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On the Quantum Mechanical Treatment of Solvent Effects

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A new formalism is proposed for incorporating solvent effects into the quantum mechanical description of molecular electronic states. In contrast to existing methods, it does not lead to a non-linear effective hamiltonian, while both the solvent/solvent and the solute/solvent interactions are treated self-consistently. It also accounts more accurately for the solute's electrical field than the usual dipole approximation. Although formally treated on the Hartree–Fock level, the method incorporates dispersion interactions between solute and solvent.

Key words: Solvent effects – Quantum mechanical treatment of ~ – Dispersion forces.

1. Introduction

Most quantum mechanical treatments of molecular properties and interactions refer to vacuum states. In particular for the description of events taking place in solution or in a macro-molecular environment, this is a serious drawback which makes comparison between theoretical and experimental results often hard, if not impossible. Therefore, it is not surprising that over the past decade or so, an increasing number of studies have been dedicated to the representation of environmental effects on the electronic structure of molecules and molecular complexes [1–20].

So far, most of the studies on solvent effects are based on Onsager's [21] reaction field model, in which the solute molecules are described as point-dipoles, situated in cavities within a dielectric continuum or even immersed in such a medium [19]. This simple model, although very useful for discussing trends, poses several

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problems if more accurate descriptions of the solute are desired. First, the dimensions of a cavity are hard to define. In fact, tractable formulations are only obtained for spherical cavities, which are not very realistic for molecules of general shape. Second, bulk dielectric constants, whether obtained from theory or experiment, are most likely not adequate in representing the solute's direct environment. Finally, the use of the dipole moment only for calculating the inductive effects of a molecular charge distribution, may lead to serious errors in cases where the charges are separated over large distances.

Three papers should be commented upon explicitly. First, Kleiner and Elder [9], in their work on environmental effects on the relative stability of the purine tautomers, gave a formal analysis of the quantum mechanical, self-consistent treatment of a solute/solvent system within the frame work of McWeeny's theory for separable groups [22]. In their *ab initio* calculations they used – for practical reasons – a "polarizable dipole in cavity" model. Second, Tapia and Goscinski [14] presented a formalism, in which also the solute's dipole moment is used to generate a reaction field. They do not use a cavity, however, but introduce a response tensor $\boldsymbol{G}$, related to the solvent's permittivity, which may be calculated from a microscopic representation of the solute's environment. Although these authors stress the necessity of obtaining the solute's charge distribution in the reaction field in a self-consistent way, they do not treat the induced effects in the solvent self-consistently. In the numerical illustrations of their method [14–18], using the Hartree–Fock approximation within the CNDO/2 scheme, $\boldsymbol{G}$ was merely used as a parameter. Nevertheless, their results show the importance of environmental effects, in particular in charge transfer processes. Finally, Warshel and Levitt [10], in their work on lysozyme, presented a "total energy" method in which a self-consistent solution was obtained for the complete enzyme/substrate complex, using a semi-empirical quantum mechanical method for part of the system, and a classical empirical energy expression for the remaining part. In the electrostatical part of their energy expression, partial charges on the atoms occur in addition to polarizabilities in the classical regions of the system. The quantum mechanical part is treated in the field produced by the point charges and induced dipoles. The resulting charge distribution, also represented in terms of atomic partical charges, is (re-)introduced in the total energy expression, and this process is repeated until self-consistency. Although the method looks nice, and has been extended and adapted in various papers by Warshel [20], the computational schemes depend on empirical parameters to an extent, that the theoretical value of the results is doubtful. Moreover, representing the total molecular charge distribution by atomic partial charges, again, may lead to errors. All the methods reviewed here, have in common that the reaction field is introduced *after* obtaining the molecular charge distribution within some quantum mechanical method – mainly the Hartree–Fock approximation – thus leading to non-linear equations in which the electrons "feel" the reaction field in a completely classical way.

In this paper we present a general derivation of these methods, as well as a formalism which incorporates the reaction field directly into the molecular hamiltonian. The latter does not lead to any non-linearity in the equations, and is also more elegant from a computational point of view.

