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On the Theory of Solvent Effects

The Virtual Charge Model to Represent the Solvent Polarization

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A simple electrostatic analysis is given of the virtual charge (solvaton) model to represent the environment effect on the electronic wave function of a solute immersed in a polarizable surrounding. New features of this model are found. The classical aspects are discussed and secondly the quantal implications are considered. A correct Hartree–Fock-like operator is derived which represents an electron in a molecular orbital subjected to the average effect of the other electrons and to the reaction field produced by the virtual charges on the atomic centers.

A general formalism based on the preceding model is presented in appendix. The final equations have a form similar to Newton's equation to represent a solvated electron. Unlike some other theories in this field, there is no cut-off involved in the evaluation of the molecular integrals.

Key words: Solvent effects – Solvation theory.

1. Introduction

The theoretical representation of environmental effects on the electronic structure of solute molecules is receiving an increasing attention [1, 20]. However, this representation involves a number of problems to which different answers have been given by various authors. Firstly, the correct choice of the functional to be minimized in order to introduce self-consistently the solute–solvent interaction has raised some confusion. Secondly, and in relation to the previous one, one has to decide how to account for the solvent reorganization or polarization effects. While both aspects have been discussed within the basic principles of quantum mechanics and statistics by one of us [16], the use of the method based on net charges on the atomic centers of a given molecular system and Born's formula for

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the solvation energy has led to apparently incorrect treatments. It therefore seems worthwhile to further discuss these points.

A simple classical electrostatic analysis, based on the virtual (polarization) charge approximation to represent the solvent polarization leads to the unnoticed result that one cannot reproduce simultaneously the solvent potential field acting over the solute, which is produced by the virtual charges, and the total electrostatic energy of the solute–solvent charge system. The latter is the total sum of 1) the self-energy of the net charge system in vacuum, 2) the interaction potential energy between the net charges and the virtual charges, and 3) the self-energy of the virtual charge system, which would represent the work necessary to create and to assemble the virtual charges.

At the level of an optimization procedure one can take either the energy of the solute in the field of the polarized solvent or the total electrostatic energy of the solute–solvent charge system. A decision has to be made between them. These points are discussed in what follows.

Thereafter we examine the transposition of these results in the framework of the SCF theory and an expression of the effective Hartree–Fock (HF) operator, which takes into account the solvation effects, is derived.

As the detailed nature of the microscopic model is not relevant to our discussion, we restrict ourselves to the one introduced by Klopman [5] and later on implemented by Germer [12, 13] within the framework of a semi-empirical SCF scheme. This model is promising due to the simplicity of the formulas and to the fact that ions as well as neutral molecules can be treated on the same basis.

2. The Virtual Charge Model (Classical Aspects)

We restrict ourselves to describe those solute-solvent interactions whose effects are of electrostatic nature and, therefore, are accounted for by the formula of Born [21, 22]. Thus, consider first a singly uniformly charged sphere $(0, a)$ with net charge Q_0, of center 0 and radius a, immersed in a dielectric continuum of relative permitivity ε. The solvation energy is simply the difference of the electrostatic self-energy of that sphere considered respectively in the vacuum $(E(1))$ and in the continuous dielectric $(E(\varepsilon))$:

$$E_{\mathrm{Solv}}=E(\varepsilon)-E(1)=\frac{1}{2\varepsilon}\frac{Q_0^2}{a}-\frac{Q_0^2}{2a}=-(1-\varepsilon^{-1})\frac{Q_0^2}{2a}. \tag{1}$$

To represent the medium effect upon the sphere one seeks for the reaction field potential due to the medium polarization. For the sphere immersed in the dielectric the potential of the charge Q_0 in the medium is given by

$$V_e(\varepsilon, M)=Q_0/\varepsilon d, \quad d>a. \tag{2}$$

This potential looks like the one produced by a point charge Q_0 situated at the origin of the sphere $(0, a)$. The reaction field potential of this latter set-up is well known [23] and is given by

$$V_R = -(1-\varepsilon^{-1})Q_0/a \tag{3}$$

which is the difference between the potential inside the sphere immersed in the dielectric $V_i(\varepsilon, 0) = Q_0/\varepsilon a$ and the potential inside the isolated sphere $V_i(1, 0) = Q_0/a$.

