

A STATISTICAL THERMODYNAMICS INTERPRETATION OF THE SOLVATIONS ENERGY WITHIN THE CONTINUUM APPROACH

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ABSTRACTS

A Statistical Thermodynamics discussion on the nature of solvation energy within the continuum approach, is presented. A full partition of the total solute-solvent free energy is given. The simple model adopted in the present work allowed us to show that even in the case where the solute-solvent interactions are treated by means of perturbation theory, the physical meaning of each contribution to the total energy of the solute-solvent system may be clearly stated. The results of the statistical analysis are used to discuss the quantum mechanical treatment of solvation within the reaction field approach.

RESUMEN

En este trabajo, se presenta una discusión sobre la naturaleza física de la energía de solvatación basada en un modelo termodinámico estadístico. A partir de él se puede obtener una partición completa de la energía libre total del sistema soluto-solvente. El modelo simple considerado para este estudio, permite mostrar que aún en el caso en que las interacciones soluto-solvente se tratan mediante teoría de perturbación, el significado físico de cada contribución a la energía total puede ser establecido claramente. Los resultados del análisis estadístico se usan como base para la discusión del tratamiento cuántico de la solvatación dentro de la teoría de campo de reacción.

INTRODUCTION

The definition of solvation energy in quantum-chemical methods is usually based on a simplified description of the solute-solvent system. Therefore, the identification of the solvation energy contribution in the formal expression of the total energy of this model system, can be either difficult or inconsistent with the true nature of solvation process.

Within the discrete or supermolecule (SM) approach for example, where the solvent is represented by a finite number of molecules, the solvation energy is equated to the solute-solvent interaction energy. However this identification is conceptually erroneous since this calculated energy corresponds to an enthalpy rather than to a free energy change. The temperature averaging effects of the liquid state are not explicitly included in this type of calculation (1-3), and these are the effects which are responsible for the

entropy variation in the solvation process.

This is not a formal problem. It is particularly confusing when, for instance, the chemist is confronted with the task of obtaining theoretical estimates of experimental thermodynamic properties (like pKa), from a SM type of calculation. It is well known that the relevant quantity in chemical equilibrium is the free energy change of the system, whereas the actual calculated property corresponds to an enthalpy change. In spite of the numerical results, it is clear that such a procedure can be misleading. The only solution to this problem is to complement the SM approach with simulation techniques of the liquid state, such as Monte Carlo calculations (4-5).

Another relevant approach for the calculation of solvation energies are the, so called, continuum models. In these models, the solvent is represented by a dielectric polarizable medium characterized by its dielectric constant (6-8), and the solute-solvent interaction is described by means of the reaction field (RF) theory.

The influence of the polarized environment upon the molecular properties of the solute must be included in the SCF treatment of the system in continuum type calculations. Thus, the main problem in these models is to define a physically acceptable Fock operator which includes the RF potential due to the polarized medium. The definition of this operator is strongly related to a correct interpretation of the solvation energy (9-12). In fact, a variationally incorrect operator has been used in several papers dealing with the quantum mechanical treatment of solvent effects (13-14).

In this paper we present a statistical thermodynamic definition of the solvation energy within a continuum model framework which satisfies the physical requirements mentioned above. The results obtained through the statistical analysis will be used to discuss the partition of the total energy of the solute solvent system. The different contributions to this energy will be shown to have clearly defined physical meaning in terms of a simple model.

Finally, two relevant applications of our calculation are presented. First, a derivation of the Onsager RF theory and, secondly, a simple manner of deriving a correct effective Fock operator for the quantum mechanical treatment of solvent effects is discussed.

THEORY

a) Definition of the Electrostatic Solvation Energy

We will choose for our preliminary discussion the case of the simplest possible solute: a monoatomic ion. We will show later that the generalization to molecular solutes is straightforward.

In the absence of forces other than those of purely electrostatic nature, we may consider an atomic ion as represented by a rigid sphere, $S(0,a)$, where "a" is the radius of the sphere centered at the origin 0. We further assume that the sphere carries a net charge Q_0 , uniformly distributed on its surface. The solvated ion may be represented, within this framework, as the same sphere immersed in a continuum dielectric medium characterized by its macroscopic dielectric constant ϵ_m . The solvation energy may be defined as

$$(1) \quad E_{\text{solv}} = E(\epsilon_m) - E(\epsilon_0)$$

where $E(\epsilon_m)$ and $E(\epsilon_0)$ are the electrostatic self energy of $S(0,a)$ in the presence of the polarizable medium and in vacuum, respectively.

