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Theoretical basis of the empirical reaction field approximations through continuum model

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We derive from exact integral equations of classical electrostatics some approximate expressions of the interaction energy of a point charge distribution with a dielectric medium. We show how they can be used for computing the wave functions of solvated species imbedded in cavities formed by interlocking spheres in a polarizable continuum. We discuss the relation between these formulae and the ones proposed earlier on empirical basis and we especially emphasize the improvement that they bring out.

Key words: Reaction field theory — Continuum model — Solvaton and desolvaton effects

1. Introduction

The thermodynamical approach to the solvaton problem brings into light the importance of the insertion energy concept [1, 2]. The insertion energy is the free energy change occurring when a molecule, in a given nuclear configuration, is transferred from the gas to the liquid phase without being polarised by its surrounding. For usual solvent polarization, it can be shown by means of statistical mechanics [3-5], that the insertion energy is simply related to the solute-solvent (s-S) electrostatic interaction energy which therefore appears to be the central quantity of any theoretical development.

The modelization of the solvent by a continuum characterized by its bulk macroscopic properties (e.g. the dielectric constant) gives an useful mean for estimating the s-S interaction energy. Up to date, a lot of applications of the continuum model has been reported in the field of quantum chemistry [5-8]. They can be roughly divided in two classes: that handling with the exact formulation of the Reaction Field (RF) theory and that using empirical representations mainly derived from the original Born formula [9]. In the first case, we are placed in the following dilemma: we can use explicit formulae for the only cavities having simple shape [10-13] or we must have recourse to heavy numerical integration techniques for more realistic cavities defined as a system of interlocking spheres [14, 15]. In the second case, the simplicity of the formulation is often paid by the unreality of the model or by the physically unacceptable character of its basic assumptions.

An example of the deficiency of the model is provided by the generalized Born (GB) formula [16, 17]: as we will clearly show below, it is legitimate only for a system of charges lying in separated cavities of the solvent, so that its use to account for the solvaton of a molecule is not satisfactory. For the same grounds, this model is not able to reproduce the desolvaton effects (i.e., the effects due to the cavities overlap) which have some influence in the study of chemical associations. In this respect, the solvaton model [18, 19] is no more suitable and the improvements suggested later [20] were not decisive.

An attempt has been made for introducing the desolvaton effects by an adequate modification of the solvaton definition [21]. Following this idea, we have proposed an extension of the GB formula able to account for this effect [22]. Unfortunately, the preliminary calculations on solvated ionic pairs using the extended generalized Born (EGB) formula showed an unexpected behaviour at large distances [4]. This feature was initially attributed to a poor representation of the ionic species in the CNDO/2 approximation.

The aim of this paper is to explain the real origin of this incorrect behaviour and to propose a completely satisfactory solution taking account carefully of the thermodynamic considerations (an outline of which is given in the appendix) and preserving the internal coherence of the theory as it was discussed in our preceding work [22]. After some essential preliminary results have been recalled at the beginning of the second section, we propose a mean for replacing some basic integral equations of the classical electrostatic theory of the dielectric media by a system of approximate linear equations. In the third section, different approximations of this system are proposed and compared with the empirical ones. We show how they can be used for the study of the chemical reactivity in solution and we examine in particular the behaviour of the energy of an ion pair at large separation.

2. Polarization of a dielectric by a charge distribution

2.1. *Definition of the polarization charge densities [23]*

We consider a linear and isotropic dielectric for which the polarization vector $\boldsymbol{P}$, that is the density of the dipole distribution, is related to the electric field strength $\mathscr{E}$ by

$$\boldsymbol{P} = (\varepsilon - \varepsilon_0)\mathscr{E}, \tag{1}$$

where ε is the dielectric constant.

We know that the potential due to such a distribution is identical to the superposition of potentials produced by a volume polarization charge density ρ^* within the dielectric

$$\rho^* = -\text{div}\,\boldsymbol{P} \tag{2}$$

and by a surface polarization charge density σ^*

$$\sigma^* = \boldsymbol{nP}, \tag{3}$$

where $\boldsymbol{n}$ stands for a vector with length unity and direction along the outward normal of the dielectric surface S.

For a homogeneous dielectric, we can write

$$\text{div}\,\boldsymbol{P} = (\varepsilon - \varepsilon_0)\,\text{div}\,\mathscr{E} \tag{4}$$

and the Gauss theorem takes the form

$$\text{div}\,\mathscr{E} = \rho/\varepsilon, \tag{5}$$

where ρ is the source charge density: accordingly, the density ρ^*, as given by the Eq. (2), vanishes if the source charges lie outside the dielectric volume. In particular, when the source charges are localized in a cavity created inside the dielectric medium, it is concluded that the potential due to the polarized dielectric can be replaced by that of the surface density σ^* alone. We will restrict ourselves to this special case in all that follows.

2.2. Exact calculation of the surface polarization charge density

It has been shown by E. Durand [24] that the polarization surface density $\sigma^*(M)$ on each point M of S is formally given by the following integral equation

$$\frac{\varepsilon_0 + \varepsilon}{\varepsilon_0 - \varepsilon}\sigma^*(M) = 2\varepsilon_0(\boldsymbol{n}_M \cdot \mathscr{E}_0(M)) + (1/2\pi)\int_S \sigma^*(N)\frac{\boldsymbol{n}_M \cdot \boldsymbol{NM}}{NM^3}\,ds_N, \tag{6}$$

where $\mathscr{E}_0(M)$ is the electric field produced at M by the source charges. The second term of this expression represents the contribution due to the field produced at M by the elementary polarization charges lying around each point N of the surface S. It should be noted that, in general, the magnitude of this last term is comparable to that of the first one: it can be neglected only in the case of weak polarization.

Although in most cases this equation cannot be solved exactly, it may provide a rigorous starting point for examining the validity of various analytical formulae which have been empirically proposed for simulating the polarization charge distribution on S.

For instance, if we perform the summation of both sides of the Eq. (6) over all points of the surface S, we obtain

$$\frac{\varepsilon_0+\varepsilon}{\varepsilon_0-\varepsilon} Q^* = 2Q + (1/2\pi) \int_{\mathrm{S}} \sigma^*(N)\, ds_N \int_{\mathrm{S}} \frac{\boldsymbol{n}_M \cdot \boldsymbol{NM}}{NM^3}\, ds_M, \tag{7}$$

where Q is the sum of the source charges inside the cavity and Q^* is the total polarization charge on the surface S. The first term is immediately obtained by using the Gauss theorem. In the second one, we have

$$\int_{\mathrm{S}} \frac{\boldsymbol{n}_M \cdot \boldsymbol{NM}}{NM^3}\, ds_M = 2\pi, \tag{8}$$

because this integral is the solid angle by which the entire surface S is subtended from any of its point N. As a result, we find the well known Born formula [9]

$$Q^* = -(1 - \varepsilon_0/\varepsilon)Q, \tag{9}$$

which appears to be valid for internal cavity of any shape.