One can now reproduce exactly these potentials by the method of virtual charges if one replaces the system already considered by an equivalent system formed by a conveniently charged sphere in vacuum. Thus, if we consider the potential (2), clearly the same potential can be reproduced at the same point in the vacuum if we introduce a virtual charge Q distributed on the surface of the sphere; we must have

$$V(\varepsilon, M) = \frac{Q_0 + Q}{d} = \frac{Q_0}{\varepsilon d} \tag{4}$$

a relation inferring that

$$Q = -(1-\varepsilon^{-1})Q_0. \tag{5}$$

The potential produced by this virtual charge Q inside the sphere is precisely the reaction field (3); and the total potential $V_i(\varepsilon, M)$ is precisely $Q_0/\varepsilon a$. In this way, the charge Q allows us to represent the environmental effect upon the charge Q_0. The interaction potential energy between the solute charge distribution ($Q_0 \equiv Q_\Sigma$) and the polarisable solvent represented by the virtual charge ($Q \equiv Q_S$) will be designated by $E_{\Sigma S}$; it is given by

$$E_{\Sigma S} = Q_0 V_R = \frac{Q_0 Q}{a} = -(1-\varepsilon^{-1})Q_0^2/a. \tag{6}$$

Thus, one can write the total energy $E(\varepsilon)$ of the system as follows:

$$E(\varepsilon) = E_\Sigma + E_{\Sigma S} + E_S \tag{7}$$

where E_Σ is the electrostatic energy of the charged sphere in vacuum, $E_{\Sigma S}$ has already been defined, and E_S is the electrostatic energy spent to polarize the solvent when there are no free charges in it. A problem arises now, since E_S is the energy produced in charging the sphere from 0 up to Q against its reaction field [24]:

$$E_S = \int_0^Q V_R(Q')\, dQ' = (1-\varepsilon^{-1})^2 Q_0^2/2a \tag{8}$$

then $E(\varepsilon) = Q_0^2/2a\varepsilon^2$, and therefore the solvation energy

$$E'_{\text{Solv}} = E(\varepsilon) - E(1) = -(1-\varepsilon^{-2})Q_0^2/2a \tag{9}$$

differs from Born's expression by a factor of $(1+\varepsilon^{-1})$. It is interesting to notice that within the image approximation to the reaction field, Friedman [25] has found that the free energy of solvation of an ion of radius a differs from the Born equation by the same factor as found by us.

One is confronted now with a dilemma. Either one reproduces the potentials according to the electrostatic of a dielectric or one reproduces the total energy of the system so as to recover Born's equation for the solvation energy. Clearly, in consideration of the medium polarizability, the determination of the equilibrium charge distribution will necessarily be achieved by the optimization of the total energy. Thus, this later quantity appears as having an essential role and, consequently, a correct expression for it has to be taken, i.e., an expression which leads to Born's formula.

Therefore, to obtain the correct formula (within this model) of the total energy $E(\varepsilon)$, it is necessary to define the virtual charge as follows

$$Q = -(1 - D^{-1})Q_0 \tag{10}$$

where D is a function of the dielectric constant, in fact is given by: $D = \sqrt{\varepsilon}$, and will be called effective dielectric constant.

Of course, with this choice of virtual charge the potentials produced by the system of charge Q_0 and Q in vacuum are no longer those produced by Q_0 in the medium of dielectric constant ε. The replacement of ε by D in the reaction field potential leads to a better distinction among the solvents of high dielectric constant. It follows now that, if this elementary approach is correct, the solvent effect upon the net charges is not directly correlated with the overall solvation effect. This is a new feature that seems not to be perceived by other workers.

