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On the application of some solvation models to the water dimer

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Three different solvation models are applied to a simple molecular system: the water dimer. The first order perturbation scheme of Hoijtink and Jano, Miertus and Kysel implementation of Klopmans' solvaton model and the virtual charge model of Constanciel and Tapia are used to study some aspects of proton potential curves. The calculations indicate that the solvent reorganization energy is important for the realistic reproduction of solvation. The solvent effect in correlation energy is also investigated using a second order perturbative approach. Finally some difficulties found when using the solvaton method are discussed by means of the Hartree–Fock instabilities theory of Paldus and Cizek and Stanton.

Key words: Solvation—Solvaton model—Water dimer—Hartree–Fock instabilities.

1. Introduction

During the last decade it has been an increasing interest in the development of models for the interaction of molecules with their neighbors. Among these, the most proficient work was done on solvation models [1–72] either by the explicit consideration of the solvent molecules [1–13] or by considering a polarizable environment in which the solute is immersed [10–30]. This latter point of view usually takes the relative permittivity of the solvent as an external macroscopic parameter, exploiting the known dependence of the equilibrium and velocity constants on the dielectric constant [61–64]. A theory which does not use the dielectric constant as a parameter is the Self-Consistent Reaction Field (SCRF) model [22, 6–29]. Here, a parameter *g*, related to the reaction field strength operating at the solute molecule, is used instead. This method has been used semi-empirically within the CNDO/2 parametrization and the MINDO/3 one in a scheme known as MINDO/3-SCRF [65]. An extension of the SCRF method to simulate protein core effects [66] has been used to describe enzyme reactions [3] and, in particular, the proton relay system of liver alcohol dehydrogenase [67]. An example of a mixed method, where some aspects of both the supermolecule and continuous methods appear, is that of Warshel [68, 69]. The main features of this "surface constrained soft sphere dipoles" (SCSSD) model are twofold. In the first place, it avoids the problems of the dielectric continuum approaches by explicitly considering the solvent molecules. In the second place, it overcomes the difficulties of the supermolecule approach by representing the solvent molecules as soft sphere point dipoles (SSPD). In this model the solute molecules are surrounded by a cluster of "solvent molecules" represented as SSPD. This cluster is also surrounded by a surface of SSPD constrained to fixed centers which correspond to the structure of the bulk solvent and all this system is embedded in a continuum characterized by the dielectric constant of the solvent. A simpler model where the solvent molecules are also represented by point dipoles is the one of Berndt and Kwiatkowski [70]. Here the potential due to the solvent is described by the multipole expansion, where the charge interaction term has been substituted by a classical parametric expression of the electrostatic interaction contribution. Instead of point dipoles, it is also possible to use point polarizabilities. This is done, for example, in the method of Thole and van Duijnen [71]. The advantages of this model are that it does not lead to a non-linear effective Hamiltonian, as point dipole techniques do, and that it accounts more accurately for the solute's electrical field. Also in this spirit is the polarization model of Stillinger and David [72] which has been recently applied to the proton transfer in the water dimer [94] and to the behavior of LiF solutions in water [73]. Other approximation to the problem is that of Clementi and coworkers [42–60], who used theoretical pair interaction potentials combined with a statistical approach to the possible disposition of the water molecules, to calculate the energy of hydration.

In this work we want to compare the results given by three different solvation methods when they are applied to a simple problem: the proton potential curves (PPC) in the water dimer system. This is a quite important problem in biology and chemistry which has been already examined by Tapia et al. [22, 26] using the SCRF method.

2. Models

We have used the semi-empirical CNDO/2 method [74] to obtain the wavefunctions for the water dimer in its experimental geometry [75] and for different values of the OH distance (x in Fig. 1). No geometry optimization was done for any of the calculations due to the known failure of the CNDO/2 method to reproduce the experimental conformation of this system [76, 77]. However, we have calculated the PPC for different values of the OO-distance (y in Fig. 1)

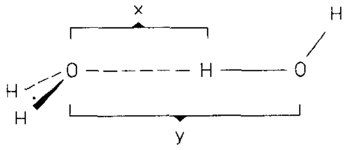

Fig. 1. Water dimer in its experimental geometry

around the experimental equilibrium one and also at the equilibrium distance obtained by the CNDO/2 method.

The calculations have been done for the system in vacuum and for the solvated one. Three models were used to take into account the solvent effect. First, the Jano–Hoijtink [78, 79] first order perturbative correction to the total energy was used, without modifying the molecular orbitals of the system because of the presence of the solvent (i.e. no solvent-dependent terms were added to the Hartree–Fock operator). Secondly, the solvaton model of Klopman [80] both in the versions of Miertuš and Kyseľ [16] and Constanciel and Tapia [23] was employed.

In the first part of this paper the PPC for each method, obtained with a fixed value of the dielectric constant ($\varepsilon = 80$) are compared with those obtained when no solvent is present ($\varepsilon = 1$). Also the energy decomposition in Constanciel's method is done. In the second part, the influence of the solvent in the second order perturbation energy is calculated and the results are compared with those of Tapia et al. [22] obtained with the SCRF model.

Finally we have examined the effect of solvation in the stability of the Hartree–Fock solution to the problem. The Hartree–Fock instabilities were considered using the formulation of Thouless [81] and Paldus and Cizek [82, 83] and the results were also analyzed from the point of view of Stanton [84, 85]. Some of the results obtained have points of contact with the work of Contreras and coworkers [86, 87].

3. Theoretical framework

According to the Jano–Hoijtink use of Born's formule [78, 79, 88] we can write

$$E_T(\varepsilon) = E_T(1) - 0.5(1 - \varepsilon^{-1}) \sum_{A} \sum_{B} (Z_A - P_{AA})(Z_B - P_{BB})\gamma_{AB} \tag{1}$$

where $E_T(\varepsilon)$ is the total energy of the molecule immersed in a solvent of dielectric constant ε, $E_T(1)$ is the total energy of the system in vacuum, Z_A is the atomic core charge of atom A, P_{AA} is the electronic charge of atom A, and γ_{AB} is the two-center electronic repulsion integral. Our first model consists of the use of formule (1) taking P_{AA} and P_{BB} as the electronic charges of atoms A and B when the system is in vacuum, i.e. they are solvent independent. This method gives the electrostatic coulombic energy of solvation.

In the method of Miertuš et al. [14–18, 77] the solvent effect is incorporated by representing the solvent as induced point charges, called solvatons, in the surroundings of the solute molecule. The solvaton model was originally developed by Klopman [80] and recently applied within the context of the MINDO/3 method by Klopman and Andreozzi [89]. In the formulation of Miertuš and Kyseľ [16] the hamiltonian for a molecule with N valence electrons, M atomic cores with charges Z_m^c is obtained from the unperturbed Hamiltonian $\mathscr{H}$ by

$$\mathscr{H}(\varepsilon)=\mathscr{H}_0-\left[\sum_{\mu=1}^{N}\sum_{s=1}^{M}Q_s r_{\mu s}^{-1}-\sum_{m=1}^{M}\sum_{s=1}^{M}Z_m^c Q_s r_{ms}^{-1}\right] \tag{2}$$

where the first and second terms of the perturbation in formule (2) represent the interaction between electrons and solvatons and between nuclei and solvatons respectively. The solvaton charges, Q_s, are assumed to be proportional to the charges in the solute atoms, Z_A–P_{AA}, using a proportionality constant which depends on the dielectric constant ε

$$Q_s=-0.5(1-\varepsilon^{-1})(Z_A-P_{AA}). \tag{3}$$

Taking into account that in the solvaton model the electrostatic coulombic energy can be expressed by the Jano–Hoijtink equation we can write the solvation energy in the form

$$E_T(\varepsilon)=E^{\text{el-coul}}(\varepsilon)+E^{\text{pol}}(\varepsilon) \tag{4}$$

where $E^{\text{el-coul}}(\varepsilon)$ is calculated by the second term in the right-hand side of Eq. (1) using the electronic charges calculated with the modified Hamiltonian of Eq. (2). $E^{\text{pol}}(\varepsilon)$ is calculated as the difference between the total energy of the solvated molecule and the electrostatic-coulombic energy $E^{\text{el-coul}}(\varepsilon)$. Since this model does not include the polarization energy of the medium, the energy $E^{\text{pol}}(\varepsilon)$ could be adscribed to the polarization of the solute molecule in the presence of the solvent [18].