The definition of the solvation energy as given in equation (1), contains two important approximations: i) it neglects the variation of the ionic radius when ions go from the gas phase to the solution and ii) it does not

consider explicitly the energy required to form the cavities for the ions within the dielectric. These problems can be handled in a rather simple way if we are only interested in obtaining numerical values of the solvation energies of atomic ions (15). However, being interested in the physical interpretation of the solvation energy, we propose to accept this model as a working hypothesis in order to discuss the solvation process in the most simple framework. We will show later, that the general ideas that we shall develop in this work are quite independent of the approximations mentioned above.

The electrostatic self energies $E(\epsilon_m)$ and $E(\epsilon_0)$ are given by the work required to charge the sphere $S(0,a)$ in the presence of the dielectric and in vacuum respectively (7,8)

$$(2) \quad E(\epsilon_0) = \frac{1}{2} \frac{Q_0^2}{\epsilon_0 a}$$

and

$$(3) \quad E(\epsilon_m) = \frac{1}{2} \frac{Q_0^2}{\epsilon_m a}$$

Substitution of equation 2 and 3 into eq 1, leads to the well known Born formula for the solvation energy

$$(4) \quad E_{\text{solV}} = -\frac{1}{2} (1 - 1/\epsilon) \frac{Q_0^2}{a} = \Delta E(\epsilon)$$

where $\epsilon = \epsilon_m/\epsilon_0$, is the effective dielectric constant of the medium (7).

b) Calculation of Electrostatic Solute-Solvent Interaction Energy

The basic assumption of the RF theory is that the presence of the charged species $S(0,a)$ polarizes the medium. This polarization induces the creation, at the surface of $S(0,a)$, of a polarization charge distribution which we shall refer as to "polarization charges" (7-9). The polarization charges may be determined from the electrostatic potential $V(\epsilon)$ produced by the solvated ion and defined by:

$$(5) \quad V(\epsilon) = \frac{Q_0}{a \cdot \epsilon}$$

Alternatively, we can think of this potential as arising from the interaction between the source and the polarization charges in vacuum, Q_0 and $Q^{\text{pol}}(\epsilon)$ respectively,

$$(6) \quad V(\epsilon) = \frac{Q_0 + Q^{\text{pol}}(\epsilon)}{a}$$

From eqs 5 and 6 the following expression for the polarization charges is obtained:

$$(7) \quad Q^{\text{pol}}(\epsilon) = -(1 - 1/\epsilon) Q_0$$

The RF potential is given by /5/.

$$(8) \quad V_R(\epsilon) = \frac{Q^{\text{pol}}}{a} = -(1 - 1/\epsilon) \frac{Q_0}{a}$$

$V_R(\epsilon)$ is the fundamental quantity of the RF theory: it is directly related to the electrostatic solute-solvent interaction energy $E_{\Sigma-S}(\epsilon)$ by /16/

$$(9) \quad E_{\Sigma-S}(\epsilon) = Q_0 V_R(\epsilon) = -(1 - 1/\epsilon) \frac{Q_0^2}{a} = 2\Delta E_{\text{solV}}(\epsilon).$$

From eqs (9) and (1) the total energy of the solute-solvent system becomes

$$(10) \quad E(\epsilon) = E(\epsilon_0) + E_{\Sigma-S}(\epsilon) - \frac{1}{2} E_{\Sigma-S}(\epsilon)$$

Equation (10) provides a full partition of the total energy of the ion in solution.

It is easy to recognize from this expression the first and second term as being the total energy of the isolated solute, $E(\epsilon_0)$, and the solute-solvent electrostatic energy, $E_{\Sigma-S}(\epsilon)$. The third term in eq (10), $-1/2 E_{\Sigma-S}(\epsilon)$, does not have an obvious meaning. Furthermore, from eq (9), it is clear that the identification of the solvation energy with the solute-solvent interaction energy, an assumption that is used in all SM approaches, is incorrect.