2.3. *Approximate calculation of local polarization charges*

Further informations about the local distribution of the total polarization charge Q^* on the surface can be obtained through the preceding procedure by limiting the summation to a given part S_i of the surface S resulting from any partition of it in a finite number of elements i $(i = a, b, \dots)$ such that

$$\bigcup_i \mathrm{S}_i = \mathrm{S} \quad \text{and} \quad \mathrm{S}_i \cap S_j = \delta_{ij}\mathrm{S}_i. \tag{10}$$

From the Eq. (6) we obtain

$$\frac{\varepsilon_0+\varepsilon}{\varepsilon_0-\varepsilon} \int_{\mathrm{S}_i} \sigma^*(M)\, ds_M = 2\varepsilon_0 \int_{\mathrm{S}_i} \mathscr{E}_0(M)\boldsymbol{n}_M\, ds_M + (1/2\pi) \int_{\mathrm{S}} \sigma^*(N)\, ds_N \int_{\mathrm{S}_i} \frac{\boldsymbol{n}_M \cdot \boldsymbol{NM}}{NM^3}\, ds_M. \tag{11}$$

With the further assumption that the source of the electric field $\mathscr{E}_0$ is a point charge distribution Q_I $(I = A, B, \dots)$, we have

$$\mathscr{E}_0(M) = (1/4\pi\varepsilon_0) \sum_I Q_I \frac{\boldsymbol{IM}}{IM^3} \tag{12}$$

and the first term becomes

$$(2/4\pi) \sum_I Q_I \int_{\mathrm{S}_i} \frac{\boldsymbol{n}_M \cdot \boldsymbol{IM}}{IM^3}\, ds_M = (2/4\pi) \sum_I Q_I \Omega_{Ii}, \tag{13}$$

where Ω_{Ii} is the solid angle by which the surface element S_i is subtended from the point I.

In the same way as before, we obtain for the second term

$$(1/2\pi) \int_{\mathrm{S}} \sigma^*(N)\, ds_N \int_{\mathrm{S}_i} d\Omega_{NM} = (1/2\pi) \int_{\mathrm{S}} \sigma^*(N)\, ds_N\, \Omega_{Ni}. \tag{14}$$

If we suppose that the density $\sigma^*(N)$ can be considered with a good accuracy as a constant quantity when the point N is moving anywhere on any of the surface elements, we may transform the second member of the Eq. (14) according to

$$(1/2\pi)\sum_j \int_{S_j} \sigma^*(N)\, ds_N \Omega_{Ni} = (1/2\pi)\sum_j \sigma_j^* \int_{S_j} ds_N\, \Omega_{Ni} \tag{15}$$

and, in a second step,

$$(1/2\pi)\sum_j \sigma_j^* S_j \bar{\Omega}_{ji} = (1/2\pi)\sum_j Q_j^* \bar{\Omega}_{ji}, \tag{16}$$

where we have introduced the quantity

$$\bar{\Omega}_{ji} = \left(\int_{S_j} ds_N \Omega_{Ni}\right) / S_j, \tag{17}$$

which is the mean value of the solid angle by which the element S_i is subtended from a point of S_j.

By introducing the normalized quantities

$$\omega_{Ii} = (1/4\pi)\Omega_{Ii} \tag{18}$$

and

$$\bar{\omega}_{ji} = (1/2\pi)\bar{\Omega}_{ji} \tag{19}$$

we may write the Eq. (11) in the simpler form

$$\frac{1+k}{1-k} Q_i^* = 2\sum_J Q_J \omega_{Ji} + \sum_j Q_j^* \bar{\omega}_{ji}, \tag{20}$$

where we have substituted the relative constant symbol k to the ratio $\varepsilon/\varepsilon_0$ used up to now. Thus, the procedure which consists in replacing the continuous summation over a set of elementary surface parts by a discrete summation over a set of finite surface elements, leads to replace the exact integral equation (6) by the approximate system of linear equations

$$\boldsymbol{Q}^* = \boldsymbol{\Pi}\, \boldsymbol{Q}, \tag{21}$$

with

$$\boldsymbol{\Pi} = 2\left(\frac{1+k}{1-k}\mathbb{1} - \bar{\omega}^t\right)^{-1} \cdot \omega^t. \tag{22}$$

We point out however that the Born relation (9) established for the total charges remains true independently on the choice of the surface partition. This can be easily verified by summing the Eq. (20) over all the surface elements

$$\frac{1+k}{1-k}\sum_i Q_i^* = 2\sum_J Q_J \left(\sum_i \omega_{Ji}\right) + \sum_j Q_j^* \left(\sum_i \bar{\omega}_{ji}\right) \tag{23}$$

and by using the sum rules

$$\sum_i \omega_{Ji} = \sum_i \bar{\omega}_{ji} = 1, \tag{24}$$

which express, according to the definition of Ω_{Ji} and $\bar{\Omega}_{ji}$
i) that the solid angle by which the entire surface S is subtended from any internal point is equal to 4π.
ii) that the mean solid angle by which the entire surface S is subtended from any point belonging to a given surface element is equal to 2π.

2.4. *Approximate calculation of the interaction energy*

The exact expression of the interaction energy between the source charges (s) and the polarized dielectric (S) (i.e. the polarization density on the surface S) is [25]

$$E^{\mathrm{s\text{-}S}} = \int_{\mathrm{S}} \sigma^*(M)\, V_0(M)\, ds_M. \tag{25}$$

where $V_0(M)$ is the potential at M of the electric field due to the source charges.

Taking account of the partition of the surface S, we define a vector $V_{0\mathrm{S}}$ the components of which are the mean values of the potential on each surface element. Thus we write

$$E^{\mathrm{s\text{-}S}} = (\boldsymbol{Q}^*)^t \boldsymbol{V}_{0\mathrm{S}}. \tag{26}$$

Moreover, using the relation (21) and defining

$$\boldsymbol{V}_R = \mathbb{\Pi}^t \boldsymbol{V}_{0\mathrm{S}} \tag{27}$$

we get

$$E^{\mathrm{s\text{-}S}} = \boldsymbol{Q}^t \boldsymbol{V}_R. \tag{28}$$

This is an expression of the exact s-S interaction energy, valid if the source of the electric field is a set of point charges, in which each component $(V_R)_I$ of $\boldsymbol{V}_R$ is the so called reaction field (RF) [26] potential produced at I by the polarization charges.