In Constanciel's model the solvation energy can be expressed as [30, 90]

$$E_s(\boldsymbol{P})=E_s^{\text{el}}(\boldsymbol{P})+E_s^{\text{core-med}}(\boldsymbol{P})+E_s^{\text{med-med}}(\boldsymbol{P}) \tag{5}$$

where

$$E_s^{\text{el}}(\boldsymbol{P})=\operatorname{Tr}\boldsymbol{P}(\boldsymbol{F}_\varepsilon(\boldsymbol{P})-0.5\boldsymbol{G}(\boldsymbol{P})) \tag{6}$$

$$E_s^{\text{core-med}}(\boldsymbol{P})=-(1-\varepsilon^{-1/2})\sum_A\sum_B Z_A(Z_B-P_{BB})\gamma_{AB} \tag{7}$$

$$E_s^{\text{med-med}}(\boldsymbol{P})=0.5(1-\varepsilon^{-1/2})^2\sum_A\sum_B(Z_A-P_{AA})(Z_B-P_{BB})\gamma_{AB}. \tag{8}$$

Here we used the notation of Constanciel's paper [30]. The elements of the modified Hartree–Fock matrix are

$$[\boldsymbol{F}_\varepsilon(\boldsymbol{P})]_{\mu\mu}=[\boldsymbol{F}_1(\boldsymbol{P})]_{\mu\mu}+(1-\varepsilon^{-1/2})\sum_B(Z_B-P_{BB})\gamma_{AB} \qquad \mu\in A \tag{9}$$

$$[\boldsymbol{F}_\varepsilon(\boldsymbol{P})]_{\mu\nu}=[\boldsymbol{F}_1(\boldsymbol{P})]_{\mu\nu} \quad \text{for all } \mu\neq\nu. \tag{10}$$

$\boldsymbol{F}_1(\boldsymbol{P})$ is the Hartree–Fock matrix of the unperturbed molecular system in vacuum. This model allows for a more flexible representation of the solvent because it includes the medium electrostatic self interaction energy, Eq. (8), which takes into account the reorganization of the solvent due to the action of the solute. Besides this, the major difference between the VCM and Miertuš model is the behavior of the ε-dependent coupling constant in the Hartree–Fock matrix [90]. While in the VCM this constant, $\alpha(\varepsilon) = 1 - \varepsilon^{-1/2}$, has limits zero when $\varepsilon \to 1$ and one when $\varepsilon \to \infty$, the same as in the SCRF method [3, 26–29], in the procedure of Miertuš we have the values zero and $\frac{1}{2}$ for the same limits. A thorough analysis of these models is given in the paper of 0. Tapia, where it is shown that Miertuš and Kyseľ (MK) model does not emerge when the variational principle is applied to Klopman's total energy functional [80, 91] (see Eqs. (46) and (43) in Ref. [92]). It may be seen that this problem is caused by a $\frac{1}{2}$ factor in MK Hamiltonian. Consequently, the agreement with the variational principle can be achieved if one assumes that the dielectric constant in the MK model, $\varepsilon_{\mathrm{MK}}$, is really a function of the dielectric constant in Klopman's model, ε_K, and they are related by the equation

$$\varepsilon_{\mathrm{MK}} = \frac{\varepsilon_K}{2 - \varepsilon_K}. \tag{11}$$

This clearly shows that the MK factor, $\varepsilon_{\mathrm{MK}}$, cannot be taken as the relative permittivity of the medium if Klopman's model is used as the starting point. This will be further discussed later.

Finally, the stability of the CNDO/2 wavefunctions was investigated by diagonalizing the $\boldsymbol{E}''$ matrix related to the second order variation of the energy by the equation [81–83]

$$\delta^2 E = \frac{1}{2}\begin{bmatrix} \boldsymbol{D} \\ \boldsymbol{D}^* \end{bmatrix}^{\dagger} \left[\begin{bmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^* & \boldsymbol{A}^* \end{bmatrix}\right] \begin{bmatrix} \boldsymbol{D} \\ \boldsymbol{D}^* \end{bmatrix} \tag{12}$$

$$\boldsymbol{E}'' = \begin{bmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^* & \boldsymbol{A}^* \end{bmatrix}$$

where $\boldsymbol{D}$ is the column matrix of the u_{ji}, the coefficients of the variation

$$\phi_i \to \phi_i' = \phi_i + \sum_j \phi_j u_{ji} \tag{13}$$

of the orbitals, and $\boldsymbol{A}$ and $\boldsymbol{B}$ are matrices defined as

$$A_{li,kj} = \langle \phi_l | \mathscr{F} | \phi_k \rangle \delta_{ij} - \langle \phi_i | \mathscr{F} | \phi_j \rangle \delta_{lk} + (li, jk) - (lk, ji) \tag{14}$$

$$\boldsymbol{B}_{li,kj} = (li, kj) - (lj, ki) \tag{14'}$$

where $\mathscr{F}$ is the Fock operator, i, j denote occupied orbitals, k, l are virtual orbitals and the integrals are, as usual,

$$(li, jk) = \int \phi_l^*(1)\phi_i(1)\phi_j^*(2)\phi_k(2) r_{12}^{-1}\, d\tau_1\, d\tau_2. \tag{15}$$

We also investigated the instabilities according to Stanton by the absolute value of the largest eigenvalue of matrix $\boldsymbol{Q}$ defined as [84, 85]

$$\boldsymbol{Q}_{ij,rs} = -(\varepsilon_i - \varepsilon_j)^{-1/2}(\varepsilon_r - \varepsilon_s)^{-1/2}[4(ij, rs) - (ir, js) - (is, jr)]. \tag{16}$$

In all the cases investigated we have calculated the four possible types of instabilities: singlet, triplet, non-real and Stanton.

4. The proton potential curves

In Fig. 2 we have represented E_T vs. OH distance for the following four cases: (a) without solvation, (b) with the Jano correction to the total energy, (c) with Miertuš model, and (d) with Constanciel's model, for an OO distance of 3.0Å in each case.

In Table 1 we give the total energies for the two minima found, the energy difference between them, and the barriers for each one of them.

From Fig. 2 and Table 1 we can see that the progressive consideration of more terms in the total energy expression has the following effects

1. creates a secondary minimum at a geometry consistent with the ionic pair $H_3O^+HO^-$,
2. progressively diminished the energy gap between the two minima, and
3. progressively diminished the energy barrier that precludes the inter-conversion of the ionic and hydrogen-bonded forms of the system.

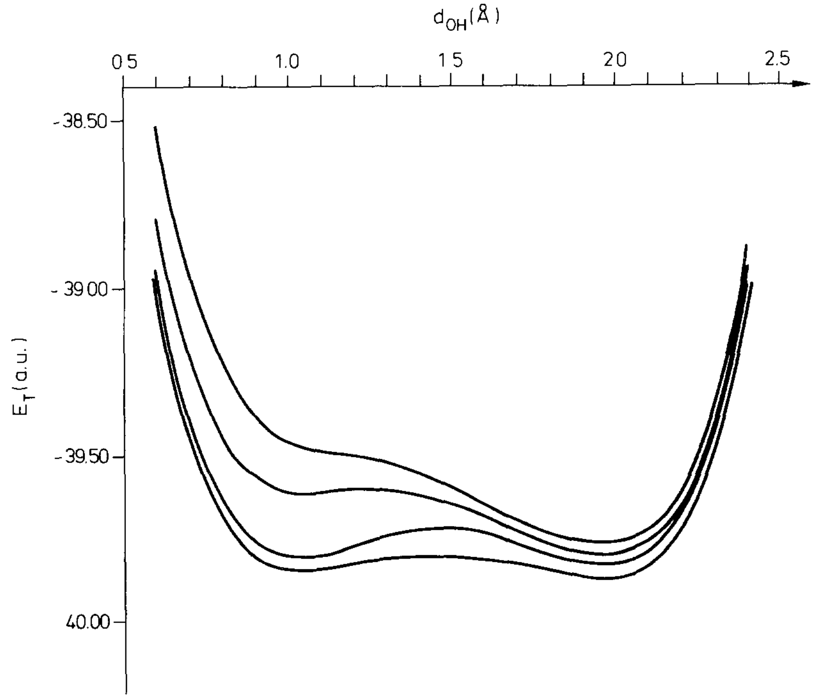

Fig. 2. Curves of total energy against OH distance. From top to bottom: for the unsolvated molecule; using the Jano correction; using Miertuš' model and using Constanciel's model

