

Some Remarks on the SCRF Theory of Solvent Effects and the Calculation of Proton Potentials

O. Tapia

Centre de Mécanique Ondulatoire Appliquée, C.N.R.S., 23, rue du Maroc, F-75019 Paris, France

Some aspects concerning the self-consistent reaction field theory of solvent effects are discussed. In particular, the variational solution to the non-linear Schrödinger equation is considered; a necessary and sufficient constraint to be added to the standard variational procedure is discussed. The exact solution of the non-linear equation is presented within the molecular orbital approach; correlation defaults to the Hartree–Fock like solutions are stated. Some thermodynamical correspondences are established with the magnitudes calculated with the self-consistent reaction field theory. Finally, we have commented upon the proton potentials calculated within this theory. An INDO calculation of a water trimer has been used as an example to discuss different types of proton translocation potentials.

Key words: Solvent effect – Proton potentials – Self-consistent reaction field

1. Introduction

The self-consistent reaction field (SCRF) theory of solvent effects [1] leads to a non-linear Schrödinger equation that represents the solute *in* a polarizable medium. Recently, a similar theory [2] has been proposed to describe a dipolar system inside a globular protein. Several applications to the study of environmental effects upon H-bonded systems [2–5] have been published. However, the papers published so far have not given any details concerning the molecular orbital (MO) formalism used to solve the non-linear equation. But continued work has made the author aware of the fact that clarifications and developments concerning the whole formalism may be desirable.

The first remark concerns the application of the variational principle and corresponding calculus to obtain an exact or an approximate solution of the non-linear Schrödinger equation. The problems discussed have a wider scope; they are related

to the variational solutions of the so-called Hückel self-consistent methods [6]. The discussion of these topics forms Sect. 2.

The well established MO formalism [7] as it is applied to obtain the exact wave-function and energy of the ground electronic state is introduced in Sect. 3. There, some of the new features concerning the SCRf theory are discussed. The energy expressions used to obtain the previous numerical results are more explicitly re-defined. Within this theory it is possible to calculate the electronic energy E of the molecule subjected to the surrounding medium effect, together with the total energy ε which corresponds to E plus the energy necessary to polarize the environment.

The total energy ε turns out to be the electrostatic contribution to the internal energy of the whole system. In Sect. 4 some further thermodynamical analogies are discussed. They illustrate the double character of the SCRf theory. This double character is related to the statistical mechanical nature of the reaction field and to the quantummechanical description of the solute molecule (or system of interest).

Sect. 5 closes the paper; therein an INDO-MO [8] study of a tetrahedrally arranged water trimer is presented. The study illustrates the difference between the E and the ε proton potentials.

2. Variational Solution of the Non-Linear Schrödinger Equation

The SCRf theory of solvent effects on dipolar systems replaces the standard electronic Schrödinger equation

$$H_0\Phi = E(Q)\Phi \quad (1)$$

where H_0 is the electronic Hamiltonian, E and Φ the energy eigenvalue and eigenfunction, by the non-linear equation

$$[H_0 - \mu \cdot \bar{g} \cdot \langle Y | \mu | Y \rangle] Y = H[Y] Y = E(Q) Y; \quad (2)$$

Q stands for the set of nuclear coordinates; μ is the total electric dipole moment operator:

$$\mu = \sum_{k=1}^m Z_k Q_k - \sum_{i=1}^u \gamma_i \quad (3)$$

where γ_i and Q_k are respectively the position vector operators of the i 'th electron and k 'th nucleus, Z_k being the charge of the latter. Y represents the molecular wave function *in* the medium; therefore, it should contain the polarization effects of that medium. The coupling between the molecular system of interest and the polarizable medium is given by the reaction field R ,

$$R(Y) = \bar{g} \cdot \langle Y | \mu | Y \rangle = \bar{g} \cdot M(Y) \quad (4)$$

