

COMMON THEORETICAL FRAMEWORK FOR QUANTUM CHEMICAL SOLVENT EFFECT THEORIES

János G. ÁNGYÁN*

Institut für Physikalische und Theoretische Chemie der Universität Bonn, Wegelerstrasse 12, 5300 Bonn 1, Germany

Abstract

Quantum chemical solvent effect theories deal with the description of the electronic structure of a molecular subsystem embedded in a solvent or other molecular environment. The average reaction field theories, which describe electrostatic and polarization interactions between solute and solvent, can be formulated in terms of a nonlinear reaction potential operator. This operator depends on the one hand on the reaction potential function of the solvent, and on the other hand on the charge density operators, which appear in the solute–solvent interaction. The former quantity is determined by the physical model of the solvent (e.g. dielectric continuum, discrete model, crystal lattice, etc.). The charge density operator can be approximated at different levels, like exact, one-centered and multicentered multipolar forms. These two ingredients of the theory, the reaction potential response function and the specific charge density operator, define unequivocally different solvent effect models. Various versions of average reaction field models are critically reviewed on the basis of this common theoretical framework.

1. Introduction

Recently, a great deal of effort has been devoted to the modeling of physico-chemical processes in condensed phases, e.g. solids, liquids, solutions, or biological environments. The progress in various fields, like in the theory of intermolecular forces, in computer simulation techniques and in solid-state physical methods, enabled us to have a better understanding of many of these important phenomena. It became evident that, at least in certain cases, the influence of the intermolecular interactions on the electronic structure of the constituents is essential.

In particular, the electronic structure of solute molecules can be strongly coupled to the solvent structure and conversely. This effect can be the key element, for example, in the understanding of the microscopic mechanism of certain reactions in solution [1].

*On leave from Quantum Theory Group, Institute of Physics, Technical University of Budapest, Budafoki út 8, H-1521 Budapest, Hungary. Present address: Laboratoire de Chimie Théorique, Université de Nancy I, P.B. 239, Vandœuvre-lès-Nancy, F-54506, France.

Quantum chemical solvent effect theories [2,3] provide a self-consistent description of the solute electronic structure, which is strongly coupled to a polarizable environment. Such calculations are indispensable to get an insight into molecular properties [4–6] and reactivity [7–10] in condensed phases. This goal is usually achieved by means of a *solute-only model Schrödinger equation*, corresponding to some simplified representation of the solvent.

Many semi-empirical and *ab initio* models have been proposed in the past twenty-five years, beginning with the heuristic solvation model of Klopman in 1967 [11] and the reaction field models of Rinaldi and Rivail [12], Newton [13] in 1973, and of Tapia and Goscinski [14] in 1975. These models and later developments [8, 15–26] sometimes seem to be very different although it is widely accepted that the underlying basic physical model in all the cases is the reaction field idea, attached to the name of Onsager [27]. This model assumes that the polar solute system, which is embedded in a solvent, polarizes its surroundings. The polarized environment creates a field, the reaction (or polarization) field which, in turn, acts back on the solute subsystem.

This simple picture has been originally formulated for a point dipole, embedded in a dielectric continuum, and many quantum chemical adaptations of the continuum model followed this line. Later, refinements improved the representation of both the solute charge distribution and the solvent, and led to various forms of the corresponding effective quantum chemical solute operator. Unfortunately, the differences of the mathematical formulations were an obstacle to having a direct comparison of different models, which is badly lacking in this field.

In the present contribution, it is attempted to formulate the most important quantum chemical solvent effect models within a relatively simple, common mathematical framework. By doing this, we extend in some sense earlier efforts of Tapia, outlined in some of his review papers [2,28].

Why is it important to get a kind of unified view of the various quantum chemical solvent effect models? We think that this can be rewarding from several different aspects. First, a unified view may render it easier to appreciate the physical significance of the models, which are quite often of rather different origin, and makes it easier to analyse their scope of validity. Secondly, the application of various perturbational schemes to the solute-only effective Schrödinger equation can be done directly on the generally formulated case, thus avoiding eventual pitfalls due to specific aspects of certain simplified models and reducing considerably the analytical effort [29]. Thirdly, the computational implementation of the various solvent effect models can be greatly simplified. In particular, the very same quantum chemical code can be used to take into account the effect of very different solvent (or environmental) models. Such a computer program system is under development in our laboratories [30].

The solvent effect models are based on the assumption that there exists a free energy functional (or at zero absolute temperature, a total energy functional) $J(\psi, X)$ which depends on the solute wave function ψ and on some generalized

solvent coordinates, which will be denoted here by \mathbf{X} . (A list of symbols can be found at the end of the paper). This energy functional takes the general form

$$J(\psi, \mathbf{X}) = \langle \psi | \hat{H}^S | \psi \rangle + \langle \psi | \hat{\rho}_r | \psi \rangle V_r^B + \frac{1}{2} \langle \psi | \hat{\rho}_r | \psi \rangle \mathbf{G}_{r,r'}^B \langle \psi | \hat{\rho}_{r'} | \psi \rangle. \quad (1.1)$$

The detailed meaning of these quantities will be given later. For the time being, it is sufficient to note that $\hat{\rho}_r$ stands for the solute charge density operator, V_r^B is the *solvent permanent potential* and $\mathbf{G}_{r,r'}^B$ is the *solvent reaction potential response function*. A kind of summation convention is followed for the repeated lower indices r and r' , which means integration with respect to these space variables (see later).

The interpretation of $J(\psi, \mathbf{X})$ depends on the physical model for the solvent or environment. As far as our model system is considered to be at zero absolute temperature, J corresponds to a total internal energy. On the other hand, as far as V_r^B and $\mathbf{G}_{r,r'}^B$ are derived from a statistical mechanical model at nonzero absolute temperatures, one should consider J as a free energy.

A nonlinear Schrödinger-like equation can be derived from this energy (or free energy) functional by the straightforward application of the variation principle, i.e. by requiring that the first variation of J with respect to the solute wave function ψ vanishes,

$$\frac{\partial J(\psi, \mathbf{X})}{\partial \psi} = 0 \quad (1.2)$$

and taking into account the normalization condition of the solute electronic wave function [31,32]. This procedure leads to the following Schrödinger-like equation:

$$\{\hat{H}^S + \hat{\rho}_r V_r^B + \hat{\rho}_r \mathbf{G}_{r,r'}^B \langle \psi | \hat{\rho}_{r'} | \psi \rangle\} | \psi \rangle = E | \psi \rangle, \quad (1.3)$$

where E is the Lagrange multiplier, introduced for the wave function normalization condition.

Special properties of this nonlinear Schrödinger equation have been discussed in the literature [33], and it has also been pointed out that an improper application of the variation principle may lead to erroneous solvent effect models [25,32,34–37].

The average potential V_r^B can be very important in order to have a physically complete solvent model [2,31]. Many solvent models are limited to only this term, which is relatively easy to include in existing quantum chemical computer codes, usually as the potential of effective point charges [38,39].

The treatment of the reaction potential operator

$$\hat{W} = \hat{\rho}_r \Pi_r^B = \hat{\rho}_r \mathbf{G}_{r,r'}^B \langle \psi | \hat{\rho}_{r'} | \psi \rangle, \quad (1.4)$$

where the reaction potential function Π_r^B has been introduced as

$$\Pi_r^B = \mathbf{G}_{r,r'}^B \langle \psi | \hat{\rho}_{r'} | \psi \rangle, \quad (1.5)$$

is considerably more delicate because this is the term responsible for the nonlinearity of the solute-only model Schrödinger equation. Our main concern in this review will be to develop different models for the reaction potential and discuss their implementation in quantum chemical computational schemes.

The various average reaction field type solvent effect models will be grouped according to the type of the underlying physical model. The following different cases will be considered:

- continuum solvent model with various cavity shapes,
- discrete solvent model with fixed nuclear configuration,
- discrete solvent model with thermal averaging,
- identical subsystems in ordered phase (molecular crystals),
- identical subsystems in disordered phase (molecular liquids).

Explicit expressions of the reaction potential response function will be given and/or derived for the above situations.

Two different approaches can be followed to evaluate the matrix elements of the reaction potential for a given solvent model.

The first one consists in the numerical calculation of the reaction potential $\Pi^B(\mathbf{r})$, i.e. the potential of the polarized charge density of the solvent and taking its matrix elements:

$$\langle \mu | \hat{W} | \nu \rangle = \int d^3r \chi_\mu^*(\mathbf{r}) \Pi^B(\mathbf{r}) \chi_\nu(\mathbf{r}). \quad (1.6)$$

The advantage of this approach is that the reaction potential is handled as a one-electron perturbation, like the external potential.

The second type of approach is based on the knowledge of the reaction potential response function $\mathbf{G}^B(\mathbf{r}, \mathbf{r}')$ and on an analytical treatment of the reaction potential operator. For this purpose, one needs the explicit quantum chemical expression of the molecular charge density as a sum of nuclear and electronic contributions:

$$\rho(\mathbf{r}) = \langle \psi | \hat{\rho}(\mathbf{r}) | \psi \rangle = \sum_a Z_a \delta(\mathbf{r} - \mathbf{R}_a) - \sum_{\lambda\sigma} P_{\sigma\lambda} \chi_\lambda^*(\mathbf{r}) \chi_\sigma(\mathbf{r}), \quad (1.7)$$

where Z_a is the nuclear charge and the electronic charge density is expanded in terms of the $\chi_\lambda(\mathbf{r})$ basis functions and of the first-order density matrix $P_{\sigma\lambda}$. The solute–solvent interaction matrix elements (1.6) can be written as:

$$\begin{aligned} \langle \mu | \hat{W} | \nu \rangle &= \sum_a Z_a \int d^3r \mathbf{G}^B(\mathbf{R}_a, \mathbf{r}) \chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r}) \\ &\quad - \sum_{\lambda\sigma} P_{\sigma\lambda} \iint d^3r d^3r' \chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r}) \mathbf{G}^B(\mathbf{r}, \mathbf{r}') \chi_\lambda^*(\mathbf{r}') \chi_\sigma(\mathbf{r}'). \end{aligned} \quad (1.8)$$

These integrals are analogous to the usual Coulomb and nuclear attraction integrals, where the Coulomb-kernel has been replaced by the *effective interaction kernel* $G^B(\mathbf{r}, \mathbf{r}')$.

