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*Original investigations*

# Self consistent field theory of solvent effects representation by continuum models: Introduction of desolvation contribution*

**Raymond Constanciel and Renato Contreras****

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

We examine the representation of solvent effects by continuum models in the frame of the Reaction Field Theory. Particular attention is devoted to the problem raised by the adaptation of the current methods of Quantum Chemistry in the Self Consistent Field approximation especially at a semi-empirical level.

A critical examination of the literature in the field shows that, for the main part, the proposed methods suffer from theoretical internal incoherence.

As an illustration of this study, we propose an extension of the generalized Born formula which is able to account for the desolvation effects produced by the specific neighborhood of each center of the solvated species.

**Key words:** SCF reaction field theory—generalized born formula—solvation and desolvation effects

## 1. Introduction

For a long time, the influence of a polarizable medium on the properties of a molecular system occupied the attention of the chemists. In the field of Quantum Chemistry, this problem has been encountered rather recently; however, considerable effort has already been exerted on taking into account the solvent effects by modifying existing methods of calculation for isolated molecules [1, 2].

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** *Present address*: Department of Chemistry, Faculty of Basic and Pharmaceutical Sciences, University of Chile, Casilla 653, Santiago, Chile

In order to simplify the theoretical approach, the solvent is often replaced by an homogeneous continuous medium characterized by its macroscopic dielectric constant $\varepsilon$: the electrostatic interactions between the solute species and the solvent are accounted for by means of the Reaction Field (RF) theory [3]. In this respect, several techniques have been developed within the SCF method of calculation [4–15]. A common difficulty of such approaches comes from the fact that there are two different ways of defining the effective Fock operator of the solute which takes into account the solvent influence. The first way consists in adding to the isolated solute Fock operator a term representing the potential produced by the polarized solvent. The second one leads directly to the effective Fock operator by applying the variation method.

A survey of the recent literature in the field shows that, unless one proceeds rigorously, the operators obtained by these methods are different [16]. Most of the published work suffers from this internal incoherence and, to our knowledge, this problem has not yet been raised.

The main points discussed in this paper are the following: a) We stress the very fact that a correct use of the variation method in the self-consistent field approximation requires a careful definition of the quantity that must be minimized. Moreover, a rigorous analysis of the interactions between the various parts of the physical system of interest will be of value for interpreting each term of the Fock operator. It is naturally expected that the answers given to these questions will be in mutual close agreement in such a way that the theory displays a full internal coherence. b) We examine critically the current continuum solvation models based on the RF Theory within the SCF method of calculation and more particularly that using the Generalized Born (GB) formula. c) We discuss the theoretical problems related to an extension of the GB formula which is able to account for the desolvation effects due to the specific neighborhood of the atomic centers of a solvated species and we propose a solution that maintains the internal coherence of the theory.

## 2. Energetic aspects of the problem

Let us start by defining the solvation energy [17]. We consider a system formed by an isolated solute molecule and by an assembly of interacting solvent molecules. In the initial state, the solvent molecules are in thermal equilibrium at a given temperature $T$. Then, through an isothermal process, we introduce the solute into the solvent: a new equilibrium is attained corresponding to the final state. The energy variation of the whole solute–solvent ($s$–$S$) system between the initial and the final state, which is generally revealed by heat liberation, is called solvation energy.

Since the process considered is an isothermal one, we can immediately conclude [18] that the solvation energy is the difference of the free energy of the $s$–$S$ system between both equilibrium states. In the final state, the free energy can be partitioned according to

$$A = E^s + \Delta E^s + A^S + \Delta A^S + E^{s-S} \tag{1}$$

where $E^s$ is the energy of the isolated solute molecule, $A^S$ is the free energy of the pure solvent at the temperature $T$, $E^{s-S}$ is the $s$–$S$ interaction energy and $\Delta E^s$ and $\Delta A^S$ are respectively the solute and the solvent polarization energies. Thus, we find for the solvation energy

$$E^{\mathrm{Solv}} = \Delta E^s + \Delta A^S + E^{s-S} \tag{2}$$

When the solute is unpolarizable, the energy variation is reducible to the last two terms of Eq. (2) and it has been called "insertion energy" [17, 19]. In this particular case, and only if the electrostatic $s$–$S$ interactions are taken into account, it can be shown that the following relation holds