Table 1. Total energies for the minima, energy differences and barriers for the interconversion between them. All energies are in a.u. See text for the meaning of the last two lines

	$E_T(H_3O^+HO^-)$	$E_T(H_2OH_2O)$	ΔE^a	$B1^b$	$B2^c$
Unsolvated		−39.764906			
Jano	−39.602329	−39.794586	−0.192	0.006	0.198
Miertuš I	−39.790270	−39.823864	−0.034	0.086	0.120
Constanciel	−39.838072	−39.859101	−0.021	0.052	0.073
Miertuš II	−39.696303	−39.810296	−0.114	0.035	0.149
Constanciel (S.O.P.)	−39.881615	−39.923514	−0.042	0.043	0.085

[a] ΔE is the energy difference between the second and first minima.
[b] $B1$ is the barrier measured from the first minimum.
[c] $B2$ is the barrier measured from the second minimum.

In Fig. 3 we have drawn the components of the total energy in the VCM for $\varepsilon = 80.0$. It can be seen that while the core-medium interaction energy is responsible for the barrier between the two forms of the system, it is the medium self interaction energy which is responsible for the greater stability of the hydrogen-bonded form.

It is certainly true that the OO-distance in the dimer will influence the shape of the PPC. To explore this aspect of the problem we have calculated them for

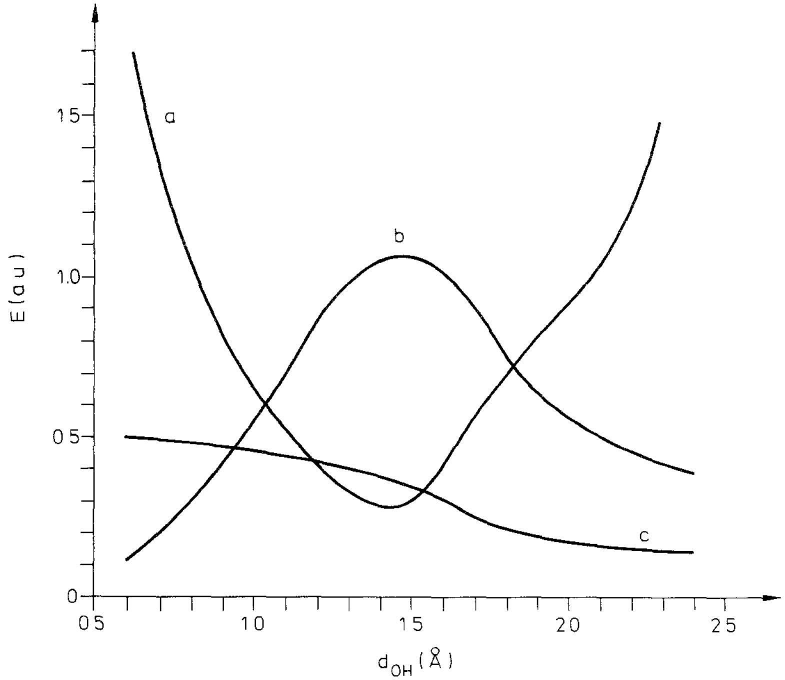

Fig. 3. Energy decomposition of total energy in Constanciel's model (a) $E^{el}+E^{rep}+43.5$ (a.u.) (b) $E^{core\text{-}med}-2.0$ (a.u.) (c) $E^{med\text{-}med}$ (a.u.)

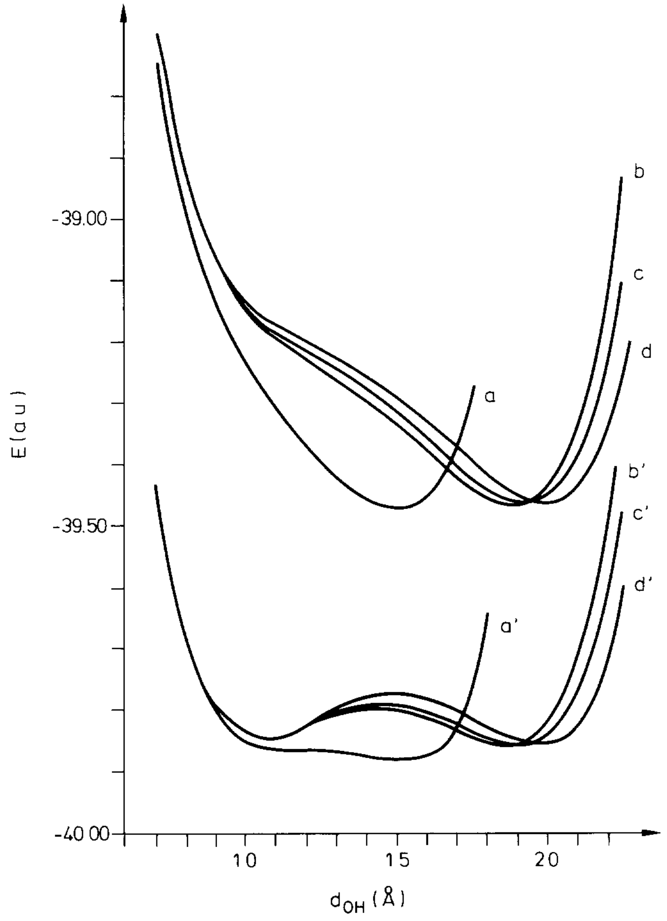

Fig. 4. PPC for different OO-distances. Primed letters represent the curves including solvation, unprimed ones the unsolvated cases. Unsolvated curves have been shifted 0.30 a.u. upwards for clarity in the drawing. (a) 2.55 Å, (b) 2.92 Å, (c) 2.96 Å and (d) 3.02 Å

some different OO-distances around the experimental one. The results obtained are plotted in Fig. 4 for $\varepsilon = 1.0$ and $\varepsilon = 80.0$.

We have also obtained the best OO-distance, according to the CNDO/2 method, using the experimental geometry of the monomers. The result, $d_{OO} = 2.55$ Å is, as expected, much shorter than the experimental one. The PPC calculated for this OO-distance is also depicted in Fig. 4. The analysis of these curves does not give any unexpected result. The increment in the monomers separation merely allows the decrease in the overlapping of the two attractive potentials for the proton. This motivates the appearance of double-minima-shaped curves but does not influence markedly neither the profoundness of the well, nor the position of the two minima (i.e. the distance of the proton to the oxygen to which it is bonded, see Table 2.)

Table 2. Total energies (in a.u.) and OH distances (in Å) for the minima obtained with different values of the OO distance. The values in parenthesis are the distances of the hydrogen to the oxygen to which it is bonded. The first row corresponds to the equilibrium OO distance determined by the CNDO/2 method. The other values were taken around the experimental equilibrium distance

	First minimum With solvation		Second minimum With solvation		Without solvation	
d_{OO}	E_T	d_{OH}	E_T	d_{OH}	E_T	d_{OH}
2.55			−39.774820	1.50 (1.05)	−39.878416	1.40 (1.15)
2.92	−39.840795	1.05	−39.768106	1.90 (1.02)	−39.863818	1.85 (1.07)
2.96	−39.840795	1.05	−39.766803	1.[illegible] (1.03)	−39.862973	1.90 (1.06)
3.02	−39.839050	1.05	−39.766544	2.00 (1.03)	−39.861091	1.95 (1.07)

In the VCM one is led to a factor depending on the $\frac{1}{2}$-power of the dielectric constant by the assumption that Born's equation for the solvation energy must be recovered [23]. The other possibility is preferring to reproduce the reaction field according to the electrostatic of a dielectric. In this case we have

$$E_s = -1/2(1-\varepsilon^{-1})E_{\Sigma s} \tag{17}$$

using the notation of reference [23]. Miertus has proposed [93] to use the basic features of VCM and the weighting factor $\frac{1}{2}(1-\varepsilon^{-1})$ in Fock operator and in $E_{\Sigma s}$, instead of $(1-\varepsilon^{-1/2})$ and to evaluate E_s according to

$$E_s = -1/2[1/2(1-\varepsilon^{-1})]E_{\Sigma s} \tag{18}$$

where $E_{\Sigma s}$ is the solute-solvent coulombic interaction energy at the end of the SCF procedure. This is exactly the same as Constanciel does, except that the "dielectric constant" in VCM, ε_C, is related with the one in MK model by the formula

$$\varepsilon_C = \frac{4\varepsilon_M^2}{(1+\varepsilon_M)^2}. \tag{19}$$

The analysis of Eq. (19) shows clearly that in this last model proposed by Miertuš only modest polarizations can be achieved (i.e. ε_c less than 4.0) as compared with the original Constanciel's model (in particular, the relation with the ω-technique [30, 90] could never be reached). For instance, in Fig. 5 we have drawn the PPC for the VCM and this method of Miertuš, both of them corresponding to $\varepsilon = 80.0$. The relevant data for the latter one are grouped in the fifth row of Table 1.

