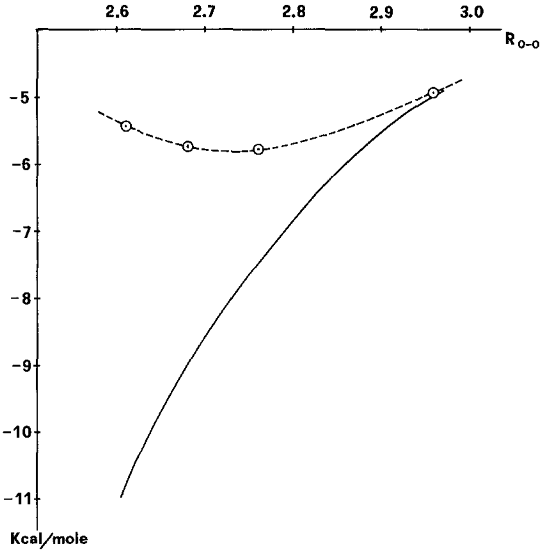

Fig. 2. Variations of the SCF stabilization energy (dotted line) and the electrostatic interaction energy (solid line) with respect to the R_{O-O} distance

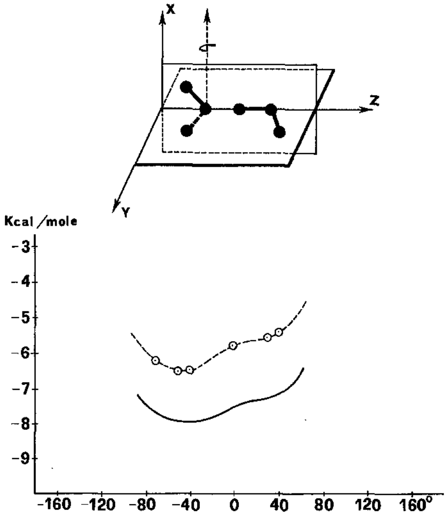

Fig. 3. Variations of the SCF stabilization energy (dotted line) and the electrostatic interaction energy (solid line) with respect to the rotation of molecule A around the X_A axis

the direction O···H–O[1]. The dotted line (SCF values) runs parallel to the solid one (electrostatic values) and hence, in this case the electrostatic assumption is confirmed.

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[1] The canonical SCF orbitals of H_2O have been transformed into localized ones according to the method suggested by Foster, J. M., Boys, S. F.: Rev. mod. Physics 32, 300 (1960).

Other comparisons are not reported here, suffice it to say that for all the rotations corresponding to the geometries of Table 1 the electrostatic assumption results are almost completely valid. It is perhaps necessary to specify that it is not necessary to have complete parallelism between the SCF and the electrostatic curve; it is sufficient that the minima (and the maxima) are in the same positions.

4. The Construction of the Model

The verification of the electrostatic assumption is only the first step in our attempt to formulate the model. The calculation of ΔE_{ei} according Eq. (1) is decidely simpler than a complete SCF calculation; still, it requires a great number of coulomb integrals between A and B.

Our ultimate goal is to use only the information arising from the wavefunctions of the solvated molecules and only the integrals necessary to build them up. Eq. (1) may also be written in the following way:

$$\Delta E_{ei} = \int d\tau_1 \left[\varrho_A(\mathbf{x}_1) - \sum_{\alpha} Z_\alpha \delta(\mathbf{x}_1 - \mathbf{x}_\alpha)\right] \cdot V_B(\mathbf{x}_1), \tag{5}$$

where

$$V_B(\mathbf{x}_1) = \int d\tau_2 \mid \varrho_B(\mathbf{x}_2) - \sum_{\beta} Z_\beta \delta(\mathbf{x}_2 - \mathbf{x}_\beta) \cdot \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \tag{6}$$

is the molecular electrostatic potential, whose features and potential utility as an interpretative tool were examined previously [17]. The electrostatic potential $V(\mathbf{x}_i)$, which is a by product of the SCF calculation gives immediately the electrostatic interaction energy with a point charge placed at the point $\mathbf{x}_i$.