This field is produced by the surrounding medium which was polarized by the molecular dipole electric field; the tensor \bar{g} represents a reaction field sus-

ceptibility. If the surrounding medium is inhomogeneous, a finite electric field produced by the molecular multipoles in the medium should be added [2]. From (3) and (4) it is seen that, in fact, the reaction field depends on the first order density matrix associated to \mathcal{Y} . A number of procedures are based upon a variational solution of either (1) or (2). For the linear case, cf. Eq. (1), the Euler–Lagrange equation derived from the variational principle is the corresponding Schrödinger equation [9], provided that the variation is allowed within the whole relevant Hilbert space. A different result is obtained once the variational calculus is applied to the functional

$$J(\tilde{\phi}) = \langle \tilde{\phi} | H[\tilde{\phi}] | \tilde{\phi} \rangle / \langle \tilde{\phi} | \tilde{\phi} \rangle \quad (5)$$

This functional has the standard form used for the linear case. Consider a variational wave function $\tilde{\phi}$ such that

$$\tilde{\phi} = \mathcal{Y} + \varepsilon\phi \quad (6)$$

where ε is a positive, otherwise arbitrary, real number, ϕ belongs to a family of variational functions orthogonal to \mathcal{Y} , this later being the exact wave function of (2). We first expand $H[\tilde{\phi}]$ around the exact wave function up to terms of first order in ε ,

$$H[\tilde{\phi}] = H[\mathcal{Y}] + H'[\mathcal{Y}]\varepsilon\phi + O(\varepsilon^2) \quad (7)$$

where $H'[\mathcal{Y}]$ is the first Fréchet derivative [10] of $H[\tilde{\phi}]$ taken at \mathcal{Y} . For the Hamiltonian used in (2) one has:

$$H'[\mathcal{Y}] = -\varepsilon\boldsymbol{\mu} \cdot \langle \phi | \bar{\boldsymbol{g}} \cdot \boldsymbol{\mu} | \mathcal{Y} \rangle \quad (8)$$

The transition-like integral $\langle \phi | \bar{\boldsymbol{g}} \cdot \boldsymbol{\mu} | \mathcal{Y} \rangle$ will be referred to as $\mathbf{R}(\phi, \mathcal{Y})$. The first variation of $\mathbf{R}(\tilde{\phi})$ is written as

$$\delta\mathbf{R} = 2\varepsilon \operatorname{Re}\{\mathbf{R}(\phi, \mathcal{Y})\} \quad (9)$$

The first variation of J is therefore given by

$$\delta J = 2\varepsilon \operatorname{Re} \{ \langle \phi | H[\mathcal{Y}] - J(\mathcal{Y}) | \mathcal{Y} \rangle - \mathbf{M}(\mathcal{Y}) \cdot \mathbf{R}(\phi, \mathcal{Y}) \} \quad (10)$$

where \mathcal{Y} is taken normalized to unity.

Thus, unlike the linear case, the stationary value of (5) at $\phi = \mathcal{Y}$, i.e., $\delta J(\mathcal{Y}) \equiv 0$ does not lead to (2), but to a different Euler–Lagrange equation, unless \mathcal{Y} fulfils the condition

$$2\varepsilon \operatorname{Re} \{ \mathbf{M}(\mathcal{Y}) \cdot \mathbf{R}(\phi, \mathcal{Y}) \} \equiv 0 \quad (11)$$

This is therefore a necessary condition for the variational functional (5) to lead to the proper solution of (2). This condition is also a sufficient condition. This statement can be proved using the functional forms of Ref. [1]. The MO theory requires a variational solution of (5) with a trial wave function $\tilde{\phi}$ satisfying some shape restriction, such as being a single-determinant wave function. Assume that $\tilde{\mathcal{Y}}$ is the one of such functions that leads to a stationary value of (5). Replacement

of \mathcal{Y} by $\tilde{\mathcal{Y}}$ in the preceding formulas leads to

$$\delta J = 2\varepsilon \operatorname{Re} \{ \langle \phi | H[\tilde{\mathcal{Y}}] - J(\tilde{\mathcal{Y}}) \tilde{\mathcal{Y}} \rangle - \mathbf{M}(\tilde{\mathcal{Y}}) \cdot \mathbf{R}(\phi, \tilde{\mathcal{Y}}) \} = 0 \quad (12)$$

where ϕ is now orthogonal to $\tilde{\mathcal{Y}}$. Therefore, if the approximate wave function $\tilde{\mathcal{Y}}$ is going to be a solution of a non-linear Schrödinger equation similar to (2), i.e.,

$$H[\tilde{\mathcal{Y}}] \tilde{\mathcal{Y}} = J(\tilde{\mathcal{Y}}) \tilde{\mathcal{Y}} \equiv \tilde{E} \tilde{\mathcal{Y}} \quad (13)$$