2. General Theory

2.1. *The Group Function Approximation*

The wave function describing any number of weakly interacting groups of electrons is – in the limit of zero interaction – given by [22]

$$\psi(1\cdots N) = M\hat{\mathscr{A}}\Phi_{\mathrm{Q}}(1\cdots N_{\mathrm{Q}})\Phi_{\mathrm{S}}(N_{\mathrm{Q}}+1,\ldots,N_{\mathrm{Q}}+N_{\mathrm{S}})\cdots \tag{1}$$

where Φ_{Q} is the anti-symmetric wave function for the N_{Q} electrons in group Q, etc. The factor M is a normalizing constant, $\hat{\mathscr{A}}$ the inter group anti symmetrizer. If the group functions are strongly orthogonal, fairly simple energy expressions can be derived:

$$E = \sum_{\mathrm{Q}} H^{\mathrm{Q}}(qq) + \sum_{\mathrm{Q}<S} \{J^{\mathrm{QS}}(qq, ss) - K^{\mathrm{QS}}(qq, ss)\} \tag{2}$$

with

$$\hat{\mathscr{H}}^{\mathrm{Q}} = \sum_{i=1}^{N_{\mathrm{Q}}} \hat{h}(i) + \tfrac{1}{2}\sum_{i\neq j}^{N_{\mathrm{Q}}} r_{ij}^{-1} \tag{3a}$$

$$H^{\mathrm{Q}}(qq) = \langle\Phi_{\mathrm{Q}}|H^{\mathrm{Q}}|\Phi_{\mathrm{Q}}\rangle \tag{3b}$$

$$J^{\mathrm{QS}}(qq, ss) = \int \frac{1}{r_{12}} P_1^{\mathrm{Q}}(qq|\mathbf{r}_1)P_1^{\mathrm{S}}(ss|\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \tag{3c}$$

$$K^{\mathrm{QS}}(qq, ss) = \int \frac{1}{r_{12}} P_1^{\mathrm{Q}}(qq|\mathbf{r}_1\mathbf{r}_2)P_1^{\mathrm{S}}(ss|\mathbf{r}_2\mathbf{r}_1)\, d\mathbf{r}_1\, d\mathbf{r}_2 \tag{3d}$$

with $P_1^{\mathrm{Q}}(qq)$ the one-particle density function for the group Q electrons, etc. Leaving the zeroth order approximation, a variation condition for (2) can be derived for each group separately in the presence of other groups:

$$E_{\mathrm{eff}}^{\mathrm{Q}} = H_{(qq)}^{\mathrm{Q}} + \sum_{\mathrm{Q}\neq\mathrm{S}} [J^{\mathrm{QS}}(qq, ss) - K^{\mathrm{QS}}(qq, ss)] \tag{4}$$

and the wave function and energy can be optimized considering only one group at a time. This is a Hartree–Fock like description, in which each group experiences only the averaged charge distributions of the other groups. It can be shown [22] that if the resulting equations are solved self-consistently, no further polarization effects, i.e. changes in the one electron charge distributions, can be obtained, and further improvements have to do with correlation effects.

Even if the strong orthogonality condition, which necessitates the evaluation of all two-electron integrals, is relaxed [23], the group function approach is out of practical bounds for large clusters of molecules, and more drastic approximations are needed. Since we are mainly interested in the electronic structure of a single solute molecule surrounded by a cluster of apolar solvent molecules, the actual state of which is considered less important, we absorb the zero-order interactions i.e. the total energy of the cluster *without* the solute molecule, in the energy scale, and write for the self-consistent total electronic energy:

$$E^{\mathrm{QS}} = H^{\mathrm{Q}} + \Delta[J^{\mathrm{QS}} - K^{\mathrm{QS}}] + \Delta\left[\sum_{\mathrm{S}} H^{\mathrm{S}} + \sum_{\mathrm{S}<\mathrm{S}'} J^{\mathrm{SS}'} - K^{\mathrm{SS}'}\right]. \tag{5}$$

If we describe the *changes* in the solvent's charge distribution by means of an effective polarizability, accounting for the self-consistency, we may write (5) in the Onsager form:

$$E^{\mathrm{QS}} = H^{\mathrm{Q}} + E^{\mathrm{RF}} + E^{\mathrm{PQL}}. \tag{6}$$

Where E^{RF} is the interaction energy and E^{POL} the work done in changing the solvent's charge distribution. As will be shown in the next section, the construction of an effectively self-consistent solvent polarizability poses no severe problems. For the solute/solvent interaction two possible approaches will be discussed in following sections.

