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# Nonequilibrium solvation: An *ab initio* quantum-mechanical method in the continuum cavity model approximation

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The electrostatic relationships necessary for the quantum-mechanical evaluation of the properties of a solute experiencing sudden changes in its internal charge distribution are here presented in a form suitable to perform accurate quantum-mechanical calculations of the solute properties. Attention has been paid to express the boundary conditions in the most convenient form and to avoid further constraints on the elaboration of the computational procedures. The approach exploits the separation of orientational (inertial) and electronic (inertialess) components of the polarization and complements the polarizable continuum method [Chem. Phys. **65**, 239 (1982)], usually employed for static descriptions. Examples of application of the method to photoionization and electronic transitions processes are shown.

## I. INTRODUCTION

Almost all the processes of chemical interest occurring in solution present some dynamical characteristics, the nature of which strongly depends on the nature of the process. We shall consider in this paper processes in which a fast variation of the solute charge distribution characterizes the dynamical aspects of the phenomenon. Typical cases are the photoionization processes, the electronic transitions, the charge transfer reactions, but many other chemical processes may be included in this category.

Problems involving dynamical aspects are often treated with the help of the adiabatic approximation. In this approximation the evolution of the solute charge distribution along the opportune set of internal coordinates is accompanied by an averaged description of the solvent degrees of freedom, determined for each point of the internal coordinate subspace. It corresponds to an equilibrium response model, based on the assumption that the solvent instantly adjusts itself to any change of the solute charge distribution. In a real fluid the solvent molecules will require a finite time to relax from a state of equilibrium when a change in the solute occurs: Hence, at any time during the phenomenon the solvent polarization degree (state) is determined by the ratio perturbation velocity/relaxation velocity. For sudden perturbations or long relaxation times the process is better described by a nonequilibrium model. In this case the total polarization of the solvent is no more equilibrated with the actual charge distribution and the use of the adiabatic approximation may give origin to serious errors.

Equilibrium solvation has been studied for many years, and there are a sizable number of methods exhibiting a progressive increase in the "realism" of the description of the system (and of the process) and then in the sophistication of the model. Computer simulation methods, for example, have recently increased their range of applicability and are at present able to describe many properties of

the solvent with the use of interaction potentials which may be, when necessary, quite realistic. On the side of the solute system, the recent progress has mainly regarded the effective Hamiltonian methods (EHM) which in their different and numerous versions (for a recent overview see Ref. 1) are able to treat a restricted portion of the system (i.e., the "solute") interacting with the bulk of the solvent at practically every level of the molecular quantum theory one needs.

Also the study of nonequilibrium solvation processes has a long history.<sup>2</sup> There has been in the last years an increasing interest in the development of the theory,<sup>3</sup> as well as in the realism of the computer simulation descriptions.<sup>4</sup> What is still missing, in our opinion, is an equivalent progress in the realism of the description of the solute subsystem. The aim of the present paper is just that of making some progress in this direction; accurate quantum-mechanical description of molecular systems in solution undergoing nonequilibrium solvation phenomena.

We stress here that we are using a "semiclassical" approach, in which the quantum description of the solute is coupled to a classical description of the solvent polarization  $\mathbf{P}$ . So far, the theory has mainly been developed at this level: continuum model for the solvent and classical description of the components of  $\mathbf{P}$ . Quite recently a quantum description of the "fast" component of  $\mathbf{P}$  has been introduced;<sup>3(f),3(g),3(i)</sup> this new approach may introduce significant corrections to the semiclassical approach when the solute electron motions characterizing the solute electronic readjustments are "slow" with respect to the electronic motions of the solvent.<sup>3(f)</sup> We shall return to this point later. The accurate quantum mechanical description we are searching for requires the introduction of cavity in the continuum model (the so-called Kirkwood-Onsager model); the semiclassical theoretical models neglect, with a few exceptions<sup>3(d),3(i)</sup> the additional problems due to the boundary conditions associated with the cavity, and the

"quantum" description has not yet considered this point.

The approach we are following is similar to that we have already used for equilibrium descriptions and belongs to the family of EHM's in the version making use of a continuous dielectric representation of the solvent.

The approach, developed by our group and sometimes indicated as the polarizable continuum model (PCM), retains the formalism of the *in vacuo* molecular calculations. The solute-solvent interactions are accounted for by means of an effective potential operator  $V_\sigma$  added to the solute Hamiltonian  $H^0$ . A realistic description of the cavity, modeled on the molecular van der Waals surface, is accompanied by a direct and self-consistent expression of  $V_\sigma$  which does not make use of truncated multipole expansions. The PCM is well suited for designing computational schemes adaptable to current programs for the evaluation of molecular wave functions and properties. In particular it may be used at the Hartree-Fock level (RHF and UHF) as well as at the MCSCF and CI levels, and we will exploit these features in the expanded version presented in this paper.

The paper is organized as follows. In Sec. II we derive energy expressions for the nonequilibrium cases. Section III details the free energies expressions. Some test calculations are described in Sec. IV and compared with the analytical results. Section V contains the application of the model to some typical processes of chemical interest. Section VI collects our conclusions.

## II. BASIC FORMULATION OF THE METHOD

In the dielectric continuum model the solvent is described by a polarization field  $\mathbf{P}(r)$ . When the solvent remains in equilibrium,  $\mathbf{P}(r)$  is determined by the electric field  $\mathbf{E}(r)$

$$\mathbf{P}(r) = \chi \cdot \mathbf{E}(r) \quad (1)$$

with

$$\chi = \frac{\epsilon_0 - 1}{4\pi}, \quad (2)$$

where  $\epsilon_0$  is the solvent static dielectric constant.

If the solvent polarization  $\mathbf{P}(r)$  is out of equilibrium, Eq. (1) is no longer valid. In this case it is convenient to consider the polarization field as the sum of an electronic part  $\mathbf{P}_e$  and of a slower part  $\mathbf{P}_{or}$  due to the solvent molecules vibrational and orientational motions. In many processes of chemical interest we may introduce the approximation of taking  $\mathbf{P}_{or}$  as the equilibrium response to a given charge distribution, usually the solute charge distribution itself at an earlier stage of the process. In the same approximation  $\mathbf{P}_e$  is assumed to adjust itself without time lag to any change in the electric field of the system, being thus in equilibrium with the actual charge distribution of the solute and with the electric field described by  $\mathbf{P}_{or}$ .

We introduce here this approximation in the basic PCM procedure.