In the following, the names “reaction potential response function” and “effective interaction kernel” will be used practically as synonyms. In effect, there are two complementary views of a charge distribution in a polarizable surrounding. One possibility is to consider the interaction of the charge distribution with the potential of the induced charge density of the surroundings, i.e. with the reaction potential. Alternatively, the polarizable surroundings can be regarded as the mediator of an effective interaction (analogous to the usual Coulomb interaction, mediated by the vacuum). These views are just different readings of the same mathematical expression of the energy of charge distribution on a polarizable environment.

The quantum chemical implementation of the above solute-only model Schrödinger equation proceeds through the specification of the above matrix elements, usually through an approximate representation of the solute charge density $\hat{\rho}_r$. One of the following three possibilities can be considered:

- exact solute charge density,
- multi-center (distributed) multipole expansion,
- one-center (molecular) multipole expansion.

An important feature is that the representation of the solute charge density should be identical both in the perturbation operator and in the reaction potential expression. The use of different (usually approximate) operators in these two places may lead eventually to the violation of the variation principle [25,37].

The first possibility, the exact calculation of all integrals of the above type, may be impractical even for simple solvent models and one may wish to introduce reasonable approximations by replacing the elementary charge distributions of the orbital products by their multipolar expansion. This kind of approximation has been used to accelerate integral evaluation in extended systems, like crystals [40], and has been proposed to evaluate intermolecular electrostatic interactions in the framework of various distributed multipole schemes [41–47].

A convenient mathematical tool to introduce multipolar expansions of the solute charge distributions in the expression of the reaction potential matrix elements is provided by the concept of equivalent charge density [48–50]. As is explained in the appendix, one can define an equivalent charge density operator, and use formally the same expressions, which are valid for continuous charge distributions. The formal equivalent charge density operator reads as

$$\hat{\rho}(r) = \sum_a \sum_n \frac{(-1)^n}{(2n-1)!!} \hat{\xi}_{\alpha\beta\dots\nu}^{(n)a} \nabla_\alpha \nabla_\beta \dots \nabla_\nu \delta(a-r), \quad (1.9)$$

where $\hat{\xi}_{\alpha\beta\dots\nu}^{(n)a}$ are operators of distributed (e.g. atomic) multiple moments, associated with the following kernel in the traceless Cartesian definition according to Buckingham:

$$\xi_{\alpha\beta\dots\nu}^{(n)}(\mathbf{r}) = \frac{(-1)^n}{n!} r^{2n+1} \frac{\partial^n}{\partial r_\alpha \partial r_\beta \dots \partial r_\nu} \left(\frac{1}{r} \right). \quad (1.10)$$

n is the order of multipole and the Greek subscripts stand for the x, y, z Cartesian components. The specific recipe of distributing the charge density is not important here: it can be one of the standard procedures [42,44,45] or any related method.

The reaction field interaction energy

$$W = \frac{1}{2} \langle \psi | \hat{\rho}_r | \psi \rangle \mathbf{G}_{r,r'}^B \langle \psi | \hat{\rho}_{r'} | \psi \rangle \quad (1.11)$$

in the multicentered multipolar approximation can be expressed as:

$$W = \frac{1}{2} \sum_{ab} \sum_{n n'} \frac{(-1)^n}{(2n-1)!(2n'-1)!!} \xi_{\alpha\beta\dots\nu}^{(n)a} \xi_{\alpha'\beta'\dots\nu'}^{(n')b} \mathbf{G}_{\alpha\beta\dots\nu, \alpha'\beta'\dots\nu'}^{ab}. \quad (1.12)$$

The effective interaction kernel tensors $\mathbf{G}_{\alpha\beta\dots\nu, \alpha'\beta'\dots\nu'}^{ab}$ are defined as:

$$\begin{aligned} \mathbf{G}_{\alpha\beta\dots\nu, \alpha'\beta'\dots\nu'}^{ab} &= (-1)^{n'} \nabla_\alpha^r \nabla_\beta^r \dots \nabla_\nu^r \nabla_{\alpha'}^{r'} \nabla_{\beta'}^{r'} \dots \nabla_{\nu'}^{r'} \mathbf{G}(\mathbf{r}, \mathbf{r}') \Big|_{r=a, r'=b} \\ &= (-1)^{n'} \nabla_\alpha^a \nabla_\beta^a \dots \nabla_\nu^a \nabla_{\alpha'}^b \nabla_{\beta'}^b \dots \nabla_{\nu'}^b \mathbf{G}^{ab}. \end{aligned} \quad (1.13)$$

The effective interaction kernels are defined with a sign factor $(-1)^{n'}$ in order to preserve the similarity with the corresponding interaction energy formula with usual Coulomb interaction kernels.

The explicit expressions for the first few effective interaction tensors are:

$$\mathbf{G}_\alpha^{ab} = \nabla_\alpha^a \mathbf{G}^{ab}, \quad (1.14)$$

$$\mathbf{G}_\alpha^{ba} = -\nabla_\alpha^b \mathbf{G}^{ab}, \quad (1.15)$$

$$\mathbf{G}_{\alpha,\beta}^{ab} = -\nabla_\alpha^a \nabla_\beta^b \mathbf{G}^{ab}, \quad (1.16)$$

$$\mathbf{G}_{\alpha\beta}^{ab} = \nabla_\alpha^a \nabla_\beta^a \mathbf{G}^{ab}, \quad (1.17)$$

$$\mathbf{G}_{\alpha\beta}^{ba} = \nabla_\alpha^b \nabla_\beta^b \mathbf{G}^{ab}. \quad (1.18)$$

The solute–solvent electrostatic energy becomes in this approximation a sum of multipolar terms of different order:

$$\begin{aligned} W &= \frac{1}{2} \sum_a \sum_b \left\{ Q^a \mathbf{G}^{ab} Q^b + Q^a \mathbf{G}_\alpha^{ba} \mu_\alpha^b - \mu_\alpha^a \mathbf{G}_\alpha^{ab} Q^b \right. \\ &\quad \left. - \mu_\alpha^a \mathbf{G}_{\alpha,\beta}^{ab} \mu_\beta^b + \frac{1}{3} Q^a \mathbf{G}_{\alpha\beta}^{ba} \Theta_{\alpha\beta}^b + \frac{1}{3} \Theta_{\alpha\beta}^a \mathbf{G}_{\alpha\beta}^{ab} Q^b + \dots \right\}. \end{aligned} \quad (1.19)$$

The components of the effective multipolar interaction kernels are defined as successive derivatives of the reaction potential response functions, in strict analogy with the usual Coulomb interaction tensors. A considerable difference is that while the Coulomb interaction is isotropic, the \mathbf{G} -tensors reflect the eventual anisotropy of the polarizable environment. For example, one has for the Coulomb tensors

$$T_{\alpha}^{ab} = -T_{\alpha}^{ba}, \quad (1.20)$$

but

$$\mathbf{G}_{\alpha}^{ab} \neq -\mathbf{G}_{\alpha}^{ba}. \quad (1.21)$$

The use of the multicentered multipolar expansion of the solute charge distribution is indispensable to treat larger systems with a reasonable accuracy.

The organization of the paper is as follows. First, in section 2, some of the continuum models will be overviewed and the explicit form of the effective Hamiltonian will be given in terms of reaction potential response functions and approximate charge density and/or multipole operators.

A quantum chemical embedding equation will be derived in section 3 for a solute subsystem, coupled to an electronically polarizable surrounding with fixed nuclear configuration. This model is developed further to a statistical mechanical mean field model.

The special case of a system composed of identical molecules is discussed in section 4. The translational symmetry imposes the equivalence of the constituents in the case of the crystals, while for molecular liquids, this equivalence holds only in the sense of a mean field model.

In all examples, the emphasis will be laid on the derivation of the reaction potential response function. Eventual computational realizations of the models are also briefly discussed, pointing out the approximations used by them for the representation of the solute charge density.

2. Embedding in dielectric continuum

The overwhelming majority of quantum chemical solvent effect calculations uses dielectric continuum methods, based on the model of a solute sitting in a cavity in a continuous dielectric medium.

A considerable effort has been devoted to refine the method, starting from the simple case of a spherical cavity to more general cavities, like ellipsoids or other forms, which are better adapted to the molecular structure (geometry) of the solute. Another attempt to generalize the continuum models was to drop the uniformity of the dielectric. It should not be forgotten, however, that the validity of these continuum models is quite limited. Therefore, sophisticated refinements of such a crude model, where the solvent is a structureless macroscopic body, seem to be hardly justifiable.

On the other hand, simple dielectric models are able to reproduce the most essential qualitative features of the solvent reaction potential response function and

they provide an invaluable tool for obtaining a qualitative–semiquantitative idea about the possible role of solvent effects, even when our knowledge about the solvent is very limited.

The fundamental equations yielding the reaction potential inside a cavity embedded in a dielectric medium can be found in many papers and textbooks [48]. Instead of rederiving these formulae for different cavity shapes, explicit expressions will be given directly for the reaction potential response function. Some improvements with respect to the conventional calculation of the reaction potential can be proposed using the distributed multipole expansion of the molecular charge distribution.