Then a condition analogous to (11) must be fulfilled. It follows now that (11) with $\tilde{\mathcal{Y}}$ instead of \mathcal{Y} is a necessary condition to be satisfied by the approximate solutions to (2). As was already stated this condition is also a sufficient one. In fact (11) may be recast to read

$$\frac{1}{2} \delta(\mathbf{R}(\tilde{\phi}) \cdot \mathbf{M}(\tilde{\phi})) |_{\tilde{\phi} = \tilde{\mathcal{Y}}} = 0 \quad (14)$$

where, for the sake of simplicity, real functions are assumed throughout. Now, one assumes that (14) is fulfilled. Furthermore, one has

$$\delta \langle \tilde{\phi} | \tilde{\phi} \rangle = 0 \quad (15)$$

and using the method of undefined Lagrange multipliers the functional

$$J_1(\tilde{\phi}) = \langle \tilde{\phi} | H[\tilde{\phi}] | \tilde{\phi} \rangle - \lambda \langle \tilde{\phi} | \tilde{\phi} \rangle + \frac{\lambda'}{2} \mathbf{R}(\tilde{\phi}) \cdot \mathbf{M}(\tilde{\phi}) \quad (16)$$

leads to (13) once λ' is taken as 1. For an energy origin defined by $J(\tilde{\mathcal{Y}}) \equiv 0$, λ is given by

$$\lambda = \tilde{E} + \frac{1}{2} \mathbf{R}(\tilde{\mathcal{Y}}) \cdot \mathbf{M}(\tilde{\mathcal{Y}}) \quad (17)$$

λ represents the total value of the molecular electronic energy in the medium and the energy spent to polarize the medium. It should be noticed that λ itself may be taken as a variational functional although it is not the expectation value of any Hamiltonian. The λ -functional has been used by some authors in connection with Onsager's approximation to the reaction field [11, 12].

The discussion presented so far may also be applied to any non-linear operator which is a function of the first-order density matrix. This is the case of the self-consistent Hückel molecular orbital method [16, 13]. Here the effective Hamiltonian depends upon the wave function through the charge distribution. Iterative extended Hückel methods also belong to this class of effective Hamiltonians. Therefore, according to the preceding scheme, once the linear variational technique is applied to minimize the energy functional an equation analogous to (12) will be obtained. This was first pointed out by F. Harris but he missed the restriction to be imposed to build up an adequate variational functional (c.f. Eq. (16)). The secular equation derived in this manner is bound to misrepresent the problem that one wants to solve. Moreover, in some other cases it would lead to finding difficulties with either interpretation of the parameters [6] or with convergence of the iterative procedure [15]. Some of these problems have been discussed by Sanhueza *et al.* [16]; the reader is referred to this work for further details.

3. Exact Energy and Wave Function, MO-Approach

3.1. The SCRF MO Formalism

For the sake of simplicity we consider a closed-shell non-degenerate electronic state of a system having $n = 2m$ electrons. Assume that a basic set of one-electron functions exists (i.e., the molecular orbitals). Hence a n -electron determinantal wave function can be built up out of the m MO's of lower energy taken twice, first with the α and then with the β spin function.

Once the variational principle is applied to the energy expectation value $\langle \tilde{\psi} | H[\tilde{\psi}] | \tilde{\psi} \rangle$, subjected to the normalization and dipole moment restrictions, a set of Hartree-Fock (HF)-like equations for the MO's is obtained,

$$[f_0(\tilde{\phi}) + \gamma \cdot \bar{g} \cdot \mathbf{M}(\tilde{\phi})] \phi_k = f \phi_k = \varepsilon_k \phi_k. \quad (18)$$

f_0 is the conventional HF operator; ϕ_k and ε_k stand for the k 'th MO and its corresponding energy [8, 9].

In principle (18) provides a complete set of MO's. By assumption the set of m MO's having the lower orbital energy is non-degenerate.

Eq. (18) can be solved either by *ab initio* or semiempirical or approximate procedures. Usually the linear combination of atomic orbitals (LCAO) approximation is made to represent the MO's.