2.2. Solvent Polarizability

Like Warshel and Levitt [10], let us represent the solute's environment by a collection of points with position vectors $\mathbf{p}$ and dipole polarizabilities $\boldsymbol{\alpha}_p$. Any electrical field will induce dipoles in this system, and, assuming linear response, the actual moment in a point $\mathbf{p}$ will be given by

$$\mathbf{m}_p = \boldsymbol{\alpha}_p\left[\mathbf{f}_p + \sum_{q \neq p} \mathbf{f}(\mathbf{m}_q, \mathbf{p})\right]. \tag{7}$$

Where $\mathbf{f}_p$ is the original field in $\mathbf{p}$ and $\mathbf{f}(\mathbf{m}_q, \mathbf{p})$ is the contribution to the field due to the induced dipole in $\mathbf{q}$. For the collection of points $\{\mathbf{p}\}$, a system of linear equations in $\{\mathbf{m}_p\}$ is obtained, the self-consistent solution of which is given by

$$\mathbf{m} = [\mathbf{1} - \mathbf{A}'\mathbf{B}]^{-1}\mathbf{A}'\mathbf{f} \tag{8}$$

with

$$\mathbf{m} \equiv \begin{pmatrix} \mathbf{m}_1 \\ \mathbf{m}_2 \\ \vdots \\ \mathbf{m}_p \end{pmatrix} \quad \mathbf{A}' \equiv \begin{pmatrix} \boldsymbol{\alpha}_1 & & 0 \\ & \ddots & \\ 0 & & \boldsymbol{\alpha}_p \end{pmatrix} \quad \mathbf{f} \equiv \begin{pmatrix} \mathbf{f}_1 \\ \mathbf{f}_2 \\ \vdots \\ \mathbf{f}_p \end{pmatrix} \tag{8a}$$

and $\mathbf{B}$ is the interaction tensor between the dipoles:

$$\mathbf{B} = \begin{pmatrix} \mathbf{0} & \mathbf{B}_1^2 & \mathbf{B}_1^3 & \cdots & \mathbf{B}_1^p \\ \vdots & \ddots & & & \\ & & \ddots & & \\ & & & \ddots & \\ \mathbf{B}_p^1 & & & & \mathbf{0} \end{pmatrix} \tag{8b}$$

with

$$\mathbf{B}_p^q = \left(\mathbf{1} - 3\frac{(\mathbf{p}-\mathbf{q})(\mathbf{p}-\mathbf{q})^{\dagger}}{|\mathbf{p}-\mathbf{q}|^2}\right)\frac{1}{|\mathbf{p}-\mathbf{q}|^3}. \tag{8c}$$

This solution only depends on the choice of points $\mathbf{p}$ and the polarizabilities $\boldsymbol{\alpha}_p$. Hence, for a self-consistent, effective polarizability we have

$$\mathbf{A}=[\mathbf{1}-\mathbf{A}'\mathbf{B}]^{-1}\mathbf{A}' \tag{9}$$

and any interaction of a (molecular) charge distribution with this model solvent may be assumed to be self-consistent without any further iterations in the solvent part of the system. For later reference it is useful to note that we may write

$$\mathbf{A}=\mathbf{L}\mathbf{L}\dagger \tag{9a}$$

where $\mathbf{L}$ is a lower triangle matrix. Of course, one must make sure that the inverse matrix in (9) exists, and that it has a physical meaning. A discussion of these points has to wait until numerical results are available, and is beyond the scope of this paper.

At any time, the total energy of polarization is given by

$$E^{\mathrm{POL}}=\tfrac{1}{2}\sum_p \mathbf{m}_p^{\dagger}\boldsymbol{\alpha}_p^{-1}\mathbf{m}_p \tag{10}$$

which for isotropic polarizabilities takes the probably more familiar form [24]

$$E^{\mathrm{POL}}=\sum_p \frac{|m_p|^2}{2\alpha_p}. \tag{11}$$

For a self-consistent solution it can be shown [25] that E^{POL} is related to the total interaction energy (E^{RF} in (6)) with the system (S) generating the inductive field as:

$$E^{\mathrm{POL}}=-\tfrac{1}{2}E^{\mathrm{RF}}. \tag{12}$$

2.3. The Average Reaction Field Method

Starting from Eq. (5), and neglecting the exchange term, the solute/solvent interaction can be described in terms of the electrical field of the solute's charge distribution P_1^Q. Let $\rho(r)$ be the electronic charge distribution of Q, and let

$$\hat{\mathscr{f}}_p\equiv\frac{\mathbf{p}-\mathbf{r}}{|\mathbf{p}-\mathbf{r}|^3},\qquad \mathbf{f}_p^n\equiv\sum_c Z_c\frac{\mathbf{p}-\mathbf{r}_c}{|\mathbf{p}-\mathbf{r}_c|^3} \tag{13}$$

define the electronic and nuclear contributions, respectively, to the field operator relative to $\mathbf{p}$, then we have:

$$\mathscr{f}_p=\langle\mathbf{f}\rangle_p+\mathbf{f}_p^n=\int d\mathbf{r}p(\mathbf{r})\hat{\mathscr{f}}_p+\mathbf{f}_p^n. \tag{14}$$