In the equilibrium PCM procedure the polarization of a homogeneous infinite dielectric medium is reduced to the creation of a system of virtual charges on the surface  $S$  of

the cavity containing the solute. (In homogeneous dielectric  $\nabla \cdot \mathbf{P} = 0$  in the dielectric bulk so that there are no effective volume charges). These virtual charges have a density  $\sigma(r)$  which is related to  $\mathbf{P}(r)$  and then to  $\mathbf{E}(r)$

$$\sigma = -[\mathbf{P}(r) \cdot \mathbf{n}(r)]_o = -\frac{\epsilon_0 - 1}{4\pi} E_n(r)_o = -\frac{\epsilon_0 - 1}{4\pi\epsilon_0} E_n(r)_i, \quad (3)$$

where the indexes "o" and "i" indicate points lying immediately outside and inside the cavity,  $\mathbf{n}$  is the outward normal unit vector at the surface cavity at the point  $r \in S$  and  $E_n$  is the component of the total electric field (including as sources also the apparent charges) along  $\mathbf{n}$ .

To obtain the last relation the following boundary condition on the cavity surface has been employed:

$$\left(\frac{\partial V}{\partial n}\right)_i = (1 + 4\pi\chi) \left(\frac{\partial V}{\partial n}\right)_o, \quad (4)$$

where  $V$  is the electrostatic potential originated by all the real and apparent charges of the system.

The electronic wave functions of the solute are obtained via the following effective Schrödinger equation:

$$(H^0 + V_\sigma) |\Psi\rangle = W |\Psi\rangle \quad (5)$$

with

$$V_\sigma(r) = \int_S \frac{\sigma(r')}{|r - r'|} d^2r' \quad (6)$$

and where  $H^0$  is the Hamiltonian of the solute system *in vacuo*.

The PCM method in its standard version arrives at the following definition of the free energy of the system:<sup>5</sup>

$$G = \langle \Psi | H^0 + V_\sigma | \Psi \rangle - \frac{1}{2} \int_S \sigma(r) V(r, \rho) d^2r. \quad (7)$$

Here  $V(r, \rho)$  is the electrostatic potential arising from the charge distribution  $\rho$  associated with the electronic state  $|\Psi\rangle$  in solution and  $\sigma(r)$  is defined by Eq. (3).

Strictly speaking,  $G$  is the electrostatic contribution to the free energy of the system: For a more precise definition of its thermodynamics state, as well as for the methods used to evaluate in the PCM the other contributions to a free energy change with respect to a given reference state see, e.g., Ref. 6.

The equilibrium version of the PCM program is provided by adequate computational recipes able to give a detailed and realistic description of all the quantities defined in Eqs. (5)–(7) which can be used at any level of the quantum molecular theory one needs (semiempirical or *ab initio*, Hartree-Fock or post-H-F). We pass now to apply this approach to nonequilibrium situations. The following treatment generalizes and supersedes a preceding version.<sup>7</sup>

Equation (7) is no longer valid. In the nonequilibrium case we need to find the electronic and orientational surface charge densities and then to use them in a different expression of the free energy.

Formally, one may rewrite  $\sigma(r)$ , Eq. (3), in terms of the sum of an electronic and an orientational contribution

$$\sigma_e(r) = -[\mathbf{P}_e \cdot \mathbf{n}(r)]_o = -\chi_e E_n(r)_o = -\frac{\chi_e}{\epsilon_0} E_n(r)_i, \quad (8)$$

$$\sigma_{or}(r) = -[\mathbf{P}_{or} \cdot \mathbf{n}(r)]_o = -\chi_{or} E_n(r)_o = -\frac{\chi_{or}}{\epsilon_0} E_n(r)_i. \quad (9)$$

Here the static susceptibilities  $\chi_e$  and  $\chi_{or}$  are related to the solvent static and optical dielectric constants  $\epsilon_0$  and  $\epsilon_\infty$  by

$$\chi_e = \frac{\epsilon_\infty - 1}{4\pi}, \quad (10)$$

$$\chi_{or} = \frac{\epsilon_0 - \epsilon_\infty}{4\pi}. \quad (11)$$

The orientational surface charge  $\sigma_{or}(r)$  can be calculated from  $\mathbf{P}_{or}(r)$ , the orientational polarization in equilibrium with the electric field due to the solute charge distribution  $\rho^E(r)$  existing at an earlier time (we shall discuss in Sec. IV the meaning of this assumption),

$$\mathbf{P}_{or} = \chi_{or} \mathbf{E}(\rho^E, \sigma_{or}^E, \sigma_e^E)_o. \quad (12)$$

In this case  $\sigma_{or}(r)$  reads

$$\sigma_{or}^E = -\frac{\chi_{or}}{\epsilon_0} \mathbf{E}(\rho^E, \sigma_{or}^E, \sigma_e^E)_i \cdot \mathbf{n}, \quad (13)$$

where  $\mathbf{E}(\rho, \sigma_{or}, \sigma_e)$  is the total electric field associated with the charge distributions  $\rho$ ,  $\sigma_{or}$ , and  $\sigma_e$ .

An additional computational task is the determination of the electronic polarization  $\mathbf{P}_e(r)$  in equilibrium with the electric field due to the actual charge distribution  $\rho^A(r)$  and to the orientational polarization

$$\mathbf{P}_e(r) = \chi_e \mathbf{E}(\rho^A, \sigma_{or}^E, \sigma_e)_o. \quad (14)$$

The relation

$$\sigma_e = -[\mathbf{P}_e(r) \cdot \mathbf{n}(r)]_o \quad (15)$$

is always valid, but this is not the case for the boundary condition (4). The new boundary condition is (see Ref. 8)

$$\left(\frac{\partial V}{\partial n}\right)_i - (1 + 4\pi\chi_e) \left(\frac{\partial V}{\partial n}\right)_o = 4\pi\sigma_{or}, \quad (16)$$

and hence  $\sigma_e$  can be expressed as

$$\sigma_e(r) = \frac{\chi_e}{\epsilon_\infty} \left[ \frac{\partial V(r)}{\partial n} \right]_i - \frac{\epsilon_\infty - 1}{\epsilon_\infty} \sigma_{or}(r). \quad (17)$$

Here  $V(r)$  is the total electric potential deriving from the solute charge distribution  $\rho^A(r)$  and from the polarization charge densities  $\sigma_e$  and  $\sigma_{or}$

$$V(r) = V(r; \rho^A) + V(r; \sigma) = V(r; \rho^A, \sigma_{or}^E, \sigma_e). \quad (18)$$

Following the computational setup tested for the equilibrium PCM, we represent the continuous charge distributions  $\sigma_e$  and  $\sigma_{or}$  by a set of discrete point charges  $(q_e)_j$  and  $(q_{or})_j$  defined over the cavity surface

$$(q_e)_j = \sigma_e(r_j) \Delta S_j, \quad (19)$$

$$(q_{or})_j = \sigma_{or}(r_j) \Delta S_j. \quad (20)$$

$\Delta S_j$  is a surface element small enough to consider  $\sigma$  constant at its interior. It is easy to show that

$$(q_{or})_j = -\frac{\chi_{or}}{\epsilon_0} \Delta S_j \mathbf{E}(r_j, \rho^E, \sigma_{or}^E, \sigma_e^E)_i \cdot \mathbf{n}. \quad (21)$$