Since both f_0 and \mathbf{M} depend on the set of m MO's of lower energy, in practice (18) is solved iteratively until a prescribed numerical threshold is attained. The solutions obtained thereby will be referred to as SCRFMO's, whatever the actual numerical technique used might be. The determinantal wave function so obtained will be designed by ψ_{SCRF} .

For the MO's belonging to the lowest energy configuration, (18) describes the electron orbital motion subjected to the nuclei-electron potential and the averaged effect of the remaining $n - 1$ electrons plus the simultaneous polarization field produced by the SCRFMO dipole moment ($\mathbf{M}(\psi_{\text{SCRF}}) = \mathbf{M}_{\text{SCRF}}$).

Therefore, once the self-consistency threshold has been attained, most of the surrounding medium polarization effects, derived from the reaction field, are implicitly included in the MO's as well as explicitly in the orbital energies.

However, as is well known, the independent particle approach, and in particular the one described so far, fails to incorporate the instantaneous correlation interactions between the electrons. Since we have taken up the supermolecule approach to study the intermolecular interactions, neglecting the instantaneous correlations amounts to leaving the London-van der Waals dispersion interaction out of the scheme. Moreover, the correlation default of the wave function may also affect the SCRF MO dipole moment and therefore, errors in the energy calculated with it may be important.

To recover the London-van der Waals effects and allow for the correlation default to the dipole moment (\mathbf{M}_c), one should go beyond the single particle

model. In the following paragraph an exact scheme starting from the one given here is developed.

3.2. The Exact Wave Function and Energy

Starting from the basis set $\{\phi_k\}$ of eigenfunctions of (18) any selection of n functions $\phi_{k_1}, \phi_{k_2}, \dots, \phi_{k_n}$ with $K_1 < K_2 < \dots < K_n$ is called an ordered configuration K , and it can be shown that any antisymmetric wave function ψ may be expanded in terms of Slater determinants (ψ_K) over such configurations. In comparison to the Slater determinant ψ_{SCRF} over the occupied one-electron functions $\phi_1, \phi_2, \dots, \phi_n$ (fundamental configuration), the various configurations which may be described as singly-, doubly-... , n -excited; $\psi_k^\lambda, \psi_{k_1}^{\lambda\gamma}$, etc., are the corresponding Slater determinants derived by replacement of $\phi_k, \phi_k\phi_1$ out of the fundamental configuration by respectively $\phi_\lambda, \phi_\lambda\phi_\gamma$ of the orthogonal complement. The exact wavefunction may now be written as [7]

$$\psi = \psi_{\text{SCRF}} + \psi_1 + \psi_2 + \dots + \psi_n \quad (19)$$

where $\psi_1 = \sum_{k,\lambda} C_k^\lambda \psi_k^\lambda$; $\psi_2 = \sum_{k_1\lambda_1\gamma} C_{k_1}^{\lambda_1\gamma} \psi_{k_1}^{\lambda_1\gamma}$, etc.; and the C 's are coefficients to be determined, either with a variational approach (the method of configuration interaction) or with a perturbative scheme.

The wave function (19) fulfills the intermediate normalization condition

$$\langle \psi_{\text{SCRF}} | \psi \rangle = \langle \psi_{\text{SCRF}} | \psi_{\text{SCRF}} \rangle = 1 \quad (20)$$

the total energy E is obtained from (1), (11), (12) and (13)

$$E = \langle \psi_{\text{SCRF}} | H_0 | \psi_{\text{SCRF}} \rangle + \langle \psi_{\text{SCRF}} | V | \psi_2 \rangle - \mathbf{M}_{\text{SCRF}} \cdot \bar{\mathbf{g}} \cdot \mathbf{M} \quad (21)$$

where V is the bielectronic Coulomb repulsion operator appearing in H_0 [7].

The first two terms of (21) are similar to those appearing in the conventional theory [7]. Therefore, when an interacting pair of molecules is treated as a supermolecule, interpretation in terms of the theory of intermolecular interactions is possible. Since this general scheme is used to study H-bonded systems, a summary of the intermolecular theory interpretation of (21) is given below.