The collection of dipoles induced by this field is, according to (9) given by

$$\mathbf{m}=\mathbf{A}\{\langle\mathbf{f}\rangle+\mathbf{f}^n\}. \tag{15}$$

A dipole in $\mathbf{q}$ contributes to the potential in $\mathbf{s}$, in the region of ρ, an amount:

$$\Delta V^{\mathrm{RF}}(q,s)=\mathbf{m}_q^{\dagger}\frac{\mathbf{s}-\mathbf{q}}{|\mathbf{s}-\mathbf{q}|^3}=-\mathbf{m}_{\mathrm{q}}^{\dagger}\hat{\mathscr{f}}_q \tag{16a}$$

from which we arrive at the reaction field operator:

$$\hat{H}^{\mathrm{RF}} = \mathbf{m}\dagger\hat{\mathscr{f}} = \{\langle\mathbf{f}\rangle + \mathbf{f}^n\}\dagger\mathbf{A}\hat{\mathscr{f}}. \tag{16b}$$

The effect of the reaction field on the electronic energy is

$$E^{\mathrm{RF}}_{\mathrm{e1}} = \langle\Phi_{\mathrm{Q}}|H^{\mathrm{RF}}|\Phi_{\mathrm{Q}}\rangle = -\{\langle\mathbf{f}\rangle + \mathbf{f}^n\}\dagger\mathrm{A}\dagger\langle\mathbf{f}\rangle \tag{17}$$

and the effect on the total interaction energy is

$$E^{\mathrm{RF}} = -\{\langle\mathbf{f}\rangle + \mathbf{f}^n\}\dagger\mathbf{A}\{\langle\mathbf{f}\rangle + \mathbf{f}^n\}.$$

For the total energy of the solute/solvent system we have to imply (12), and find for the electronic contribution:

$$E^{\mathrm{QS}}_{\mathrm{e1}} = \langle\Phi_{\mathrm{Q}}|H^{\mathrm{Q}}|\Phi_{\mathrm{Q}}\rangle - \tfrac{1}{2}\langle\mathbf{f}\rangle\dagger\mathbf{A}\langle\mathbf{f}\rangle + \langle\mathbf{f}\rangle\dagger\mathbf{A}\mathbf{f}^n. \tag{18}$$

Hence, this energy cannot directly be obtained as the expectation value of the electronic operator

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}^{\mathrm{Q}} + \hat{\mathscr{H}}^{\mathrm{RF}}. \tag{19}$$

In order to arrive at (18) the expectation value of $\hat{\mathscr{H}}^{\mathrm{RF}}$ has to be evaluated separately, after which it is to be reduced so as to account for the polarization energy. Moreover, the wave function Φ_{Q} has to be obtained from a non-linear equation

$$[\hat{\mathscr{H}}^{\mathrm{Q}} + \hat{\mathscr{H}}^{\mathrm{RF}}(\Phi_{\mathrm{Q}})]\Phi_{\mathrm{Q}} = E(\Phi_{\mathrm{Q}})\Phi_{\mathrm{Q}} \tag{20}$$

which poses several formal problems discussed by Sanhueza *et al.* [26].

2.4. The Direct Method

In order to avoid the problems mentioned in the foregoing section we introduce the effect of the solvent directly into the solute's hamiltonian, prior to any reference to the charge distribution or the wave function:

$$\hat{\mathscr{H}}^{\mathrm{Q}}_{\mathrm{eff}} = \hat{\mathscr{H}}^{\mathrm{Q}} - \tfrac{1}{2}\sum_{i,j}\hat{\mathscr{f}}_i^{\dagger}\mathbf{A}\hat{\mathscr{f}}_j + \sum_i \mathbf{f}^{n\dagger}\mathbf{A}\hat{\mathscr{f}}_i \tag{21}$$

where $\hat{\mathscr{f}}_i$ etc., defined as in (13), now refer to an electronic coordinate rather than to an arbitrary point in space. Using the decomposition of **A** (cf. Eq. (9a)), we have more simply:

$$\hat{\mathscr{H}}^{\mathrm{Q}}_{\mathrm{eff}} = \hat{\mathscr{H}}^{\mathrm{Q}} - \tfrac{1}{2}\sum_{i,j}\hat{\mathscr{g}}_i^{\dagger}\hat{\mathscr{g}}_j + \sum_i \mathbf{g}^{n\dagger}\hat{\mathscr{g}}_i \tag{22}$$

The use of the factor one half in this expression is warranted because of the effective self-consistency of the solvent implied in **A**. The interpretation of the additional terms in the hamiltonian (22) may be two-fold. Either one considers them as effective forms of the $\hat{\mathscr{J}}$ and $\hat{\mathscr{K}}$ operators in the formal group function treatment, or one simply takes them as introducing an effective dielectric constant reducing all coulombic interactions. In either case, the solvent reacts instantaneously to the solute's electrons, and this is bound to produce differences with the preceding average field method.