2.1. CONTINUUM MODELS WITH REGULAR CAVITY SHAPE

Although cavities of simple shapes, like spheres or ellipsoids, are not always well-adapted to the envelope of the molecular electronic charge density, their advantage is that the reaction potential response function takes a closed analytical form in these cases.

2.1.1. Spherical cavity in a dielectric continuum

The simplest form of the solute cavity is a sphere with radius a . The solution of the Laplace equation for a charge distribution sitting inside the cavity is relatively straightforward [48,51]. The standard expression of the reaction potential response function $\mathbf{G}(\mathbf{r}_i, \mathbf{r}_j)$ is

$$\mathbf{G}(\mathbf{r}_i, \mathbf{r}_j) = \sum_{n=0}^{\infty} f_n (r_i r_j)^n P_n(\cos \gamma_{ij}), \quad (2.1)$$

where $P_n(x)$ are the associated Legendre functions and γ_{ij} is the angle of vectors \mathbf{r}_i and \mathbf{r}_j . The vector \mathbf{r}_i pointing from the center of the cavity to the i th point of the charge distribution is characterized by the polar coordinates $(r_i, \theta_i, \phi_i) = (r_i, \omega_i)$.

According to the addition theorem

$$P_n(\cos \gamma_{ij}) = \frac{4\pi}{2n+1} \sum_{m=-n}^n Y_{nm}^*(\omega_i) Y_{nm}(\omega_j), \quad (2.2)$$

the associated Legendre functions can be expanded in the spherical harmonics $Y_{nm}(\omega_i)$. Introducing the modified spherical harmonic $C_{nm}(\omega)$:

$$C_{nm}(\omega) = \sqrt{\frac{4\pi}{2n+1}} Y_{nm}(\omega) \quad (2.3)$$

and the regular spherical harmonic $R_{nm}(\mathbf{r})$:

$$R_{nm}(\mathbf{r}) = r^n C_{nm}(\omega), \quad (2.4)$$

the following expression is obtained for the reaction potential response function:

$$G(r_i, r_j) = \sum_{n=0}^{\infty} \sum_{m=-n}^n f_n R_{nm}(r_i) R_{nm}(r_j). \quad (2.5)$$

The reaction potential factors f_n depend on the dielectric constant ε and the radius of the cavity a . For a homogeneous dielectric medium, one has [51]

$$f_n(\varepsilon, a) = \frac{(1 - \varepsilon)(n + 1)}{\varepsilon(n + 1) + 1} \frac{1}{a^{2n+1}}. \quad (2.6)$$

An obvious shortcoming of the homogeneous dielectric medium model is that it does not take into account the existence of a cybotactic region around the solute. The fact that the solvent structure is different from that of the bulk can be accounted for by considering a nonuniform dielectric constant.

In the spherical cavity model, proposed by Beveridge and Schnuelle [52], the dielectric constant in the immediate neighborhood of the cavity is different from the bulk value ε_0 . The molecule is sitting inside a cavity of radius a , characterized by ε_i . The internal cavity is surrounded by an intermediate region ($a \leq r \leq b$), where the dielectric constant is ε_{loc} . The corresponding reaction potential factors are given by the expressions:

$$f_n(\varepsilon_0, \varepsilon_{loc}, a, b) = \frac{(n + 1)(1 - \varepsilon'_a)}{(n + 1)\varepsilon'_a + n} \frac{1}{a^{2n+1}} + \frac{(n + 1)(1 - \varepsilon_b)}{(n + 1)\varepsilon_b + n} \left[1 - \frac{n(1 - \varepsilon'_a)}{(n + 1)\varepsilon'_a + n} \right] \frac{1}{b^{2n+1}}, \quad (2.7)$$

where $\varepsilon_a = \varepsilon_{loc}/\varepsilon_i$, $\varepsilon_b = \varepsilon_0/\varepsilon_{loc}$, and

$$\varepsilon'_a = \varepsilon_a \left[1 + \frac{(n + 1)(1 - \varepsilon_a)(1 - \varepsilon_b)}{(n + 1)\varepsilon_b + n} \frac{a^{2n+1}}{b^{2n+1}} \right]^{-1}. \quad (2.8)$$

Other forms of the reaction potential factors corresponding to a nonuniform dielectric medium can also be found in the literature. For example, Block and Walker studied a dipolar solute in a spherical cavity embedded in a medium with an exponentially varying dielectric constant [53], and Raudino et al. considered a diffuse interface of two dielectric regions with different permittivities [54].

Exact molecular charge distribution in a spherical cavity

In most of the applications of the spherical cavity model, the charge density operator is “exact” and the solute–solvent interaction energy is

$$W = \frac{1}{2} \sum_n \sum_{m=-n}^n f_n \langle \hat{Q}_{nm} \rangle \langle \hat{Q}_{nm} \rangle, \quad (2.9)$$

where $\langle \hat{Q}_{nm} \rangle$ is the expectation value of the molecular spherical harmonic multipole moment component of order n

$$\langle \hat{Q}_{nm} \rangle = \int d^3r \langle \psi | \hat{\rho}(r) | \psi \rangle R_{nm}(r). \quad (2.10)$$

Although the representation of the charge density operator is formally “exact” in this approach, one has to truncate the molecular multipole moment components at relatively low order. This kind of method has been extensively used by the Nancy group [4,6] and by Ågren and coworkers in Sweden [55].

Distributed multipoles in a spherical cavity

An alternative approach, which has been explored until now only in the context of classical molecular charge densities, consists in using a distributed multipoles approximation of the molecular charge density [56].

Let us suppose that the molecular charge density is represented by a set of atomic (or other kind of distributed) multipole moments $\xi_{\alpha\beta\dots\nu}^{(n)a}$. The solute–solvent interaction energy is:

$$W = \frac{1}{2} \sum_{ab} \sum_{l'l'} \frac{(-1)^l}{(2l-1)!!(2l'-1)!!} \xi_{\alpha\beta\dots\nu}^{(l)a} \xi_{\alpha'\beta'\dots\nu'}^{(l')b} \mathbf{G}_{\alpha\beta\dots\nu,\alpha'\beta'\dots\nu'}^{ab}, \quad (2.11)$$

where the reaction potential response tensor elements are:

$$\begin{aligned} & \mathbf{G}_{\alpha\beta\dots\nu,\alpha'\beta'\dots\nu'}^{ab} \\ &= (-1)^{n'} \nabla_{\alpha}^a \nabla_{\beta}^a \dots \nabla_{\nu}^a \nabla_{\alpha'}^b \nabla_{\beta'}^b \dots \nabla_{\nu'}^b \sum_n \sum_{m=-n}^n f_n R_{nm}(r_a) R_{nm}(r_b). \end{aligned} \quad (2.11)$$

A possible advantage of this expression is that precise results can be obtained by relatively low-order distributed multipole moments $\xi_{\alpha\beta\dots\nu}^{(l)a}$, provided that the sum over n is sufficiently convergent.

2.1.2. Ellipsoidal cavity in uniform dielectrics

The shape of the cavity should follow as closely as possible the molecular shape and in effect the spherical cavity model often turns out to be inappropriate for molecules with strongly non-spherical shape.

Rivail and Terryn [57] derived analytical expressions for the electrostatic energy of a charge distribution in an ellipsoidal cavity. The solution of the Laplace equation for this case can be most conveniently expanded in terms of ellipsoidal multipole moment functions \tilde{Q}_{LM} of the charge distribution sitting in the cavity.

The reaction field response function in this model is:

$$\mathbf{G}(\mathbf{r}_i, \mathbf{r}_j) = \sum_L \sum_{M=0}^{2L} \mathcal{F}_{LM} \tilde{R}_{LM}(\mathbf{r}_i) \tilde{R}_{LM}(\mathbf{r}_j). \quad (2.13)$$

For practical calculations, it is more convenient to expand the ellipsoidal multipoles in terms of the usual spherical harmonic multipole moment components R_{lm} , where l is of like parity as L and $l \leq L$. Expanding the ellipsoidal multipoles in terms of spherical moments,

$$\tilde{R}_{LM}(\mathbf{r}) = \sum_{l=0}^L \sum_{m=-l}^l \mathcal{A}_{LM,lm} R_{lm}(\mathbf{r}), \quad (2.14)$$

the reaction potential response function can be cast in a similar form as in the spherical cavity case:

$$\mathbf{G}(\mathbf{r}_i, \mathbf{r}_j) = \sum_{lm} \sum_{l'm'} f_{lm,l'm'} R_{lm}(\mathbf{r}_i) R_{l'm'}(\mathbf{r}_j), \quad (2.15)$$

where the reaction potential factor [58] reads as

$$f_{lm,l'm'} = \sum_{LM} \mathcal{A}_{lm,LM} \mathcal{F}_{LM} \mathcal{A}_{LM,l'm'}. \quad (2.16)$$

Remark that these reaction potential factors depend not only on l , the order of the spherical multipole moment, but also on m , the angular quantum number, which reflects that the reaction potential is not spherically symmetrical in the ellipsoidal cavity. Cross-terms appear also, involving multipole components of different order, which were missing in the more symmetrical spherical cavity case.

2.2. CONTINUUM MODELS WITH IRREGULAR CAVITY SHAPE

Considerable effort has been devoted to the development of continuum models with cavity shapes, which are better adapted to the molecular shape than simple spheres or ellipsoids. A reasonable choice is to construct the molecular cavity from interpenetrating Van der Waals spheres of the constituting atoms. The price to pay for this refinement is that the reaction potential response functions can no longer be calculated analytically.

2.2.1. Multipolar reaction field factors

The classical method to find the multipolar reaction field factors $f_l(\epsilon)$ or $f_{lm,l'm'}(\epsilon)$ is to write the general analytical expression of the potential inside and outside the cavity, and determine the reaction field factors from the continuity conditions on the cavity surface.