The expectation value of H_0 with respect to ψ_{SCRF} essentially contains the electrostatic permanent multipole interaction and the inductive effects, as well as the charge transfer, overlap, and exchange interactions. Moreover, if the charge density is suitably represented by ψ_{SCRF} , the Pauli repulsive forces between interacting closed shell molecules (ions) are embodied there. The second term $\langle \psi_{\text{SCRF}} | V | \psi_2 \rangle$ takes care of the correlation effects from which the London-van der Waals forces are derived. More detailed analysis can be found elsewhere (7, 17, 18). The interaction energy between the model dipole moment and the exact reaction field forms the third term of (21). In this formalism there is no self-consistency associated with the exact reaction field. The dominant central role is played by \mathbf{M}_{SCRF} in (21). In fact (1) has been transformed into a new non-linear Schrödinger equation for the SCRF approximate wave function. The corresponding energy

expectation value

$$E_{\text{SCRf}} = \langle \psi_{\text{SCRf}} | H[\psi_{\text{SCRf}}] | \psi_{\text{SCRf}} \rangle, \quad (22)$$

can be obtained once (18) has converged.

The exact energy can be written as a sum of a SCRf energy plus electron correlation corrections. Besides the electron-electron dynamic correlation one finds a correction associated with the correlation default to the SCRf dipole moment. Writing $\mathbf{M} = \mathbf{M}_{\text{SCRf}} + \mathbf{M}_c$ formula (21) can be recast to read

$$E = E_{\text{SCRf}} + \langle \psi_{\text{SCRf}} | V | \psi_2 \rangle - \mathbf{M}_{\text{SCRf}} \cdot \bar{\mathbf{g}} \cdot \mathbf{M}_c \quad (23)$$

This formula shows the difference between the standard self-consistent field (SCF) energy and the corresponding SCRf one. E_{SCRf} is an upper bound to $\langle \Psi | H_0 | \Psi \rangle$ [7], while E_{SCRf} , due to the linear term in \mathbf{M}_c , does not necessarily share that property. In particular, one should be sufficiently cautious in selecting the actual calculational scheme. Thus in order for it to be useful, it *must* provide good dipole moments; otherwise, the error introduced by only considering E_{SCRf} will depend linearly on the correlation default to the SCRf dipole moment.

4. SCRf Theory and Thermodynamics Correlates

4.1. Electrostatic Contribution to the Internal Energy

The effective Hamiltonian $H[\mathcal{Y}](H[\psi_{\text{SCRf}}])$ represents the molecule under the effect of the polarization field $\bar{\mathbf{g}} \cdot \mathbf{M}(\bar{\mathbf{g}} \cdot \mathbf{M}_{\text{SCRf}})$. In fact, the molecular system corresponds to an open system in a thermodynamical sense. The polarization term derives from the potential produced by the molecules (or charge distribution representing molecular groups [2]) in the medium at a given point ρ . Let it be denoted by $V_{\text{ext}}(\rho)$. For an electrically neutral system the Taylor expansion of V_{ext} around a given origin inside the molecular system of interest leads to the following interaction operator:

$$H' = \sum_{i=1}^{n+m} (\delta V_{\text{ext}} / \delta \rho_i)_0 \cdot \rho_i = - \sum_{i=1}^n (\delta V_{\text{ext}} / \delta \gamma_i)_0 \cdot \gamma_i + \sum_{k=1}^m (\delta V_{\text{ext}} / \delta \mathbf{Q}_k)_0 z_k \mathbf{Q}_k \quad (24)$$

where terms of higher than linear order have been neglected. For all i, k the partial derivatives are equivalent to a constant electric field acting at the chosen origin $\Gamma(0)$. Therefore, the interaction operator becomes $-\boldsymbol{\mu} \cdot \Gamma(0)$, a form similar to the one appearing in (2). Within the theoretical framework developed up to now [1, 2], the statistical averaging of $\Gamma(0)$ over the medium configurations leads to the appearance of a reaction field. In order for this to be so, it is implied in the argument that the medium has already been polarized by the system of interest. The work necessary to perform this polarization amounts to $+\frac{1}{2} \mathbf{M} \cdot \bar{\mathbf{g}} \cdot \mathbf{M}$. This result may be derived from a virtual charging process whereby the dipole moment is changed reversibly from zero to its full value [19].