$$\Delta A^S = -E^{s-S}/2. \tag{3}$$

This can be done by statistical calculations [17, 18] when the solvent polarization is temperature dependent (for instance, when the solvent is formed by unpolarizable molecules with permanent dipole moments so that $\Delta A^S$ is entirely determined by the variation of the solvent orientation). However, relation (3) is also valid when the coupling with the thermostat can be completely neglected [20] (that is, when the polarization results from the displacement of the solvent charges so that $\Delta A^S$ is the variation of the potential energy related to an internal force constant). Accordingly, the insertion energy can be written in both cases [2, 21–23]

$$E^{\mathrm{Ins}} = E^{s-S}/2. \tag{4}$$

In the case of a polarisable solute, the solvation energy is obtained by adding the solute polarization term to the insertion energy according to Eq. (2) [9].

In order to illustrate these preliminary theoretical considerations, we will verify the main results in the particularly simple case of a single uniformly charged sphere immersed in an homogeneous dielectric medium with a dielectric constant $\varepsilon$.

The work necessary for charging a sphere $S(0, a)$ of center 0 and radius $a$, with a charge $Q$ can be calculated quite easily by simple electrostatics. The difference of the work respectively calculated with and without solvent gives the well-known Born formula for the solvation energy [24] which is, in fact, the insertion energy since the sphere is unpolarizable

$$E^{\mathrm{Ins}}_{\varepsilon} = -(1-1/\varepsilon)\cdot Q^2/2a. \tag{5}$$

On the other hand, it is well established that the solvent polarization may be reduced to the creation of a polarization charge $Q^{\mathrm{pol}}_{\varepsilon}$ uniformly distributed at the surface of $S(0, a)$. The determination of such a polarization charge can be achieved by a classical procedure from which [3]

$$Q^{\mathrm{pol}}_{\varepsilon} = -(1-1/\varepsilon)\cdot Q. \tag{6}$$

Thus, the electrostatic interaction energy between the charge $Q$ (which may be associated to the solute) and the polarized medium (assimilable to the solvent) is given by

$$E^{s-S}_{\varepsilon} = Q\cdot V^R_{\varepsilon}(Q) = -(1-1/\varepsilon)\cdot Q^2/a \tag{7}$$

where

$$V_\varepsilon^R(Q) = Q_\varepsilon^{\text{pol}}/a = -(1-1/\varepsilon)\cdot Q/a \tag{8}$$

is the so called *RF* potential due to the solvent polarization.

By comparing Eqs. (5) and (7), we verify the relation (4) between the insertion energy and the *s–S* electrostatic interaction energy.

## 3. Self-consistent field theory of solvent effects

In the frame of the *RF* theory, the electrostatic interaction energy between a solute molecule and the solvent is a function of the one particle density matrix *P* of the solute. Thus, we can write

$$E_\varepsilon^{s-S}(P) = \sum_I Z_I(V_\varepsilon^R(P))_I - \operatorname{Tr} P\cdot V_\varepsilon^R(P) \tag{9}$$

where $Z_I$ is the nuclear charge on the center $I$ of the solute molecule, $V_\varepsilon^R(P)$ is the RF potential operator and $\varepsilon$ is the solvent dielectric constant.

If we denote by $F_1(P)$ the Fock operator of the isolated solute molecule, it seems natural to define the effective Fock operator as

$$F_\varepsilon(P) = F_1(P) - V_\varepsilon^R(P). \tag{10}$$

In this way, we simply express that each electron of the solute molecule which is already submitted to the action of the nuclei and of the other electrons, lies in the potential field created by the polarized solvent.

Another means for deriving the expression of the effective Fock operator is to seek the minimum of the *s–S* free energy defined by the Eq. (1) through the variation method. Considered as a function of *P*, this energy can be written

$$A_\varepsilon(P) = E^s(P) + E_\varepsilon^{s-S}(P)/2 + A^S \tag{11}$$

where $A^S$ is independant of *P*.