An important result comes out of the preceding discussion once an assembly $\{Q_{0i}, Q_i\}$ of interacting net and virtual charges is considered. The total electrostatic energy is given by

$$E(\varepsilon) = \tfrac{1}{2}\sum_{i,j}\frac{Q_{0i}Q_{0i}}{(r_{ij}+a_i\,\delta_{ij})} + \sum_{i,j}\frac{Q_{0i}Q_j}{(r_{ij}+a_i\,\delta_{ij})} + \tfrac{1}{2}\sum_{i,j}\frac{Q_iQ_j}{(r_{ij}+a_i\,\delta_{ij})} = E_\Sigma + E_{\Sigma S} + E_S \tag{11}$$

with obvious notations. For the case of $i=2$, and only when the virtual charge Q given by (10) is taken, one recovers from (11) the correct energy formula

$$E_{12}(\varepsilon) = \frac{Q_{01}^2}{2a_1\varepsilon} + \frac{Q_{02}^2}{2a_2\varepsilon} + \frac{Q_{01}Q_{02}}{\varepsilon r_{12}} \tag{12}$$

of two ions of radii a_1 and a_2 immersed in a continuum of dielectric constant ε separated by a distance r_{12}.

Henceforth, if the virtual charge approach to simulate the polarizable medium effect upon a given charge system is going to be consistently used, the potential produced by the polarization charge must be given by

$$V_R = -(1 - 1/\sqrt{\varepsilon})Q_0/a \tag{13}$$

and the total electrostatic energy will acquire the form (11) which is consistent with Born's formulation.

3. The Effective Hamiltonian (Quantum Aspects)

Since the self-consistent field (SCF) calculations involve the optimization of total energy functionals [26], the dilemma raised in the preceding section must be solved in favor of a correct representation of this energy functional.

To derive an effective Hamiltonian we have to consider the system formed by two interacting subsystems Σ and S as a charge subsystem Σ (e.g. S) in the field of the other S (e.g. Σ). Thus, provided the intersystem correlation effects may be neglected, the search for the equilibrium charge distribution through the solution of the Schrödinger equation of the whole system, may be replaced [27] by the search for the optimal charge distribution of each subsystem through the solution of the coupled Schrödinger equations involving the effective Hamiltonians

$$H_\Sigma^{\text{eff}}(S) = H_\Sigma + V_\Sigma(S) \tag{14}$$

and

$$H_S^{\text{eff}}(\Sigma) = H_S + V_S(\Sigma) \tag{15}$$

describing each subsystem in the average Coulomb field of the other. The total energy can be expressed in either of two manners

$$E = E_\Sigma + E_S(\Sigma) \quad \text{or} \quad E = E_S + E_\Sigma(S) \tag{16}$$

where

$$E_S(\Sigma) = E_S + E_{S\Sigma} \quad \text{and} \quad E_\Sigma(S) = E_\Sigma + E_{S\Sigma} \tag{17}$$

with obvious meaning.

In the particular case where a given subsystem is fixed all the considerations on E can be deduced from the knowledge of the effective energy of the variable subsystem only. Clearly, this is not the case as far as selfconsistent treatment of the solvation effect is concerned, since we have assumed that the virtual charge distribution simulating the solvent reorganization was defined explicitly in terms of the real charges and consequently varies with them. In fact, the contribution $E_{\Sigma S}$ to the effective energy $E_\Sigma(S)$ of the solute subsystem is negative; it characterizes the stabilization coming from the appearance of opposite charges in the solvent around the solute. But appearance of these charges is energy consuming; this destabilization contribution is just given by E_S which is a positive term. Neglecting this term without further ado may lead to physically senseless results.