Therefore, if there are N dipolar systems in the sample, and the degrees of freedom of the medium besides those associated with the polarization process are not

changed during the charging process, the energy $\varepsilon(\bar{g})$, defined by:

$$\varepsilon(\bar{g})/N = E + \frac{1}{2} \mathbf{M} \cdot \bar{\mathbf{g}} \cdot \mathbf{M} \quad (25)$$

represents the electrostatic contribution to the internal energy of the whole system; each dipolar system is taken at a fixed but otherwise arbitrary orientation with respect to a laboratory frame.

Eq. (25) may be recast to read

$$\varepsilon(\bar{g})/N = [E_{\text{SCRF}} + \frac{1}{2} \mathbf{M}_{\text{SCRF}} \cdot \bar{\mathbf{g}} \cdot \mathbf{M}_{\text{SCRF}}] + \langle \psi_{\text{SCRF}} | V | \psi_2 \rangle + \frac{1}{2} \mathbf{M}_c \cdot \bar{\mathbf{g}} \cdot \mathbf{M}_c \quad (26)$$

This equation shows that $\varepsilon(\bar{g})$ contrary to E is quadratic in \mathbf{M}_c ; the term in square brackets define $\varepsilon_{\text{SCRF}}$.

When $\varepsilon(\bar{g})$ is used as an energy functional in the variational calculation, the correct Euler equation comes out from the first variation. Nevertheless, one should remember that $\varepsilon(\bar{g})$ is a magnitude associated to the whole system, while E describes the energy of the polarizing system only. The information which may be obtained from these quantities is necessarily different. This situation is further discussed in Sect. 5.

4.2. Other Thermodynamic Correlates

The free energy variation associated with the charging process at constant volume (V) and temperature (T), is given by [20]

$$\Delta G(\bar{g}) = G(\bar{g}) - G(0) = -\frac{1}{2} N \mathbf{M} \cdot \bar{\mathbf{g}} \cdot \mathbf{M} \quad (27)$$

It follows that the internal energy variation is

$$\Delta U(\bar{g}) = U(\bar{g}) - U(0) = -T \Delta S - \frac{1}{2} N \mathbf{M} \cdot \bar{\mathbf{g}} \cdot \mathbf{M} \quad (28)$$

where ΔS is the corresponding change in entropy.

Now, according to (25) the internal energy variation for the assembling of N dipoles will be: $\Delta \varepsilon = \varepsilon(\bar{g}) - \varepsilon(0)$. From (2) and (25) the following equation may be written for $\Delta \varepsilon$:

$$\Delta \varepsilon = N \{ \langle Y | H_0 | Y \rangle - \langle Y_0 | H_0 | Y_0 \rangle \} - \frac{1}{2} N \mathbf{M} \cdot \bar{\mathbf{g}} \cdot \mathbf{M} \quad (29)$$

where Y_0 is the eigenfunction of H_0 corresponding to its ground state. In principle (28) and (29) represent the same process and should be correlated. Since the term in curly brackets in (29) is always positive by the variational principle, it follows that the entropy variation is negative. The presence of a dipole moment increases the order around it, therefore the entropy associated to the setting up of a reaction field is decreased. The result is entirely consistent with the physical picture associated to the polarization process [1].

5. *E*- and ϵ -Proton Potentials. A Numerical Comparison

The *E*- or ϵ -energy as a function of the proton coordinate is referred to as an *E*- or ϵ -proton potential. It is not necessarily the potential driving the actual proton motion since there may be non-equilibrium medium polarization effects involved [21].

There exists a fundamental difference between both potentials. The *E*-potential would drive the proton motion whenever there exists an external source providing the polarization work needed to set up the reaction field. In the absence of this latter, the proton motion should be driven by the ϵ -potential, and the *E*-proton potential would inform about a possible intrinsic behaviour of the molecular system coupled to the environment. Therefore, such potentials have only qualitative value. On the other hand, if quantitative information is sought, for instance the variation of the equilibrium or the rate constant with the \bar{q} coupling between the system and the medium, the ϵ -energy values have to be used.

5.1. Model and Method

To illustrate the different shapes of both types of potential, and the information obtained therefrom, we have chosen a hydrogen-bonded water trimer arranged tetrahedrally. The geometry and the proton paths are indicated in Fig. 1.