In the frame of the self-consistent field approximation, the minimization of $A_\varepsilon(P)$ is achieved by varying *P* under the constraint

$$P^2 = 2P \tag{12}$$

which insures that we restrict the search to a subspace of one particle density operators that can be represented by a single closed-shell Slater determinant. This condition may be taken into account by using the Lagrange multiplier technique, setting that the first variation of the functional

$$J_\varepsilon(P) = A_\varepsilon(P) + \operatorname{Tr} \Lambda(P^2 - 2P) \tag{13}$$

must vanish. One gets [25]

$$\delta J_\varepsilon(P) = \operatorname{Tr}\,(\partial A_\varepsilon/\partial P + \Lambda P + P\Lambda - 2\Lambda)\cdot\delta P = 0 \tag{14}$$

and taking into account that the variation $\delta P$ is arbitrary, we obtain after elimination of the Lagrange multiplier matrix $\Lambda$

$$[\partial A_\varepsilon/\partial P, P] = 0. \tag{15}$$

This last relation, together with the condition (12) forms the well-known system of Hartree–Fock equations: the solution of these equations is usually obtained by solving the pseudo-eigenvalue problem for the effective Fock operator

$$F_\varepsilon(P) = \partial A_\varepsilon/\partial P \tag{16}$$

relative to the solute molecule in the field of the polarized solvent. It can be verified that in vacuum (i.e. when $A_1(P) = E^s(P)$) the formula (16) leads to the usual expression of the Fock operator for the isolated solute molecule.

By using the expressions (11) and (16) we obtain

$$F_\varepsilon(P) = F_1(P) + \tfrac{1}{2}(\partial E_\varepsilon^{s-S}/\partial P). \tag{17}$$

We see that this last expression of the effective Fock operator, derived by application of the variational method, is identical with that of Eq. (10), obtained by physical arguments, if and only if

$$V_\varepsilon^R(P) = -\tfrac{1}{2}(\partial E_\varepsilon^{s-S}/\partial P). \tag{18}$$

Taking account of the Eq. (9), this condition can be written as

$$V_\varepsilon^R(P) = -\left(\sum_I Z_I \cdot \partial(V_\varepsilon^R(P))_I/\partial P - \mathrm{Tr}\, P \cdot \partial V_\varepsilon^R(P)/\partial P\right). \tag{19}$$

## 4. Applications

A usual simplification in the treatment of the $s$–$S$ interaction is to consider that the solute molecule can be represented by a set of so-called net charges $Q_I$ which are the sum of the nuclear and electronic charges of each atomic center $I$. In this case, the $s$–$S$ electrostatic interaction energy is given by an expression like

$$E_\varepsilon^{s-S}(P) = \sum_I Q_I(P) \cdot (V_\varepsilon^R(P))_I \tag{20}$$

where the $RF$ potential can be linearly expanded in terms of the net charges

$$(V_\varepsilon^R(P))_I = \sum_J Q_J(P) \cdot (c_\varepsilon^R)_{IJ}. \tag{21}$$

Having in mind that $\partial/\partial P = -\partial/\partial Q$, we may replace the condition (19) by

$$(V_\varepsilon^R(P))_I = \sum_J Q_J(P) \cdot \partial(V_\varepsilon^R(P))_J/\partial Q_I. \tag{22}$$

For instance, in the Kirkwood's cavity model [26], one considers net point charges localized inside a sphere $S(0, a)$ within an homogeneous dielectric medium simulating the solvent: the theory leads to the following expression for the coefficients

$$(c_\varepsilon^R)_{IJ} = \frac{1}{a} \sum_l \frac{(l+1)(1-\varepsilon)}{\varepsilon(l+1)+l} \left(\frac{r_I r_J}{a^2}\right)^l P_l(\cos\theta_{IJ}) \tag{23}$$

and it is easy to make sure that the condition (21) is satisfied.