2.5. *Approximate calculation of the reaction field potential*

For the sake of theoretical coherence, it is interesting to verify that, under the same assumptions that have been made above, the relation (27) can be derived independently from exact integral equations also given by E. Durand [27]. The first one

$$\frac{1+k}{2} V(M) = V_0(M) + \frac{1-k}{4\pi} \int_{\mathrm{S}} V(N)\, d\Omega_{MN} \tag{29}$$

gives the total potential V (i.e. the sum of potentials due to the source charges and to the polarization charges) on each point M of the surface S. Once it has been solved, the second equation

$$V(M) = V_0(M) + \frac{1-k}{4\pi} \int_S V(N)\, d\Omega_{MN} \tag{30}$$

yields the total potential in any point M inside the cavity.

The RF potential in any point M inside the cavity can be directly derived by making the substitution

$$V(M) = V_0(M) + V_R(M) \tag{31}$$

in the Eq. (30): we have then

$$V_R(M) = \frac{1-k}{4\pi} \int_S V(N)\, d\Omega_{MN}. \tag{32}$$

In the framework of the previous approximations this last equation can be immediately rewritten

$$\boldsymbol{V}_R = (1-k)\omega \boldsymbol{V}_S, \tag{33}$$

where the components of the vector $\boldsymbol{V}_S$ are the mean values of the total potential on a given part of S. In the same way the Eq. (29) is transformed into (having in mind that, in this equation, the point M belongs to S)

$$\frac{1+k}{2} \boldsymbol{V}_S = \boldsymbol{V}_{0S} + \frac{1-k}{2} \bar{\omega} \boldsymbol{V}_S, \tag{34}$$

which allows to express $\boldsymbol{V}_S$ in term of $\boldsymbol{V}_{0S}$ as follows

$$\boldsymbol{V}_S = \frac{2}{1-k} \left(\frac{1+k}{1-k} \mathbb{1} - \bar{\omega} \right)^{-1} \boldsymbol{V}_{0S}. \tag{35}$$

Then we make sure that the relation (27) holds by inserting the Eq. (35) into the Eq. (33).

2.6. Calculation of the approximate Green function

Now we express that $\boldsymbol{V}_{0S}$ is a linear combination of the source charges.

$$\boldsymbol{V}_{0S} = \boldsymbol{\Gamma} \boldsymbol{Q}, \tag{36}$$

where the matrix elements Γ_{iI} are the mean values of the potential created on a surface element S_i by an unitary charge lying at the point I inside the cavity. Thus we get for the interaction energy

$$E^{s\text{-}S} = \boldsymbol{Q}^t \mathbb{G} \boldsymbol{Q}, \tag{37}$$

with

$$\mathbb{G} = \boldsymbol{\Pi}^t \boldsymbol{\Gamma} \tag{38}$$

that is a quadratic expansion in term of the source charges. By definition [28], $\mathbb{G}$ is the Green function of the system: an element G_{IJ} is the potential created at I (resp. J) by the polarization charge that an unitary point charge at J (resp. I) induces on S. These matrix elements can also be considered as the coulombic interaction between the source charges via the dielectric medium.

The symmetry of the $\mathbb{G}$ matrix can be intuitively conjectured from its definition: it can also be rigorously proved by mathematical analysis [29]. However, we must stress the fact that the rigorous proof holds for the exact Green function only; in particular, the procedure of partition of S that we used leads in general to a non symmetric approximate $\mathbb{G}$ matrix.

The problem raised by this symmetry breaking can be easily solved by remarking that $E^{\text{s-S}}$ can be written in the equivalent form

$$E^{\text{s-S}} = \boldsymbol{Q}^t\tilde{\mathbb{G}}\boldsymbol{Q}, \tag{39}$$

where $\tilde{\mathbb{G}}$ is the symmetrized Green function

$$\tilde{\mathbb{G}} = 1/2(\mathbb{G}+\mathbb{G}^t). \tag{40}$$

Naturally, this choice requires a new definition of the RF potential

$$\boldsymbol{V}_R = \tilde{\mathbb{G}}\boldsymbol{Q}, \tag{41}$$

which is different from the initial ones.

Although this redefinition can seem to be somehow artificial and physically unsound, we may argue that both expressions of the RF potential (i.e. the symmetrized and the initial ones) would be identical for an exact calculation and that their difference, strongly dependent on the approximations involved in the numerical calculations, can be substantially reduced by a proper choice of the surface partition (the difference will theoretically vanish if S is partitioned into an increasingly great number of small elements).

Another argument for using $\tilde{\mathbb{G}}$ in place of $\mathbb{G}$ is provided by the application of the variational principle as we will show in the next section.

3. Application to the calculation of solvent effects in quantum chemistry

3.1. Variational calculation of the solute wave function

Our purpose is to use the results of the preceding sections for the study of the electronic structure of a polarizable solute molecule embedded in a polarizable solvent. If the effect of the temperature on the electronic motion can be neglected, we can assume that the electronic structure of the s–S system is determined by a wave function ψ. Here, we suppose that ψ is separable so that the electronic structure of the solute is determined by a solute wave function φ: then, we will find the optimal φ through a variational procedure in the Born–Oppenheimer (BO) approximation.

As it is shown in the Appendix, the effective hamiltonian of the s–S system (which depends only on the solute coordinates) is given by the Eq. (A11) or by the Eq. (A21) in the weak s–S interaction approximation (when (s) is in a preformed cavity). In the BO approximation, the first term of the Eq. (A21), which is the nuclear hamiltonian of the solute, reduces to the potential function $U^{s}_{\varphi}(\boldsymbol{r})$: considered as a function of φ, parametrically depending on $\boldsymbol{r}$, this term is the quantum mechanical energy, noted $E^{s}_{\boldsymbol{r}}(\varphi)$, of the solute in the nuclear configuration $\boldsymbol{r}$. The second term is one half the mean s–S electrostatic interaction energy: its calculation requires the knowledge of the averaged nuclear and electronic structure of the solvent in thermal equilibrium and polarized by the solute, fixed in the configuration $\boldsymbol{r}$, with the electronic wave function φ. In spite of its limitations, the continuum model provides a simple way for estimating this term as far as the solute can be replaced by a set of point charges $\boldsymbol{Q}$. In what follows, we assume that the point charges Q_I are the solute net charges (i.e. the difference between the nuclear and the electronic charges on each atom I) and we estimate the mean s–S interaction energy by the Eq. (39) (we use the more explicit notation $E^{s\text{-}S}_{\boldsymbol{r}}(Q)$) in such a way that the solvent is characterized by its macroscopic dielectric constant and the shape of the cavity only.