If we solve Φ_Q with the hamiltonian (22) on the Hartree–Fock level, we find in terms of an orthonormal set of doubly occupied MOs:

$$\begin{aligned} E_{\mathrm{el}} = {} & \langle\Phi_Q|H^Q|\Phi_Q\rangle - \sum_i \langle i|\mathbf{g}^\dagger(1)\mathbf{g}(1)|i\rangle \\ & + 2\mathbf{g}^{n\dagger} \sum_i \langle i|\mathbf{g}(1)|i\rangle - \sum_{i,j} 2\langle i|\mathbf{g}(1)|i\rangle^\dagger \langle j|\mathbf{g}(1)|j\rangle \\ & + \sum_{i,j} \langle i|\mathbf{g}(1)|j\rangle^\dagger \langle i|\mathbf{g}(1)|j\rangle \end{aligned} \tag{23}$$

where i,j are orbital indices.

First, we note that, indeed, the total electronic energy of the system is obtained as the expectation value of the corresponding operator, and no special arrangements are needed in its evaluation. Also, there is no non-linearity problem involved in finding Φ_Q. Writing (18) in the same form as (23) we have:

$$E'_{\mathrm{el}} = \langle\Phi_Q|H^Q|\varphi_Q\rangle + 2\mathbf{g}^{n\dagger} \sum_i \langle i|\mathbf{g}(1)|i\rangle - \sum_{i,j} 2\langle i|\mathbf{g}(1)|i\rangle^\dagger \langle j|\mathbf{g}(1)|j\rangle \tag{24}$$

which, at first sight, looks rather different from Eq. (23). In the difference

$$\Delta E = E_{\mathrm{el}} - E'_{\mathrm{el}} = -\sum_i \langle i|\mathbf{g}(1)^\dagger\mathbf{g}(1)|i\rangle + \sum_{i,j} \langle i|\mathbf{g}(1)|j\rangle^\dagger \langle i|\mathbf{g}(1)|j\rangle \tag{25}$$

we see two terms, the first of which contains the stabilization of each electron in its own reaction field, while the second comes from imposing the Pauli principle on Φ_Q. After applying the closure relation to the first term:

$$\sum_i \langle i|\mathbf{g}(1)^\dagger\mathbf{g}(1)|i\rangle = -\sum_{i=1}^{n_{\mathrm{occ}}} \sum_{K=1}^{\infty} \langle K|\mathbf{g}(1)|i\rangle^\dagger \langle K|\mathbf{g}(1)|i\rangle \tag{26}$$

we have:

$$\Delta E = -\sum_{i=1}^{n_{\mathrm{occ}}} \sum_{K=n_{\mathrm{occ}}+1}^{\infty} \langle K|\mathbf{g}(1)|i\rangle^\dagger \langle K|\mathbf{g}(1)|i\rangle . \tag{27}$$

Now, the operators $\hat{g}$ are associated with the polarizability of the solvent molecules, and for each of these we may write:

$$\boldsymbol{\alpha} = \sum_{v\neq 0} \frac{|\langle 0|\mathbf{m}|v\rangle|^2}{E_0 - E_v} \tag{28}$$

i.e. a sum of matrix elements connecting singly excited states. On combining the two forms (27) and (28), we obtain an expression coupling single excitations of the solute molecule to single excitations in the solvent, and, hence, Eq. (27) is a representation of the second order terms arising from applying perturbation theory within the self-consistent group function formalism [22]. This means, that our description, if Eq. (23) is obtained self-consistently, contains dispersion contributions up to third order, a result obtained in a much more direct way than that outlined by Tapia [27]. Moreover, the direct method, in comparison with the average field approach, leads to much less computational difficulties, as will be pointed out in the next section.

3. Practical Considerations

In this section we develop the formalism of the foregoing section for use in actual computations in the LCAO approximation. For simplicity, the discussion is restricted to closed shell Hartree–Fock wave functions.