Let us also mention that in calculations by semi-empirical methods of Quantum Chemistry a useful approximation is to consider the coefficients as adjustable parametric functions. Thus, in the frame of the CNDO/2 parametrization, one defines

$$(c_\varepsilon^R)_{IJ} = -(1-1/\varepsilon) \cdot \gamma_{IJ} \tag{24}$$

where the $\gamma_{IJ}$ are the electronic repulsion integrals and, taking account of Eqs. (6) and (21) we obtain

$$(V_\varepsilon^R(P))_I = \sum_J (Q_\varepsilon^{\text{pol}}(P))_J \cdot \gamma_{IJ}. \tag{25}$$

Through the use of Eq. (20) we get

$$E_\varepsilon^{s\text{-}S}(P) = -(1-1/\varepsilon) \cdot \left( \sum_I \sum_J Q_I(P) \cdot Q_J(P) \cdot \gamma_{IJ} \right) \tag{26}$$

and Eq. (26) leads to the GB formula [27–30] previously used by many authors. Here again, the condition (22) is satisfied. However, one may wonder that such a result can be derived for an expression of the interaction energy which has been empirically established, in contrast with the Kirkwood's model where this energy was rigorously derived by electrostatic laws. In fact, the symmetry property of the coefficients $(c_\varepsilon^R)_{IJ}$, as defined, for instance, in Eq. (23), suffices to entail the internal coherence condition (19). This is also the case for the coefficients of Eq. (24) if we suppose that the repulsion integrals are also symmetric. If the $\gamma_{IJ}$ were dissymmetric, a physically senseless additional term would appear in the effective Fock operator expression derived by means of the formula (17). This difficulty will generally arise for an arbitrary empirical choice of the $s$–$S$ interactions as we shall see below.

## 5. Extension of the generalized Born formula

In order to take into account the steric inhibition to solvation due to the specific neighborhood of each atomic center of the solvated molecule, it has been recently proposed to replace the definition of the polarization charges, given by Eq. (6), by the following one [15]

$$(Q_\varepsilon^{\text{pol}}(P))_J = \alpha_J(\varepsilon) \cdot Q_J(P) \tag{27}$$

where $\alpha_J(\varepsilon)$ is a function of the dielectric constant characteristic of the atomic center $J$. However, if one adopts such an expression for the polarization charges the condition (22) is no longer verified because in general

$$\alpha_I(\varepsilon)\gamma_{IJ} \neq \alpha_J(\varepsilon)\gamma_{JI} \tag{28}$$

and then the coefficients $(c_\varepsilon^R)_{IJ}$ are not symmetric.

A consequence of this inegality is that the effective Fock operator, calculated by the variation method, differs from the physically deduced one by a corrective term which is meaningless from a physical viewpoint.

To remove this difficulty, we propose to retain the "ansatz" (27) and to define [31]

$$\alpha_J(\varepsilon) = -(1-1/\varepsilon)\cdot(1-f_J) \tag{29}$$

where $f_J$ is a parameter characterizing the neighborhood of the center $J$; but, in order to maintain the internal coherence, we write the RF potential as

$$(V_\varepsilon^R(P))_I = \sum_J (Q_\varepsilon^{\text{pol}}(P))_J \cdot \tilde{\gamma}_{IJ} \tag{30}$$

where the dissymmetric $s$–$S$ interaction matrix $\tilde{\gamma}$ is related to a symmetrical one $\gamma$ by

$$\tilde{\gamma}_{IJ} = (1-f_I)\cdot\gamma_{IJ}. \tag{31}$$

With these assumptions, it can be easily verified that the coefficients $(c_\varepsilon^R)_{IJ}$ are symmetric so that the condition (22) is necessarily satisfied.

Unfortunately, the introduction of the neighborhood factors $f_J$ raises a new kind of problem. In effect, it is generally accepted that charged particles do not interact between themselves when they are immersed in a highly polarizable solvent [32]. This suggests that the polarization charge induced in the solvent around each ionic particle is exactly the opposite of the ionic charge so that the ion screened by its polarization charge behaves like a neutral particle. As expected, Eqs. (27) and (29) show that this is exactly the case of a one center ion (for which the factor $f$ vanishes). For many center ions however the factors $f$ have nonvanishing values and it is necessary to modify our scheme in order to preserve the electroneutrality in highly polarizable solvent.