It can be observed the complete parallelism between both PPC. From the data in Table 1 we can deduce that this model suggests an easy conversion from

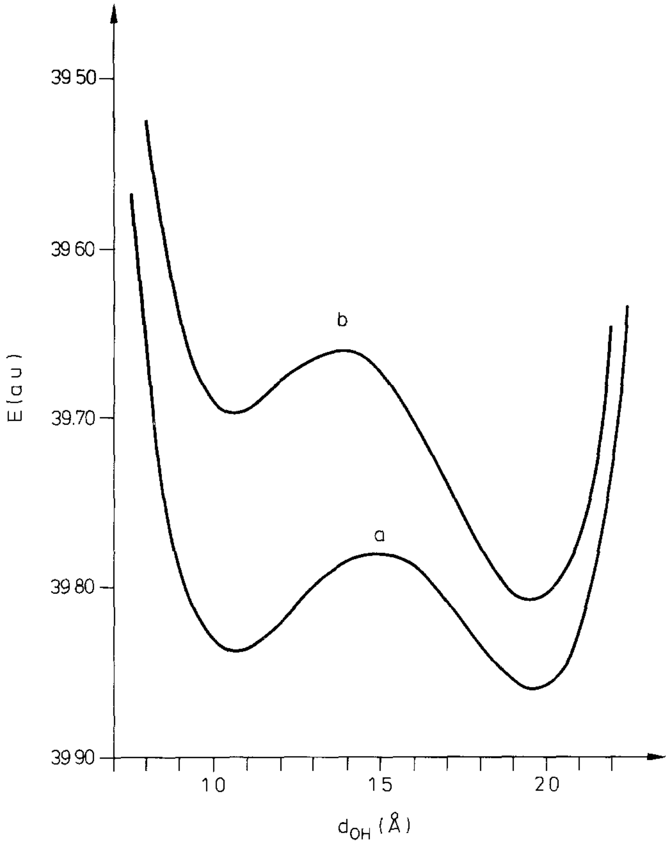

Fig. 5. PPC for Constanceil's method and for the second method of Miertus. (a) VCM, (b) Miertus' second method. In both cases the curves have been drawn with $\varepsilon = 80.0$

the ionic pair to the hydrogen-bonded system which may be, in the conditions of this study, a more faithful representation of the true situation. As a whole, it can be said that there is no reason to definitely prefer one of the models over the other. Something which is certainly sure however, is that the dielectric constant must not be taken too seriously but as a semi-empirical parameter which, in some way, is connected to the dielectric properties of the solvent. Its value, however, can vary greatly as the connection between the different "dielectric constants" in Klopman's, Miertuš' and Constanciel's models prove.

5. The Second Order Perturbation Energy

The methods discussed so far do not take into account the dispersion energy since they are of electrostatic nature only. The dispersion energy could be considered by a second order perturbation [27] and this is what we have done. In Fig. 6 we have plotted the S.O.P. energy against OH distance using the wavefunction calculated with Constanciel's solvation model ($\varepsilon = 80.0$). The

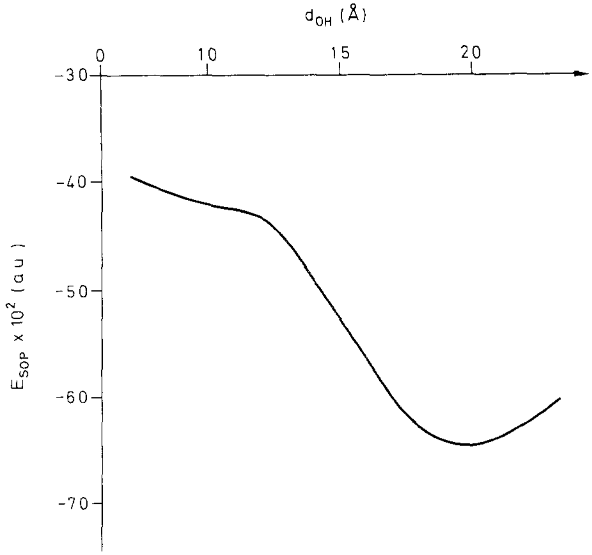

Fig. 6. Second order perturbation energy, in a.u., vs. OH-distance, in Å, for $\varepsilon = 80.0$

behavior of this perturbation term is the expected one. It is greater for the hydrogen-bonded form of the complex than for the ionic pair, where the electrostatic interactions are thought to be dominant. However small (only 1% of the total energy) the difference between the values for the two minima gives a net stabilization of the hydrogen-bonded form by 0.0209 a.u. This is similar to the energy difference between them calculated without the perturbation energy, which is 0.0210 a.u. Summing up these contributions we obtain an energy

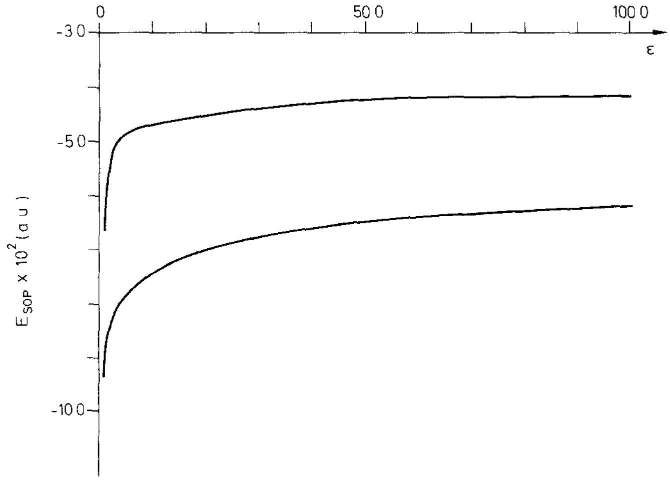

Fig. 7. Second order perturbation energy, in a.u., against dielectric constant for the ionic pair (top), and the hydrogen-bonded (bottom) forms of the system

difference of 0.0409 a.u. These values have been included as the sixth line of Table 1. In Fig. 7 we have drawn the curves of the S.O.P. energy vs. the dielectric constant for the two forms of the system. It can be seen that the behavior is similar in both situations. This implies that the S.O.P. energy will not substantially modify the curves of total energy whichever the dielectric constant may be. This is supported by Fig. 8 where the total energy and the total energy plus S.O.P. energy have been plotted against the dielectric constant. We can see that the two curves are very similar. Since the hydrogen-bonded form of the system is likely to be the more affected one, we can conclude that the results obtained for $\varepsilon = 80.0$ will be valid for other values of the dielectric constant.