At the SCF level of approximation, the search for the optimal wave function φ is replaced by that of the optimal density matrix $\mathbb{P}$. The quantity to be minimized is then

$$A^{s\cup S}(\mathbb{P}) = E^{s}_{\boldsymbol{r}}(\mathbb{P}) + 1/2E^{s\text{-}S}_{\boldsymbol{r}}(\boldsymbol{Q}) + A^{S}, \tag{42}$$

where $\boldsymbol{Q}$ is depending on $\mathbb{P}$ and A^{S} is a constant term relative to the solvent alone. In this expression we can replace the last two terms by the sum of $E^{s\text{-}S}_{\boldsymbol{r}}$ and a contribution of the polarized solvent $A^{S}+\Delta A^{S}$ (i.e. the term $-1/2E^{s\text{-}S}_{\boldsymbol{r}}$ is considered as the solvent polarization ΔA^{S} [11]) so that $A^{s\cup S}$ is the free energy of the s–S system, S being polarized by the solute fixed in a given nuclear configuration.

The variational calculus leads to the general expression of the effective Fock operator [22] taking account of the solvent

$$\mathbb{F}_k(\mathbb{P}) = \partial A^{s\cup S}/\partial\mathbb{P}. \tag{43}$$

By developing the total free energy $A^{s\cup S}$ as indicated above we derive the more explicit expression

$$\mathbb{F}_k(\mathbb{P}) = \mathbb{F}_1(\mathbb{P}) + 1/2(\partial E^{s\text{-}S}_{\boldsymbol{r}}/\partial\mathbb{P}), \tag{44}$$

where the first term is the Fock operator of the isolated solute and the second one is a potential correction due to the interaction with the polarized solvent. That can be verified immediately having in mind that, in a OAO basis (μ, ν, . . .), we have $\partial Q_J/\partial P_{\mu\nu} = -\delta_{\mu\nu}\delta_{IJ}$ if μ belongs to the center I: thus, if we express $E^{s\text{-}S}_{\boldsymbol{r}}$ in term of the Green function according to the Eq. (39) we find

$$1/2\partial E^{s\text{-}S}_{\boldsymbol{r}}/\partial P_{\mu\nu} = -(\mathbb{G}\boldsymbol{Q})_I\delta_{\mu\nu}. \tag{45}$$

Taking account of the Eq. (41) we see that the diagonal elements of F_k contain a solvent correction which is the RF potential to which an electron on I is submitted. Let us emphasize that one directly derives from the variational principle an expression of V_R in terms of the symmetrized Green function or, in other words, that the free energy minimum of the solute–solvent system can be reached only by using the effective Fock operator defined in term of the symmetrized Green function.

3.2. Simplified formulae

Let us examine at first the strong approximation which results from the weak polarization assumption. The $\mathbb{\Pi}$ matrix of the Eq. (21) is calculated by neglecting the contribution of the polarization charges in the second member of the Eq. (20): we thus obtain

$$Q_i^* = -(1-1/k)\sum_J Q_J \omega_{Ji}, \tag{46}$$

where we have replaced the numerical factor $2(1-k)/(1+k)$ by $-(1-1/k)$ because they are equal to first order for small k values. A satisfactory consequence of this small modification is that the Born relation (9) will be fulfilled for any k value. Equation (46) is a natural extension of the GB formula [16, 17] where the local polarization charges depend linearly on all the source charges. We point out that if the matrix ω is replaced by the unity matrix $\mathbb{I}$ we obtain the GB formula as a limit case. However, it is clear that this simplication, which amounts to suppose that each source charge is isolated in its own cavity, is not convenient for describing the solvated molecules.

When the polarization is more important, the contribution just neglected in the Eq. (20) must be taken into account. Unfortunately, the computer calculation of the $\bar{\omega}_{ji}$ matrix elements is time and space consuming because it requires an averaging over each surface element. Thus, when the continuum model is coupled with semi-empirical techniques of calculation of the solute wave function, it may be acceptable, in regard to the number of crude approximations made elsewhere, to estimate this matrix elements by the formula

$$\bar{\omega}_{ji} = \omega_{Ji} \tag{47}$$

if the point J associated to j is carefully chosen. Let us point out that this relation holds for a single spherical cavity of surface S_a and center A as it results from the relation between the solid angles

$$\Omega_{Na} = 1/2\Omega_{Aa}, \tag{48}$$

where N is any point of S_a.

3.3. Application to the study of chemical reactions in solution

The case of a cavity formed by the union of non-connected different volume is interesting for the theoretical study of the chemical reactivity of molecules or ions in solution. As E. Durand pointed out [30], this problem can be solved by means of their integral equations which are always valid provided that the different volumes are clearly distinguished in it. As a consequence, for a cavity formed by n distinct volumes, each of the equations that we derived above (e.g. the Born relation) must be replaced by a set of n equations (i.e. the GB formula which is rigorously valid in that case).

From classical electrostatic, we expect that the solute-solute (s-s) interaction energy $E^{\mathrm{s-s}}_{\mathrm{X-Y}}$ between two species, X and Y, in a polarizable solvent will behave as $1/kR_{\mathrm{XY}}$ when the intersystem distance R_{XY} becomes greater than a critical value R_{C} for which the solutes are trapped in two distinct cavities.

In order to verify this property, we first define $E^{\mathrm{s-s}}_{\mathrm{X-Y}}$ by adding to the mutual interaction term in vacuum

$$E^{\mathrm{Vac}}_{\mathrm{X-Y}} = \sum_{I}^{\mathrm{X}} \sum_{J}^{\mathrm{Y}} Q_I Q_J 1/R_{IJ} \tag{49}$$

the mutual interaction of charges via the solvent

$$E^{\mathrm{Solv}}_{\mathrm{X-Y}} = \sum_{I}^{\mathrm{X}} \sum_{J}^{\mathrm{Y}} Q_I \tilde{G}_{IJ} Q_J \tag{50}$$

according to the Eq. (39).

Using the definitions (40) and (38), we may write

$$\tilde{G}_{IJ} = 1/2 \sum_{k} (\Pi^{t}_{Ik}\Gamma_{kJ} + \Gamma^{t}_{Ik}\Pi_{kJ}). \tag{51}$$

In the present case however, the matrix ω and $\bar{\omega}$ defined by the Eq. (18) and (19) are bloc diagonal because the solid angles by which a surface element of X (resp. Y) is subtended from any point of Y (resp. X) vanish identically. We conclude that the Π matrix defined by Eq. (22) is also bloc diagonal. Thus, for two points I and J belonging respectively to X and Y, we have

$$\tilde{G}_{IJ} = 1/2 \left(\sum_{k}^{\mathrm{X}} \Pi^{t}_{Ik}\Gamma_{kJ} + \sum_{l}^{\mathrm{Y}} \Gamma^{t}_{Il}\Pi_{lJ} \right) \tag{52}$$

and, taking account of the definition (21), we consequently obtain from the Eq. (50)

$$E^{\mathrm{Solv}}_{\mathrm{X-Y}} = 1/2 \sum_{k}^{\mathrm{X}} \sum_{J}^{\mathrm{Y}} Q^{*}_{k}\Gamma_{kJ}Q_J + 1/2 \sum_{I}^{\mathrm{X}} \sum_{l}^{\mathrm{Y}} Q_I \Gamma^{t}_{Il} Q^{*}_{l}. \tag{53}$$

This is no no more than one half the s-S (Y-X plus X-Y) interaction energy in agreement with the relation (42).