To do that it is convenient to consider that each polarization charge is a sum of two terms [31]

$$(Q_\varepsilon^{\text{pol}}(P))_I = ({}^iQ_\varepsilon^{\text{pol}}(P))_I + ({}^eQ_\varepsilon^{\text{pol}}(P))_I \tag{32}$$

where

$$({}^iQ_\varepsilon^{\text{pol}}(P))_I = -(1-1/\varepsilon)\cdot(1-f_I)\cdot Q_I(P) \tag{33}$$

and

$$({}^eQ_\varepsilon^{\text{pol}}(P))_I = -(1-1/\varepsilon)\cdot f_I\cdot Q_I(P). \tag{34}$$

This entails

$$\lim_{\varepsilon\to\infty} ((Q_\varepsilon^{\mathrm{pol}}(P))_I + Q_I(P)) = 0 \tag{35}$$

so that the electroneutrality condition is satisfied for the whole solute.

The reaction field potential at the center $I$ is now a sum of two terms

$$\begin{aligned}(V_\varepsilon^R(P))_I &= ({}^iV_\varepsilon^R(P))_I + ({}^eV_\varepsilon^R(P))_I \\ &= \sum_J ({}^iQ_\varepsilon^{\mathrm{pol}}(P))_J\, {}^i\gamma_{IJ} + \sum_J ({}^eQ_\varepsilon^{\mathrm{pol}}(P))_J\, {}^e\gamma_{IJ}\end{aligned} \tag{36}$$

where we have introduced the interaction integrals defined by

$${}^i\gamma_{IJ} = (1 - f_I) \cdot \gamma_{IJ} \tag{37}$$

and

$${}^e\gamma_{IJ} = f_I \cdot \gamma_{IJ}. \tag{38}$$

The $s$–$S$ interaction energy can be written

$$E_\varepsilon^{s-S}(P) = \sum_I Q_I(P) \cdot ({}^iV_\varepsilon^R(P) + {}^eV_\varepsilon^R(P))_I \tag{39}$$

and consequently, according to Eq. (4), the insertion energy is given by

$$E_\varepsilon^{\mathrm{Ins}}(P) = -\tfrac{1}{2}(1 - 1/\varepsilon) \sum_I \sum_J Q_I(P) \cdot Q_J(P) \cdot \gamma_{IJ} \cdot (1 - (f_I + f_J - 2f_If_J)) \tag{40}$$

We remark that this expression contains a first term which is the GB formula and a corrective term depending on the neighborhood factors. If we suppose that

$$f_J \leq 1; \quad \forall J \tag{41}$$

the corrective term has a sign opposite to that of the GB-like term so that it can be assimilated to a desolvation contribution. As expected, this desolvation term disappears when the distances between the atomic centers are larger than overlapping ones (i.e. when $f_J = 0, \forall J$).

Finally, if we restrict the variation of the factor $f$ to the interval $(0, 1/2)$ Eqs. (37) and (38) give

$${}^i\gamma_{IJ} \geq {}^e\gamma_{IJ} \tag{42}$$

which implies that $({}^iQ_\varepsilon^{\mathrm{pol}}(P))_J$ is closer to the $J$-center than $({}^eQ_\varepsilon^{\mathrm{pol}}(P))_J$. Thus, $({}^iQ_\varepsilon^{\mathrm{pol}}(P))$ can be considered as an internal polarization charge whereas $({}^eQ_\varepsilon^{\mathrm{pol}}(P))$ is an external one. We deduce that, from a physical point of view, the desolvation appears to be the consequence of a polarization charge transfer from an internal to an external solvation shell, in agreement with the desolvation mechanism proposed by Grunwald [32].

## 6. Discussion

Let us first emphasize the necessity of having a precise definition of the solvation energy. As shown in Eq. (2), this quantity is obtained by adding the solute polarization contributions, due to the nuclear or electronic rearrangement of the solute in the presence of the solvent, to the insertion energy. The physical sense of the insertion energy is clearly displayed by statistical thermodynamics: it is the free energy variation of the $s$–$S$ system, maintained at a given temperature, when the polarized solute is transferred into the solvent with fixed nuclear configuration and electron cloud. It can simply be calculated through the Eq. (3) from the $s$–$S$ electrostatic interaction energy.