In terms of a basis set $\{\chi\}$ of, e.g. atomic orbitals, the molecular electronic charge distribution is represented by a density matrix $2\mathbf{R}$ [28], and the total charge distribution is, in atomic units:

$$\rho(\mathbf{r}) = -2\chi\dagger(r)\mathbf{R}\chi(r) + \sum_{c} Z_c\delta(\mathbf{r}-\mathbf{r}_c). \tag{29}$$

The total energy (23) in terms of the basis $\{\chi\}$ is:

$$\begin{aligned} E_{\mathrm{T}} = {} & \sum_{ij} 2R_{ij}\{h_{ij} - \tfrac{1}{2}(\mathbf{g}\dagger\mathbf{g})_{ij} + \mathbf{g}^{n}\dagger\mathbf{g}_{ij}\} + \sum_{ijkl}(2R_{ij}R_{kl} - R_{ik}R_{jl})\{(ij|kl) - \mathbf{g}^{\dagger}_{ij}\mathbf{g}_{kl}\} \\ & + \sum_{c<d} Z_c Z_d r_{cd}^{-1} - \tfrac{1}{2}\mathbf{g}^{n}\dagger\mathbf{g}^{n} \end{aligned} \tag{30}$$

with h_{ij} the usual one-electron matrix elements and $(ij|kl)$ the two-electron integrals, and the last term representing the nuclear–nuclear interactions. The form of (30) points directly to the way in which the solvent effect can be incorporated into an actual calculation. Once the additional interaction matrix elements have been evaluated, they are simply combined with the corresponding terms in the standard Hartree–Fock energy expression, and there is no need for special procedures on the SCF level. However, the evaluation of these matrix elements may present some problems. If P is the number of points representing the solvent, we have

$$\mathbf{g}^{\dagger}_{ij}\mathbf{g}_{kl} = \mathbf{f}^{\dagger}_{ij}\mathbf{L}\mathbf{L}\dagger\mathbf{f}_{kl} = \sum_{p,q=1}^{P} \mathbf{f}^{\dagger}_{p_{ij}}\mathbf{A}_{pq}\mathbf{f}_{q_{kl}}. \tag{31}$$

The implication is, that for every point in the solvent a *matrix* has to be constructed for each cartesian direction:

$$\mathbf{f}_{p_{ij}} = \left\langle \chi_i \middle| \frac{\mathbf{p}-\mathbf{r}}{|\mathbf{p}-\mathbf{r}|^3} \middle| \chi_j \right\rangle \tag{32}$$

and the construction of the matrix elements $\mathbf{g}^{\dagger}_{ij}\mathbf{g}_{kl}$ involves, since $\mathbf{A}$ is a $3P\times 3P$ matrix, the evaluation, storage and retrieval of $3P(3P+\frac{1}{2}n(n+1))$ quantities (n being the basis size), a number which, depending on P, can easily be prohibitive. Therefore, we introduce an approximation which simplifies the integrals (32), reduces their number, and enables us to avoid reference to the individual solvent points during the quantum mechanical parts of the calculations.

Expanding the local field operator in a Taylor series around a – for the moment arbitrary – origin $\mathbf{a}$, we have:

$$\frac{\mathbf{p}-\mathbf{r}}{|\mathbf{p}-\mathbf{r}|^3} \approx \mathbf{v}^{a}_{p} - \mathbf{B}^{a}_{p}(\mathbf{r}-\mathbf{a}) \tag{33}$$

with

$$\mathbf{v}^a = \frac{\mathbf{p}-\mathbf{a}}{|\mathbf{p}-\mathbf{a}|^3} \tag{33a}$$

and $\mathbf{B}_p^a$ defined in (8c). Relative to this origin a matrix element of $\mathbf{f}_p$ is

$$\mathbf{f}^a_{p_{ij}} = \langle \chi_i | \mathbf{v}_p^a + \mathbf{B}_p^a \mathbf{a} - \mathbf{B}_p^a \mathbf{r} | \chi_j \rangle = (\mathbf{v}_p^a + \mathbf{B}_p^a \mathbf{a}) S_{ij} - \mathbf{B}_p^a \mathbf{r}_{ij} \tag{34}$$

which contains only overlap and dipole moment integrals. Here, we note, that taking one and the same origin for all charge distributions $\chi_i \chi_j$ would lead to a reaction field operator (cf. Eq. (20)) with matrix elements

$$\hat{\mathscr{H}}_{ij}^{\mathrm{RF}} = -\sum_{p,q} \langle \mathbf{f} \rangle_p^{\dagger} \mathbf{A}_{pq} (\mathbf{v}_q S_{ij} - \mathbf{B}_q \mathbf{r}_{ij}) \tag{35}$$

which, apart from the monopole term and the self consistency of the solvent implied in $\mathbf{A}$, would give us back Tapia and Goscinski's [14] approach, with $\mathbf{B}\dagger\mathbf{A}\mathbf{B}$ instead of their tensor $\mathbf{G}$.