Coming back to Eq. (19), we obtain from Eqs. (17) and (18)

$$(q_e)_j = \frac{\chi_e}{\epsilon_\infty} \Delta S_j \left[ \frac{\partial V(r_j, \rho^A, \sigma_{or}^E, \sigma_e)}{\partial n} \right]_i - \frac{\epsilon_\infty - 1}{\epsilon_\infty} (q_{or})_j. \quad (22)$$

This equation permits the calculation of  $(q_e)_j$  via an iterative procedure, because the right side of the equation depends on the  $q_e$ 's values. The details of the computational methods for the definition of the surface  $S$ , of the surface elements and for the computation of all the necessary intermediate elements are similar to those already elaborated and tested for solvent equilibrium calculations and are documented elsewhere.<sup>9</sup>

The continuum model assumes that all the real charges are inside the cavity. Actually, the quantum-mechanical definition of  $\rho$  implies the presence of exponential tails going to zero for  $r \rightarrow \infty$ . These tails produce an erroneous value of the virtual charges  $Q$ . This discrepancy between numerical finding and "a priori" analytical prevision, can be corrected by distributing an extra charge,  $\Delta Q$ , over the cavity surface in order to find the correct value

$$\Delta Q = Q^{\text{num}} - Q^{\text{an}}. \quad (23)$$

In equilibrium processes  $Q^{\text{an}}$  reads

$$Q^{\text{an}} = \frac{1 - \epsilon_0}{\epsilon_0} Q(\text{solute}), \quad (24)$$

where  $Q(\text{solute})$  is the charge of the isolated molecular system *in vacuo*. In nonequilibrium processes we must correct independently  $Q_{or}$  and  $Q_e$ . The orientational charge is related to  $Q^{\text{tot}}$  by the expression

$$Q_{or} = \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 - 1} Q^{\text{tot}}(\text{surface}), \quad (25)$$

and hence,  $Q_{or}^{\text{an}}$  can be written as

$$Q_{or}^{\text{an}} = \frac{(\epsilon_0 - \epsilon_\infty)}{(\epsilon_0 - 1)} \frac{(1 - \epsilon_0)}{(\epsilon_0)} Q(\text{solute}). \quad (26)$$

To correct  $Q_e$  we must use a different expression because in this case there exists an already fixed orientational surface charge (see the Appendix)

$$Q_e^{\text{an}} = \frac{1 - \epsilon_\infty}{\epsilon_\infty} \cdot [Q(\text{solute}) + Q_{or}]. \quad (27)$$

Equations (21) and (22) determine the nonequilibrium surface charge distribution. From this distribution it is immediate to derive the reaction potential  $V_\sigma$  and then the wave function of the solute via the effective Schrödinger Eq. (5).

In conclusion, we have here, as in the equilibrium case, two nested iterative cycles, the first regarding the definition of the system of charges at a fixed solute charge distribution, the second the modification of this charge distribution via the solution of Eq. (5).

### III. FREE ENERGY

The free energy functional for a system in the electronic state  $\Psi$  in the presence of arbitrary electronic and orientational polarizations  $P_e$  and  $P_{or}$  of the medium is<sup>3(d),10</sup>

$$G = \langle \Psi | H^0 | \Psi \rangle + \frac{1}{2\chi_e} \int_V |\mathbf{P}_e(r)|^2 d^3r + \frac{1}{2\chi_{or}} \int_V |\mathbf{P}_{or}(r)|^2 d^3r - \frac{1}{2} \int_V [\mathbf{P}_e(r) + \mathbf{P}_{or}(r)] \cdot \mathbf{E}_p(r, P_e, P_{or}) d^3r - \int_V [\mathbf{P}_e(r) + \mathbf{P}_{or}(r)] \cdot \mathbf{E}(r, \rho^A) d^3r. \quad (28)$$

Here  $\rho^A$  is the solute charge density related to  $|\Psi\rangle$ ,  $\mathbf{E}(r, \rho^A)$  the electric field due to the solute charge distribution  $\rho^A$  and  $\mathbf{E}_p(r, P_e, P_{or})$  the electric field arising from the polarization fields  $\mathbf{P}_e$  and  $\mathbf{P}_{or}$ :

$$\mathbf{E}_p(r, \sigma_e, \sigma_{or}) = - \int_V T(r', r) [\mathbf{P}_e(r') + \mathbf{P}_{or}(r')] d^3r', \quad (29)$$

where  $T(r', r)$  is the dipole tensor

$$T(r', r) = \nabla \nabla' |r' - r|^{-1}. \quad (30)$$

When the orientational polarization is given by Eq. (12) and the electronic polarization by Eq. (14), Eq. (28) assumes the simpler form

$$G = \langle \Psi | H^0 | \Psi \rangle - \frac{1}{2} \int_V [\mathbf{P}_e(r) + \mathbf{P}_{or}(r)] \cdot \mathbf{E}(r, \rho^A) d^3r + \frac{1}{2} \int_V \mathbf{P}_{or} \cdot [\mathbf{E}(\rho^E, \sigma_{or}^E, \sigma_e^E) - \mathbf{E}(\rho^A, \sigma_{or}^E, \sigma_e)] d^3r. \quad (31)$$

We can write now the relation between the free energy  $G$  and the energy eigenvalue  $W$  in Eq. (5) as

$$G = W + \frac{1}{2} \int_V [\mathbf{P}_e(r) + \mathbf{P}_{or}(r)] \cdot \mathbf{E}(r, \rho^A) d^3r + \frac{1}{2} \int_V \mathbf{P}_{or} \cdot [\mathbf{E}(\rho^E, \sigma_{or}^E, \sigma_e^E) - \mathbf{E}(\rho^A, \sigma_{or}^E, \sigma_e)] d^3r. \quad (32)$$

With the aid of Green's integral theorem the volume integrals can be written as

$$\begin{aligned} & \int_V \mathbf{P}(r) \cdot \mathbf{E}(r) d^3r \\ &= - \int_V \mathbf{P}(r) \cdot \nabla V(r) d^3r \\ &= - \int_S [\mathbf{P}(r) \cdot \mathbf{n}(r)] V(r) d^2r + \int_V \nabla \cdot \mathbf{P}(r) V(r) d^3r. \end{aligned} \quad (33)$$

If the dielectric is homogeneous,  $\nabla \cdot \mathbf{P} = 0$ , the volume integral vanishes and we obtain

$$\int_V \mathbf{P}(r) \cdot \mathbf{E}(r) d^3r = - \int_S \sigma(r) V(r) d^2r. \quad (34)$$

We have used here the relation  $\sigma(r) = -[\mathbf{P}(r) \cdot \mathbf{n}(r)]$ . Using Eq. (33) it is easy to show that

$$G = W - \frac{1}{2} \int_S [\sigma_e(r) + \sigma_{or}^E(r)] V(r, \rho^A) d^2r - \frac{1}{2} \int_S \sigma_{or}^E(r) \times [V(r, \rho^E, \sigma_{or}^E, \sigma_e^E) - V(r, \rho^A, \sigma_{or}^E, \sigma_e)] d^2r. \quad (35)$$