As has been pointed out recently by Rivail et al. [6], this procedure, which leads to closed expressions in the case of regular cavities, like spheres or ellipsoids, can be applied in a straightforward manner to a numerical determination of the reaction field factors for arbitrary cavity shapes.

The potential inside the cavity is the superposition of the multipolar potential $V_M(\mathbf{r})$:

$$V_M(\mathbf{r}) = \sum_{lm} I_{lm}(\mathbf{r}) Q_{lm} \quad (2.17)$$

and of the reaction potential $V_R(\mathbf{r})$:

$$V_R(\mathbf{r}) = \sum_{lm} \sum_{l'm'} f_{lm,l'm'} R_{lm}(\mathbf{r}) Q_{l'm'} \quad (2.18)$$

Here, $R_{lm}(\mathbf{r})$ is the regular spherical harmonic, defined in eq. (2.4), and $I_{lm}(\mathbf{r})$ is the irregular spherical harmonic:

$$I_{lm}(\mathbf{r}) = \sum_{lm} r^{-(l+1)} C_{lm}(\omega). \quad (2.19)$$

Q_{lm} is the multipole moment component of the solute charge distribution in the cavity and $f_{lm,l'm'}$ is the multipolar reaction field factor.

The potential outside the cavity must satisfy the Laplace equation, which has the general solution:

$$V_S(\mathbf{r}) = \sum_{lm} \gamma_{lm} I_{lm}(\mathbf{r}). \quad (2.20)$$

The continuity of the potential means that for an arbitrary point s on the surface of the cavity:

$$V_M(s) + V_R(s) = V_S(s). \quad (2.21)$$

The normal components of the electric field must satisfy

$$[\nabla V_M(s)]_n + [\nabla V_R(s)]_n = \varepsilon [\nabla V_S(s)]_n, \quad (2.22)$$

where ε is the relative dielectric constant of the continuum. The tangential components of the field satisfy the simple continuity condition:

$$[\nabla V_M(s)]_t + [\nabla V_R(s)]_t = [\nabla V_S(s)]_t. \quad (2.23)$$

These equations, applied to a sufficiently large number of surface points, lead to an overdetermined system for the unknown multipolar reaction field factors $f_{LM,lm}$:

$$\begin{aligned}
 & I_{l'm'}^n(s)I_{LM}^n(s) - \varepsilon I_{l'm'}^n(s)I_{LM}(s) \\
 &= \sum_{lm} f_{LM,lm} [\varepsilon R_{lm}(s)I_{l'm'}^n(s) - R_{lm}^n(s)I_{l'm'}(s)].
 \end{aligned}
 \tag{2.24}$$

The corresponding expression of the reaction potential response function is formally identical with the case of the ellipsoidal cavity:

$$\mathbf{G}(\mathbf{r}_i, \mathbf{r}_j) = \sum_{lm} \sum_{l'm'} f_{lm,l'm'} R_{lm}(\mathbf{r}_i) R_{l'm'}(\mathbf{r}_j).
 \tag{2.25}$$

2.2.2. Integral equation method of Durand

The case of a cavity of general shape has been discussed by the Pisa group [8,59], Constanciel [36] and Claverie [60]. The solution of the electrostatic problem is based on an integral equation [61], which determines the polarization charge density $\sigma(s)$ on the cavity surface S containing the charge distribution $\rho(\mathbf{r})$ of the solute:

$$f(\varepsilon)\sigma(s) = \mathbf{n}(s) \cdot \mathbf{E}^0(s) - \int_S d^2s' \mathbf{n}(s') \cdot \mathbf{T}(s, s')\sigma(s'),
 \tag{2.26}$$

where $\mathbf{n}(s)$ is the normal vector directed outwards from the surface at the surface point s . $\mathbf{E}^0(s)$ is the electric field of the solute charges:

$$\mathbf{E}^0(s) = - \int d^3r \mathbf{T}(s, \mathbf{r})\rho(\mathbf{r}).
 \tag{2.27}$$

$\mathbf{T}(s, \mathbf{r})$ is the charge–dipole interaction kernel:

$$\mathbf{T}(s, \mathbf{r}) = - \frac{1}{4\pi\varepsilon_0} \frac{\mathbf{s} - \mathbf{r}}{|\mathbf{s} - \mathbf{r}|^3},
 \tag{2.28}$$

and $f(\varepsilon)$ is a factor depending on the solvent dielectric constant:

$$f(\varepsilon) = \frac{1}{2\varepsilon_0} \frac{1 + \varepsilon}{1 - \varepsilon}.
 \tag{2.29}$$

A thorough analysis of this integral equation in the context of continuum models of the solvent effect description has been given by Constanciel [36]. His aim was twofold. First, to obtain a discretized form of eq. (2.26), which is adapted to numerical calculations, and secondly, to get some insight into the nature of approximations inherent to the so-called solvation models.

In the forthcoming discussion, addressed to the first issue, we follow quite closely the derivation given by Constanciel.

One can divide the surface S of the cavity into M disjoint subsets $S = \cup_i^M S_i$. A discretized matrix equation can be obtained by integrating separately on the s_i surface elements and summing these contributions afterwards:

$$Q_i = Q_i^0 + \sum_j \omega_{ij} Q_j. \quad (2.30)$$

In this equation, the total surface charge Q_i , the zeroth order surface charge Q_i^0 and the interaction matrix ω_{ij} are defined by:

$$Q_i = \int_{S_i} d^2s \sigma(s), \quad (2.31)$$

$$f(\epsilon) Q_i^0 = \int_{S_i} d^2s \mathbf{n}(s) \cdot \mathbf{E}^0(s), \quad (2.32)$$

$$f(\epsilon) \omega_{ij} = - \int_{S_i} d^2s \mathbf{n}(s) \cdot \mathbf{T}(s, s_j). \quad (2.33)$$

Introducing the M -element vectors \mathbf{Q} , \mathbf{Q}^0 and the $M \times M$ matrix $\boldsymbol{\omega}$. (2.30) reads

$$\mathbf{Q} = \mathbf{Q}^0 + \boldsymbol{\omega} \mathbf{Q}, \quad (2.34)$$

which can be solved formally, yielding

$$\mathbf{Q} = (\mathbf{I} - \boldsymbol{\omega})^{-1} \mathbf{Q}^0 = \mathbf{S} \mathbf{Q}^0. \quad (2.35)$$

Here, the screening matrix \mathbf{S} is defined as

$$\mathbf{S} = (\mathbf{I} - \boldsymbol{\omega})^{-1}. \quad (2.36)$$

The reaction potential Π_r is the potential of the surface charge distribution. Taking into account eqs. (2.27) and (2.32), and introducing

$$\bar{\omega}(s_i, \mathbf{r}) = \int_{S_i} d^2s \mathbf{n}(s) \cdot \mathbf{T}(s, \mathbf{r}), \quad (2.37)$$

the reaction potential response function is

$$\tilde{\mathbf{G}}_{r,r'} = \sum_{ij} T(\mathbf{r}, s_i) S_{ij} \bar{\omega}(s_j, \mathbf{r}'), \quad (2.38)$$

where $T(\mathbf{r}, s_i) = |\mathbf{r} - s_i|^{-1}$ is the Coulomb interaction kernel.

As was pointed out by Constanciel [36], this reaction potential response function is not symmetrical with respect to the interchange of \mathbf{r} and \mathbf{r}' as a consequence of the discretized approximation. Since a non-symmetric reaction potential response

function is not consistent with the variational treatment of the solute–solvent free energy, it is recommended to symmetrize $\bar{\mathbf{G}}_{r,r'}$,

$$\mathbf{G}_{r,r'} = \frac{1}{2} \sum_{ij} \{T(r, s_i) S_{ij} \bar{\omega}(s_j, r') + T(r', s_i) S_{ij} \bar{\omega}(s_j, r)\}. \quad (2.39)$$

This expression provides the most general, essentially numerical, solution of the reaction potential response function in a cavity of general shape.

Constanciel suggested the use of Korobov's grid technique, originally used by Claverie et al. in a similar context [62], to calculate the integrals needed for the definition of the ω_{ij} matrices. An alternative approach, avoiding the explicit numerical integrations, has been proposed and implemented by the Pisa group.

2.2.3. Pisa model

In contrast to the direct solution of the above equation by matrix inversion, suggested by Constanciel [36], the Pisa group developed an iterative scheme [8, 59], based on the recursion formula:

$$\mathbf{Q}^n = \mathbf{Q}^0 + \omega \mathbf{Q}^{n-1}, \quad (2.40)$$

where \mathbf{Q}^n is the n th approximation to the surface charges.

Miertuš et al. [8, 59] approximated Q_i^0 and ω_{ij} by the simplified expressions, without doing any numerical integration on the surface elements, as:

$$f(\epsilon) Q_i^0 = \Delta s_i \mathbf{n}_i \cdot \mathbf{E}_i^0, \quad (2.41)$$

$$f(\epsilon) \omega_{ij} = -\Delta s_i \mathbf{n}_i \cdot \mathbf{T}_{ij}, \quad (2.42)$$

$$f(\epsilon) \omega_{ii} = \left(1 + \left(\frac{\Delta s_i}{4\pi R_i^2} \right)^{1/2} \right), \quad (2.43)$$

where R_i is the radius of the sphere S_i (Van der Waals sphere) associated with the point i .

Unfortunately, according to our best knowledge, no direct comparisons were done of this scheme with the Korobov grid technique/direct matrix inversion procedure. Therefore, it is quite difficult to judge a priori the eventual advantages of the two different computational approaches.

2.3. SOLVATON AND GENERALIZED BORN MODELS

Finally, one has to mention the continuum model, which was implemented first in a self-consistent quantum chemical calculation: the solvaton model [11]. This model was introduced in a rather heuristic manner as a kind of generalization of the Born model for ionic solvation [63].