In the following sections a reinterpretation of the energetics of ion solvation based on thermodynamics relationships is given. This procedure will allow us to give a physical meaning to the third term in eqn (10).

c) Statistical Thermodynamics Analysis of the Solute-Solvent Interactions. The Independent Dipoles Approach

In order to give a physical interpretation to each contribution of the total energy of the solute-solvent system given by eq (10), we will consider a microscopic model of the polarized dielectric medium. In a first step, and with the purpose of illustrating the statistical thermodynamic calculation in the simplest way, we will assume that the solvent may be represented by a set of N non-interacting identical dipoles, $\vec{\mu}_k (1 < k < N)$; with $|\vec{\mu}_k| = \mu_k$. Let further assume that the dipoles are unpolarizable. The interaction of this system with the solute will be represented by the set $\vec{\mu}_k$ interacting with an external field \vec{E}_0 . This external electric field could arise, in the most general case, from any electric moment associated with the charge distribution of the solute. It is this frame that allows us to generalize our conclusions from the particular situation where the solute is represented by a net charge (monoatomic ions) to molecules or molecular ions. Finally, we will assume that the whole system is coupled to a thermostat at the temperature T .

Let $\rho(\Omega)$ be the probability density of finding a dipole in the direction of the solid angle Ω . The probability of finding a dipole forming with \vec{E}_0 a solid angle within the element $(\Omega, \Omega + d\Omega)$ is:

$$(11) \quad p(\Omega) = \rho(\Omega) d\Omega$$

If N is the total number of dipoles, then

$$(12) \quad \rho(\Omega) = \frac{n(\Omega)}{N}$$

where $n(\Omega)d\Omega$ represents the number of dipoles forming with \vec{E}_0 a solid angle within the element $(\Omega, \Omega + d\Omega)$; from the normalization condition (i.e. the conservation of the total number of dipoles),

$$(13) \quad \int n(\Omega) d\Omega = N$$

the entropy of the system as a function of $\rho(\Omega)$ is given by

$$(14) \quad S = -kN \int \rho(\Omega) \ln \rho(\Omega) d\Omega$$

where k is the Boltzmann constant. Since the independent dipoles model has been assumed, the average potential energy as a function of $\rho(\Omega)$ becomes

$$(15) \quad U = \int u(\Omega) \rho(\Omega) d\Omega$$

where $u(\Omega)$ is the potential energy of a dipole oriented in the direction of the solid angle Ω .

From Eqs (14) and (15) the Helmholtz free energy F , is given by

$$(16) \quad F = U - TS = \int n(\Omega)u(\Omega)d\Omega - kT[N \ln N - \int n(\Omega) \ln n(\Omega) d\Omega]$$

At equilibrium, $\delta F = 0$, and therefore

$$(17) \quad \delta F = \int \delta n(\Omega)(u(\Omega) + kT \ln n(\Omega))d\Omega = 0$$

From this condition the angular distribution of dipoles at thermodynamic equilibrium is

$$(18) \quad n(\Omega) = \frac{N}{Z} e^{-u(\Omega)/kT}$$

with Z , the partition function of the system given by

$$(19) \quad Z = \int e^{-u(\Omega)/kT} d\Omega$$

Substitution of eq (18) into eq (16) allows us to immediately verify that

$$(20) \quad F = -kT \ln Z$$

which is the statistical thermodynamic definition of the Helmholtz free energy.

We may further try to relate the thermodynamic magnitudes to the electric properties of the system. We start by writing the explicit form of $u(\Omega)$ (16)

$$(21) \quad u(\Omega) = -\vec{\mu} \cdot \vec{E}_0 = -\mu E_0 \cos\theta$$

where θ is the angle formed by the vectors $\vec{\mu}$ and \vec{E}_0 and where axial symmetry is assumed in the system. By introducing the well known change of variables (16)

$$(22) \quad a = \frac{\mu E_0}{kT}$$

we obtain

$$(23) \quad Z = \int_0^\pi \int_0^{2\pi} e^{-a \cos\theta} \sin\theta d\theta d\phi = 4\pi \frac{\sinh(a)}{a}$$

and

$$(24) \quad U = \int_0^\pi \int_0^{2\pi} e^{-a \cos\theta} (-a k T \cos\theta) \sin\theta d\theta d\phi = -N a k T L(a)$$

where

$$(25) \quad L(a) = \coth a - \frac{1}{a}$$

is the Langevin function (16).