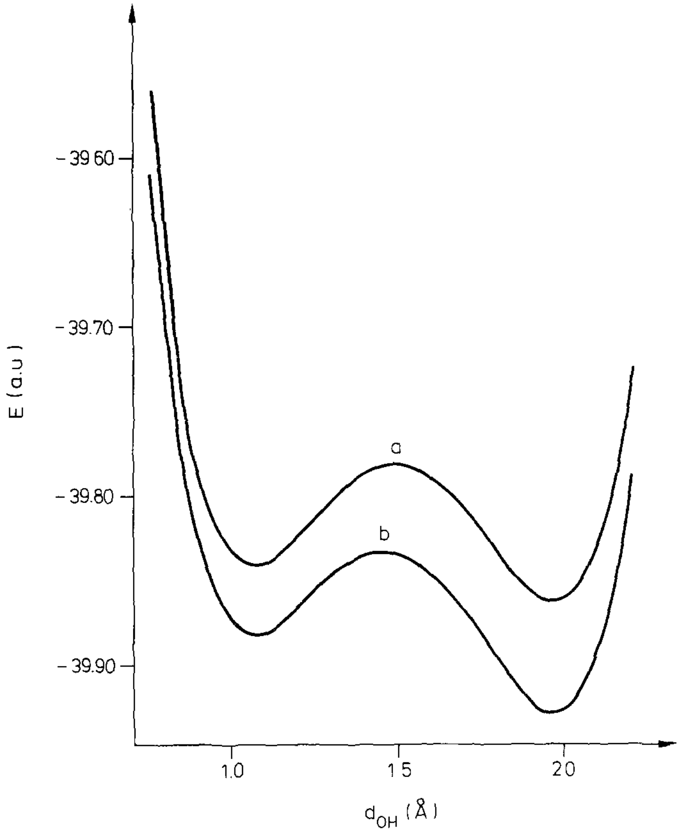

Fig. 8. Curve of total energy (a), and total energy plus S.O.P. energy (b) vs. dielectric constant. Energies are in a.u., $\varepsilon = 80.0$

6. Discussion and conclusions

From the calculations presented here it can be seen that of the three models, it is Constanciel's one the most capable of reproducing the solvent field, at least in a qualitative way. However, all the models predict a secondary minimum energy conformation which corresponds to the ionic pair.

The behavior of the S.O.P. energy in Constanciel's model is completly analogous to that obtained by Tapia et al. [22] in the framework of the SCRF model. This suggests that it may be a relation between the dielectric constant and the *g* factor, a fact which is also supported by the plot of the S.O.P. energy against the dielectric constant, the α factor and the *g* factor done in Figs. 9 and 10. This point has

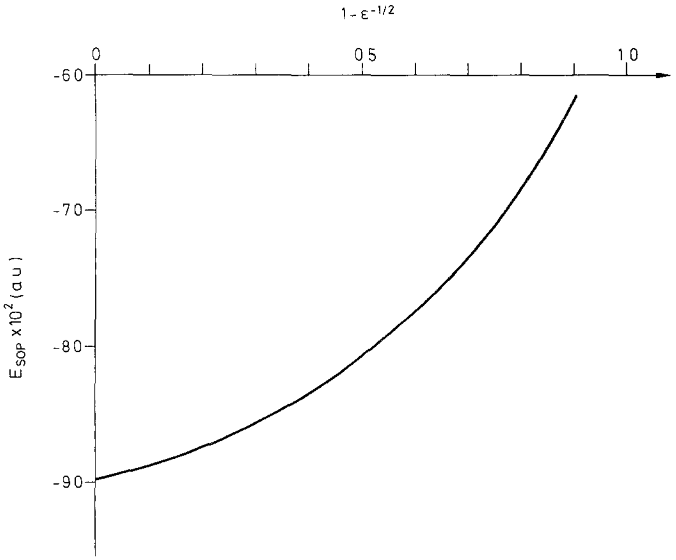

Fig. 9. Second order perturbation energy, in a.u., against $1-\varepsilon^{-1/2}$

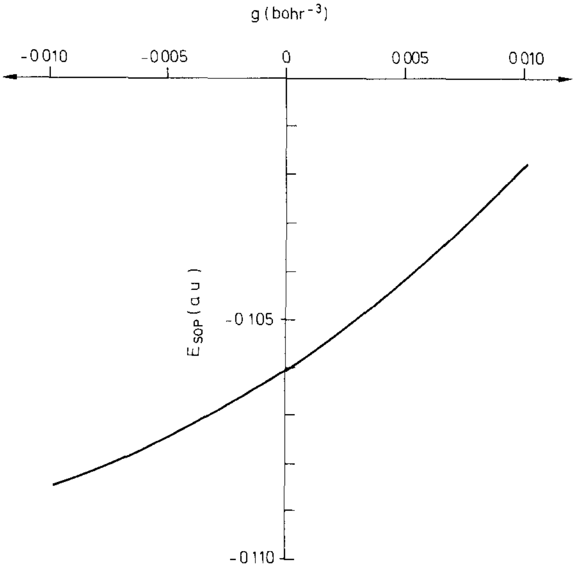

Fig. 10. Second order perturbation energy, in a.u., against *g* factor, in bohr^{-3}, in Tapia's calculation for a similar system than the one studied in this paper [9]

already been discussed in detail by Lamborelle and Tapia [29], Tapia and Silvi [65], and Tapia [92] where a thorough substantiation of this relation can be found.

It is clear that the main advantage of these models is the stabilization of ionic structures. This can be of great help in the study of reactions where the reactants are ionic or highly polarizable. However some care must be exercised when studying these systems. An example of the problems which may be encountered is provided by the $H_3O^+HO^-$ system. If the PPC for $\varepsilon = 80.0$ is calculated normally (i.e. without convergence-forcing methods) it is observed that the state of the system changes abruptly when the OH distance is greater than 1.1 Å. Comparing

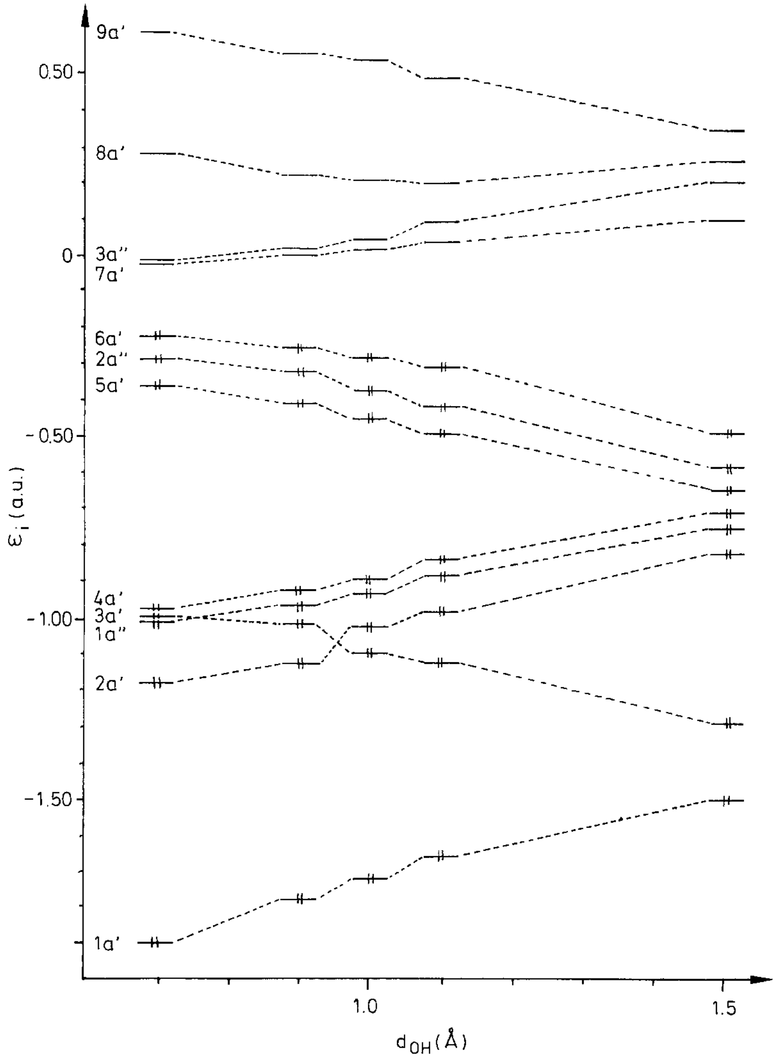

Fig. 11. Energies, in a.u., for the molecular orbitals of the ionic pair at OH distances between 0.7 and 1.5 Å, $\varepsilon = 1.0$

the ordering of the molecular orbitals in the zone of the PPC corresponding to the ionic pair we can observe the great difference between the unsolvated and solvated systems (see Figs. 11 and 12). Most important is that the crossing of the orbitals for OH distances between 1.0 Å and 1.1 Å involves the HOMO and LUMO of the system changing completely, at least in principle, its properties. An analysis of the charge distribution at OH distances of 1.0 Å and 1.1 Å shows that the wavefunction at the lower distance corresponds formally to the structure $H_3O^-HO^+$ a direct consequence of the fact that the molecular orbital which represents one lone pair of the oxygen in HO^- is unoccupied in this case leading to a transfer of two electrons from one fragment to the other and to this unphysical situation. To correct this error we used a simple linear mixing algorithm for the