For sufficiently large intersystem distance, say $R_{\mathrm{XY}} \gg R_{\mathrm{C}}$, we have then approximately

$$E^{\mathrm{Solv}}_{\mathrm{X-Y}} \sim 1/2(Q^{*}_{\mathrm{X}}Q_{\mathrm{Y}} + Q_{\mathrm{X}}Q^{*}_{\mathrm{Y}})1/R_{\mathrm{XY}} \tag{54}$$

and, taking account of the set of Born relations like Eq. (9), the interaction energy, sum of Eqs. (49) and (54), is found to be $Q_{\mathrm{X}}Q_{\mathrm{Y}}/kR_{\mathrm{XY}}$ as expected.

4. Discussion

Our aim is to account for the solvent effects by considering as well as possible, although in an approximate way, the shape of the solute. Rather than to use analytical but also too simple surfaces (as are spheres or ellipses) and in order to deal with a representation of the cavity which would be together tractable and realistic enough, we choose to define it as a system of spheres of radii R_I the centers of which are located at the positions I of the solute charges. With this assumption, there is a one to one correspondence between each point I and a surface element S_i defined in Eq. (10). The adjustment of the parameters R_I to get the effective volume of the solute has been discussed previously [14]. In the same paper, the authors indicated how to use the Korobov's grid technique for numerical computation of surface integrals: this method can be applied for estimating the elements of the matrices ω, $\bar{\omega}$ and Γ.

As it comes out from the Eq. (2), (4) and (5), a proper account of the s–S interaction energy only necessitates the knowledge of the polarization charge density on the surface of the solvent cavity. From a physical point of view, that results from both hypotheses: the dielectric homogeneity and the localisation of the source charges inside the cavity. This contrasts with our previous work [22] in which we assumed two kinds of polarization charges: the "internal and the external" ones. In fact, it appears that the introduction of the external charge concept was only an artefact for a priori maintaining the validity of the Born relation for the total charges. Simultaneously, this invalidates the interpretation of the desolvation effects as a polarization charge transfer from an internal to an external solvation shell [31], at least in the framework of the continuum model that we have defined from the beginning. In respect of this point, we must add that the presence of source charges inside the medium [15] is incompatible with the consideration of the only surface polarization density: however, the problem can be solved by introducing an additional potential into the solute hamiltonian which constrains the source charges to remain inside the cavity [12].

We have shown in the section 3.2 how simplified formula could be derived by successive approximations. The simplified formula (46) can be compared with other empirical approaches. If we remember the sum rule (24) for the ω matrix elements, we may rewrite the Eq. (46)

$$Q_I^* = -(1-1/k)\left(Q_I\left(1-\sum_J{}' \omega_{IJ}\right)+\sum_J{}' Q_J\omega_{JI}\right), \tag{55}$$

where, as stated above, we have identified the indices I and i. We recognize, in the first term of the second member, the expression

$${}^iQ_I^* = -(1-1/k)Q_I(1-f_I) \tag{56}$$

defining the internal polarization charges of the extended GB (EGB) formula [22]. The merit of the new formula (55) with respect to the original one is to provide an explicit expression of the neighbourhood factor f_I which, in some previous works [4, 32], was only estimated with the aid of the atomic orbitals overlap integrals. Moreover, the validity of the Born relation for the total charges directly proceeds from the presence of the second term in the Eq. (55) which depends on the charges Q_J at the points $J \neq I$. In this respect, the formulae that we propose significantly differ from the other attempts for improving the GB formula [21, 22, 33, 34].

They also provide a new explanation of the desolvation effect which can be presented in a simple way by considering the example of two monocentric solute species A and B, with opposite charges, the distance R_{AB} of which is varying from infinity to zero. When R_{AB} is very large, A and B are the centers of two spherical cavities S_{A} and S_{B}, with radii R_{A} and R_{B}, and there is a stabilizing (solvation) solvent effect given by the GB formula. A destabilizing (desolvation) solvent effect appears when R_{AB} becomes smaller than $R_{\text{C}} = R_{\text{A}} + R_{\text{B}}$, which is the critical value for which S_{A} and S_{B} overlap, giving rise to non-vanishing values of the solid angles Ω_{AB} and Ω_{BA}. Then, both polarization charges Q^*_{A} and Q^*_{B} are modified by the influence of the charges (source and polarization ones) of the other center. This modification is responsible of a destabilization (desolvation) with respect to the energy given by the GB formula. If we suppose that $R_{\text{A}} > R_{\text{B}}$, the sphere S_{B} is totally included in S_{A} when $R_{\text{AB}} < R_{\text{A}} - R_{\text{B}}$. In this case, the unique cavity S_{A} contains two opposite charges and the polarization charge Q^*_{A} vanishes: thus the desolvation is maximum and there is no more solvent effect. As a result, the total free energy curve can display two stationary points separated by a barrier [31].

We have seen in Eq. (54) that the correct behaviour of the ionic pair interaction energy at large distances is a direct consequence of the Born relation provided that the Green function has been adequately defined as in Eq. (40). In order to precise the origin of the failure of the EGB formula [22], we will remake the analysis of the s–s interaction energy as it has been done in the section 3.3. The EGB Green function is defined in term of the neighbourhood factor f_I by

$$\tilde{G}_{IJ} = -(1-1/k)((1-f_I)\cdot(1-f_J)+f_I f_J)\gamma_{IJ}, \tag{57}$$

where the γ_{IJ} are the CNDO/2 electronic repulsion integrals.

Taking account of the external polarization charge definition, ${}^eQ^*_I = -(1-1/k)f_I Q_I$, we can derive the interaction energy between two solvated species X and Y via the solvent

$$E^{\text{Solv}}_{\text{X-Y}} = -(1-1/k)\left(\sum_I^{\text{X}}\sum_J^{\text{Y}} Q_I Q_J - \sum_I^{\text{X}}\sum_J^{\text{Y}} {}^eQ^*_I Q_J - \sum_I^{\text{X}}\sum_J^{\text{Y}} Q_I {}^eQ^*_J \right.$$
$$\left. -2k/(k-1)\sum_I^{\text{X}}\sum_J^{\text{Y}} {}^eQ^*_I {}^eQ^*_J\right). \tag{58}$$

The s–s interaction energy is obtained as before by adding the mutual interaction terms in vacuum; at large distance, we get the approximate form

$$E^{\text{s-s}}_{\text{X-Y}} \sim Q_{\text{X}}Q_{\text{Y}}/kR_{\text{XY}} - ({}^eQ^*_{\text{X}}Q_{\text{Y}} + Q_{\text{X}}{}^eQ^*_{\text{Y}} + 2k/(k-1){}^eQ^*_{\text{X}}{}^eQ^*_{\text{Y}})1/R_{\text{XY}}. \tag{59}$$

We see that there remains a spurious term which only disappears when the total external charges vanish. This fact explains why the behaviour of a system formed by two monocentric species is apparently correct (at large distance, the factors f_I vanish and so do the external charges). However, the disagreement is particularly evident when we study the interaction of any solute X with a monocentric one B for very high values of the dielectric constant [4]: we have now

$$E^{\mathrm{s-s}}_{\mathrm{X-B}} \sim -{}^{e}Q^{*}_{\mathrm{X}}Q_{\mathrm{B}}/R_{\mathrm{XB}} \tag{60}$$

that is an unexpected attractive interaction in the case of ionic species having opposite charges. Clearly, the unrealistic external charge concept is mainly responsible of this anomalous trend.