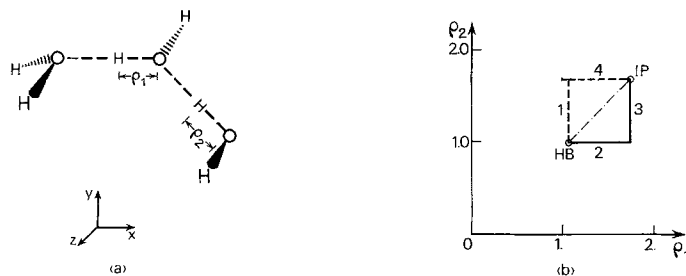


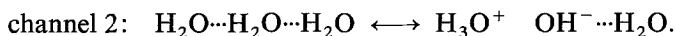
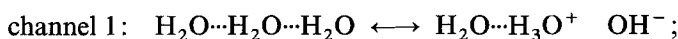
Fig. 1a and b. (a) Geometrical setup of the water trimer studied. The O...O' distance between the nearest neighbors is of 2.75 Å, and the frozen O-H distances are taken equal to 1.04 Å. (b) Different pathways of the proton displacements in the trimer

The standard linear combination of valence atomic orbitals approximation to the MO's has been used. The corresponding matrix elements of f_0 have been evaluated within the INDO approximation scheme [8]; the matrix elements associated with the operator γ in this basis set are given in Table 1. In what follows only the energy quantities calculated at the SCRF level are discussed. While the introduction of the second order perturbation energy produces some changes in the potential curves, the overall trend is nevertheless retained [3].

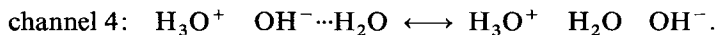
Table 1. Matrix elements of the position vector operator appearing in the LCAO approximation to the self-consistent reaction field theory of solvent effects within the ZDO approximation. The s , p , and d orbitals are those used in the INDO version of Pople

	s	p_x	p_y	p_z	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
s	R_A								
p_x	$\frac{5}{\sqrt{3}} \alpha_A^{-1} i$	R_A							
p_y	$\frac{5}{\sqrt{3}} \alpha_A^{-1} j$	0	R_A						
p_z	$\frac{5}{\sqrt{3}} \alpha_A^{-1} k$	0	0	R_A					
d_{z^2}	0	$\frac{-7 i}{\sqrt{15} \alpha_A}$	$\frac{-7 j}{\sqrt{15} \alpha_A}$	$\frac{-14 k}{\sqrt{15} \alpha_A}$	R_A				
d_{xz}	0	$\frac{7 k}{\sqrt{5} \alpha_A}$	0	$\frac{7 i}{\sqrt{5} \alpha_A}$	0	R_A			
d_{yz}	0	0	$\frac{7 k}{\sqrt{5} \alpha_A}$	$\frac{7 j}{\sqrt{5} \alpha_A}$	0	0	R_A		
$d_{x^2-y^2}$	0	$\frac{7 i}{\sqrt{5} \alpha_A}$	$\frac{-7 j}{\sqrt{5} \alpha_A}$	0	0	0	0	R_A	
d_{xy}	0	$\frac{7 j}{\sqrt{5} \alpha_A}$	$\frac{7 i}{\sqrt{5} \alpha_A}$	0	0	0	0	0	R_A

Four proton paths have been chosen. Channels 1 and 2 represent proton translocation between nearest neighbor water molecules. They can be depicted as:



The corresponding proton potentials are plotted in Fig. 2. Channels 3 and 4 correspond to ion migration, both channels ending at the same point. They are depicted by:



The corresponding proton potentials are displayed in Fig. 3. As in other works reported by us, a scalar \bar{g} -tensor is used in practical calculations. The g -value is chosen so that it produces a relatively high reaction field strength (RFS) for the H-bonded complex $\text{H}_2\text{O}\cdots\text{H}_2\text{O}\cdots\text{H}_2\text{O}$. For this particular case the RFS attains a value of 1.52 Volt/Å. This strength may be too high for ice or liquid water, but the example chosen here could better be considered as representative of a more general class of proton relay systems [4, 5].