The difficulties of interpretation of the underlying physical model provide at least a partial explanation of the surprisingly high number of erroneous publications with this kind of model [15, 17, 64], and of the many slightly different versions of the solvaton theory. A quite satisfactory rationalization of the solvaton models has been given by Constanciel [36], who was able to derive the Generalized Born formula [63] and the Extended Generalized Born formula [25] from the integral eq. (2.26). He shows that quite drastic approximations are needed for that and explained the failure of these models. Nevertheless, in the context of semi-empirical quantum chemical schemes, the use of these models can be judged as acceptable, and there is a continuing interest in novel parametrization schemes of the solvaton models [65].

A possible interpretation of the solvaton models emerges from a picture where the corresponding reaction potential response function is considered as the kernel of a uniformly screened interaction of the solute charges:

$$\mathbf{G}_{r,r} = g(\epsilon) \frac{1}{|\mathbf{r} - \mathbf{r}|}, \quad (2.44)$$

where $g(\epsilon)$ is a simple function of the solvent dielectric constant. This interpretation points to the major deficiency of the underlying physical model, supported by the analysis of Constanciel: implicitly, all the solute charges are sitting in their own cavity, immersed in a dielectric medium. Obviously, this is a quite unrealistic picture of a solvated molecule.

3. Embedding in discrete environment

With the development of diffraction and spectroscopic techniques and increasing computer simulation possibilities, the construction of reliable microscopic models of liquid and condensed phase solutions becomes almost a routine task. Although the simple continuum models have the advantage that one can estimate the solvent (environmental) effects on the electronic structure without detailed structural data, such a crude model is not always satisfactory.

In the following, the average reaction field model will be derived for a set of interacting molecules using quantum chemical considerations, related to the theory of intermolecular forces. First, an effective “solute-only” equation will be derived for a set of interacting solute and solvent molecules at fixed nuclear configuration, and this model is then generalized to statistical ensembles.

3.1. DISCRETE SOLVENT MODEL

Solvent effect models represent typical embedding situations, where one deals with a small system of interest, which is surrounded by a considerably larger environment, the solvent. The usual model system consists of a solute (S) subsystem and a solvent (“bath”, B), characterized by the total Hamiltonian:

$$\hat{H} = \hat{H}^S + \hat{H}^B + \hat{H}^{SB}, \quad (3.1)$$

where the \hat{H}^{SB} interaction operator can be written in the Longuet–Higgins [66] notation as:

$$\hat{H}^{SB} = \iint d^3r d^3r' \hat{\rho}^S(\mathbf{r}) T(\mathbf{r}, \mathbf{r}') \hat{\rho}^B(\mathbf{r}'). \quad (3.2)$$

This operator can be written with the summation convention introduced before as

$$\hat{H}^{SB} = \hat{\rho}_r^S T_{r,r'} \hat{\rho}_{r'}^B. \quad (3.3)$$

Here, $\hat{\rho}^X(\mathbf{r})$ is the total charge density operator of the system $X (= S \text{ or } B)$ involving N_X nuclei and n_X electrons:

$$\hat{\rho}^X(\mathbf{r}) = \sum_a^{N_X} Z_a \delta(\mathbf{r} - \mathbf{R}_a) - \sum_i^{n_X} \delta(\mathbf{r} - \mathbf{r}_i). \quad (3.4)$$

$T(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$ is the Coulomb interaction kernel and $\delta(\mathbf{r})$ is the three-dimensional delta function.

The usual Born–Oppenheimer approximation can be used to separate the electronic and nuclear motions in the solute–solvent supersystem, leading to an electronic Hamiltonian, which depends parametrically on the nuclear coordinates. According to the general philosophy of embedding, a model Hamiltonian should be constructed which depends explicitly only on the electronic coordinates of the solute subsystem.

3.2. SOLUTE ELECTRONIC STRUCTURE AT FIXED SOLVENT CONFIGURATION

3.2.1. Solute-only Schrödinger equation

It shall be assumed that the solute and solvent subsystems are separated from each other by a distance, where the overlap between them is sufficiently small and the total wave function can be expressed as a simple Hartree product of the n_S - and n_B -electron wave functions ψ^S and ψ^B :

$$|\Psi\rangle \approx |\psi^S \psi^B\rangle. \quad (3.5)$$

In practice, this means that we have to assume that a repulsive potential energy term E_{rep}^{SB} keeps the subsystems in the region of small or negligible overlap, thus rendering acceptable the product approximation.

Another important physical interaction, neglected in the simple mean field approximation, which will be introduced in the following is the dispersion energy, E_{disp}^{SB} . Since the dispersion forces, like the repulsion forces at the negligible overlap region, have little influence on the electronic structure of the constituents, we can

neglect their effect on the electronic Schrödinger equation, but not in the total energy. Accordingly, we can write the approximate total energy of the solute–solvent supersystem as the energy in the Hartree approximation, corrected by the physically most important repulsion and dispersion terms:

$$E = \langle \Psi | \hat{H} | \Psi \rangle \approx \langle \psi^S \psi^B | \hat{H} | \psi^S \psi^B \rangle + E_{\text{rep}}^{SB} + E_{\text{disp}}^{SB}. \quad (3.6)$$

In the simple product approximation, the electronic Schrödinger equation for the total system at a fixed nuclear configuration is:

$$\{\hat{H}^S + \hat{H}^B + \hat{H}^{SB}\} | \psi^S \psi^B \rangle = \mathcal{E} | \psi^S \psi^B \rangle. \quad (3.7)$$

Let us introduce the *mean field approximation*, which leads to the following set of coupled equations:

$$\begin{aligned} \{\hat{H}^S + \langle \hat{H}^{SB} \rangle_B\} | \psi_k^S \rangle &= \{\mathcal{E} - \langle \hat{H}^B \rangle_B\} | \psi_k^S \rangle, \\ \{\hat{H}^B + \langle \hat{H}^{SB} \rangle_S\} | \psi_0^B \rangle &= \{\mathcal{E} - \langle \hat{H}^S \rangle_S\} | \psi_0^B \rangle. \end{aligned} \quad (3.8)$$

Here, the brackets stand for normalized expectation values

$$\langle \hat{A} \rangle_X = \frac{\langle \psi^X | \hat{A} | \psi^X \rangle}{\langle \psi^X | \psi^X \rangle}. \quad (3.9)$$

The solvent is supposed to be in its ground electronic state, and the solute can be, in principle, in an arbitrary ground or excited electronic state k .

By replacing the exact intermolecular potential operator \hat{H}^{SB} with its average value $\langle \hat{H}^{SB} \rangle$, the intersystem correlation effects are neglected. This error has been compensated for by adding a dispersion energy term E_{disp}^{SB} to the total energy at each nuclear configuration of the solvent–solute system.

The coupled mean field eqs. (3.8) can be solved at different levels, namely

- (1) a self-consistent solution can be obtained iteratively by optimizing both subsystems in the field of the other;
- (2) the solvent subsystem can be kept rigid and the solute wave function optimized in the permanent field of the solvent;
- (3) linear polarization of the solvent subsystem can be allowed and the solute wave function optimized in the permanent + polarization potential of the solvent.

The iterative solution, when both subsystems are treated on an equal footing, has been advocated by Otto and Ladik in their Mutually Consistent Field method [67–71], by Weinstein in the Interaction Modified Field Approach [72], and in the Hartree–Hartree–Fock method [73–75]. A very similar iterative procedure has

been used by several authors to describe the electrostatic interaction of strictly localized two-electron bonds in large covalent systems [76].

A trivial way to uncouple the mean field eqs. (3.8) is to evaluate the mean potential from the charge density of the unperturbed solvent wave functions. This method has been frequently applied for solvent effect problems in the context of the so-called discrete models [38,39].

As far as the solute is polar, the mutual polarization of the two subsystems cannot be neglected. In such cases it seems reasonable to uncouple the mean field equations by the following first-order perturbational Ansatz on the solvent wave function $|\psi_0^B\rangle$:

$$|\psi_0^B\rangle = |\phi_0^B\rangle - \sum_{b \neq 0} \frac{\langle \phi_b^B | \hat{V}_k^S | \phi_0^B \rangle}{\Delta E^B(0 \rightarrow b)} |\phi_b^B\rangle = |\phi_0^B\rangle + \hat{R}_0^B \hat{V}_k^S |\phi_0^B\rangle. \quad (3.10)$$

Here, $|\phi_b^B\rangle$ is an eigenfunction of the unperturbed solvent Hamiltonian operator with eigenvalues E_b^B :

$$\hat{H}^B |\phi_b^B\rangle = E_b^B |\phi_b^B\rangle, \quad (3.11)$$

the excitation energies are defined as

$$\Delta E^B(0 \rightarrow b) = E_b^B - E_0^B,$$

and \hat{R}_0^B is the reduced resolvent associated with B :

$$\hat{R}_0^B = \frac{1 - |\phi_0^B\rangle\langle\phi_0^B|}{E_0^B - \hat{H}^B}. \quad (3.12)$$

The operator of the mean potential created by the solute is

$$\begin{aligned} \hat{V}_k^S &= \langle \psi_k^S | \hat{H}^{SB} | \psi_k^S \rangle \\ &= \iint d^3r d^3r' \hat{\rho}^B(\mathbf{r}) T(\mathbf{r}, \mathbf{r}') \langle \psi_k^S | \hat{\rho}^S(\mathbf{r}') | \psi_k^S \rangle \\ &= \hat{\rho}_r^B T_{r,r'} \langle \psi_k^S | \hat{\rho}_r^S | \psi_k^S \rangle. \end{aligned} \quad (3.13)$$

In the last expression, the simplified notation introduced earlier has been used again, where repeated lower indices \mathbf{r}, \mathbf{r}' mean integration over these space variables.