Concerning the Green function definition, we must mention that, in our preceding work [22], we imposed the symmetry property by an adequate adjustment of the mean interaction integrals Γ_{IJ} which were related to the symmetric matrix γ of the electronic repulsion integrals. By this way, we avoided the problem of defining the shape of the cavity. In the case of weak polarization, where the $\mathbb{\Pi}$ matrix is a product of ω by a numerical factor depending on k, this procedure would consist to define the Γ matrix by

$$\Gamma = \gamma\omega \tag{61}$$

in such a way to obtain the following symmetric Green matrix

$$\tilde{\mathbb{G}} = -(1-1/k)\omega^{t}\gamma\omega. \tag{62}$$

in the general case however, $\mathbb{\Pi}$ is not factorizable and its use instead of ω in Eq. (61) would give mean interaction integrals depending on the dielectric constant. Thus, the symmetrization procedure that we propose in Eq. (40) seems to be the one, only, satisfactory in general.

5. Conclusion

We have shown how simplified formula can be derived through successive approximations from the basic integral equations which implicitly give the rigorous s–S interaction energy. The stronger approximation gives the well known GB formula, the weaker one amounts to a numerical treatment the accuracy of which can be theoretically indefinitely increased. Between these extreme cases, we propose intermediate solutions the simpler of which seem particularly well suited to be adapted to the semi-empirical methods of quantum chemistry. We hope that the more elaborate formula will be of value for computations by ab-initio *methods.*

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6. Appendix. Statistical study of a system of two molecular interacting groups in thermal equilibrium

We consider a system $(s \cup S)$ containing two interacting groups, one (s) formed by solute molecules, the other (S) formed by solvent molecules. This system is maintained in thermal equilibrium at a fixed temperature T and we assume that the nuclei are classical particles governed by Boltzmann's statistic. On the other hand, the electrons are treated as quantum particles the motion of which is temperature independent: thus, the electron cloud can be described by a wave function that, in a first step, we assume to be separable $(\Psi = \varphi\Phi)$ and unpolarizable. After quantum averaging of the electronic motion in the Born-Oppenheimer approximation, the nuclear hamiltonian of $(s \cup S)$ in the phase configuration $(\boldsymbol{p}, \boldsymbol{x}; \boldsymbol{P}, \boldsymbol{X})$ can be written

$$H^{s\cup S}(\boldsymbol{p}, \boldsymbol{x}; \boldsymbol{P}, \boldsymbol{X}) = H^{s}(\boldsymbol{p}, \boldsymbol{x}) + U^{s-S}(\boldsymbol{x}; \boldsymbol{X}) + H^{S}(\boldsymbol{P}, \boldsymbol{X}). \tag{A1}$$

In this expression, $H^{s}(\boldsymbol{p}, \boldsymbol{x})$ (resp. $H^{S}(\boldsymbol{P}, \boldsymbol{X})$) is the hamiltonian of the isolated solute (resp. isolated solvent) group lying in the configuration $(\boldsymbol{p}, \boldsymbol{x})$ (resp. $(\boldsymbol{P}, \boldsymbol{X})$). Each hamiltonian H is a sum of a kinetic term T and of a potential term U depending only on the generalized space coordinates $\boldsymbol{x}$. The third term of the Eq. (A1) is the interaction potential between both groups which depends only on the space coordinates.

Although the potential functions are parametrically depending on the electronic wave function $\varphi\Phi$ of $(s \cup S)$ the simple notation U^{s}, U^{S} and U^{s-S} will be employed instead of the more explicit ones U^{s}_{φ}, U^{S}_{Φ} and $U^{s-S}_{\varphi\Phi}$ that we will use only if needed.

In what follows, it may be useful to distinguish, among the various space coordinates $\boldsymbol{x}$, the coordinates σ which define the position and the orientation of the solute molecules and the internal coordinates $\boldsymbol{r}$ which determine the relative positions of their nuclei. With these notation conventions in mind, we have

$$H^{s}(\boldsymbol{p}, x) = T(\boldsymbol{p}, x) + U^{s}(\boldsymbol{r}). \tag{A2}$$

6.1. Definition of an effective hamiltonian for the system (s)

If we consider the canonical ensemble consisting of a large number of systems like $(s \cup S)$, we know that the free energy of $(s \cup S)$ can be derived from the canonical ensemble partition function which is (we neglect an unessential constant factor)

$$Z^{s\cup S} = \int\!\!\int e^{-H^{s\cup S}(\boldsymbol{p}, \boldsymbol{x}; \boldsymbol{P}, \boldsymbol{X})/kT}\, d\boldsymbol{p}\, d\boldsymbol{x}\, d\boldsymbol{P}\, d\boldsymbol{X}, \tag{A3}$$

where the $\boldsymbol{x}$ and $\boldsymbol{X}$ integrations are taken over the volume V of a container: our aim is to define an effective hamiltonian such that

$$Z^{s\cup S} = \int\!\!\int e^{-H^{s}_{\mathrm{eff}}(\boldsymbol{p}, \boldsymbol{x})/kT}\, d\boldsymbol{p}\, d\boldsymbol{x}. \tag{A4}$$

By using the expression (A1) of the total energy, we may write

$$Z^{s\cup S} = \int e^{-H^{s}(\boldsymbol{p}, \boldsymbol{x})/kT} \int e^{-(H^{S}(\boldsymbol{P}, \boldsymbol{X}) + U^{s-S}(\boldsymbol{x}; \boldsymbol{X}))/kT}\, d\boldsymbol{P}\, d\boldsymbol{X}\, d\boldsymbol{p}\, d\boldsymbol{x}. \tag{A5}$$

We emphasize that, for sufficiently strong dilution, the sum over the solvent phase coordinates is a function of $\boldsymbol{r}$ only because it is invariant under any translation or rotation of the solute molecules.