Although these considerations are rather general, and are valid irrespective of the actual computational technique that may be employed, they can be used to get an effective operator within the framework provided by the preceding virtual charge model. In what follows, the CNDO semiempirical scheme [26] is used to get a form of the effective Fock-operator associated to a solute molecule Σ in the solvent S. The real charge distribution Q^Σ is that of the calculated net charges Q of the molecule, i.e., the difference between the nuclear (core) charges Z_A and the electronic ones P^A:

$$Q_\text{A}^\Sigma = Z_\text{A} - P^\text{A} = Q_\text{A} \quad \text{for all atoms A,} \tag{18}$$

the virtual charges simulating the solvent S are according to (10):

$$Q_A^S = -(1-D^{-1})Q_A \quad \text{for all atoms.} \tag{19}$$

Let us stress the fact that retaining the relation (19) gives us directly the virtual charge distribution without performing the optimization of $E_S(\Sigma)$ (that is, without handling the effective operator $H_S^{\mathrm{eff}}(\Sigma)$). In this way, we do not achieve the optimization of the total energy in the more general manner, but we only determine its optimal value with a constraint (as we have shown in the first chapter, this constraint on the virtual charges assures that they simulate the influence of the medium so that the total energy obtained leads us to recover the Born expression).

Following Jano one may define a virtual charge distribution operator and build up the potential that acts over the Σ-molecule. An explicit form of the interaction operator can be obtained which displays explicitly the dependence on the Σ-wave function. This is done in the appendix. Here instead the interaction energy $E_{\Sigma S}$ is immediately written down within the CNDO-approximation (see appendix)

$$E_\Sigma{}^S = \sum_A \sum_B Q_A^S Q_B^\Sigma \gamma_{AB} \tag{20}$$

where γ_{AB} is a two-electron integral which depends only on the nature of the atoms A and B [26]. As is well known from Pople's theory [26] γ_{AB} is an average electrostatic repulsion between any electron on A and any electron on B. For large interatomic distances r_{AB}, γ_{AB} will be approximately equal to r_{AB}^{-1}, which leads (20) back to $E_{\Sigma S}$ given by (11). A simple derivation is proposed now which takes advantage of the energy expression obtained in the LCAO approximation.

Therefore, using the definition (18), $E_{\Sigma S}$ can be written as a sum of two terms

$$E_{\Sigma S} = -\left(1-\frac{1}{D}\right)\sum_A \sum_B Z_A Q_B \gamma_{AB} + \left(1-\frac{1}{D}\right)\sum_A \sum_{\mu\in A} \sum_B P_{\mu\mu}^A Q_B \gamma_{AB}. \tag{21}$$

The first term is the core-solvent interaction; the second one is the electron-solvent interaction from which we derive the solvent field one electron operator

$$\hat{G}(S) = \sum_A \sum_{\mu\varepsilon A} \left(1-\frac{1}{D}\right) \sum_B Q_B \gamma_{AB} |\mu\rangle\langle\mu|. \tag{22}$$

By addition of the operator $\hat{G}(S)$ to the one-electron operator $\hat{h}$ of the isolated molecule, we define the effective core operator $\hat{h}(S)$ associated to the solute in the field of the solvent

$$\hat{h}(S) = \hat{h} + \hat{G}(S). \tag{23}$$

The modification to the Fock operator can be deduced from the preceding ones; in regard to the usual definition [26]

$$\hat{F} = \hat{h} + \hat{G} \tag{24}$$

where $\hat{G}$ is the electron field operator, we obtain for the effective Fock operator including the solvent interaction

$$\hat{F}(S) = \hat{h}(S) + \hat{G} = \hat{F} + \hat{G}(S). \tag{25}$$

The expression of the effective electronic energy $\varepsilon_\Sigma^{\mathrm{eff}}(S)$ is easily obtained by substitution of $\hat{h}$ and $\hat{F}$ by $\hat{h}(S)$ and $\hat{F}(S)$ in the usual formal expression of the electronic energy [26] in the AO basis

$$\varepsilon_\Sigma^{\mathrm{eff}}(S)=\tfrac{1}{2}\sum_{\mu}\sum_{\gamma}P_{\mu\gamma}(h_{\mu\gamma}(S)+F_{\mu\gamma}(S)). \tag{26}$$