When  $\rho^E \rightarrow \rho^A$  one has  $V(\rho^E, \sigma_{or}^E, \sigma_e^E) = V(\rho^A, \sigma_{or}^E, \sigma_e)$  and the last integral in Eq. (35) vanishes. In this case the equilibrium expression (7) is obtained. The free energy, Eq. (35), can be also expressed in terms of  $V(r; \sigma)$  and  $V(r; \sigma_{or})$ , the reaction potentials due to the total and orientational charge, respectively,

$$\begin{aligned} G &= W - \frac{1}{2} \int V(r; \sigma_{or}^E, \sigma_e) \rho^A(r) d^3r \\ &\quad - \frac{1}{2} \int V(r; \sigma_{or}^E) [\rho^E(r) - \rho^A(r)] d^3r \\ &\quad - \frac{1}{2} \int V(r; \sigma_{or}^E) [\sigma_{or}^E(r) - \sigma_e(r)] d^2r, \end{aligned} \quad (36)$$

where we have used the relation [9b]

$$\int V(r; \rho) \sigma(r) d^2r = \int V(r; \sigma) \rho(r) d^3r.$$

Coming back to Eq. (35), the free energy can be cast into its final form by replacing the continuous charge distribution with a discrete set of point charges

$$\begin{aligned} G &= W - \frac{1}{2} \sum_j (q_{ej} + q_{orj}) V(r; \rho^A) \\ &\quad - \frac{1}{2} \sum_j q_{orj} [V(r; \rho^E, \sigma_{or}^E, \sigma_e^E) - V(r; \rho^A, \sigma_{or}^E, \sigma_e)]. \end{aligned} \quad (37)$$

### IV. TEST CALCULATIONS

In this section we examine some simple numerical examples addressed to check the internal consistency of the computational procedure. To this end a spherical cavity

has been chosen. In this case it is possible to give analytical expressions for all quantities in Eq. (36), (the Appendix).

The reaction potential assumes the form

$$V(r; \sigma) = V(r; \sigma_{\text{or}}^E) + V(r; \sigma_e); \quad (38)$$

with

$$V(r; \sigma_{\text{or}}^E) = - \sum_n \sum_m \frac{(n+1)(\epsilon_0 - \epsilon_\infty)}{n + \epsilon_0(n+1)} \times E_n^m(\rho^E) \frac{r^n}{a^{2n+1}} P_n^m(\cos \theta) e^{im\phi} \quad (39)$$

and

$$V(r; \sigma_e) = \sum_n \sum_m \left[ \frac{(n+1)(1-\epsilon_\infty)}{n + \epsilon_\infty(n+1)} E_n^m(\rho^A) - \frac{(n+1)^2(\epsilon_0 - \epsilon_\infty)(1-\epsilon_\infty)}{[n + \epsilon_\infty(n+1)][n + \epsilon_0(n+1)]} E_n^m(\rho^E) \right] \times \frac{r^n}{a^{2n+1}} P_n^m(\cos \theta) e^{im\phi}. \quad (40)$$

Here "a" is the cavity radius,  $P_n^m$  the Legendre polynomial, and  $E_n^m(\rho)$  is defined by

$$E_n^m(\rho) = \frac{(n-|m|)!}{(n+|m|)!} \int \rho(R) R^n P_n^m(\cos \theta') e^{im\phi'} dR. \quad (41)$$

If we sum the orientational and electronic terms, we obtain

$$V(r; \sigma) = \sum_n \sum_m \frac{(n+1)(1-\epsilon_0)}{n + \epsilon_0(n+1)} \times E_n^m(\rho^E) \frac{r^n}{a^{2n+1}} P_n^m(\cos \theta) e^{im\phi} + \sum_n \sum_m \frac{(n+1)(1-\epsilon_\infty)}{n + \epsilon_\infty(n+1)} [E_n^m(\rho^A) - E_n^m(\rho^E)] \times \frac{r^n}{a^{2n+1}} P_n^m(\cos \theta) e^{im\phi} \quad (42)$$

and now by using the Green functions  $Q$  defined by

$$V(R) = \int Q(r, R) \rho(r) d^3r = Q|\rho \quad (43)$$

the reaction potential can be cast in the more compact form

$$V(r; \sigma) = Q(\epsilon_0)|\rho^E + Q(\epsilon_\infty)|\rho^A - \rho^E = (Q(\epsilon_0) - Q(\epsilon_\infty))|\rho^E + Q(\epsilon_\infty)|\rho^A = Q_\mu|\rho^E + Q(\epsilon_\infty)|\rho^A \quad (44)$$

where the last relation defines  $Q_\mu$ . The  $Q_\mu|\rho^E$  term describes the effect on the reaction potential of the orientational charges and the electronic charges in equilibrium

with them. The same result has been obtained by Newton and Friedman<sup>11</sup> using the superposition theorem of potentials.

In the special case of an atomic ion, the charge distribution has a spherical symmetry ( $l=m=0$ ) and Eq. (38) reduces to

$$V(r; \sigma) = \frac{1-\epsilon_0}{\epsilon_0} \frac{q^E}{a} + \frac{1-\epsilon_\infty}{\epsilon_\infty} \frac{q^A - q^E}{a} = \left( \frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty} \right) \frac{q^E}{a} + \left( \frac{1}{\epsilon_\infty} - 1 \right) \frac{q^A}{a}. \quad (45)$$

In Table I we compare the results obtained with our numerical method with the analytical ones for the evaluation of the solvation shifts in the photoionization spectra of a few atomic ions.

The solvation shift is defined as the difference between the vertical ionization free energy of the system in solution and *in vacuo*

$$\Delta \text{I.P.} = \text{I.P.}^{\text{sol}} - \text{I.P.}^{\text{vac}} \quad (46)$$

or well as the difference in the solvation free energies between the states  $\rho^A$  and  $\rho^E$

$$\Delta \text{I.P.} = [G^{\text{sol}}(\rho^A) - G^{\text{sol}}(\rho^E)] - [G^{\text{vac}}(\rho^A) - G^{\text{vac}}(\rho^E)] = \Delta G^{\text{sol}}(\rho^A) - \Delta G^{\text{sol}}(\rho^E). \quad (47)$$

When  $G$  is given by Eq. (36) and the cavity is a sphere,  $\Delta \text{I.P.}$  reads

$$\Delta \text{I.P.} = \frac{1-\epsilon_\infty}{\epsilon_\infty} \frac{q^A q^A}{2a} - \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 \epsilon_\infty} \frac{q^E q^A}{a} + \left( 1 + \frac{1}{\epsilon_\infty} - \frac{2}{\epsilon_0} \right) \frac{q^E q^E}{2a}, \quad (48)$$

where we have used the expressions for  $V(r; \sigma)$ ,  $V(r; \sigma_{\text{or}})$ , and  $\sigma_e$  given in the Appendix.