If $\varrho_A(\mathbf{x}_1)$ is approximated by a suitable point charge distribution, it will be possible to calculate ΔE_{ei} as a simple summation:

$$\Delta E_{ei} = \sum_{k}^{\text{model}} q_k(\mathbf{k})\, V(\mathbf{k}); \tag{7}$$

where the $q_k(\mathbf{k})$ are the charges of the model, placed at the points $\mathbf{k}$.

It would be possible to go a step further representing also the charge distribution of the B molecule by a discrete number of point charges. We have the impression, however, that it is a not such a simple matter to find a realistic point charge model for more complicated molecules, although this task may be relatively easy for H_2O. Bearing in mind that our purpose is to build up a model for the hydration of large molecules, we shall (as mentioned above) approximate in the dimeric system considered here the first order density distribution of one molecule by the point charge while for the other molecule the SCF electrostatic potential will be employed.

The degree of reliability of the model may be tested in two different ways:

a) By comparing the values of $V(\mathbf{x}_i)$ obtained through Eq. (6) with those pertinent to the selected point charge distribution. A visual comparison may be obtained by justaposition, in selected planes, of the corresponding maps.

b) By comparing the ΔE_{ei} values obtained through Eq. (7) with the corresponding SCF stabilization energies. This comparison offers a check of both the model and of the electrostatic assumption.

All the attempts and all the steps for the elaboration of the point charge model which at present we consider as an acceptable compromise between reliability and simplicity will not be described here in detail. Schematically the procedure adopted may be summarized as follows:

i) A first set of suitable point charges is placed at the position of the nuclei and of the centroids of the localized orbitals; the model has the same electric dipole moment as the SCF wavefunction employed in the localization.

ii) The model is refined by introducing corrections dictated by requirements a) and b) quoted above.

The corrections of step ii) lead to a substitution of each lone-pair point charge with three charges symmetrically disposed around each lone-pair centroid, and to a substitution of each bond orbital charge with two charges on the O–N axis, symmetrical with respect to the centroid. The coordinates and the charge values are reported in Table 2. As a further check of the reliability of the point

Table 2. *Coordinates and charge values for the point charge model of* H_2O[a]

x	y	z	q
1.43153	0.	−1.10942	1.
−1.43153	0.	−1.10942	1.
1.23371	0.	−0.96759	−1.
0.44329	0.	−0.35501	−1.
−1.23371	0.	−0.96759	−1.
−0.44329	0.	−0.35501	−1.
0.	0.30631	0.62280	−0.66667
−0.32909	0.59659	0.13225	−0.66667
0.32909	0.59659	0.13225	−0.66667
0.	−0.30631	0.62280	−0.66667
−0.32909	−0.59659	0.13225	−0.66667
0.32909	−0.59659	0.13225	−0.66667
0.	0.	0.	6.

[a] Atomic units.

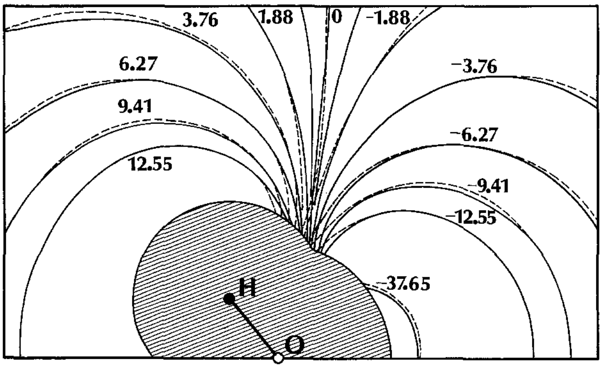

Fig. 4. Electrostatic molecular potential map for H_2O in the molecular plane. Solid lines refer to SCF values, dotted lines to point charge model values