It is easy to verify that the effective total energy is the sum of the just defined effective electronic energy and of the core-solvent interaction term

$$E_\Sigma(S)=\varepsilon_\Sigma^{\mathrm{eff}}(S)-\left(1-\frac{1}{D}\right)\sum_{\mathrm{A}}\sum_{\mathrm{B}}Z_{\mathrm{A}}Q_{\mathrm{B}}\gamma_{\mathrm{AB}}. \tag{27}$$

Thus, the SCF procedure including solvation effects can be reduced to the standard SCF procedure on the isolated molecule by retaining as Fock operator that of Eq. (25). However, we would like to emphasize that although the effective and the total energy attain a stationary value simultaneously, (i.e., the correct charge distribution is obtained either way) the only physically relevant quantity for discussing equilibrium and rate constants is the total energy E [28]. It is easy to check within this approach that $E_S=-E_{\Sigma S}(1-D^{-1})/2$ at selfconsistency, so that one has to form this quantity at the end of the selfconsistent field calculation.

4. Discussion

The currently used virtual charge model to represent the environmental effect upon the electronic properties of molecular systems has been revised. It has been shown that if a proper representation of the electrostatic contribution to the solvation energy is sought, there is need of an effective dielectric constant in the potential function appearing in the Hartree–Fock molecular orbital equations. The theory developed here differs from that proposed by Klopman. Klopman's theory [5] made the strong assumption that $E_S = 0$ and therefore obtained

$$E=E'_\Sigma+E'_{\Sigma S}=Q_0^2/2a\varepsilon. \tag{28}$$

Since $E'_\Sigma=Q_0^2/2a$, it follows that

$$E'_{\Sigma S}=-(1-\varepsilon^{-1})Q_0^2/2a \tag{29}$$

at variance with formula (13), not only with respect to the replacement of the dielectric constant, but also in so far as a spurious factor $\frac{1}{2}$ is present in (29). While this theoretical approach is physically unsound, it appears to work correctly within the first-order perturbation theory used by Klopman [5]; nevertheless, it is no longer adequate to provide a meaningful reaction field potential acting on the atomic charges.

It should be noted that within a proper reaction field theory [18], the preceding difficulties do not arise. There, the potential and the electrostatic contribution to the solvation energy are adequately defined [18].

An effective Hamiltonian for the solute has been built up in the appendix. A procedure proposed by Jano [4] has been followed. The one-electron solvent field operator $\hat{G}(S)$ was derived from it within the CNDO approximate scheme. The formalism is general and can be used in *ab initio* calculations; the integrals appearing in Eqs. (A6) and (A14) are the standard integrals in molecular orbital calculations. The medium effect is present through the function $f(D)$. It is noteworthy that these integrals do not present cut off problems as in some other works [2, 9, 14, 15, 17]. The reason is simple, since the system of charges (virtual and net) are interacting in vacuum, therefore there is no need of cavities or to use non-convergent expansions to represent the coupling between the solute and the medium.

Another procedure can be envisaged to build up an effective Hamiltonian. The Eq. (11) can be used to propose the following Hamiltonian:

$$H_\Sigma^{\text{eff}}(S) = H_\Sigma - \sum_i^{\text{electr.}} \sum_s^{\text{nuclei}} Q_s/r_{is} \tag{30}$$

where we have dropped the term $a_s\,\delta_{is}$ in the denominator of $E_{\Sigma S}$ (cf. Eq. (11)). The Hamiltonian H_Σ is given by

$$H_\Sigma = \sum_i \left(\tfrac{1}{2}\nabla_i^2 + \sum_s^{\text{nuclei}} \frac{Z_s}{r_{is}} + \tfrac{1}{2} \sum_{j \neq i} \frac{1}{r_{ij}} \right). \tag{31}$$