Photoionization processes occur on time scales similar to the time scale of electronic polarization relaxation and they are considered as typical examples of nonequilibrium solvation processes. We have performed calculations on  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{F}^-$ , and  $\text{Cl}^-$  in glycol. For these systems there are experimental values to which our results in the equilibrium and nonequilibrium approximation can be compared.

The values assigned to the radii of the spherical cavities have been selected by the following rule:

anions: the ionic radius;

cations: the ionic radius + 0.5 Å.

By making use of the ionic and covalent radius for the anions and cations, respectively, Rashin and Namboodiri<sup>12</sup> obtain hydration enthalpies in good agreement with the experimental values. For cations, our choice provides a radius somewhat smaller than the covalent radius, but we obtain a better agreement with the experimental shifts.

The ionic radii have been taken from Ref. 13. The calculations have been performed with the 6-31G\*\* basis set. As the solute charge distribution is spherically symmetric, there would be no self-consistent contribution to the solvation energy (the second outer cycle in our iterative process) and the solvation shift should be insensitive

TABLE I. Photoelectron binding energy shift (a.u.) of monovalent ions in glycol solution.

Ion	Eq( $\epsilon_0$ )	Eq( $\epsilon_\infty$ )	NoEq(num)	NoEq(anal)	Expt. <sup>a</sup>
Li <sup>+</sup>	-0.7023	-0.3694	-0.5925	-0.5911	-0.562
Na <sup>+</sup>	-0.5346	-0.2813	-0.4516	-0.4488	-0.456
F <sup>-</sup>	+0.1860	+0.0996	+0.2749	+0.2791	+0.364
Cl <sup>-</sup>	+0.1345	+0.0707	+0.1979	+0.2097	+0.206

<sup>a</sup>Experimental values from Ref. 14.

to the basis set. Actually there is a small BS dependence, due to the "tails" of the solute wave function going outside the cavity boundary.

Columns 1 and 2 of Table I display self-consistent solvation shifts that account for equilibrium dielectric interaction with two values of the dielectric constant corresponding to the static ( $\epsilon_0=37.7$ ) and optical ( $\epsilon_\infty=2.050$ ) values for glycol. In neither case is a correct value obtained (the experimental values are reported in column 5 of the same table).

Columns 3 and 4 of Table I report the nonequilibrium values obtained using the numerical PCM expression (column 3) and the analytical expression. The values are quite similar, with differences near to 1%. This difference decreases when the size of the cavity is enlarged and it is due, as anticipated above, to the occurrence of tails of the solute wave function in the space filled by the dielectric. The entity of these tails depends slightly on the basis set. The tails produce an excess charge  $Q$  on the cavity surface and some errors in the value of the solute electrostatic potential  $V(\rho)$  (with respect to the hypothetical case in which all the solute charge is within the cavity). The excess charge is corrected by using Eqs. (23) and (25), but nothing is done for the correction to  $V(\rho)$ ; the  $Q$  error is larger than the  $V(\rho)$  one, and on the whole they amount for our processes to approximately 1% of the whole effect, as Table I documents. The tail effects are present in all methods coupling an *ab initio* description of the solute with a dielectric-plus-cavity description of the medium: A correction is always advisable though in many applications the effect of this artifact is negligible.

Coming back to the nonequilibrium values of the solvent. I.P. shift, the values obtained with the PCM procedure may be considered in satisfactory agreement with the experimental ones.

As Table I shows, the signs of the shifts found for the cations are opposed to those obtained for the anions. In cations, the polarization of the dielectric stabilizes the core state (charge = +2) more than the ground state. This

TABLE II. Orientational and electronic contributions to  $\Delta G^{\text{int}}$  (a.u.) for the core states of monovalent ions.

Ion	Eq( $P_{\text{or}}$ )	Eq( $P_e$ )	NoEq( $P_{\text{or}}$ )	NoEq( $P_e$ )
Li <sup>2+</sup>	-0.9096	-0.0268	-0.6819	-0.1447
Na <sup>2+</sup>	-0.6919	-0.0204	-0.5176	-0.1117
F <sup>0</sup>	0.0000	0.0000	+0.1839	-0.0950
Cl <sup>0</sup>	0.0000	0.0000	+0.1382	-0.2748

TABLE III. Photoelectron binding energy shifts of water (a.u.).

State	Eq( $\epsilon_0$ )	Eq( $\epsilon_\infty$ )	NoEq
1s <sup>1</sup>	-0.146 22	-0.063 50	-0.071 20
3A <sub>1</sub>	-0.137 84	-0.060 74	-0.063 29
1B <sub>1</sub>	-0.138 99	-0.061 16	-0.064 41

leads to a redshift of I.P. in solutions relative to the gas phase. In anions the opposite occurs; the ground state (charge = -1) is more stabilized than the core state (charge = 0).

In Table II we report the solute-solvent interaction free energy,  $\langle \Psi | V(r; \sigma) | \Psi \rangle$ , for the core states obtained as indicated in Sec. III. We also display the orientational and electronic component of  $\Delta G$ . In the equilibrium approximation the largest contribution to  $\Delta G$  is associated with the orientational polarization (97% in all cases). In the nonequilibrium approximation the contributions of the electronic and of the orientational polarizations are similar. The corresponding difference in the solvation shift is largely determined by the electronic term. This indicates that the electronic polarization plays an important role in stabilizing nonequilibrium states more than equilibrium states. A similar conclusion for electronic transitions has been reached by Kim and Hynes.<sup>3(e)</sup>

## V. MOLECULAR SOLUTES

In this section we present calculations for some molecular solutes. In all cases the cavity is expressed in terms of intersecting spheres centred on the solute atoms. We assign the values of the cavity radii by applying a procedure described in an earlier paper.<sup>15</sup> This method takes into account the dependence of atomic radii on the net charge  $Q_i$  over the  $i$ th atom and on the characteristics of the basis set used. The calculations were performed for a medium having dielectric constants  $\epsilon=78.5$  and  $\epsilon_\infty=1.776$  corresponding to the static and optical dielectric constants of liquid water.

### A. Photoionization

Two molecular solutes, water and methanol, have been studied. For these molecules the solvation effects are very important and there exist a few experimentally determined solvation shifts to compare with our calculations. The energies for the ground, valence, and core states are obtained by the ROHF method. All orbitals, including the core ones, have been optimized. The 6-311G\*\* basic set has been used for both molecules.

We find for the core I.P. *in vacuo* the values of 19.82 a.u. for water and 19.78 a.u. for methanol. The experimental values are 19.84 and 19.80 a.u.,<sup>16</sup> respectively. As we can see the basis set describes the energetics of the core hole electronic states adequately. In neutral molecules, as well as in cations, the polarization of the dielectric stabilizes the core state more than the ground state leading to a redshift of I.P. in solution relative to the gas phase. The shift increases with increasing dielectric constant and, gen-

TABLE IV. Photoelectron binding energy shifts of methanol (a.u.).