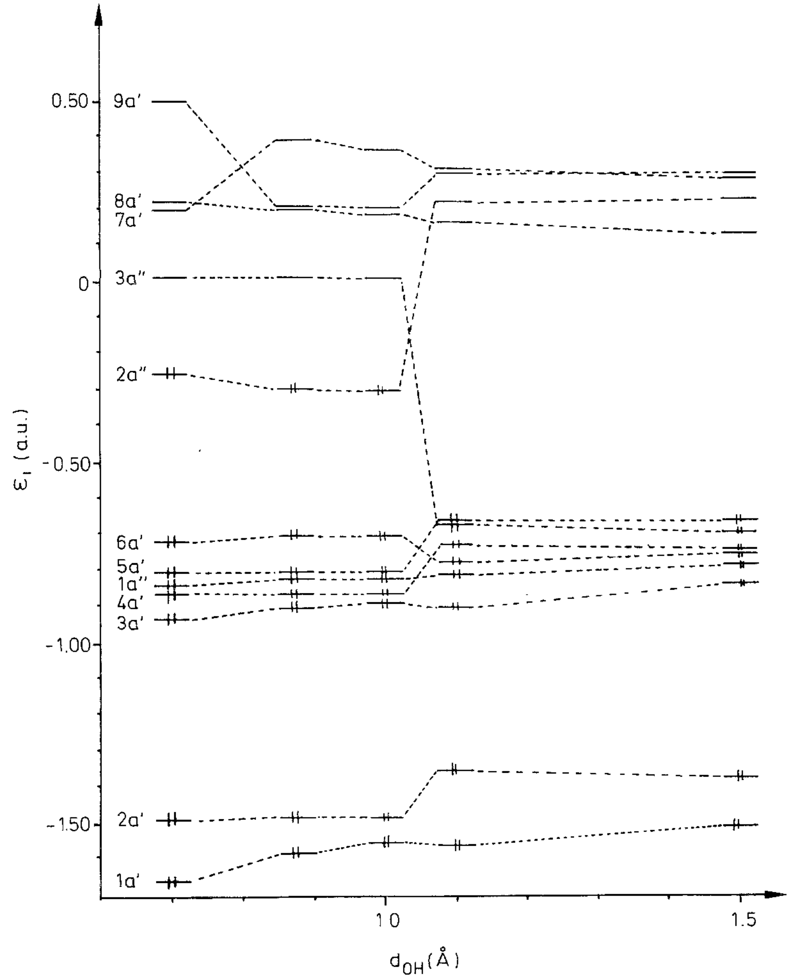

Fig. 12. Energies, in a.u., for the molecular orbitals of the ionic pair at OH distances between 0.7 and 1.5 Å, $\varepsilon = 80.0$

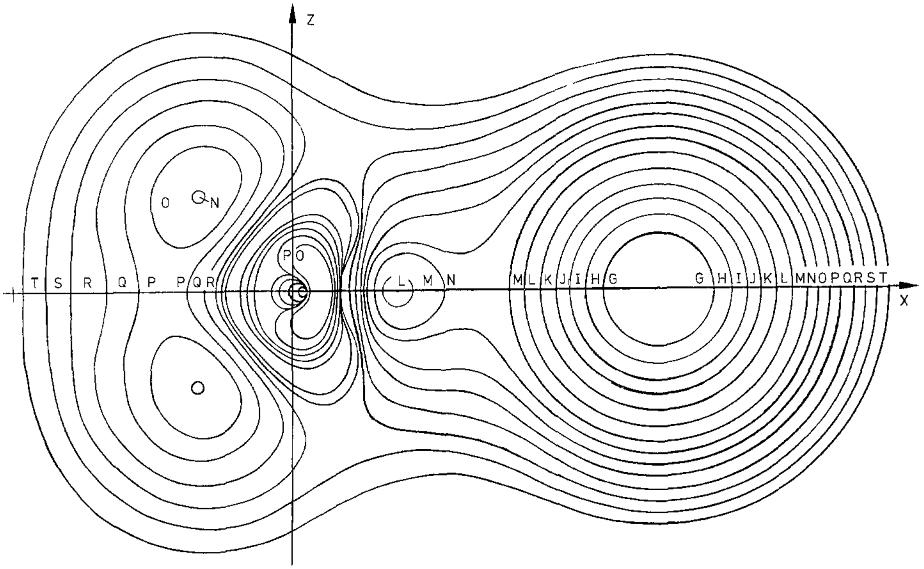

Fig. 13. Isoenergetic contours for the contribution of the HOMO of the system to its total density, $\varepsilon = 1.0$, $\lambda = 0.5$. The values of the contours are obtained dividing by 2.0 the value of the preceeding contour and beginning with $A = 32.0$ kcal/mol

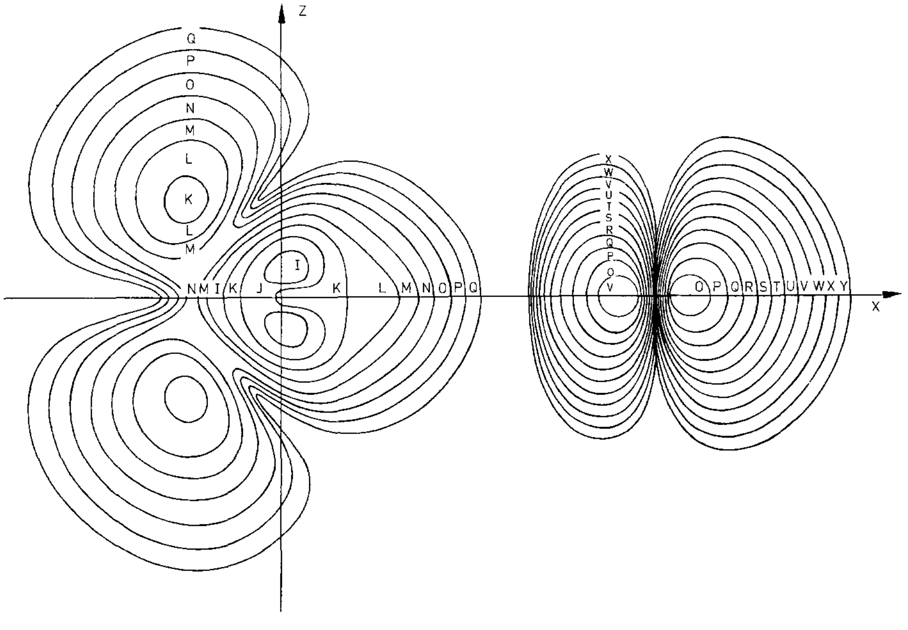

Fig. 14. Isoenergetic contours for the contribution of the HOMO of the system to its total density, $\varepsilon = 80.0$, $\lambda = 0.0$. The values of the contours are the same as in Fig. 13