Within the weak field approximation (which is equivalent to apply first order perturbation theory), we may develop $L(a)$ in powers of a . By combining eqs (23) and (20), and neglecting the terms higher than second order, we get

$$(26) \quad F = -NkT(\ln 4\pi + \frac{a^2}{3}) = F_0 - \frac{1}{2} NkT \frac{a^2}{3}$$

and

$$(27) \quad U = -NakT(\frac{a}{3}) = -NkT\frac{a^2}{3}$$

where $F_0 = -TS_0$, with S_0 the entropy corresponding to the perfect disorder (i.e. in the absence of \vec{E}_0). By combining eqs (26) and (27) we obtain

$$(28) \quad \Delta F = F - F_0 = \frac{1}{2} U.$$

On the other hand we have

$$(29) \quad \Delta F = \Delta U - T\Delta S = U - T\Delta S$$

with $U_0 = 0$, in the absence of \vec{E}_0 . By comparing eqs (28) and (29), we may conclude that

$$(30) \quad F = F_0 + U - T\Delta S$$

and

$$(31) \quad -T\Delta S = \frac{1}{2} U$$

Expression 30 is formally comparable to expression 10. However, the statistical calculation allowed us to obtain a more precise interpretation of the different contributions to the total energy of the solute-solvent system as given in eq (10). First, we may conclude that the quantity $1/2U$ represents the free energy variation of the system. In second place, by comparing eqs (30) and (10), we can see that the third term of expression 10 is related to the entropy variation of the system (i.e. the solvent reorganization energy around the solute). This second conclusion may be naturally explained within the simple microscopic model considered, by recognizing that the equilibrium state of the system results from the competition of two opposite trends: on one hand, the trend to the order due to the coupling with \vec{E}_0 , which forces the dipoles to adopt an ordered configuration (i.e. following the direction of \vec{E}_0) and, on the other hand, the trend to the disorder due to the coupling with the thermostat. This argument is also consistent with the fact that the average orientation of the solvent dipoles at thermal equilibrium, taking into account the coupling with \vec{E}_0 , is determined by the minimization of a well defined potential function: the free energy of the system. Furthermore, it is quite clear from the above calculations that the minimization of the total energy of the system, neglecting the influence of the temperature (as in the case of the SM approach), would lead to a situation where all the solvent dipoles would be strictly oriented in the direction of \vec{E}_0 . It is the $-T\Delta S > 0$ contribution in expression 30, which causes that the minimum of F is obtained for a non vanishing value of the angle θ . Physically, $T\Delta S < 0$ term represents the heat transferred to maintain the temperature until the equilibrium state is attained, under the influence of \vec{E}_0 .

d) Introduction of the Onsager Reaction Field Theory

The hypothesis of independent dipoles introduced in the previous section, considerably diminishes the reliability of the model when applied to liquid

solutions. In this section, we will use a more general approach to show that the introduction of the interaction between the solvent dipoles, does not modify the conclusions already obtained.

Let us consider a system formed by a reduced number of solute molecules (Σ) in interaction with a big number of solvent molecules (S). We further assume that the Σ and S systems are in the configurations ω and Ω , respectively. The total energy of the system $U(\omega, \Omega)$ in the configuration (ω, Ω) is written as:

$$(32) \quad U(\omega, \Omega) = U_{\Sigma}(\omega) + U_S(\Omega) + U_{\Sigma-S}(\omega, \Omega)$$

where $U_{\Sigma}(\omega)$ and $U_S(\Omega)$ are the total energies of the pure solute and pure solvent respectively in the absence of interaction, and $U_{\Sigma-S}(\omega, \Omega)$ is the solute-solvent interaction energy. The partition function Z of the whole system is given by

$$(33) \quad Z = \int e^{-U(\omega, \Omega)/kT} d\omega d\Omega$$

By combining eqs (32) and (33), Z becomes

$$(34) \quad Z = \int e^{-U_{\Sigma}(\omega)/kT} \left[\int e^{-[U_S(\Omega) + U_{\Sigma-S}(\omega, \Omega)]/kT} d\Omega \right] d\omega$$