State	Eq( $\epsilon_0$ )	Eq( $\epsilon_\infty$ )	NoEq
$1s^1$	-0.114 84	-0.050 53	-0.051 08
$1B_1$	-0.111 79	-0.049 53	-0.047 73

erally, decreases with the increase of the size of the molecule. Tables III and IV list the solvation shift obtained as indicated in Sec. IV. The water core shift  $O(1s^1)$  measured in liquid water is  $-0.070$  a.u.<sup>17</sup> The shift calculated with the static dielectric constant,  $-0.146$  a.u., is too large. Equilibrium calculations with the optical dielectric constant give a better, but not correct, value:  $-0.063$  a.u. The result obtained with our model,  $-0.071$  a.u., is in a satisfactory agreement with the experimental value.

In methanol, like in water, the core shift  $O(1s_1)$  calculated with the static dielectric constant is too large. The values of core shift obtained by the optical dielectric constant and with our method are similar,  $0.050$  and  $0.051$  a.u., respectively. The only available result proposed by Lundholm *et al.* is  $-0.059$  a.u.<sup>17</sup>

## B. Excited states of formaldehyde in water

We shall now consider the solvent effects on the solvatochromic shift of the  $(n \rightarrow \pi^*)^1$  transition of formaldehyde in water. In this case it may be necessary to go beyond the one-determinantal SCF approximation for the description of the excited state. We have calculated the wave function at three levels: ROHF, MCSCF, and CI. Ground state and excited state are optimized *in vacuo* and in the presence of the solvent. The process we use to include the effect of the solvent on the correlated wave functions is the same as indicated for SCF wave functions elsewhere.<sup>9</sup> From the density matrix obtained *in vacuo*, one calculates the surface charges and the reaction potential as indicated in Sec. II. This potential is introduced in the molecular Hamiltonian, and with the wave function at the desired level, we solve the Schrödinger equation (5) and obtain a new density matrix, which is used to iterate the process. In the CI calculation we have considered two possibilities: single excitations (S-CI) and single and double excitations (SD-CI) with frozen core. In MCSCF we took eight active electrons and eight active orbitals. These calculations show the potentialities of the method and stress the differences between equilibrium and nonequilibrium calculations.

Table V (first row) lists the excitation energies in vacuum. The value computed at the Hartree-Fock level is  $0.124\,75$  a.u., some  $0.03$  a.u. below the experimental gas-

TABLE V. Excitation energy,  $G^{\text{exc}} - G^{\text{ground}}$  (a.u.), of  $\text{H}_2\text{CO}$  in vacuum and in aqueous solution.<sup>a</sup>

	ROHF	MCSCF	CI(s)	CI(sd)
Vacuum	0.124 75	0.191 51	0.173 05	0.150 39
Eq( $\epsilon_0$ )	0.130 64	0.194 35	0.180 15	0.153 44
NoEq	0.134 44	0.196 81	0.186 72	0.155 98

<sup>a</sup>Experimental value in gas phase:  $0.1550$  a.u. (Ref. 18).

TABLE VI. Dipole moment in solution,  $\mu$  (a.u.) of  $\text{H}_2\text{CO}$ .

	ROHF	MCSCF	CI(s)	CI(sd)
Eq(ground)	1.385	1.146	1.452	1.103
Eq(excited)	0.679	0.696	0.380	0.649
NoEq(excited)	0.747	0.746	0.501	0.684

phase maximum. MCSCF and S-CI values are too high but extension at the CI-SD level brings the computed vertical transition energy into close agreement with the experimental value. Therefore, only highly correlated calculations with large basis sets reproduce well the absolute values.

We will see now the changes in transition energies. As is well known, the  $(n \rightarrow \pi)^1$  transition causes a large reduction in the dipole moment and hence in the solute-solvent interaction energy, leading to a blueshift. Computations at the Hartree-Fock level at the ground state equilibrium geometry ( $R_{\text{CO}}=1.184$  Å,  $R_{\text{CH}}=1.093$  Å,  $\text{HCH}=122.14^\circ$ ) lead to a ground state dipole moment *in vacuo* of  $1.056$  a.u. somewhat larger than the experimental value  $0.917$  a.u. For the excited state at the same geometry we found a dipole moment of  $0.519$  a.u.

In Table VI we report the dipole moments in solution obtained at different levels: ROHF, MCSCF, CI-S, and CI-SD. The solvent increases the ROHF dipole of both ground and the excited state by about 30%. The dipole moments in the ground state at MCSCF and SD-CI levels are somewhat smaller than the ROHF value, but the agreement improves in the excited state. By contrast, the S-CI level causes a lowering of the dipole value in the excited state but not in the ground state. All these changes in the dipole moment values explain the different blueshift obtained with the equilibrium PCM (first row Table VII). The experimental blueshift for monomeric formaldehyde in water is not available due to the formation of oligomers, but is likely between the shift due to the oligomeric formaldehyde ( $1.7$  Kcal/mol) and the acetone shift ( $5.4$  Kcal/mol). Levy *et al.* in a recent molecular dynamics simulation<sup>19</sup> found a blueshift of  $5.4$  Kcal/mol; in this simulation the effect of solvent electronic polarizability was neglected and hence the actual value must be somewhat lower. Table VII displays solvation shifts for the adiabatic (equilibrium) and nonadiabatic (nonequilibrium) electronic transitions. When the static dielectric constant is used, our best calculations (CI-SD level) give a too low value:  $1.953$  Kcal/mol. (The use of optical dielectric constant leads to a still lower value:  $0.706$  Kcal/mol.) The nonequilibrium value is  $3.511$  Kcal/mol. In all cases the nonequilibrium results are much larger (80%–90%) than the corresponding equilibrium values. ROHF and CI-S methods provide a

TABLE VII. Excitation energy shifts, (Kcal/mol), of  $\text{H}_2\text{CO}$ .

	ROHF	MCSCF	CI(s)	CI(sd)
Eq( $\epsilon_0$ )	3.699	1.781	4.454	1.953
NoEq	6.082	3.327	8.574	3.511



better description of the charge distribution in the excited state than in the ground state, overestimating the solute-solvent interaction in the ground state and hence giving a too large solvent shift. The MCSCF gives better dipole moments and we found a shift close to the CI-SD calculation.

## VI. CONCLUSIONS

We have reformulated in Secs. II and III of the present paper the theory of nonequilibrium solvation effects in a form suitable for large scale *ab initio* quantum-mechanical computations. The basic assumption of the model corresponds to the one already adopted in several preceding papers by other authors, namely, a separation of the induction process into two components, the first related to translational and orientation motions of the molecular components of the medium, the second to the electronic polarization effects acting on the solvent molecules. Noticeably different relaxation times for the two phenomena are assumed, in agreement with experimental evidence, and with preceding models [the two components are sometimes denoted as the inertial and inertialess components of  $\mathbf{P}(r)$ ].