Apart from the fact that we do not want to use the operator in this form, we want a better approximation to the field operators, and therefore we take different expansion centres for different charge distributions. Of course, by taking a new centre for each charge distribution, we would be back at the problem of having too many integrals. Hence, we choose the nuclear positions as expansion centres. These are at least good for the one-centre distributions, while for two-centre distributions one may either take the nearest nuclear centre or interpolate, since it may be assumed that the reaction field varies rather smoothly within the dimensions of the solute molecule.

After some amount of algebra (see Appendix) we have:

$$(\mathbf{g}\dagger\mathbf{g})_{ij} = \gamma^{aa} S_{ij} - 2\boldsymbol{\delta}\dagger^{aa} \mathbf{r}_{ij} + (\mathbf{r}\dagger\boldsymbol{\Omega}^{aa}\mathbf{r})_{ij} \tag{36a}$$

$$\mathbf{g}_{ij}^{\dagger}\mathbf{g}_c = \xi^{ac} S_{ij} - \mathbf{r}_{ij}^{\dagger}\boldsymbol{\varepsilon}^{ac} \qquad (\mathbf{g}_c \text{ is the contribution of a single nucleus } c \text{ to } \mathbf{g}^n). \tag{36b}$$

$$\mathbf{g}_{ij}^{\dagger}\mathbf{g}_{kl} = S_{ij}\gamma^{ab} S_{kl} - S_{ij}\boldsymbol{\delta}\dagger^{ab}\mathbf{r}_{kl} - \mathbf{r}_{ij}^{\dagger}\boldsymbol{\delta}^{ba} S_{kl} + \mathbf{r}_{ij}^{\dagger}\boldsymbol{\Omega}^{ab}\mathbf{r}_{kl} \tag{36c}$$

and all terms may be obtained from the overlap and dipole moment integrals, except the last term in Eq. (36a) which is related to the matrix elements of the quadrupole operator. The greek symbols in Eq. (36) are simple constants, three-dimensional vectors and 3 × 3 matrices, independent of the basis. The upper indices indicate the expansion centre(s) to which they relate, where it is understood that "*a*" refers to "*j*" and "*b*" to "*kl*", the actual values of these parameters depend solely on the choice of solvent points, their polarizabilities and the geometry of the system, and they are obtained prior to the evaluation of the integrals. By incorporating the matrix elements $\mathbf{g}_{ij}^{\dagger}\mathbf{g}_{kl}$ directly into the corresponding coulombic integrals, the additional storage requirements are very limited, while no change in procedure is needed in the SCF part. We note, that implementation of the present approximations in the reaction field operator formalism (cf Eq. (35)) would lead to the necessity of keeping track of *four* one-electron matrices *per expansion centre*, which, again, may lead rapidly to storage problems. Moreover, in that formalism, quite drastic changes in the logic of the SCF procedures would be necessary.

4. Discussion

Starting from a formal quantum mechanical treatment of a complex system of weakly interacting molecules, we arrived at a quantum mechanical formulation of solvent effects on a single solute molecule, which is both tractable and consistent. Tractable, because the description of the solvent – represented by a collection of point polarizabilities – is reduced to a relatively small number of scalars, vectors and tensors, this number being only dependent of the number of atoms in the solute. The computational effort involved in obtaining this effective representation is – most likely – rather small, once a procedure is developed for manipulating large matrices.

The consistency of the formalism is threefold. First, the field induced in the solvent is treated self-consistently. Apart from being correct, this has the advantage that there is no need to evaluate the polarization energy separately. Second, the reaction field is introduced directly in the effective molecular hamiltonian, which leads to the – normal – situation that the total energy is obtained as the expectation value of the total hamiltonian. This, in contrast, is not the case for the "averaged reaction field" approach like that of Tapia and Goscinski [14]. Third, since the solvent/solvent interactions are treated in an approximate way, considering only dipole/dipole interactions, it is reasonable to approximate also the field operators. Our method, however, is generous to the details of the solute's charge distribution – typical for a quantum mechanical description – by not simply relating the field to a dipole [14] or a collection of point charges [10].

Within the frame work of representing the solvent by point polarizabilities, our direct method accounts to a certain extent for dispersion effects, which are not present in the average field methods. As to the detailed information on structure and properties of the environment, we assume that such information is, or may become, available, either from experiment or from computations. Structural parameters may be obtained – in the latter case – from Monte Carlo or Molecular Dynamics simulations. Polarizabilities can be computed for individual solvent molecules placed in appropriate fields.

Numerical testing of the method is in progress in this laboratory, and results as well as comparison with existing methods will be reported shortly.