By virtue of this first-order Ansatz, eq. (3.10), the solute Schrödinger equation has been uncoupled, and the following solute-only effective equation is obtained:

$$\begin{aligned}
& \left\{ \hat{H}^S + \langle \phi_0^B | \hat{H}^{SB} | \phi_0^B \rangle \right. \\
& \quad - \sum_{b(\neq 0)} \frac{\langle \phi_0^B | \hat{H}^{SB} | \phi_b^B \rangle \langle \phi_b^B | \hat{V}_k^S | \phi_0^B \rangle}{\Delta E^B(0 \rightarrow b)} \\
& \quad \left. - \sum_{b(\neq 0)} \frac{\langle \phi_0^B | \hat{V}_k^S | \phi_b^B \rangle \langle \phi_b^B | \hat{H}^{SB} | \phi_0^B \rangle}{\Delta E^B(0 \rightarrow b)} \right\} | \psi_k^S \rangle = E_k^S | \psi_k^S \rangle. \quad (3.14)
\end{aligned}$$

The first perturbation term is the permanent electrostatic potential \hat{V}^B due to the unperturbed solvent charge density:

$$\hat{V}^B = \langle \phi_0^B | \hat{H}^{SB} | \phi_0^B \rangle = \hat{\rho}_r^S V_r^B = \hat{\rho}_{r,r'}^S T_{r,r'} \langle \hat{\rho}_{r'}^B \rangle_0. \quad (3.15)$$

The two further terms correspond to the reaction (or polarization) potential. This can be made apparent if we define the charge density response function [77] (generalized polarizability function) of the solvent $\mathbf{C}_{r'',r'''}^B$, which for real wave functions reads as:

$$\mathbf{C}_{r'',r'''}^B = 2 \sum_{b(\neq 0)} \frac{\langle \phi_0^B | \hat{\rho}_{r''}^B | \phi_b^B \rangle \langle \phi_b^B | \hat{\rho}_{r'''}^B | \phi_0^B \rangle}{\Delta E^B(0 \rightarrow b)} = -2 \langle \phi_0^B | \hat{\rho}_{r''}^B \hat{R}_0^B \hat{\rho}_{r'''}^B | \phi_0^B \rangle. \quad (3.16)$$

Writing explicitly the expectation value over the solute wave function and introducing the solvent charge density response function, the following expression is obtained for $\hat{\Pi}_k^B$, the reaction potential operator:

$$\hat{\Pi}_k^B = -\hat{\rho}_r^S T_{r,r''} \mathbf{C}_{r'',r'''}^B T_{r',r'''} \langle \psi_k^S | \hat{\rho}_{r'}^S | \psi_k^S \rangle = \hat{\rho}_r^S \mathbf{G}_{r,r'}^{B,el} \langle \hat{\rho}_{r'}^S \rangle_k. \quad (3.17)$$

A further simplification can be achieved by carrying out the integration over the solvent variables. The reaction potential response function $\mathbf{G}_{r,r'}^{B,el}$ is defined as:

$$\mathbf{G}_{r,r'}^{B,el} = -T_{r,r''} \mathbf{C}_{r'',r'''}^B T_{r',r'''} \quad (3.18)$$

The above sign convention has been chosen in order to remain consistent with the usual choice of sign of the dipolar response function.

The reaction potential response function characterizes the linear electronic polarization of the solvent subsystem in a given geometrical arrangement with respect to the solute.

Thus, one can write the “solute-only” model Schrödinger equation:

$$\left\{ \hat{H}^S + \hat{\rho}_r^S V_r^B + \hat{\rho}_r^S \mathbf{G}_{r,r'}^{B,el} \langle \psi_k^S | \hat{\rho}_{r'}^S | \psi_k^S \rangle \right\} | \psi_k^S \rangle = E_k^S | \psi_k^S \rangle. \quad (3.19)$$

The effect of the solvent is fully characterized in the present approximation by its permanent potential V_r^B and its linear response function $\mathbf{G}_{r,r'}^{B,el}$. These quantities

can be calculated, in principle, with any required accuracy, provided that the exact solvent wave function is known. This is usually not the case, but the present theoretical framework allows us to introduce well-controlled approximations.

Equation (3.19) is consistent with the result obtained by Tapia [3, 28]. However, in contrast to Tapia's derivation, eq. (3.19) has been obtained uniquely with quantum chemical methods, without making reference to classical electrodynamical or macroscopical arguments. Such macroscopical arguments are usually invoked to interpret the difference of the expectation value of the Hamiltonian of eq. (3.19) and the corresponding total energy functional (see below).

The mathematical origin of this difference follows in a straightforward manner from the nonlinear character of the solute-only Schrödinger equation [33]. The physical interpretation for dielectric models is usually based on thermodynamic arguments [78], identifying the total energy functional with the approximate electrostatic free energy of the solute–solvent system at fixed solute nuclear configuration. This view, opposing the expectation value of the nonlinear Hamiltonian (internal energy), with the total energy functional (free energy), gives sometimes the fallacious impression that the difference has entropy origin.

Of course, this cannot be the case for the zero-temperature limit. As we shall see, this difference can be obtained in a straightforward manner from the zero-temperature quantum mechanical perturbation theory.

3.2.2. Decomposition of the solute–solvent total energy

Comparison of the solute-only model Schrödinger eq. (3.19) with the mean field eqs. (3.8) makes evident that the total energy of the solute–solvent system \mathcal{E} is related to the eigenvalue of the solute-only model Hamiltonian E_k^S by:

$$\mathcal{E} = E_k^S + \langle \psi_0^B | \hat{H}^B | \psi_0^B \rangle \langle \psi_0^B | \psi_0^B \rangle^{-1}. \quad (3.20)$$

The difference comes from the shifted energy of the linearly polarized solvent, which should be evaluated to second order. Expanding the normalization in a power series, one obtains

$$\begin{aligned} & \langle \psi_0^B | \hat{H}^B | \psi_0^B \rangle \langle \psi_0^B | \psi_0^B \rangle^{-1} \\ & \approx \left\{ E_0^B + \langle \phi_0^B | \hat{V}^S \hat{R}_0^B \hat{H}^B \hat{R}_0^B \hat{V}^S | \phi_0^B \rangle \right\} \left\{ 1 - \langle \phi_0^B | \hat{V}^S \hat{R}_0^B \hat{R}_0^B \hat{V}^S | \phi_0^B \rangle \right\}, \end{aligned}$$

which gives rise to one zeroth-order, two second-order and one fourth-order term. Consistently with the second-order approximation, used until now, this latter term will be neglected and up to second order one obtains the following result:

$$\mathcal{E} = E_k^S + E_0^B + \langle \psi_0^B | \hat{V}^S \hat{R}_0^B \hat{V}^S | \psi_0^B \rangle. \quad (3.21)$$

The zeroth-order term E_0^B is the unperturbed solvent energy. The second-order terms were rearranged by using the general relationship:

$$\langle \phi_0^B | \hat{V}^S \hat{R}_0^B (E_0^B - \hat{H}^B) \hat{R}_0^B \hat{V}^S | \phi_0^B \rangle = \langle \phi_0^B | \hat{V}^S \hat{R}_0^B \hat{V}^S | \phi_0^B \rangle. \quad (3.22)$$

Putting the expression (3.13) of the solute potential into eq. (3.22) and combining it with the definition of the electronic reaction potential response function, eqs. (3.16) and (3.18), one obtains that the energy of the polarized solvent is raised by half the reaction potential interaction energy in the linear response approximation:

$$\mathcal{E} = E_k^S + E_0^B - \frac{1}{2} \langle \psi_k^S | \hat{\rho}_r^S | \psi_k^S \rangle G_{r,r'}^{B,el} \langle \psi_k^S | \hat{\rho}_r^S | \psi_k^S \rangle. \quad (3.23)$$

It should be emphasized that the factor of 1/2 is a consequence of the linear response character of the reaction potential. If higher order (e.g. quadratic) hyperpolarizabilities of the solvent were also taken into account, these higher-order contributions would have appeared with a different factor, for example, with 1/6 in the case of the quadratic hyperpolarizabilities [79].

As has been noted in the introduction, the nonlinear solute-only Schrödinger eq. (3.19) can also be obtained by the application of the variation principle to the total energy:

$$\mathcal{E} = E_0^B + \langle \psi_k^S | \hat{H}^S + \hat{\rho}_r V_r^B + \frac{1}{2} \hat{\rho}_r^S G_{r,r'}^{B,el} \langle \psi_k^S | \hat{\rho}_r^S | \psi_k^S \rangle | \psi_k^S \rangle. \quad (3.24)$$

Such a variational approach will be followed to derive a solute-only mean-field Schrödinger equation for the nonzero temperature case.

Before treating this case, let us complete the analysis of the zero-temperature model by specifying the unperturbed solvent energy, the direct solvent potential and the solvent reaction potential response function in terms of the properties of the individual solvent molecules.

3.2.3. Approximate solvent properties

In the previous discussion, the solvent was treated as a “supermolecule” and it has been assumed that the *unperturbed* solvent wave function and corresponding *response properties* were known. These two quantities are necessary to evaluate the solvent charge density:

$$\hat{\rho}_r^B = \langle \phi^B | \hat{\rho}_r^B | \phi^B \rangle \quad (3.25)$$

and the solvent charge density response function:

$$C_{r,r'}^B = -2 \langle \phi^B | \hat{\rho}_r^B \hat{R}_0^B \hat{\rho}_{r'}^B | \phi^B \rangle. \quad (3.26)$$

(The lower index 0 of ϕ^B has been dropped for the sake of notational simplicity.)

Note that the solvent charge density response function describes a non-local response [77].