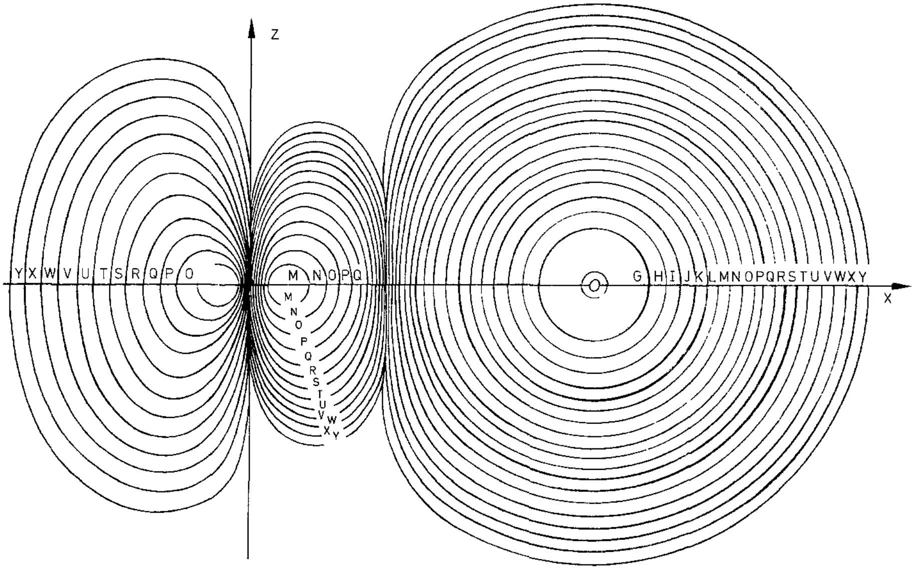

Fig. 15. Isoenergetic contours for the contribution of the HOMO of the system to its total density, $\varepsilon = 80.0$, $\lambda = 0.5$. The values of the contours are the same as in Fig. 13

density matrix in each iteration of the SCF procedure

$$P^{(i)} = (1-\lambda)P^{(i)} + \lambda P^{(i-1)}. \tag{20}$$

Using a mixing parameter $\lambda = 0.5$ it is possible to revert the situation so as to have the same state before and after the OH distance of 1.1 Å with the right occupancy for the aforementioned molecular orbital. The contribution of the HOMO to the total density shows this drastic change. As can be seen in Figs. 13, 14 and 15 it differs both from the unsolvated case and from the non-promediated one ($\lambda = 0.0$).

The explanation of this behavior can be found examining the lowest eigenvalue of the instabilities matrices E'' (according to Paldus and Cizek [82, 83]) and Q (according to Stanton [84, 85]). In Table 3 we report these values for the

Table 3. Lowest eigenvalues of the matrices of instabilities (see text). The distances are in Å. Note that the equality of the values for the singlet, triplet and non-real cases in the second, third, fourth and fifth columns is a coincidence since the other eigenvalues are different

d_{OH}	ε	λ	Singlet	Triplet	Non-real	Stanton
0.8	1.0	0.5	−0.09986	−0.29658	−0.09986	−1.41246
	80.0	1.0	−0.04983	−0.04983	−0.04983	−1.10702
	80.0	0.5	0.07400	0.07400	0.07400	−0.92321
1.1	1.0	0.5	−0.07731	−0.03203	−0.07731	−1.15911
	80.0	1.0	0.07470	0.07470	0.07470	−0.92255
	80.0	0.5	0.07470	0.07470	0.07470	−0.92255

unsolvated and solvated systems at $d_{OH} = 0.8$ Å and 1.1 Å respectively. For the solvated system we show the eigenvalues when $\lambda = 0.0$ and when $\lambda = 0.5$.

Some facts may be noted from this Table. First, the wavefunction for the unsolvated system is unstable and the effect of solvation is to reduce the absolute value of the least eigenvalue reported on this Table. However this reduction is not sufficient to make the SCF process converge to the stable wavefunction. To do this it is necessary to use the mixing of density matrices. The wavefunction obtained (to which we have referred above) is stable both from the point of view of Paldus and Cizek and from that of Stanton. The instability of the unsolvated wavefunction is obviously produced by the great separation of charge in the ionic pair. In the solvated wavefunction, on the other hand, the instability is produced by an anti-aufbau solution (see the work of Stanton) where the molecular orbital representing the oxygen lone pair should be occupied. In the second place, we can see that at $d_{OH} = 1.1$ Å (the equilibrium OH distance for the ionic pair) the unsolvated wavefunction continues to be unstable but the solvated solutions are stable for either value of λ. In fact there is no difference between the eigenvalues obtained for the two values of λ in this case.

Care must be exercised, then, because the solvent effect can influence the SCF process so as to give solutions that are really unstable but were obtained without convergence-forcing methods. In this respect we can think that the solvent perturbation of the Hamiltonian resembles the problems found in NMR calculations by Contreras and coworkers [86, 87].

Some final remarks may be done concerning the energy decomposition analysis of Constanciel's model. First it may be argued that the solvent polarization energy for the hydrogen-bonded system, $E^{\text{med-med}} = 106$ kcal/mol is too high. The calculations done shows that this energy varies very slowly with the separation of the molecules so that the principal effect on it seems to be mainly independent of the bonds between the fragments and largely dependent on the individual solvent polarization energy of each of them. In the case of the water monomer our calculations give approximately 57.9 kcal/mol for $E^{\text{med-med}}(H_2O)$. This implies that the effect in the dimer is simply connected to the effect in the monomers. Since this energy is directly connected to the formal charge of the atoms it depends on the accuracy with which the CNDO/2 method reproduces the polarity of the bonds. This is an aspect of the problem which needs further study.

Another problem is that the difference between the two minima coming from the *b*-terms is small (approx. 6 kcal/mol) and then the energy difference comes from the near cancellation of two opposite quantities (*a*- and *c*-terms). Although this may obscure the meaningfulness of the conclusions based on quantitative differences between the minima it can not alter the essential fact of the existence of them and of the existence of the barrier since these facts are provided by *b*-terms. Other information to take into account is that the dispersion energy acts in the same direction as the deduced energy difference so that any problem with the compensation can be masked by the effect of it. This is another point which merits a thorough investigation.