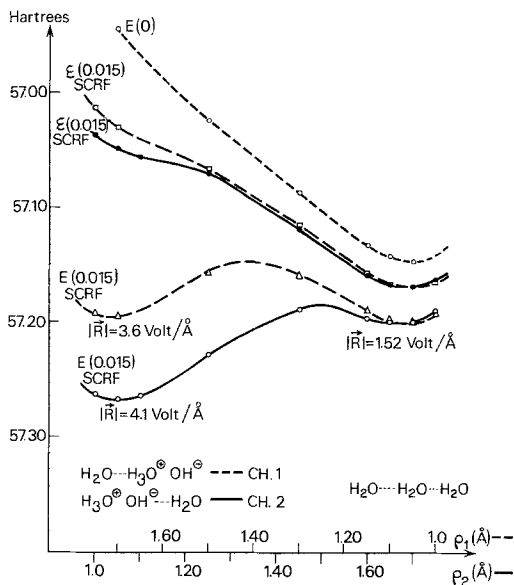


Fig. 2. Potential energy curves corresponding to an ion pair formation between the nearest neighbor molecules in the trimer. The energy terms are defined in the text

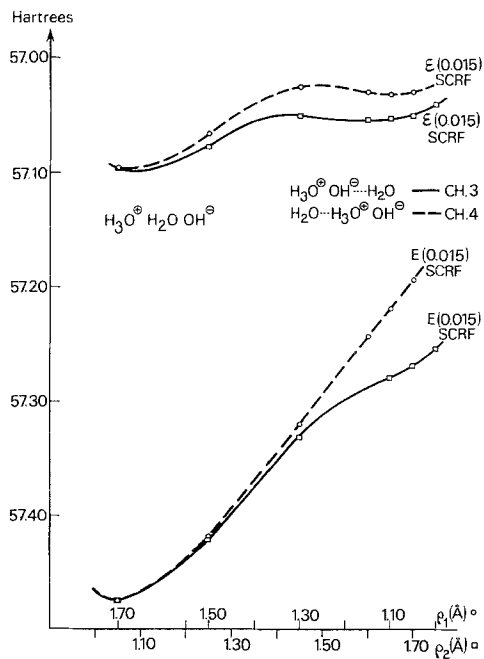


Fig. 3. Potential energy curves corresponding to an ion migration process. The energy terms are defined in the text

5.2. Numerical Results. Discussion

If there were an external source to provide the polarization work, as discussed above the E -potential would be the relevant potential. In this case, as Fig. 1 shows, the charge displacement process leads to the formation of a stable ion pair structure. Energetically, the process where the hydroxyl ion is H-bonded to a water molecule (channel 2) is favoured over the process where the hydronium ion is in a corresponding situation (channel 1). Once channels 3 and 4 are considered, the minima associated with the ion pair structures turn out to be saddle points of the E -hypersurface. The ion migration processes appear to be energetically favoured.

On the other hand, for the isolated system the ε -potentials have to be used to describe the proton energetics. In this case Fig. 1 shows that the H-bonded complex is always the most stable structure. The charge displacement process under this circumstance requires a considerable energy. But once an ion pair is formed, it is associated with a saddle like point where this time it is the ion migration process that has associated with it a small energy barrier (see channels 3 and 4).

Between these extremes the actual production of spatial charge displacement might be a process assisted by external sources like external electric fields. We have already shown the striking effects produced by a homogeneous electric field upon both the E - [4] and ε - [5] proton potentials.

It is believed that this simple numerical example illustrates sufficiently well the extreme points about which a proton potential may vary. Both produce a sort of complementary information. In the cases already studied by us, almost always the E -proton potentials were reported [3, 4]. In fact, in those papers the model studied represented systems subjected to external sources like charged ions in the vicinity or fields produced by biomembranes, etc. Thus, the qualitative information produced by the E -potentials was adequate.

Finally we would comment about the simultaneous proton pathway. As our previous study shows this channel presents a high energy barrier (see Ref. [4]), and therefore it seems likely that the actual process of proton translocation will follow the uncoupled channels.

Acknowledgments. The author wishes to thank Drs. M. E. Stephens and M. Trsic for reading the manuscript and helpful discussions. Lic. E. Sanhueza is thanked for making his unpublished work available. The author also gratefully acknowledges the hospitality and interest in this work of Prof. R. Daudel and Dr. M. Allavena.

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Received June 6, 1977