Obviously, it is usually impractical to consider the solvent as one huge supermolecule. Instead, one may divide the solvent into many subunits, the individual solvent molecules. It is reasonable to assume that these subunit wave functions are known to a sufficient accuracy. Therefore, one can expand the solvent properties by the wave functions of these subunits, the solvent molecules.

According to the spirit of our model, the solvent wave function can be expressed as the Hartree product of the non-overlapping subunit wave functions:

$$|\phi^B\rangle = |\psi^1\psi^2\psi^3\dots\rangle. \quad (3.27)$$

The ψ^j subunit wave functions are supposed to be related to the wave functions ϕ^i of the isolated solvent molecules by the first-order perturbational expression:

$$|\psi^i\rangle = |\phi^i\rangle + \hat{R}^i \hat{\rho}_p |\phi^i\rangle \sum_{j \neq i} T_{p,q} \langle \psi^j | \hat{\rho}_q | \psi^j \rangle, \quad (3.28)$$

where p and q are the space coordinate variables and \hat{R}^i is the reduced resolvent of the i th solvent molecule.

The charge distribution and the energy of the unperturbed solvent are necessary to evaluate the permanent solvent potential V_r^B and the energy of the solute E_0^B , respectively, while the approximate solvent charge density response function can be obtained by the application of first-order perturbation theory to the solvent charge density.

Solvent average potential

The solvent permanent potential V_r^B can be calculated from the solvent charge density:

$$V_r^B = T_{r,p} \langle \phi^B | \hat{\rho}_p^B | \phi^B \rangle. \quad (3.29)$$

The *solvent charge density* in the absence of the solute

$$\langle \phi^B | \hat{\rho}_r^B | \phi^B \rangle = \sum_i \langle \psi^i | \hat{\rho}_r | \psi^i \rangle \quad (3.30)$$

can be obtained from the approximate first-order wave function of the individual solvent molecules:

$$\langle \psi^i | \hat{\rho}_r | \psi^i \rangle = \langle \phi^i | \hat{\rho}_r | \phi^i \rangle - \alpha_{r,p}^i \sum_j T_{p,q}^{ij} \langle \psi^j | \hat{\rho}_q | \psi^j \rangle. \quad (3.31)$$

Here, $\alpha_{r,p}^i$ is the charge density response function (generalized polarizability) of one solvent molecule:

$$\alpha_{r,p}^i = -2\langle\phi^i|\hat{\rho}_r\hat{R}^i\hat{\rho}_p|\phi^i\rangle. \quad (3.32)$$

Equation (3.31) defines a system of linear equations for the monomer charge densities, which can be solved by iteration. (Note that all quantities refer to the absolute laboratory frame. In practical calculations, the monomer densities are given in a molecule-fixed frame, so the Coulomb interaction tensors should include the appropriate rotational transformations.) The charge density of the isolated solvent molecules is:

$$\begin{aligned} \langle\psi^i|\hat{\rho}_r|\psi^i\rangle &= \langle\phi^i|\hat{\rho}_r|\phi^i\rangle \\ &- \sum_j \alpha_{r,p}^i T_{p,q}^{ij} \left(\langle\phi^j|\hat{\rho}_q|\phi^j\rangle - \sum_k \alpha_{q,s}^j T_{s,t}^{jk} (\langle\phi^k|\hat{\rho}_t|\phi^k\rangle - \dots) \right) \\ &= \sum_j S_{r,q}^{ij} \langle\phi^j|\hat{\rho}_q|\phi^j\rangle, \end{aligned} \quad (3.33)$$

where the screening function $S_{r,q}^{ij}$ of the solvent is

$$S_{r,q}^{ij} = \delta_{r,p}\delta^{ij} - \alpha_{r,p}^i T_{p,q}^{ij} + \alpha_{r,p}^i \sum_k T_{p,s}^{ik} \alpha_{s,t}^k T_{t,q}^{kj} - \dots \quad (3.34)$$

In this expression, one can easily recognize the series expansion of the $(I + \alpha T)^{-1}$ matrix

$$S = (I + \alpha T)^{-1}, \quad (3.35)$$

and it can be approximated at first order by

$$S \approx I - \alpha T, \quad (3.36)$$

i.e. the interaction of the moments induced by the partner solvent molecules is neglected. As has been pointed out by Stone, this latter approximation is more coherent with the first-order perturbation approach, adopted for the description of the polarization [80]. In effect, a fully iterated S includes infinite order effects, while even simple third-order terms are neglected by the linear response assumption. This implies that as far as the solvent hyperpolarizability is small, the full iterative method can be justified, otherwise the use of single-molecule polarizabilities seems to be a better choice.

By virtue of expression (3.33), the solvent potential can be written as:

$$V_r^B = \sum_{ij} T_{r,s} S_{s,p}^{ij} \langle\phi^j|\hat{\rho}_p|\phi^j\rangle. \quad (3.37)$$

Neglecting self-consistency in the mutual polarization of the solvent monomers, we have an alternative expression where an inductive correction is superimposed to the potential of the unperturbed monomers:

$$V_r^B \approx \sum_i T_{r,s} \langle \phi^i | \hat{\rho}_s | \phi^i \rangle - \sum_{ij} T_{r,q} \alpha_{q',q}^i T_{q,p}^{ij} \langle \phi^j | \hat{\rho}_p | \phi^j \rangle. \quad (3.38)$$

The unperturbed solvent energy should be calculated with consistent approximations.

Approximate solvent energy

The solvent energy E_0^B

$$E_0^B = \sum_i \frac{\langle \psi^i | \hat{H}^i | \psi^i \rangle}{\langle \psi^i | \psi^i \rangle} + \frac{1}{2} \sum_{ij} \langle \psi^i | \hat{\rho}_r | \psi^i \rangle T_{r,r'}^{ij} \langle \psi^j | \hat{\rho}_{r'} | \psi^j \rangle, \quad (3.39)$$

calculated from the same wave function Ansatz as the solvent charge density:

$$|\psi^i\rangle = |\phi^i\rangle + \hat{R}^i \rho_r | \phi^i \rangle \sum_j T_{r,r'}^{ij} \langle \psi^j | \hat{\rho}_{r'} | \psi^j \rangle. \quad (3.40)$$

Inserting expression (3.33) of the solvent charge density and expanding the expectation value of the monomer Hamiltonian to second order, the following energy expression is obtained:

$$E^B = \sum_i E^i + \frac{1}{2} \sum_{ijklm} \langle \rho_p^j \rangle S_{p,q}^{jk} T_{q,r}^{ki} \alpha_{r,r'}^i T_{r',q}^{il} S_{q',p'}^{lm} \langle \rho_{p'}^m \rangle + \frac{1}{2} \sum_{ijkl} \langle \rho_r^i \rangle S_{r,p}^{ik} T_{p,q}^{kl} S_{q,r'}^{lj} \langle \rho_{r'}^j \rangle. \quad (3.41)$$

The shorthand notation $\langle \rho_r^j \rangle$ stands for the expectation value of the solvent monomer charge distributions. This can be brought to a simpler form by virtue of the relationship [81]

$$S = (I - \alpha T S), \quad (3.42)$$

which is equivalent to eq. (3.35). Using the symbolic matrix notation:

$$S T S + S T \alpha T S = S T S + (I - S) T S = T S. \quad (3.43)$$

The $T S$ matrix can be rewritten by using the series expansion of S as

$$\begin{aligned} T S &= T - T \alpha T + T \alpha T \alpha T - T \alpha T \alpha T \alpha T + \dots \\ &= T - T(\alpha - \alpha T \alpha + \alpha T \alpha T \alpha - \dots) T \\ &= T - T A T, \end{aligned} \quad (3.44)$$

where $A = S \alpha$ is the many-body polarizability matrix.

The energy of the unperturbed solvent (by the solute) can be written in terms of the monomer energies E^i of the direct Coulomb interactions of the monomers and of the polarization energy:

$$E^B = \sum_i E^i + \frac{1}{2} \sum_{ij} \langle \rho_r^i \rangle T_{r,p}^{ik} \langle \rho_{r'}^j \rangle + \frac{1}{2} \sum_{ijkl} \langle \rho_r^i \rangle T_{r,p}^{ik} A_{p,q}^{kl} T_{q,r'}^{lj} \langle \rho_{r'}^j \rangle. \quad (3.45)$$

Solvent reaction potential

The *solvent reaction potential* is the potential of the charge density induced by the solute. By virtue of the superposition of the linear perturbations, the effect of the solute perturbations on the solvent charge density can be described independently from the solvent–solvent induction interactions. In a higher-order approximation, a double perturbation approach would be necessary to handle the eventual cross terms. In the linear approximation, the wave function Ansatz is simply:

$$|\psi^i\rangle = |\phi^i\rangle + \hat{R}_0^i \hat{\rho}_p |\phi^i\rangle T_{p,q}^{is} \langle \psi^s | \hat{\rho}_q^s | \psi^s \rangle. \quad (3.46)$$

The perturbed solvent monomer charge distribution is accordingly:

$$\langle \psi^i | \hat{\rho}_r | \psi^i \rangle = \sum_j S_{r,p}^{ij} \left(\langle \phi^j | \hat{\rho}_p | \phi^j \rangle - \alpha_{p,q}^j T_{q,s}^{js} \langle \psi^s | \hat{\rho}_e^s | \psi^s \rangle \right). \quad (3.47)$$

The solute-induced solvent charge density $\Delta \langle \hat{\rho}_r^B \rangle$ can be written in this approximation as:

$$\Delta \langle \hat{\rho}_r^B \rangle = - \sum_{ij} A_{r,p}^{ij} T_{p,s}^{js} \langle \psi^s | \hat{\rho}_s | \psi^s \rangle, \quad (3.48)$$

where the many-body polarizability $A_{r,p}^{ij}$ can be considered as an approximation to the charge density response function of the total solvent:

$$C_{r,p}^B \approx \sum_{ij} A_{r,p}^{ij} = S_{r,q}^{ij} \alpha_{q,p}^j. \quad (3.49)$$

In terms of the many-body polarizability matrix, the explicit expression of the reaction potential response function is

$$C_{r,r'}^B \approx \sum_{ij} T_{r,p}^{Si} A_{p,q}^{ij} T_{q,r'}^{jS}. \quad (3.50)$$

A practical implementation of the above scheme can be done in the framework of the dipole polarizability approximation.