At this stage of the calculation it is convenient to introduce the reduced partition function $Z_i(\omega)$ of the solute proposed by Barriol (17) given by

$$(35) \quad \int e^{-[U_S(\Omega) + U_{\Sigma-S}(\omega, \Omega)]/kT} d\Omega = Z_i(\omega) \int e^{-U_S(\Omega)/kT} d\Omega$$

We can introduce a free energy term $F_i(\omega)$ associated to $Z_i(\omega)$ as

$$(36) \quad F_i(\omega) = -kT \ln Z_i(\omega)$$

In order to give a physical meaning to the free energy $F_i(\omega)$, we will assume that the system Σ is "frozen" in the configuration ω_0 and unpolarizable, that is, it conserves its configuration even under the influence of the system S. The total energy of the system $U(\omega_0, \Omega)$ is then given by:

$$(37) \quad U(\omega_0, \Omega) = U_{\Sigma}(\omega_0) + U_S(\Omega) + U_{\Sigma-S}(\omega_0, \Omega)$$

and Z may be cast into the form

$$(38) \quad Z(\omega_0) = e^{-U_{\Sigma}(\omega_0)/kT} \int e^{-[U_S(\Omega) + U_{\Sigma-S}(\omega_0, \Omega)]/kT} d\Omega$$

and

$$(39) \quad F(\omega_0) = U_{\Sigma}(\omega_0) - kT \ln \int e^{-[U_S(\Omega) + U_{\Sigma-S}(\omega_0, \Omega)]/kT} d\Omega$$

From eq (39), it is easy to verify that in the absence of interaction:

$$(40) \quad F_0(\omega_0) = U_{\Sigma}(\omega_0) - kT \ln \int e^{-U_S(\Omega)/kT} d\Omega$$

Subtracting eqs (40) and (39) we obtain

$$(41) \quad \Delta F = F(\omega_0) - F_0(\omega_0) = -kT \ln \int e^{-[U_S(\Omega) + U_{\Sigma-S}(\omega_0, \Omega)]/kT} d\Omega + kT \ln \int e^{-U_S(\Omega)/kT} d\Omega$$

$\Delta F(\omega_0)$ represents the free energy variation resulting from the interaction between the system $\Sigma(\omega_0)$ with $S(\Omega)$. In other words, F describes the free energy variation when the system $\Sigma(\omega_0)$ is inserted into the system S . Furthermore, from eqs (35) and (36) it is also seen that

$$(42) \quad \Delta F(\omega_0) = F_i(\omega_0)$$

The physical meaning of $F_i(\omega_0)$ is now quite clear: it represents the free energy of insertion of the system $\Sigma(\omega_0)$ into the system $S(\Omega)$ (18-19). This "insertion" energy represents the solvation energy of the system $\Sigma(\omega_0)$ by the system S .

The calculation developed above will be used as the basis to show that the results obtained within the independent solvent dipoles model may be generalized to the case where the interaction term is explicitly included. This is done by putting the quantity $F_i(\omega_0)$ in a more compact form and taking advantage that the reduced partition function defined in eq (35) may be rewritten as

$$(43) \quad Z_i(\omega) = \langle e^{-U_{\Sigma-S}(\omega, \Omega)/kT} \rangle_0$$

where $\langle \rangle_0$ represents the average value calculated on the basis of the partition function of the isolated $S(\Omega)$ system (which formally corresponds to a first order perturbation calculation). From eqs (43) and (36) we obtain:

$$(44) \quad F_i(\omega_0) = -kT \ln \langle e^{-U_{\Sigma-S}(\omega, \Omega)/kT} \rangle_0$$

In order to make the present calculation comparable to that of the previous section, the term in brackets in eq (44) is developed in powers of $U_{\Sigma-S}(\omega, \Omega)$. Neglecting terms higher than second order we obtain (see appendix 1).

$$(45) \quad F_i(\omega) = \frac{1}{2} \langle U_{\Sigma-S}(\omega, \Omega) \rangle$$

Expression 45 is equivalent to expression 28 and unequivocally leads to eq (30). However, eq (45) is more general since it was obtained by assuming a less restrictive hypothesis on the nature of system S . It is significant that expression 45, which describes the free energy of insertion of the system $\Sigma(\omega_0)$ into the system S is equivalent to the expression deduced by Ben-Naim (eq 3-12 of ref (20)) by using a quite different (non-perturbative) approach.