The effective Hamiltonian $H_\Sigma^{\text{eff}}(S)$ resembles the one given by Germer. However, it differs in $H_{\Sigma S}$ by a factor $\frac{1}{2}$, which is spurious in that work, and now in the new form given to the virtual charge Q_s. This Hamiltonian is not amenable to a simple form from where the variational principle can be applied. Instead, one may consider that the actual virtual charges are known. Therefore once the variational principle is applied to obtain a stationary value of $\langle \psi | H_\Sigma^{\text{eff}}(S) | \psi \rangle$ subjected to the normalization constraint $\langle \psi \mid \psi \rangle = \text{constant}$, these charges are not varied, and the following Hartree–Fock operator is obtained

$$\left(h + \sum_{j=1}^{\text{occ}} (2J_j - K_j) - \sum_s \frac{Q_s}{r_{is}} \right) \phi_\mu(1) = \varepsilon_\mu \phi_\mu(1). \tag{32}$$

This equation is valid only if the exact molecular orbitals are used. Since we do not have such orbitals, a self-consistent procedure involving also the virtual charges has to be used. This makes a difference with Germer's treatment. To end up these considerations one can easily see that in the CNDO approximation used here the one-electron solvent field operator appearing in (32) reduces to the one already obtained by us in Eq. (22). At this level of approximation these treatments are equivalent.

Recently a new application of Klopman and Germer's procedure came to our attention: a quantum chemical study of radical ions and molecules incorporating solvent effect [29] through the solvation model. We would like to emphasize that, while the theory behind this model is not well founded, the numerical results thereby obtained do reflect the solvent polarization effects upon the electronic wave function. In fact, one can assume that an "effective" dielectric constant ε' has been taken up, i.e., $\varepsilon' = \varepsilon/(2-\varepsilon)$ so that the Hartree–Fock-like equations do represent the solvent effect as in Eq. (32). The meaning of the total energy calculated with this wave function is of course doubtful.

Numerical comparisons between the SCRF theory and the virtual charge method discussed here have been done [30]. Details of them will be published elsewhere. As it could be expected both methods taken at the same approximate level, lead to similar results.

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Appendix

The approach proposed by Jano [4] is used to state an explicit form of the effective Hamiltonian within the framework of the virtual charge model of the solvent effect.

Consider the virtual charge density operator defined by

$$\hat{\rho}_v(\boldsymbol{R}')=f(D)\left[\sum_{\mathrm{A}} Z_{\mathrm{A}}\,\delta(\boldsymbol{R}'-\boldsymbol{R}_{\mathrm{A}})-\sum_{i=1}^{n}\delta(\boldsymbol{R}'-\boldsymbol{r}_i)\right] \tag{A1}$$

where n is the number of electrons; $\delta(\boldsymbol{R}'-\boldsymbol{R})$ is Dirac's delta distribution; the sum over A represents a sum over the atoms of the molecule; and $f(D)=-(1-D^{-1})$. The operator $\hat{\rho}_v$ is a simple n-electron operator.

For a one-determinant wave function $\psi(1,\ldots,n)$ build up of the $n/2$ molecular orbitals ϕ_i (1) defining the lowest-energy configuration, the expectation value of $\hat{\rho}_v(\boldsymbol{R}')$ represents the virtual charge density at a given point $\boldsymbol{R}'$:

$$\langle\psi|\hat{\rho}_v(\boldsymbol{R}')|\psi\rangle=f(D)\sum_{\mathrm{A}} Z_{\mathrm{A}}\,\delta(\boldsymbol{R}'-\boldsymbol{R}_{\mathrm{A}})-2\sum_{j=i}^{\mathrm{occ}}\phi_j^{+}\,(\boldsymbol{R}')\phi_j(\boldsymbol{R}') \tag{A2}$$

where of course the following equality holds

$$\langle\psi|\sum_{i=1}^{n}\delta(\boldsymbol{R}'-\boldsymbol{r}_i)|\psi\rangle=2\sum_{j=i}^{\mathrm{occ}}\phi_j^{+}(\boldsymbol{R}')\phi_j(\boldsymbol{R}'). \tag{A3}$$