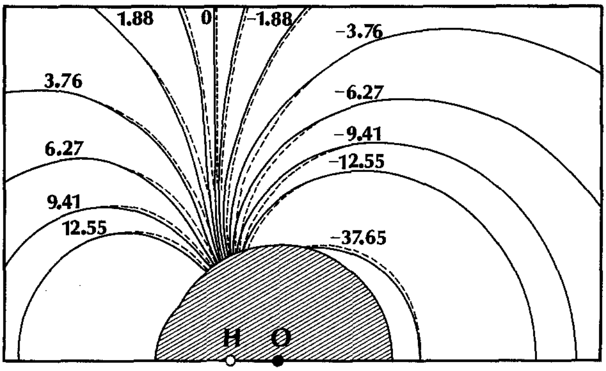

Fig. 5. Electrostatic molecular potential map for H_2O in the symmetry plane perpendicular to the molecular plane

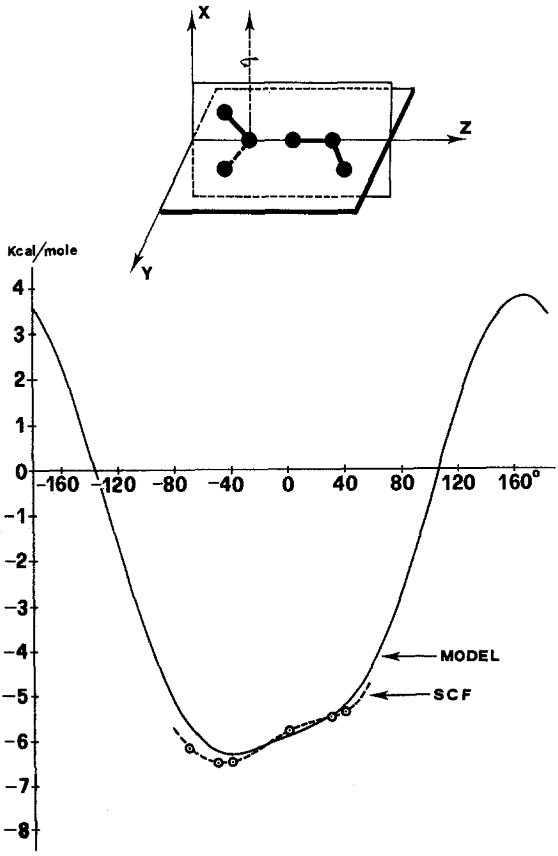

Fig. 6. Comparison of the SCF and model interaction energies with respect to rotation of molecule A around the X_A axis. $R_{O\text{-}O} = 2.76$ Å

charge model we have compared the corresponding quadrupole moment tensor with the SCF one. The latter compares favorably with the former.

The comparison between the maps of the electrostatic potential arising from the SCF wavefunction [Eq. (6)] and from the point charge distribution is performed in Figs. 4 and 5. Actually, the maps refer to the electrostatic interaction energy with a unitary point charge (energies in Kcal/mole). Fig. 4 refers to the molecular plane, Fig. 5 to the perpendicular symmetry plane (in this last figure the open circle is the parallel projection on the plane of the two H nuclei). In each case the solid line refers to the SCF potential and the dotted one to the point model's potential. Only the region outside the van der Waals radii is drawn, this being the more interesting region. We have thought it to be unnecessary at present to add to the electrostatic model a repulsive term and some calculations on this subject led us to conclude that it is a relatively simple matter to elaborate a model more realistically with respect to the distance between the two monomers.