It is our impression that until now the elaboration of nonequilibrium continuum models have not been accompanied by an equally detailed and accurate description of the molecular solute subject to nonequilibrium perturbation. Our main effort has been that of solving the quantum-mechanical problem (i.e., finding wave functions and energies) of a molecular system subject to the continuum electrostatic constraints, maintaining the rigor of the classical elaboration of this electrostatic problem. For this reason we have reported numerical data, comparing with analytical results when possible, and selecting a spectrum of quantum-mechanical methods of different complexity. The selection of methods, basis set, molecular systems, and physical process is only indicative, but sufficient to demonstrate the real possibilities of application of the computational algorithms which accompany this paper.

Future applications will show more clearly what has been hinted in the short analysis of the results presented in Sec. V, namely, that the performances of the model cannot be predicted by a simple inspection of the physical problem without making actual calculations. Actually, we have much to learn about the performances of the model, their dependence on the level of the molecular theory, basis set, and other technical points, as well as about the physics of the phenomenon and its dependence on physical parameters, explicit or implicit in the model (e.g., the ratios  $\epsilon_0/\epsilon_\infty$ , the temperature, etc.).

We have purposely omitted chemical reactions (mentioned in Sec. I as possible subjects of our investigation) from our set of examples. This exclusion is a consequence of the physical uncompleteness of the model simply based on the separation of  $\mathbf{P}$  into two components.

As we said in Sec. III, the model uses an orientational charge distribution  $\sigma_{or}$  calculated at an "earlier time." This rather vague expression becomes operationally clear when there is a physical phenomenon beginning and ending in a very short time, like photoionization or photoexcitation. In

these cases it is clear that the earlier time precedes the beginning of the phenomenon, and the actual situation (at which  $\mathbf{P}_e$  is evaluated) is not far in time, at a moment in which the relaxation of the original orientational polarization has not significantly altered  $\sigma_{or}$ .

In chemical reactions the situation is a bit different. The present scheme could be applied without significant changes to a small carefully selected portion of some reaction steps. Intentionally, we did not report here examples of the tests we have made on this subject to emphasize that in our opinion this elaboration is only partial, and that the nonequilibrium continuum approach to chemical reactions deserves further development. To do it other concepts must be introduced. The quantum description of  $\mathbf{P}_e$  mentioned in Sec. I<sup>3(f)</sup> represents a promising perspective for a description of fast motions and the coupling of this approach with more detailed quantum descriptions of the solute system will surely be attempted. There are many arguments suggesting that it is worth further efforts on the elaboration of more adequate models in the framework of the semiclassical approximation (i.e., on the approximation based on the classical description of  $\mathbf{P}_e$  we have used here): In chemical research we need, in fact, methods able to describe complex molecular events arriving at completion in relatively long times. Among the various possibilities there is a schematic modelization of the changes occurring in  $\mathbf{P}_{or}$  during the characteristic time of the elementary reaction step. We have attempted to do so by complementing the method described here with a recipe to describe  $\mathbf{P}_{or}$  changes. A preliminary study, regarding a  $S_N2$  reaction, will be published in a short time.<sup>20</sup>

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## APPENDIX: NONEQUILIBRIUM REACTION POTENTIAL FOR AN ARBITRARY CHARGE DISTRIBUTION INTO A SPHERICAL CAVITY

In this Appendix we shall consider the problem of an arbitrary charge distribution into a spherical cavity immersed in a dielectric extending to infinity, with dielectric constant  $\epsilon_\infty$ . There exists also a fixed surface charge  $\sigma_{or}$ .

We take the center of the sphere as the origin of the coordinate system. For the description of electrostatic potential we use two different functions  $V_1$  and  $V_2$ , outside and inside the sphere, respectively. The solutions can be written as

$$V_1 = \sum_n \sum_m \left( A_n^m r^n + \frac{B_n^m}{r^{n+1}} \right) P_n^m(\cos \Theta) e^{im\varphi}, \quad (A1)$$

$$V_2 = \sum_n \sum_m \left( C_n^m r^n + \frac{D_n^m}{r^{n+1}} \right) P_n^m(\cos \Theta) e^{im\varphi}. \quad (A2)$$

The boundary conditions for this problem are

(1)

$$(V_1)_{r \rightarrow \infty} = 0, \quad (\text{A3})$$

(2)

$$(V_1)_{r=a} = (V_2)_{r=a}, \quad (\text{A4})$$

(3)

$$\epsilon_\infty \left( \frac{\partial V_1}{\partial r} \right) = \left( \frac{\partial V_2}{\partial r} \right) - 4\pi\sigma_{\text{or}}, \quad (\text{A5})$$

(4) at the center of the sphere  $V_2$  must have no singularity.

The orientational surface charge  $\sigma_{\text{or}}$  can be calculated from the equilibrium potential  $V$  due to the solute charge distribution  $\rho^E(r)$  existing at an earlier time

$$\sigma_{\text{or}} = \chi_{\text{or}} \left( \frac{\partial V}{\partial r} \right)_{r=a} \quad (\text{A6})$$

$$= - \sum_n \sum_m \frac{(\epsilon_0 - \epsilon_\infty)(n+1)(2n+1)}{n + \epsilon_0(n+1)} \times \frac{E_n^m(\rho^E)}{4\pi a^{n+2}} P_n^m(\cos \Theta) e^{im\varphi}, \quad (\text{A7})$$

with

$$E_n^m(\rho^E) = \frac{(n-|m|)!}{(n+|m|)!} \int \rho(R) R^n P_n^m(\cos \Theta') e^{-im\varphi'} dR. \quad (\text{A8})$$

The terms  $(D_n/r^{n+1})P_n(\cos \Theta)$  in  $\phi_2$  are due to charges within the cavity. On account of all these conditions we found

$$A_n^m = 0, \quad (\text{A9})$$

$$C_n^m = \frac{(n+1)(1-\epsilon_\infty)}{n + \epsilon_\infty(n+1)} \frac{E_n^m(\rho^A)}{a^{2n+1}} - \frac{(n+1)(2n+1)(\epsilon_0 - \epsilon_\infty)}{[n + \epsilon_\infty(n+1)][n + \epsilon_0(n+1)]} \frac{E_n^m(\rho^E)}{a^{2n+1}}, \quad (\text{A10})$$

$$B_n^m = \frac{2n+1}{n + \epsilon_\infty(n+1)} E_n^m(\rho^A) - \frac{(n+1)(2n+1)(\epsilon_0 - \epsilon_\infty)}{[n + \epsilon_\infty(n+1)][n + \epsilon_0(n+1)]} E_n^m(\rho^E). \quad (\text{A11})$$