Then, using a classical method, it is useful to introduce the auxiliary partition function $Z^{\mathrm{Ins}}(\boldsymbol{r})$ defined as [1]

$$Z^{\mathrm{Ins}}(\boldsymbol{r}) = \frac{\displaystyle\int e^{-(H^{S}(\boldsymbol{P}, \boldsymbol{X}) + U^{s-S}(\boldsymbol{x}; \boldsymbol{X}))/kT}\, d\boldsymbol{P}\, d\boldsymbol{X}}{\displaystyle\int e^{-H^{S}(\boldsymbol{P}, \boldsymbol{X})/kT}\, d\boldsymbol{P}\, d\boldsymbol{X}} \tag{A6}$$

or by [2]

$$Z^{\mathrm{Ins}}(\boldsymbol{r}) = \langle \mathrm{e}^{-U^{\mathrm{s\text{-}S}}(\boldsymbol{x};\boldsymbol{X})/kT} \rangle_0, \tag{A7}$$

where the notation $\langle\ \rangle_0$ means that the mean value has been calculated with the canonical partition function of the isolated system (S).

If we introduce the partition function of the solvent alone Z^{S}, which is no more than the denominator of the expression (A6), we have

$$Z^{\mathrm{s}\cup\mathrm{S}} = Z^{\mathrm{S}} \int \mathrm{e}^{-H^{\mathrm{s}}(\boldsymbol{p},\boldsymbol{x})/kT}\, Z^{\mathrm{Ins}}(\boldsymbol{r})\, d\boldsymbol{p}\, d\boldsymbol{x}. \tag{A8}$$

Thus, if we define by $A^{\mathrm{Ins}}(\boldsymbol{r})$ the free energy associated to $Z^{\mathrm{Ins}}(\boldsymbol{r})$ as follows

$$A^{\mathrm{Ins}}(\boldsymbol{r}) = -kT \log Z^{\mathrm{Ins}}(\boldsymbol{r}) \tag{A9}$$

we obtain for the partition function of $(\mathrm{s} \cup \mathrm{S})$

$$Z^{\mathrm{s}\cup\mathrm{S}} = \int \mathrm{e}^{-(H^{\mathrm{s}}(\boldsymbol{p},\boldsymbol{x}) + A^{\mathrm{Ins}}(\boldsymbol{r}) + A^{\mathrm{S}})/kT}\, d\boldsymbol{p}\, d\boldsymbol{x}, \tag{A10}$$

where A^{S} is the free energy of the solvent alone.

We see that this partition function can be calculated by associating to each phase configuration $(\boldsymbol{p}, \boldsymbol{x})$ of (s) a temperature dependent effective hamiltonian defined by

$$H^{\mathrm{s}}_{\mathrm{eff}}(\boldsymbol{p}, \boldsymbol{x}) = H^{\mathrm{s}}(\boldsymbol{p}, \boldsymbol{x}) + A^{\mathrm{Ins}}(\boldsymbol{r}) + A^{\mathrm{S}}, \tag{A11}$$

where the influence of (S) is introduced through the free energy term $A^{\mathrm{Ins}}(\boldsymbol{r})$ [35, 36].

6.2. Physical meaning of the free energy $A^{\mathrm{Ins}}(\boldsymbol{r})$

Let us now consider (s) in the fixed relative space configuration $(\boldsymbol{r}_0)$. In other words, we assume that the system remains in the space configuration $(\boldsymbol{r}_0)$ even when it is submitted to the field of (S). Keeping in mind that the sum over the solvent phase coordinates in the Eq. (A5) is a function of $\boldsymbol{r}_0$ only, we find that the partition function is

$$Z^{\mathrm{s}\cup\mathrm{S}}(\boldsymbol{r}_0) = \int \mathrm{e}^{-H^{\mathrm{s}}(\boldsymbol{p},\boldsymbol{x}_0)/kT}\, d\boldsymbol{p}\, d\boldsymbol{o} \int \mathrm{e}^{-(H^{\mathrm{S}}(\boldsymbol{P},\boldsymbol{X}) + U^{\mathrm{s\text{-}S}}(\boldsymbol{x}_0;\boldsymbol{X}))/kT}\, d\boldsymbol{P}\, d\boldsymbol{X}, \tag{A12}$$

where the sum over the solute coordinates includes only the values $\boldsymbol{p}$ of the conjugate momenta compatible with the invariance of the configuration $(\boldsymbol{r}_0)$ (i.e. translation or rotation of the solute system).

We deduce that the free energy of $(\mathrm{s} \cup \mathrm{S})$, with (s) fixed in the relative space configuration $(\boldsymbol{r}_0)$, is

$$A^{\mathrm{s\text{-}S}}(\boldsymbol{r}_0) = -kT \log \int \mathrm{e}^{-H^{\mathrm{s}}(\boldsymbol{p},\boldsymbol{x}_0)/kT}\, d\boldsymbol{p}\, d\boldsymbol{o} - kT \log \int \mathrm{e}^{-(H^{\mathrm{S}}(\boldsymbol{P},\boldsymbol{X}) + U^{\mathrm{s\text{-}S}}(\boldsymbol{x}_0,\boldsymbol{X}))/kT}\, d\boldsymbol{P}\, d\boldsymbol{X}. \tag{A13}$$

If, in the preceding expression, we neglect the s–S interaction term, we obtain the free energy $A_0^{\mathrm{s}\cup\mathrm{S}}(\boldsymbol{r}_0)$ of the isolated systems (s) and (S). Thus, the variation of the free energy which is due to the interaction between (s) in the relative space configuration $(\boldsymbol{r}_0)$ and (S) is

$$A^{\mathrm{s}\cup\mathrm{S}}(\boldsymbol{r}_0) - A_0^{\mathrm{s}\cup\mathrm{S}}(\boldsymbol{r}_0) = -kT \log \int \mathrm{e}^{-(H^{\mathrm{S}}(\boldsymbol{P},\boldsymbol{X}) + U^{\mathrm{s\text{-}S}}(\boldsymbol{x}_0;\boldsymbol{X}))/kT}\, d\boldsymbol{P}\, d\boldsymbol{X} + kT \log \int \mathrm{e}^{-H^{\mathrm{S}}(\boldsymbol{P},\boldsymbol{X})/kT}\, d\boldsymbol{P}\, d\boldsymbol{X}. \tag{A14}$$

By using the Eqs. (A6) and (A9), we verify easily that this free energy variation is identical to $A^{\mathrm{Ins}}(\boldsymbol{r}_0)$. The quantity $A^{\mathrm{Ins}}(\boldsymbol{r}_0)$ has been called "insertion free energy" [1, 2]: it is the variation of the total free energy which results from the insertion in (S) of the system (s), fixed in the relative space configuration $(\boldsymbol{r}_0)$.