In summary, we have shown that in the case where the solvent is represented by non polarizable polar molecules, the magnitude to be minimized is the total free energy of the solute-solvent system. This result can be extended to the case where electronic polarization of both the solute and the solvent is considered.

APPLICATIONS

In order to illustrate the reliability and the usefulness of the given statistical analysis of the solvation process, two relevant applications will be discussed.

a) Derivation of the Onsager Reaction Field Theory

Let us assume that the Σ system is represented by a unique unpolarizable dipole $\vec{\mu}_\Sigma$ and that the solvent is representable by a set of equally unpolarizable dipoles $\vec{\mu}_i$. The interaction energy $U_{\Sigma-S}(\omega, \Omega)$ may be written as

$$(46) \quad U_{\Sigma-S}(\omega, \Omega) = -\vec{\mu}_{\Sigma}(\omega) E_S(\Omega)$$

where \vec{E}_S is the electric field created by a set of dipoles of the S system in the configuration Ω .

Since the average field created by an uniform and isotropic distribution of dipoles vanishes (see appendix 1) we have

$$(47) \quad \langle U_{\Sigma-S}(\omega, \Omega) \rangle_0 = -\vec{\mu}_{\Sigma} \cdot \langle E_S(\Omega) \rangle_0 = 0$$

In the case where the dipole distribution of the S system is perturbed by the presence of $\vec{\mu}_{\Sigma}$, the resulting average field $\langle E_S(\Omega) \rangle$ does not vanish. In fact, this average $\langle E_S \rangle$ is nothing but the reaction field. If R_S is its module, then

$$(48) \quad U_{\Sigma-S}(\Omega) = -\mu_{\Sigma} R_S$$

Finally, by using eqn (45), it is found that

$$(49) \quad F_i(\omega) = -\frac{1}{2} \mu_{\Sigma} R_S$$

which is the classical expression of the solvation energy given by the Onsager reaction field theory (16). Expression 49 is also the starting point for the quantum chemical calculation of the solvation energy in the self consistent reaction field (SCRf) model of Tapia (21) and in a variety of cavity models proposed by other authors (22-24).

b) Quantum Chemical Treatment of Solvent Effects. Derivation of the Effective Fock Operator.

In the introduction of this paper it has been mentioned that a correct interpretation of the solvation energy has a large influence in the derivation of the effective Fock operator for the quantum chemical treatment of solvation. It is also worth emphasizing that this problem is particularly relevant if the solute is a molecule or a molecular ion.

For this type of systems a usual approximation for the solvation energy is given by a generalization of Born formula (eq 4): the solvation energy of a molecular solute is built up by a sum of atomic contributions plus the interatomic interaction contributions (25-26). If we adopt such approach, we do not lose generality by considering the derivation of the Fock operator for the case of a monoatomic ion. The generalization to molecules is straightforward (9).

Let $E(1,P)$ be the total energy of the isolated solute as calculated within the self consistent field (SCF) approximation. The total energy of this system in solution $E(\epsilon,P)$ may be written as a function of the dielectric constant of the medium ϵ , and the Mulliken population matrix P , as follows

$$(50) \quad E(\epsilon,P) = E(1,P) + E_S(\epsilon,P)$$

where E_S is the correction term representing the solvation energy. To derive the effective Fock operator, $F(\epsilon,P)$, for the solute in the presence of the polarizable medium, we may adopt a very simple physical picture. Since $F(\epsilon,P)$ represents the average potential acting on each electron of the solvated solute we expect it to be the sum of the standard Hartree-Fock potential $F(1,P)$ of the isolated solute and the reaction field potential V_R , due to the solvent. Mathematically,

$$(51) \quad F(\epsilon, P) = - \frac{dE(\epsilon, P)}{dQ_A} = - \left[\frac{dE(1, P)}{dQ_A} + \frac{dE_S(\epsilon, P)}{dQ_A} \right] = F(1, P) + V_R(\epsilon, P)$$

In the case where the solute is a molecular system eq (51) holds if the net charge Q_A of the ion is replaced by the net charge $Q_A(P)$ of each atom in the valence state (the reader interested in a more formal derivation of eq (51) should consult reference (8)).