Hence the nonequilibrium potential can be written as

$$V(r; \sigma) = - \sum_n \sum_m \left[ \frac{(n+1)(1-\epsilon_\infty)}{n + \epsilon_\infty(n+1)} E_n^m(\rho^A) - \frac{(n+1)(2n+1)(\epsilon_0 - \epsilon_\infty)}{[n + \epsilon_\infty(n+1)][n + \epsilon_0(n+1)]} E_n^m(\rho^E) \right] \times \frac{r^n}{a^{2n+1}} P_n^m(\cos \Theta) e^{im\varphi}. \quad (\text{A12})$$

This potential is the sum of two terms: one due to the orientational charges, and the other to the electronic charges. The orientational term is

$$V(r; \sigma_{\text{or}}) = - \sum_n \sum_m \frac{(n+1)(\epsilon_0 - \epsilon_\infty)}{n + \epsilon_0(n+1)} E_n^m(\rho^E) \times \frac{r^n}{a^{2n+1}} P_n^m(\cos \Theta) e^{im\varphi}. \quad (\text{A13})$$

The electronic contribution is obtained as difference between the total potential and the orientational contribution

$$V(r; \sigma_e) = - \sum_n \sum_m \left[ \frac{(n+1)(1-\epsilon_\infty)}{n + \epsilon_\infty(n+1)} E_n^m(\rho^A) - \frac{(n+1)^2(1-\epsilon_\infty)(\epsilon_0 - \epsilon_\infty)}{[n + \epsilon_\infty(n+1)][n + \epsilon_0(n+1)]} E_n^m(\rho^E) \right] \times \frac{r^n}{a^{2n+1}} P_n^m(\cos \Theta) e^{im\varphi}. \quad (\text{A14})$$

The electronic surface charge can be calculated as

$$\sigma_e = \chi_e \left( \frac{\partial V_1}{\partial r} \right)_{r=a} = - \sum_n \sum_m \frac{B_n^m(n+1)\chi_e}{a^{n+2}} P_n^m(\cos \Theta) e^{im\varphi} \quad (\text{A15})$$

and the total electronic surface charge as

$$Q_e = \int_s \sigma_e d^2r. \quad (\text{A16})$$

Due to the properties of the Legendre polynomials all the terms are zero except  $n=0$

$$Q_e = \frac{1-\epsilon_\infty}{\epsilon_\infty} q^A - \frac{(1-\epsilon_\infty)(\epsilon_0 - \epsilon_\infty)}{\epsilon_\infty \epsilon_0} q^E = \frac{1-\epsilon_\infty}{\epsilon_\infty} (Q^A + Q_{\text{or}}). \quad (\text{A17})$$

<sup>1</sup> J. Tomasi, R. Bonaccorsi, R. Cammi, and F. J. Olivares del Valle, *J. Mol. Struct. (Theochem.)* **234**, 401 (1991).

<sup>2</sup> (a) Y. Ooshika, *J. Chem. Phys. Jpn.* **9**, 594 (1954); (b) R. Marcus, *J. Chem. Phys.* **24**, 966 (1956); (c) E. G. McRae, *J. Phys. Chem.* **61**, 562 (1957); (d) V. G. Levich, *Adv. Electrochem. Eng.* **4**, 249 (1966).

<sup>3</sup> (a) D. F. Calef and P. G. Wolynes, *J. Phys. Chem.* **87**, 3387 (1983); (b) J. L. Kurz, *J. Am. Chem. Soc.* **111**, 8631 (1989); (c) H. J. Kim and J. T. Hynes, *J. Phys. Chem.* **94**, 2736 (1990); (d) H. J. Kim and J. T. Hynes, *J. Chem. Phys.* **93**, 5194 (1990); (e) H. J. Kim and J. T. Hynes, *ibid.* **93**, 5211 (1990); (f) **96**, 5088 (1992); (g) J. N. Gehlen, D. Chan-

- dlar, H. J. Kim, and J. T. Hynes, *J. Phys. Chem.* **96**, 1748 (1992); (h) M. V. Basilevsky and G. E. Chudinov, *Chem. Phys.* **144**, 155 (1990); (i) M. V. Basilevski and G. E. Chudinov, *ibid.* **157**, 327 (1991); (l) R. A. Marcus, *J. Phys. Chem.* **96**, 1753 (1992).
- <sup>4</sup> (a) B. J. Gertner, K. R. Wilson, and J. T. Hynes, *J. Chem. Phys.* **90**, 3537 (1989); (b) T. Fonseca and B. Ladanyi, *J. Phys. Chem.* **95**, 2116 (1991); (c) W. P. Keirstead, K. R. Wilson, and J. T. Hynes, *J. Chem. Phys.* **95**, 5257 (1991).
- <sup>5</sup> S. Miertus and J. Tomasi, *Chem. Phys.* **65**, 239 (1982).
- <sup>6</sup> R. Bonaccorsi, R. Cammi, and J. Tomasi, *J. Comp. Chem.* **12**, 301 (1991).
- <sup>7</sup> R. Bonaccorsi, R. Cimiraglia, and J. Tomasi, *J. Comp. Chem.* **4**, 567 (1983).
- <sup>8</sup> R. A. Marcus, *J. Chem. Phys.* **24**, 979 (1956).
- <sup>9</sup> S. Miertuš, E. Scrocco, and J. Tomasi, *Chem. Phys.* **55**, 117 (1981).
- <sup>10</sup> S. Lee and J. T. Hynes, *J. Chem. Phys.* **88**, 6853 (1988).
- <sup>11</sup> M. D. Newton and H. L. Friedman, *J. Chem. Phys.* **88**, 4460 (1988).
- <sup>12</sup> A. Rashin and K. Namboodiri, *J. Phys. Chem.* **91**, 6003 (1987).
- <sup>13</sup> Y. Marcus, *Ion Solvation* (Wiley, New York, 1962).
- <sup>14</sup> H. Ågren, C. M. Llanos, and K. V. Mikkelsen, *Chem. Phys.* **115**, 43 (1987).
- <sup>15</sup> M. A. Aguilar and F. J. Olivares del Valle, *Chem. Phys.* **129**, 439 (1989).
- <sup>16</sup> A. A. Bakke, H. Wen-Chen, and W. L. Jolly, *J. Electron. Spectrosc. Relat. Phenom.* **29**, 333 (1980).
- <sup>17</sup> M. Lundholm, H. Siegbahn, S. Holmberg and M. Arbmán, *J. Electron Spectrosc. Relat. Phenom.* **40**, 163 (1986).
- <sup>18</sup> J. C. D. Brand, *J. Chem. Soc.* **1956**, 858.
- <sup>19</sup> R. M. Levy, D. B. Kitchen, J. T. Blair, and K. Krogh-Jespersen, *J. Phys. Chem.* **94**, 4470 (1990).
- <sup>20</sup> M. Aguilar, R. Bianco, S. Miertuš, and J. Tomasi (unpublished).