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References

1. Pullman, A., Armbruster, A. M.: Int. J. Quantum Chem., Symp. **8**, 169 (1974).
2. Pullman, A., Armbruster, A. M.: Chem. Phys. Letters **36**, 558 (1975).
3. Tapia, O., Johannin, G.: J. Chem. Phys. **75**, 3624 (1981).
4. Port, H. N. J., Pullman, A.: Theoret. Chim. Acta **31**, 231 (1973).
5. Port, H. N. J., Pullman, A.: Int. J. Quantum Chem. **QBS1**, 21 (1974)
6. Pullman, B., Courriere, Ph., Berthod, H.: J. Med. Chem. **17,** 439 (1974)
7. Pullman, B., Pullman, A., Berthod, H., Gresh, N.: Theoret. Chim. Acta (Berl.) **40**, 93 (1975)
8. Schnuelle, G. W., Swaminathan, S., Beveridge, D. L.: Theoret. Chim. Acta (Berl. **48**, 17 (1978)
9. Pullman, A., Perahia, D.: Theoret. Chim. Acta (Berl.) **48**, 29 (1978)
10. Claverie, P., Daudey, J. P., Langlet, J., Pullman, B., Piazzola, D.: J. Phys. Chem. **82**, 405 (1978)
11. Rivail, J. L., Rinaldi, D.: Chem. Phys. **18**, 233 (1976)
12. Bertran, J., Oliva, A., Rinaldi, D., Rivail, J. L.: Nouv. J. Chim. **4**, 209 (1980)
13. Lavery, R., de Oliveira, M., Pullman, B.: Int. J. Quantum Chem. **QBS6**, 459 (1979)
14. Miertuš, S., Kyseĺ, O.: Chem. Phys. **21**, 27 (1977)
15. Miertuš, S., Kyseĺ, O.: Chem. Phys. **21**, 33 (1977)
16. Miertuš, S., Kyseĺ, O.: Chem. Phys. **21**, 47 (1977)
17. Miertuš, S., Kyseĺ, O.: Chem. Phys. Letters **65**, 395 (1979)
18. Miertuš, S., Bartos, J.: Coll. Czechoslov. Chem. Commun. **45**, 2308 (1980)
19. Tvaroska, I., Bleha, T.: Coll. Czechoslov. Chem. Commen. **43**, 922 (1978)
20. Tvaroska, I., Bleha, T.: Coll. Czechoslov. Chem. Commun. **45**, 1883 (1980)
21. Bleha, T., Gajdos, J., Tvaroska, I.: J. Mol. Struct. **68**, 189 (1980)
22. Tapia, O., Poulain, E., Sussman, F.: Chem. Phys. Letters **33**, 65 (1975)
23. Constanciel, R., Tapia, O.: Theoret. Chim. Acta (Berl.) **48**, 75 (1978)
24. Germer, H. A.: Theoret. Chim. Acta (Berl.) **34**, 145 (1974)
25. Germer, H. A.: Theoret. Chim. Acta (Berl.) **35**, 273 (1974)
26. Tapia, O., Poulain, E.: Int. J. Quantum Chem. **11**, 473 (1977)
27. Tapia, O., Poulain, E., Sussman, F.: Theoret. Chim. Acta (Berl.) **47**, 171 (1978)
28. Tapia, O.: Theoret. Chim. Acta (Berl.) **47**, 157 (1978)
29. Lamborelle, C., Tapia, O.: Chem. Phys. **42**, 25 (1979)
30. Constanciel, R.: Theoret. Chim. Acta (Berl.) **54**, 123 (1980)
31. Pullman, B., Berthod, H., Gresh, N.: FEBS Letters **53**, 199 (1975)
32. Dashevsky, V. G., Sarkisov, G. N.: Mol. Phys. **27**, 1271 (1974)
33. Basu, S.: Adv. Quantum Chem. **1**, 145 (1964)
34. Sinanoğlu, O., in The world of quantum chemistry, p. 131. R. Daudel et al. eds. Dordrecht: Reidel, 1974.
35. Sinanoğlu, O.: Theoret. Chim. Acta (Berl.) **33**, 279 (1974)
36. Beveridge, D. L., Kelly, M. P., Radna, R. J.: J. Am. Chem. Soc. **96**, 3769 (1974)
37. Huron, H. J., Claverie, P.: J. Phys. Chem. **76**, 2123 (1972)
38. Huron, M. J., Claverie, P.: J. Phys. Chem. **78**, 1853 (1974)
39. Huron, M. J., Claverie, P.: J. Phys. Chem. **78**, 1862 (1974)
40. Beveridge, D. L., Kelly, M. P., Radna, R. J.: J. Am. Chem. Soc. **96**, 153 (1974)
41. Birnstock, F., Hoffman, H. J., Kohler, H. J.: Theoret. Chim. Acta (Berl.) **42**, 311 (1977)
42. Kistenmacher, H., Lie, G. C., Popkie, H., Clementi, E.: J. Chem. Phys. **61**, 546 (1974)
43. Matsuoka, O., Clementi, E., Yoshimine, M.: J. Chem. Phys. **64**, 1351 (1976)
44. Lie, G. C., Clementi, E., Yoshimine, M.: J. Chem. Phys. **64**, 2314 (1976)
45. Clementi, E., Cavallone, F., Scordamaglia, R.: J. Am. Chem. Soc. **99**, 5531 (1977)
46. Scordamaglia, R., Cavallone, F., Clementi, E.: J. Am. Chem. Soc. **99**, 5545 (1977)
47. Bolis, G., Clementi, E.: J. Am. Chem. Soc. **99**, 5550 (1977)
48. Clementi, E., Ranghino, G., Scordamaglia, R.: Chem. Phys. Letters **49**, 218 (1977)

49. Carozzo, L., Corongiu, G., Petrongolo, C., Clementi, E.: J. Chem. Phys. **68**, 787 (1978)
50. Romano, S., Clementi, E.: Int. J. Quantum Chem. **14**, 839 (1978)
51. Romano, S., Clementi, E.: Gazz. Chim. Ital. **108**, 319 (1978)
52. Ragazzi, M., Ferro-D. R., Clementi, E.: J. Chem. Phys. **70**, 1040 (1979)
53. Clementi, E., Corongiu, G.: Biopolymers **18**, 2431 (1979)
54. Clementi, E., Corongiu, G., Jonsson, B., Romano, S.: FEBS Letters **100**, 313 (1979)
55. Clementi, E., Corongiu, G.: Int. J. Quantum Chem. **16**, 897 (1979)
56. Clementi, E.: Gazz. Chim. Ital. **109**, 201 (1979)
57. Romano, S., Clementi, E.: Int. J. Quantum Chem. **17**, 1007 (1980)
58. Clementi, E., Corongiu, G., Jonsson, B., Romano, S.: J. Chem. Phys. **72**, 260 (1980)
59. Clementi, E., Corongiu, G.: J. Chem. Phys. **72**, 3979 (1980)
60. Clementi, E., Corongiu, G., Lelj, F.: J. Chem. Phys. **70**, 3726 (1979)
61. Barriol, J., Weisbecker, A.: C. R. Acad. Sci. **265C**, 1372 (1967)
62. Rivail, J. L., Thiebault, J. M.: J. Chem. Soc. Faraday II **70**, 430 (1974)
63. Abraham, R. J., Cavalli, L., Pachler, K. G. R.: Mol. Phys. **11**, 471 (1966)
64. Tomila, E.: Acta Chem. Scand. **13**, 662 (1959)
65. Tapia, O., Silvi, B.: J. Phys. Chem. **84**, 2646 (1980)
66. Tapia, O., Sussman, F., Poulain, E.: J. Theor. Biol. **71**, 49 (1978)
67. Tapia, O., Lamborelle, C., Johannin, G.: Chem. Phys. Letters **72**, 334 (1980)
68. A. Warshel: Chem. Phys. Letters **55**, 454 (1978)
69. A. Warshel: J. Phys. Chem. **83**, 1640 (1979)
70. Berndt, M., Kwiatkowski, J. S.: Theoret. Chim. Acta (Berl.) **50**, 223 (1978)
71. Thole, B. T., van Duijnen, P. T.: Theoret. Chim. Acta (Berl.) **55**, 307 (1980)
72. Stillinger, F. H., David, C. W.: J. Chem. Phys. **69**, 1473 (1978)
73. David, C. W., David, E. E.: J. Comput. Chem. **2**, 414 (1981)
74. Pople, J. A., Beveridge, D. L., Approximate molecular orbital theory. New York: McGraw-Hill 1970
75. Dyke, T. R., Muenter, J. S.: J. Chem. Phys. **60**, 2929 (1974)
76. Thiel, W.: Theoret. Chim. Acta (Berl.) **48**, 357 (1978)
77. Zhixing, C.: Theoret. Chim. Acta (Berl.) **54**, 169 (1980)
78. Jano, I.: C.R. Acad. Sci. **261D**, 103 (1965)
79. Hoijtink, G. J., de Beer, E., Van der Meij, P. H., Weijland, W. P.: Rec. Trav. Chim. Pays Bas. **75**, 487 (1956)
80. Klopman, G.: Chem. Phys. Letters **1**, 200 (1967)
81. Thouless, D. J.: The quantum mechanics of many body systems. New York: Academic Press 1961
82. Čižek, J., Paldus, J.: J. Chem. Phys. **47**, 3976 (1967)
83. Chambaud, G., Levy, B., Millie, P.: Theoret, Chim. Acta (Berl.) **48**, 103 (1978)
84. Stanton, R. E.: J. Chem. Phys. **75**; 3426 (1981)
85. Stanton, R. E.: J. Chem. Phys. **75**, 5416 (1981)
86. Facelli, J. C., Contreras, R. H.: J. Chem. Phys. **77**, 1076 (1982)
87. Scuseria, G. E., Engelman, A. R., Contreras, R. H.: Theoret. Chim. Acta (Berl.) **61**, 49 (1982)
88. Born, M.: Z. Physik **1**, 45 (1920)
89. Klopman, G., Andreozzi, P. : Theoret. Chim. Acta **55**, 77 (1980)
90. Constanciel, R. in: Quantum theory of chemical reactions, Vol II, p. 73. R. Daudel et al. eds., Dordrecht: Reidel 1980
91. Sanhueza, J. E., Tapia, O., Laidlaw, N. C., Trsic, M.: J. Chem. Phys. **70**, 3096 (1979)
92. Tapia, O. in: Quantum theory of chemical reactions, Vol II, p. 25. R. Daudel et al. eds. Dordrecht: Reidel 1980
93. Miertuš, S.: private communication
94. David, C. W.: Chem. Phys. Letters **78**, 488 (1981)
95. Duben, A. J., Miertuš, S.: Theoret. Chim. Acta (Berl.) **60**, 327 (1981)

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