Although this result is not original it is worth emphasizing because of the frequency in which incorrect formulations occur in recent papers, especially when the solvent effects are incorporated in quantum mechanical calculations within the SCF approximation. Errors arise mainly from a misinterpretation of the insertion energy which is often taken as an electrostatic $s$–$S$ interaction energy whereas it also contains the solvent polarization energy, as shown in Eq. (2).

This is the case, for instance, of the Klopman's solvation model [30], later incorporated into the SCF MO formalism by Germer [6, 7] and used by many authors [12, 33–37]. In these works it is assumed that the $s$–$S$ interaction energy is approximated by the GB formula: this error causes the introduction of a spurious $\frac{1}{2}$ factor in the expression of the RF potential and leads to the incorrect effective Fock operator

$$(F_\varepsilon(P))_{\mu\nu} = (F_1(P))_{\mu\nu} + n(1-1/\varepsilon)\sum_J Q_J(P)\cdot\gamma_{IJ}\delta_{\mu\nu}; \qquad \mu\in I \qquad (43)$$

where $n=1/2$, while the correct formula is obtained by setting $n=1$, according to Eqs. (10), (21) and (24). The implementation of the solvaton model [13], introducing the interaction of the solvatons among themselves, is also inappropriate because the relation (3) is not satisfied. In our opinion, none of the analyses published up to now [4, 14, 37, 38] have given a satisfactory explanation of these inconsistences.

We have verified that the minimization of the free energy of the whole $s$–$S$ system in the frame of the RF theory allows obtaining an expression of the effective Fock operator of the solute which contains an additional term representing the RF potential due to the polarized solvent [39]. Although it leads to identical results, we think that this formulation of the problem is more direct and physical than that given on the basis of the formal theory of non linear Hamiltonian [9, 40, 41]. The main point, however, is that the minimization of the enthalpy [15], instead of the free energy, is a physically unsound procedure.

The derivation of the effective Fock operator by the formula (16) confirms that many works are theoretically inconsistent [6, 12, 13, 33–37] and that the variation method has not been correctly handled [7]. We also point out that Eq. (16) gives expressions of the effective Fock operator which differ from that given in some previous works: for instance, with the original notations used by the authors, we obtain [22]

$$(F_\varepsilon(P))_{\mu\nu}=(F_1(P))_{\mu\nu}-\sum_J Q_J(P)\sum_{l=0}^{\infty}\frac{(l+1)(1-\varepsilon)}{\varepsilon(l+1)+l}\left(\frac{1}{a^{2l+1}}\right)\gamma_{IJ}^{(l)}\delta_{\mu\nu} \tag{44}$$

instead of Eqs. (26, 27) of Ref. [11], and

$$(F_\varepsilon(P))_{\mu\nu}=(F_1(P))_{\mu\nu}+\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\langle R_l^m\rangle\langle\mu|S_l^m|\nu\rangle \tag{45}$$

which is at variance with Eq. (15) of Ref. [10]. It must be noted, however, that this last result has been modified in further publications [42].

Above all, we stress the fact that both methods we have described above for obtaining the effective Fock operator (see Eqs. (10) and (16)) can give different results when arbitrary approximate formulations of the RF theory are used, as it is often the case in semi-empirical calculations. We have given the conditions under which the internal coherence of the theory can be restored. This problem seems to have been ignored in some previous work using the Friedman approximate RF potential [14] or an extension of the GB formula [15].

At last, we have discussed the difficulties which arise when we try to extend the GB formula to account for the effects of neighborhood upon the solvation of each atomic centers of the solute, while preserving the internal coherence of the theory. We have shown that the introduction of a specific neighborhood factor in the definition of the polarization charges must be necessarily followed by a dissymmetrization of the $s$–$S$ interaction integrals. Moreover, our solution naturally leads to the appearence of a corrective desolvation term in the total $s$–$S$ free energy, which is connected with the diminution of the solvation phenomena when charged centers approach within overlapping distances.

This model seems very promising in studying several problems related to Chemical Reactivity where desolvation effects may be important. Preliminary results concerning the solvent effects upon the formation of ionic pairs in the dissociation reaction of some simple systems are encouraging and illustrative of the relevance of the model: complete calculations will soon be submitted for publication.

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