6.3. The weak interaction approximation

We obtain directly from the Eqs. (A7) and (A9)

$$A^{\mathrm{Ins}}(\boldsymbol{r}) = -kT \log \langle \mathrm{e}^{-U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X})/kT} \rangle_0 . \tag{A15}$$

As the mean value is calculated with the partition function of the isolated system (S), there is strong contribution due to the (s–S) repulsion forces at short distance. This gives rise to the formation of a cavity inside the solvent: the part of A^{Ins} which is associated to this step is the cavitation energy [5]. Once the cavity is formed, the remaining (s–S) interaction (mainly the electrostatic one) is weak and we may calculate the corresponding part of A^{Ins} in an approximate way. Thus, expanding the expression (A15), we obtain

$$A^{\mathrm{Ins}}(\boldsymbol{r}) = -kT \log \left(1 - \frac{\langle U^{\mathrm{s-S}}(\boldsymbol{X};\,\boldsymbol{X}) \rangle_0}{kT} + \frac{\langle (U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X}))^2 \rangle_0}{2k^2T^2} \right) \tag{A16}$$

by neglecting the terms of higher order.

The second term of the development vanishes because it represents the averaged value of the electrostatic interaction energy between (s), fixed in the configuration ($\boldsymbol{r}$), and the isolated system (S), which is supposed to remain homogeneous and isotropic although a cavity has been formed in it. Thus we can wwrite

$$A^{\mathrm{Ins}}(\boldsymbol{r}) = -\frac{\langle (U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X}))^2 \rangle_0}{2kT} . \tag{A17}$$

If we consider now the mean value

$$\langle U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X}) \rangle = \frac{\displaystyle\int \mathrm{e}^{-H^{\mathrm{s}}(\boldsymbol{p},\boldsymbol{x})}\, d\boldsymbol{p}\, d\boldsymbol{o} \int \mathrm{e}^{-(H^{\mathrm{S}}(\boldsymbol{P},\boldsymbol{X}) + U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X}))/kT}\, U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X})\, d\boldsymbol{P}\, d\boldsymbol{X}}{\displaystyle\int \mathrm{e}^{-H^{\mathrm{s}}(\boldsymbol{p},\boldsymbol{x})}\, d\boldsymbol{p}\, d\boldsymbol{o} \int \mathrm{e}^{-(H^{\mathrm{S}}(\boldsymbol{P},\boldsymbol{X}) + U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X}))/kT}\, d\boldsymbol{P}\, d\boldsymbol{X}} \tag{A18}$$

calculated by averaging over all the phase configurations of (S) in interaction with (s), we find, after expansion of $\exp(-U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X})/kT)$

$$\langle U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X}) \rangle = -\frac{\langle (U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X}))^2 \rangle_0}{kT} . \tag{A19}$$

Comparing the expressions (A17) and (A19), we can derive an approximate relation between $A^{\mathrm{Ins}}(\boldsymbol{r})$ and the mean s–S interaction energy [5]

$$A^{\mathrm{Ins}}(\boldsymbol{r}) = \frac{\langle U^{\mathrm{s-S}}(\boldsymbol{x};\boldsymbol{X}) \rangle}{2} . \tag{A20}$$

Thus, we can write the Eq. (A11)

$$H^{\mathrm{s}}_{\mathrm{eff}}(\boldsymbol{p},\boldsymbol{x}) = H^{\mathrm{S}}(\boldsymbol{p},\boldsymbol{x}) + 1/2 \langle U^{\mathrm{s-S}}(\boldsymbol{x};\,\boldsymbol{X}) \rangle + A^{\mathrm{S}} . \tag{A21}$$

6.4. The case of electronically polarizable species

As we pointed out at the beginning of this appendix, the potentials U^{s}_{φ}, U^{S}_{Φ} and $U^{\mathrm{s-S}}_{\varphi\Phi}$ are parametrically depending on the electronic wave functions φ and Φ of (s) and (S). If these functions are different from the optimal ones, φ_0 and Φ_0, associated to the isolated systems (s) or (S), the hamiltoninan H^{s}_{φ} in the Eq. (A11) is that of the polarized solute and the free energy A^{S}_{Φ} of the solvent alone has to be interpreted as that of the polarized, but not oriented solvent.

However, the calculation of A^{Ins} has to be reexamined. In effect the term $\langle U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x};\,\boldsymbol{X}) \rangle_0$, which appears in the Eq. (A16) does not vanish any more: it represents the mean electrostatic interaction between the polarized solute and the polarized, but not oriented solvent. Thus, we find in place of the Eq. (A17)

$$A^{\mathrm{Ins}}(\boldsymbol{r}) = \langle U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X})\rangle_0 - \frac{\langle (U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X}))^2\rangle_0 - (\langle U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X})\rangle_0)^2}{2kT} \tag{A22}$$

and in place of the Eq. (A19)

$$\langle U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X})\rangle = \langle U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X})\rangle_0 - \frac{\langle (U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X}))^2\rangle_0 - (\langle U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X})\rangle_0)^2}{kT}. \tag{A23}$$

Now we obtain the relation [37]

$$A^{\mathrm{Ins}}(\boldsymbol{r}) = \langle U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X})\rangle_0 + 1/2(\langle U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X})\rangle - \langle U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X})\rangle_0) \tag{A24}$$

instead of the relation (A20).

If we remember that $\langle U^{\mathrm{s-S}}_{\varphi\Phi}(\boldsymbol{x}; \boldsymbol{X})\rangle$ is the mean electrostatic interaction of the polarized solute with the polarized and oriented solvent, we see that the expression (A24) is a sum of two contributions: the first one, due to the polarized, but not oriented solvent, the second due to the oriented, but not polarized solvent.

It must be emphasized that the polarization part, which does not depend on the temperature, is not affected by an one-half factor as it is the case for the temperature dependent part corresponding to the solvent orientation. However, if we use the results of the reaction field theory [26], (i.e. if we assume that Φ is depending on φ), the work of polarization of the solvent is

$$A^{\mathrm{s}}_{\Phi} - A^{\mathrm{S}}_{\Phi_0} = \Delta A^{\mathrm{S}}_{\varphi} = -1/2\langle U^{\mathrm{s-S}}_{\varphi}(\boldsymbol{x}; \boldsymbol{X})\rangle_0 \tag{A25}$$

so that we get

$$A^{\mathrm{Ins}} + \Delta A^{\mathrm{S}}_{\varphi} = 1/2\langle U^{\mathrm{s-S}}_{\varphi}(\boldsymbol{x}; \boldsymbol{X})\rangle. \tag{A26}$$

As a consequence, the Eq. (A21) is valid in general, provided one consider H^{s}_{φ} as the hamiltonian of the polarized solute, $\langle U^{\mathrm{s-S}}_{\varphi}(\boldsymbol{x}; \boldsymbol{X})\rangle$ as the mean electrostatic interaction between the polarized systems (s) and (S) and A^{S} as a constant quantity characteristic of the isolated solvent.

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