The electrostatic potential produced inside the molecular volume, $\tilde{V}$, is given by

$$\tilde{V}(\boldsymbol{R})=\int d\boldsymbol{R}'\,\frac{\langle\psi|\hat{\rho}_v(\boldsymbol{R}')|\psi\rangle}{|\boldsymbol{R}-\boldsymbol{R}'|}. \tag{A4}$$

This is the reaction field potential acting over the molecular system. The interaction Hamiltonian can be written as follows:

$$V_{\Sigma}(S)=\sum_{\mathrm{B}}{}' Z_{\mathrm{B}}\tilde{V}(\boldsymbol{R}_{\mathrm{B}})-\sum_{i=1}^{n}\tilde{V}(\boldsymbol{r}_i) \tag{A5}$$

where the prime over the summation indicates that the self-energy term corresponding to the core charges is to be given the form $Z_{\mathrm{B}}^2/a_{\mathrm{B}}$. It is then clear that the effective Hamiltonian $H_{\Sigma}+H_{\Sigma S}$ depends upon the wave function of the solute. A self-consistent procedure will be implied in its solution independently of the method used to calculate the MO's.

Proceeding now to calculate $E_{\Sigma S}$ in the LCAO approximation one gets

$$\langle\psi|V_\Sigma(S)|\psi\rangle = f(D)\left[\sum_{\mathrm{A,B}} \frac{Z_\mathrm{A} Z_\mathrm{B}}{|\boldsymbol{R}_\mathrm{A} - \boldsymbol{R}_\mathrm{B} + a_\mathrm{A}\ \delta_\mathrm{AB}|} - \sum_\mathrm{B} \sum_{\mu\nu}^{\mathrm{AO}} Z_\mathrm{B} P_{\mu\nu} \int \frac{\chi_\mu^*(\boldsymbol{r})\chi_\nu(\boldsymbol{r})\, d\boldsymbol{r}}{|\boldsymbol{R}_\mathrm{B} - \boldsymbol{r}|} \right.$$
$$\left. - \sum_\mathrm{A} \sum_{\mu\nu}^{\mathrm{AO}} Z_\mathrm{A} P_{\mu\nu} \int \frac{\chi_\mu^*(\boldsymbol{r})\chi_\nu(\boldsymbol{r})\, d\boldsymbol{r}}{|\boldsymbol{r} - \boldsymbol{R}_\mathrm{A}|} + \sum_{\mu\nu} \sum_{\lambda\rho} P_{\mu\nu} P_{\lambda\rho} (\mu\nu \mid \lambda\rho) \right] \qquad \text{(A6)}$$

where

$$(\mu\nu \mid \lambda\rho) = \int \frac{\chi_\mu^*(\boldsymbol{r})\chi_\nu(\boldsymbol{r})\chi_\lambda^*(\boldsymbol{r}')\chi_\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\, d\boldsymbol{r}\, d\boldsymbol{r}' \qquad \text{(A7)}$$

and

$$P_{\mu\nu} = 2 \sum_{i=1}^{\mathrm{occ}} c_{\mu i}^* c_{\nu i} \qquad \text{(A8)}$$

where $\{c_{\mu i}\}$ are the atomic orbital coefficients of the i'th MO; $P_{\mu\nu}$ is the charge-bond order matrix.

The expression (A6) is general in respect to the integrals appearing in it. Applying now the approximate scheme of Pople *et al.*, for the bielectronic integrals, and approximating the penetration integrals as follows

$$\int \frac{\chi_\mu^\mathrm{A}(\boldsymbol{r})\chi_\nu^\mathrm{A}(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{R}_\mathrm{B}|}\, d\boldsymbol{r} = \gamma_\mathrm{AB} \qquad \text{(A9)}$$

together with

$$\sum_{\mathrm{A,B}} Z_\mathrm{A} Z_\mathrm{B} / |\boldsymbol{R}_\mathrm{A} - \boldsymbol{R}_\mathrm{B} + a_\mathrm{A}\ \delta_\mathrm{AB}| = \sum_{\mathrm{A,B}} Z_\mathrm{A} Z_\mathrm{B} \gamma_\mathrm{AB} \qquad \text{(A10)}$$

one gets Eq. (20) of the text.