The results of some tests performed according to the criterium b) quoted above are reported in Figs. 6–9. The comparisons are made between SCF stabilization

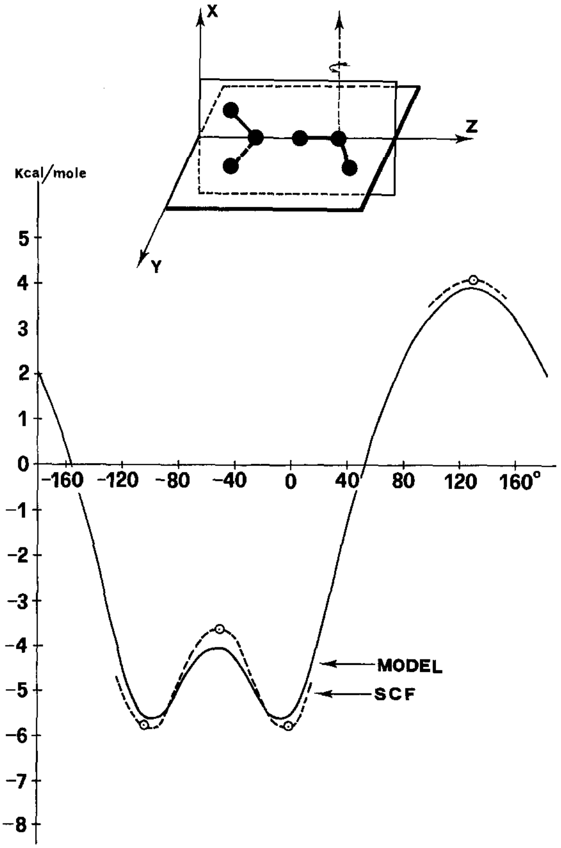

Fig. 7. Comparison of the SCF and model interaction energies with respect to rotation of molecule B around the X_B axis. $R_{O-O} = 2.76$ Å

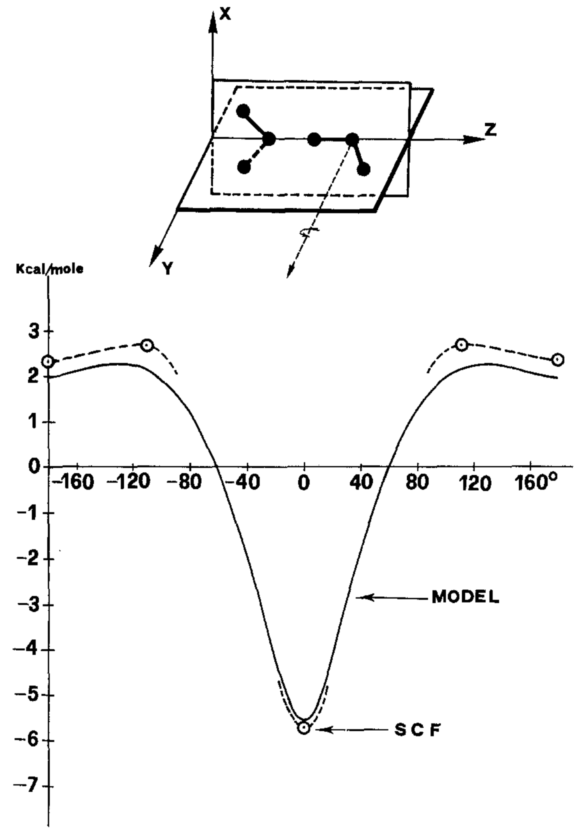

Fig. 8. Comparison of the SCF and model interaction energies with respect to rotation of molecule B around the Y_B axis. $R_{O-O} = 2.76$ Å

energies (open circles) and ΔE_{ei} values calculated according to Eq. (7). In all cases the R_{O-O} distance was kept fixed at 2.76 Å.

Fig. 6 is analogous to Fig. 3: Eq. (1) led to higher interaction energies (with respect to the SCF ones) while Eq. (7) lead to near equal values. It is pointed out here again that it is not necessary that the model reproduce exactly the electrostatic value. The model values of Fig. 6 refer to the case where molecule A is represented by the point charge distribution, while the electrostatic SCF potential refers to the B molecule.

The conformations obtained by a rotation of B molecule around the X_B axis are considered in Fig. 7. Symmetry reasons dictate that the conformation corresponding to $\hat{x}_B = -104°27'$ has the same energy as conformation with $\hat{x}_B = 0°$. The model does not predict with accuracy the SCF barrier height between these two conformations, but the location of the minima are well represented. The conformation corresponding to the barrier is a "bifurcated" dimer; its stabilization energy is decidedly smaller than in the "linear" case.