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Appendix

According to (33) we have, relative to centre **a**:

$$\begin{aligned}\frac{\mathbf{p}-\mathbf{r}}{|\mathbf{p}-\mathbf{r}|^3} &\approx \frac{\mathbf{p}-\mathbf{a}}{|\mathbf{p}-\mathbf{a}|^3} - \mathbf{B}_p^a(\mathbf{r}-\mathbf{a}) \\ &= \mathbf{v}_p^a - \mathbf{B}_p^a(\mathbf{r}-\mathbf{a}) \\ &= \mathbf{w}_p^a - \mathbf{B}_p^a\mathbf{r}\end{aligned} \tag{A.1a}$$

with

$$\mathbf{v}_p^a = \frac{\mathbf{p}-\mathbf{a}}{|\mathbf{p}-\mathbf{a}|^3}, \qquad \mathbf{w}_p^a = \mathbf{v}_p^a + \mathbf{B}_p^a\mathbf{a}. \tag{A.1b}$$

Choosing centre **a** for basis orbital product (ij) and **b** for (kl) we obtain for a typical matrix element

$$\begin{aligned}\mathbf{g}_{ij}^{\dagger}\mathbf{g}_{kl} &= \mathbf{f}_{ij}^{\dagger}\mathbf{L}\mathbf{L}\dagger\mathbf{f}_{kl} = \sum_{pq} \mathbf{f}_{p_{ij}}^{\dagger}\mathbf{A}_{pq}\mathbf{f}_{q_{kl}} = \sum_{pq} (\mathbf{w}_p^a S_{ij} - \mathbf{B}_p^a\mathbf{r}_{ij})\dagger\mathbf{A}_{pq}(\mathbf{w}_q^b S_{kl} - \mathbf{B}_q^b\mathbf{r}_{kl}) \\ &= \sum_{pq} \{S_{ij}\mathbf{w}_p^{a\dagger}\mathbf{A}_{pq}\,\mathbf{w}_q^b S_{kl} - S_{ij}\mathbf{w}_p^{a\dagger}\mathbf{A}_{pq}\mathbf{B}_q^b\mathbf{r}_{kl} \\ &\quad - \mathbf{r}_{ij}^{\dagger}\mathbf{B}_p^{a\dagger}\mathbf{A}_{pq}\mathbf{w}_q^b S_{kl} + \mathbf{r}_{ij}^{\dagger}\mathbf{B}_p^{a\dagger} A_{pq}\boldsymbol{B}_q^b\mathbf{r}_{kl}\} \\ &= S_{ij}\gamma^{ab}S_{kl} - S_{ij}\boldsymbol{\delta}\dagger^{ab}\mathbf{r}_{kl} - \mathbf{r}_{ij}^{\dagger}\boldsymbol{\delta}^{ab}S_{kl} + \mathbf{r}_{ij}^{\dagger}\boldsymbol{\Omega}^{ab}\mathbf{r}_{kl}\end{aligned} \tag{A.2}$$

with

$$\gamma^{ab} = \sum_{p,q} \mathbf{w}_p^{a\dagger}\mathbf{A}_{pq}\mathbf{w}_q^b, \qquad \boldsymbol{\delta}^{ab} = \sum_{p,q} \mathbf{B}_p^{a\dagger}\mathbf{A}_{pq}\mathbf{w}_q^b, \qquad \boldsymbol{\Omega}^{ab} = \sum_{p,q} \mathbf{B}_p^{a\dagger}\mathbf{A}_{pq}\mathbf{B}_q^b. \tag{A.3}$$

The nuclear-electron interaction terms contain:

$$\mathbf{g}_{ij}^{\dagger}\mathbf{g}_c = \sum_{pq} (\mathbf{w}_p^a S_{ij} - \mathbf{B}_p^a\mathbf{r}_{ij})\dagger\mathbf{A}_{pq}\mathbf{v}_q^c = S_{ij}\xi^{ac} - \mathbf{r}_{ij}^{\dagger}\boldsymbol{\varepsilon}^{ac} \tag{A.4}$$

with

$$\boldsymbol{\xi}^{ac} = \sum_{pq} \mathbf{w}_p^{a\dagger}\mathbf{A}_{pq}\mathbf{v}_q^c, \qquad \boldsymbol{\varepsilon}^{ac} = \sum_{pq} \mathbf{B}_p^{a\dagger}\mathbf{A}_{pq}\mathbf{v}_q^c. \tag{A.5}$$

Finally, the nuclear/nuclear term in (30) reduces to a constant:

$$E_{nn} = \tfrac{1}{2}\sum_{cd} Z_c Z_d \sum_{pq} \mathbf{v}_p^{c\dagger}\mathbf{A}_{pq}\mathbf{v}_q^d. \tag{A.6}$$

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