It is interesting to check now the derivation given in the text of the one-electron solvent field operator $\hat{G}(S)$. To proceed we use the energy functional already considered by one of us [16, 28]:

$$J(\psi) = \langle\psi|H_\Sigma^{\mathrm{eff}}|\psi\rangle + \lambda\langle\psi \mid \psi\rangle - \tfrac{1}{2}\langle\psi|V_\Sigma(S)|\psi\rangle \qquad \text{(A11)}$$

where the last term represents the solvent polarization energy. After some simple manipulations one gets for the first variation of (A11)

$$\delta J = \langle\delta\psi|(H_\Sigma - \sum_i \tilde{V}(\boldsymbol{r}_i) + \lambda)|\psi\rangle = 0 \qquad \text{(A12)}$$

Thus for a $\delta\psi$ given by the determinant $\psi_i^{i'}$ where the orbital ϕ_i has been replaced by an orbital $\phi_{i'}$ belonging to the orthogonal complement of the fundamental configuration, one easily gets

$$\left[h(\boldsymbol{r}) - \tilde{V}(\boldsymbol{r}) + \sum_j (2\hat{J}_j - \hat{K}_j)\right] \phi_i(\boldsymbol{r}) = \varepsilon_i \phi_i(\boldsymbol{r}) \qquad \text{(A13)}$$

which is the new Hartree–Fock operator from where the MO's and energies have to be obtained. By the way, this equation may be used in *ab initio* as well as semi-empirical procedures.

We have now to calculate the matrix elements of $\tilde{V}(\boldsymbol{r})$:

$$-\tilde{V}_{\mu\nu} = -f(D)\left[\sum_{\mathrm{B}} Z_{\mathrm{B}} \int \frac{\chi_\mu^*(\boldsymbol{r})\chi_\nu(\boldsymbol{r})}{|\boldsymbol{R}_{\mathrm{B}} - \boldsymbol{r}|}\, d\boldsymbol{r} - 2\sum_{j=i}^{\mathrm{occ}} \int \chi_\mu^*(\boldsymbol{r})\hat{J}_j(\boldsymbol{r})\chi_\nu(\boldsymbol{r})\, d\boldsymbol{r}\right] \tag{A14}$$

which within the approximate CNDO scheme used here leads only to diagonal matrix elements:

$$-\tilde{V}^{\mathrm{A}}_{\mu\mu} = -f(D)\sum_{\mathrm{B}} (Z_{\mathrm{B}} - P^{\mathrm{B}})\gamma_{\mathrm{AB}} \tag{A15}$$

where $P^{\mathrm{B}} = \sum_{\mu \in \mathrm{B}} P_{\mu\mu}$. The minus sign cancels the sign inside $f(D)$ and one recovers $\hat{G}(S)$ since the right hand side of (A15) does not depend on the orbital index but only on the type of atom.

Finally, we would like to emphasize that within the exact reaction field theory $-\frac{1}{2}\langle\psi|V_\Sigma(S)|\psi\rangle$ represents the work necessary to polarize the environment, i.e., E_s. On the contrary, in the method described in the main text, the solvent polarization is given by a set of interacting virtual charges where self-interaction is included. Now, due to the fact that the total energy is constrained to adopt a form in accord with Born's formula, it is no longer possible to derive the solvent polarization energy from the reaction field potential. On the other hand, the form of the functional (A11) is imposed by quite general considerations associated to the application of the variational principle to functionals containing non-linear Hamiltonians [28]. Thus, λ has only the meaning of total energy when the polarization energy is derived from a reaction field potential. Otherwise, one has to be very careful to calculate the adequate total energy of the system which is compatible with the chosen model representing the surrounding medium polarization.

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