The ΔE_{ei} value at $\hat{x}_B = 0°$ is not perfectly equal to the corresponding one of Fig. 6 the energy shift is 0.4 Kcal/mole. According to our model two different ways of

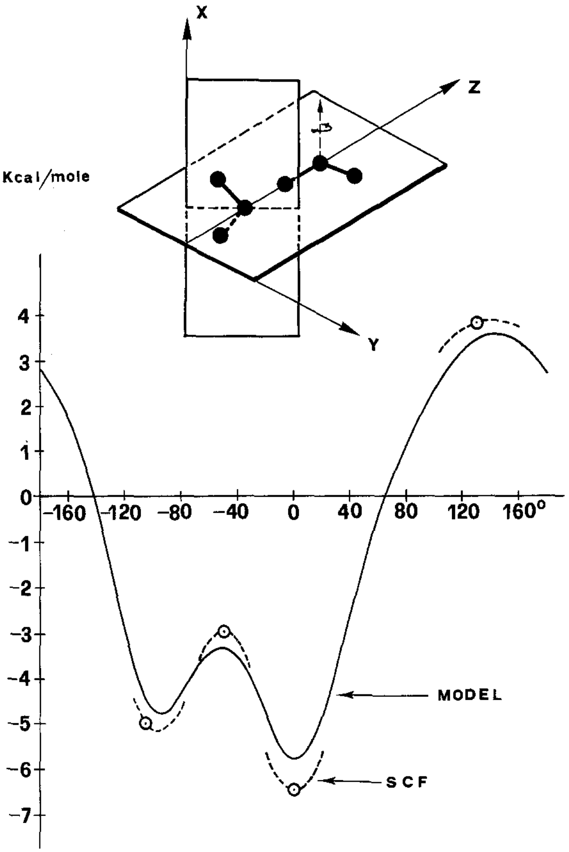

Fig. 9. Comparison of the SCF and model interaction energies with respect to rotation of molecule B around the X_B axis. The A molecule is rotated by −50° around the X_A axis and $R_{O-O} = 2.76$ Å

calculating the dimer interaction energy are possible which are not completely equivalent. In fact, when one applies Eq. (7) one must choose which of the two molecules is represented by the point charge distribution. In Figs. 6–9 we have adopted the convention of using the point charge model for the rotating molecule. If one reverses this convention, one obtains plots with different ΔE_{ei} values; however, the position of the minima remains substantially unchanged.

Fig. 8 collects the values for conformations obtained by a rotation around the Y_B axis and in this case the two plots are also seen to run parallel to each other. Finally, Fig. 9 reports the interaction energies for conformations from rotations with respect to the X_B axis and having the A molecule rotated −50° around the X_A axis with respect to the starting conformation. The conformation having $\hat{x}_B = 0°$ is very near to the configuration corresponding to the absolute minimum. With respect to Fig. 7 the situation is less symmetric. The conformation corresponding to $\hat{x}_B = -104°27'$ has not in this case the same energy as the conformation with $\hat{x}_B = 0°$, the difference being due chiefly to the long range effects of the hydrogen.

A further test of the point charge distribution may be obtained by using the point charge distribution simultaneously for both molecules A and B. Any defect of the model should be amplified in the results. Our checks show only small deviations from the above reported curves, and such deviations do not seem significant. Some years ago, Schneider [18] with a simple point charge model for both water molecules obtained a picture of the dimer that the recent *ab initio* calculations have shown to be essentially correct. This may be considered as a further indication that for such a type of hydrogen bonded system even a simple electrostatic model may give useful information.

At present, the results of this investigation enable one to consider, at least provisionally, that the approximations introduced here have been shown to be acceptable and one may pass on to examine more complex monohydrated systems.

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Prof. Jacopo Tomasi
Istituto di Chimica Fisica dell'Università
Via Risorgimento 35
I-56100 Pisa, Italy