In order to discuss the relevance of the statistical thermodynamics analysis in the derivation of $F(\epsilon, P)$, let us write the solvation energy in the following form (see eqs (4), (8), (9)):

$$(52) \quad E_S(\epsilon) = \lambda Q_A V_R(\epsilon) = -\lambda \left[1 - \frac{1}{\epsilon} \right] \frac{Q_A^2}{a}$$

where λ is a parameter which converts $E_S(\epsilon)$ into the solute-solvent interaction energy ($\lambda=1$) or into the free energy of solvation ($\lambda=1/2$).

After combining eqs (50), (52) we get

$$(53) \quad - \frac{dE_S(\epsilon)}{dQ_A} = - 2\lambda \left[1 - \frac{1}{\epsilon} \right] \frac{Q_A}{a} = 2\lambda V_R(\epsilon)$$

We immediately see that the correction to the Fock operator due to the solvent equals the reaction field potential only in the case where $\lambda = 1/2$. In other words, we obtain a variationally correct effective Fock operator only when the orientational polarization energy of the solvent is taken into account, as shown in the statistical analysis of the solvation process discussed above.

CONCLUDING REMARKS

The solvation energy in the context of the continuum approach has been discussed. A partition of the total solute-solvent interaction energy has been presented. It was shown that the classical electrostatic theory does not provide a complete interpretation of the different contributions to the free energy of a solvated system. A statistical thermodynamics discussion of the solvation process was given. The simple model adopted in the present work allowed us to show that even in the case where solute-solvent interactions are treated by means of a perturbational approach, the physical meaning of each contribution to the total energy of the solute-solvent system can be clearly identified.

Finally, in order to test the reliability of the present approach, the Onsager reaction field theory has been derived. The relevance of the statistical analysis was also illustrated in the discussion of a correct derivation of the effective Fock operator required for the quantum mechanical treatment of solvent effects.

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APPENDIX 1

Derivation of Eq (45).

Starting from eq (44):

$$F_i(\omega_0) = -kT \ln \langle e^{-U_{\Sigma-S}(\omega_0, \Omega)/kT} \rangle_0$$

we may develop the term in bracket in powers of $U_{\Sigma-S}(\omega, \Omega)$. Neglecting terms higher than second order we get

$$(A-1) \quad F_i(\omega_0) = -kT \ln \left[1 - \frac{1}{kT} \langle U_{\Sigma-S}(\omega_0, \Omega) \rangle_0 + \frac{1}{2(kT)^2} \langle U_{\Sigma-S}^2(\omega_0, \Omega) \rangle_0 \right]$$

The contribution $\langle U_{\Sigma-S}(\omega_0, \Omega) \rangle_0$ in eq A-1 vanishes because it represents the average value of the interaction energy calculated on the basis of the partition of the S system considered as isolated and therefore homogeneous and isotropic.

By using the approximation $\ln(1+x) = x$, for x small, we get

$$(A-2) \quad F_i(\omega_0) = -\frac{1}{2} \frac{1}{kT} \langle U_{\Sigma-S}^2(\omega_0, \Omega) \rangle_0$$

On the other hand, the average value of the interaction potential energy is given by

$$(A-3) \quad \langle U_{\Sigma-S}(\omega_0, \Omega) \rangle = \frac{\int e^{-[U_S(\Omega) + U_{\Sigma-S}(\omega_0, \Omega)]/kT} U_{\Sigma-S}(\omega_0, \Omega) d\Omega}{\int e^{-[U_S(\Omega) + U_{\Sigma-S}(\omega_0, \Omega)]/kT} d\Omega}$$

where $\langle \rangle$ represents the average value in the presence of the interaction. After developing the term $\exp[-U_{\Sigma-S}(\omega_0, \Omega)/kT]$ in powers of

$U_{\Sigma-S}(\omega_0, \Omega)$ we obtain

$$(A-4) \quad \langle U_{\Sigma-S}(\omega_0, \Omega) \rangle = -\frac{1}{kT} \langle U_{\Sigma-S}^2(\omega_0, \Omega) \rangle_0$$

Finally, by combining eqs A-2 and A-4, eq (45) is obtained.

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