3.2.4. Implementations of the microscopic model

The microscopic representation of the charge density and polarization density of the environment has been advocated about ten years ago by Tapia and his coworkers for the representation of protein core effects in enzyme reactions [82], in solid state [50] and in microhydrated proton transfer reactions [83]. These inhomogeneous reaction field (ISCRF) calculations were carried out at the CNDO/2 level. An atomic dipole polarizability description of the charge density response function of the environment has been adopted and atomic net charges and dipole moments were used to represent the solvent charge density. The corresponding reaction potential response function is

$$\mathbf{G}^{\text{ISCRF}}(\mathbf{r}, \mathbf{r}') = \sum_k T_\alpha(\mathbf{r}, \mathbf{r}_k) \alpha_{\alpha\beta}^k T_\beta(\mathbf{r}_k, \mathbf{r}'). \quad (3.51)$$

Unfortunately, all these ISCRF calculations involved a slight inconsistency, since the reaction potential has been calculated from the field arising from the *total molecular charge and dipole moment*, while the interaction with the reaction potential has been developed in terms of distributed *atomic charges and dipole moments*. In terms of the molecular and atomic multipole moment developments of the charge density operator $\hat{\rho}^{\text{mol}}$ and $\hat{\rho}^{\text{at}}$, respectively, the following effective operator was used:

$$\hat{W}^{\text{ISCRF}} = \iint d^3r d^3r' \hat{\rho}^{\text{at}}(\mathbf{r}) \mathbf{G}^{\text{ISCRF}}(\mathbf{r}, \mathbf{r}') \langle \psi | \hat{\rho}^{\text{mol}}(\mathbf{r}') | \psi \rangle, \quad (3.52)$$

while the appropriate operator, corresponding to the solute–solvent energy

$$W = \frac{1}{2} \iint d^3r d^3r' \langle \psi | \hat{\rho}^{\text{at}}(\mathbf{r}) | \psi \rangle \mathbf{G}^{\text{ISCRF}}(\mathbf{r}, \mathbf{r}') \langle \psi | \hat{\rho}^{\text{mol}}(\mathbf{r}') | \psi \rangle \quad (3.53)$$

would have been obtained by the application of the variation theorem:

$$\begin{aligned} \hat{W} &= \frac{1}{2} \iint d^3r d^3r' \hat{\rho}^{\text{at}}(\mathbf{r}) \mathbf{G}^{\text{ISCRF}}(\mathbf{r}, \mathbf{r}') \langle \psi | \hat{\rho}^{\text{mol}}(\mathbf{r}') | \psi \rangle \\ &+ \frac{1}{2} \iint d^3r d^3r' \hat{\rho}^{\text{mol}}(\mathbf{r}) \mathbf{G}^{\text{ISCRF}}(\mathbf{r}, \mathbf{r}') \langle \psi | \hat{\rho}^{\text{at}}(\mathbf{r}') | \psi \rangle. \end{aligned} \quad (3.54)$$

Although the \hat{W}^{ISCRF} operator does not satisfy exactly the variation principle, it is reasonable to assume that the resulting numerical error is not important and the qualitative conclusions obtained from these calculations are not affected.

In a quite recent application of the generalized SCRF model at ab initio level [84], the solvent charge density response function was represented by atomic dipole polarizabilities. The induced dipole moments were allowed to interact and in this case, the reaction potential response function can be expressed in terms of \mathbf{A} , the nonlocal many-body dipole polarizability matrix [81, 85, 86]:

$$\mathbf{G}^{\text{GSCRF}}(\mathbf{r}, \mathbf{r}') = \sum_{ij} T_{\alpha}(\mathbf{r}, \mathbf{r}_i) A_{\alpha\beta}^{ij} T_{\beta}(\mathbf{r}_j, \mathbf{r}'). \quad (3.55)$$

The solute charge density was approximated by atomic multipoles truncated at dipolar level, so the solute–solvent energy is

$$W = \frac{1}{2} \sum_a \sum_b \left\{ Q^a \mathbf{G}^{ab} Q^b + Q^a \mathbf{G}_{\alpha}^{ba} \mu_{\alpha}^b - \mu_{\alpha}^a \mathbf{G}_{\alpha}^{ab} Q^b - \mu_{\alpha}^a \mathbf{G}_{\alpha,\beta}^{ab} \mu_{\beta}^b \right\}. \quad (3.56)$$

The reaction potential response tensors are defined by the following relationships:

$$\begin{aligned} \mathbf{G}^{ab} &= \sum_{ij} T_{\alpha}^{ai} A_{\alpha\beta}^{ij} T_{\beta}^{jb} = \mathbf{G}^{ba}, \\ \mathbf{G}_{\alpha}^{ab} &= \sum_{ij} T_{\alpha\beta}^{ai} A_{\beta\gamma}^{ij} T_{\gamma}^{jb} \neq \mathbf{G}_{\alpha}^{ba}, \\ \mathbf{G}_{\alpha}^{ba} &= \sum_{ij} T_{\alpha\beta}^{bi} A_{\beta\gamma}^{ij} T_{\gamma}^{ja}, \\ \mathbf{G}_{\alpha,\beta}^{ab} &= \sum_{ij} T_{\alpha\gamma}^{ai} A_{\gamma,\delta}^{ij} T_{\delta\beta}^{jb} = \mathbf{G}_{\beta,\alpha}^{ba}. \end{aligned} \quad (3.57)$$

Atomic multipole moments can be defined in many different ways, based on various partitioning schemes of the electronic charge distribution. In the above-mentioned work, the atomic moments were calculated based on the Ruedenberg partitioning scheme [87]. The atomic charges in this scheme are the Mulliken charges:

$$Q^a = Z_a - \sum_{\mu \in a} (PS)_{\mu\mu} \quad (3.58)$$

and the α component of the atomic dipole moment is

$$\mu_{\alpha}^a = - \sum_{\mu\nu\rho \in a} (PS)_{\mu\nu} S_{(a)}^{-1}{}_{\nu\rho} \langle \chi_{\rho} | r_{\alpha} - R_{\alpha}^a | \chi_{\mu} \rangle. \quad (3.59)$$

Better representations of the reaction field can be obtained by more sophisticated distributed multipole schemes, like those proposed by Stone [43] or Sokalski [45].

3.3. SOLUTE ELECTRONIC STRUCTURE IN STATISTICAL MEAN FIELD OF THE SOLVENT

The mean field model outlined in section 3.2 provides a reasonable approximation to the total energy of the solute–solvent system at fixed nuclear configuration. A complete analysis of the problem would only be possible if the full $(3(N_S + N_B) - 6)$ -dimensional potential surface were used in a statistical mechanical simulation on the nuclear motions. Although such a program will certainly be manageable in the future by the rapid development of computer technology, it is worthwhile to develop approximate models within the framework of the embedding philosophy.

3.3.1. Free energy functional in the mean field approximation

Standard methods of statistical mechanics, involving reduced probability density functions, are available to separate the treatment of a small number of nuclear degrees of freedom. Such an approach, leading to free-energy surfaces, has been proposed for the discussion of conformational equilibria in solution [88–92].

In contrast to the relatively slow nuclear variables, like torsional coordinates, the separation of the fast electronic degrees of freedom represents a different problem. Since electrons can adapt themselves instantaneously to changes in the nuclear positions in the spirit of the Born–Oppenheimer approximation, the electronic wave function depends parametrically only on the solvent nuclear coordinates. This feature would make it impossible, at least in the strict sense, to “pre-average” over the solvent coordinates, while such a procedure might be legitimate to separate torsional variables.

In spite of the obvious drawbacks of a pre-averaged, mean field approximation, it is important to analyse in some detail this possibility too. This mean field model is the implicit physical hint of the continuum models (at least of “equilibrium” continuum models [10]), therefore the microscopical interpretation of the appropriate reaction potential response function seems to be interesting.

According to the results of the previous section, the total potential energy of the system at fixed solute internal coordinates (\mathbf{x}) and solvent configurational coordinates (\mathbf{X}) is (for the sake of simplicity, the solvent molecules are supposed to be rigid):

$$E(\mathbf{x}, \mathbf{X}) = E^B(\mathbf{x}, \mathbf{X}) + \langle \psi^S(\mathbf{x}, \mathbf{X}) | \hat{H}^S(\mathbf{x}) + \hat{V}_r^B(\mathbf{X}) + \frac{1}{2} \hat{\Pi}_r^B(\mathbf{X}) | \psi^S(\mathbf{x}, \mathbf{X}) \rangle, \quad (3.60)$$

where the “unperturbed solvent energy” $E^B(\mathbf{x}, \mathbf{X})$ defines an appropriate “zero-order” reference state of the solvent, and the potential and reaction potential operators are defined as:

$$\begin{aligned} \hat{V}_r^B(\mathbf{X}) &= \hat{\rho}_r^S(\mathbf{x}) V_r^B(\mathbf{X}), \\ \hat{\Pi}_r^B(\mathbf{X}) &= \hat{\rho}_r^S(\mathbf{x}) \Pi_r^B(\mathbf{X}). \end{aligned} \quad (3.61)$$

It is reasonable to incorporate into $E^B(\mathbf{x}, \mathbf{X})$, in addition to the solvent energy, the solute–solvent repulsion and dispersion terms also:

$$E^B(\mathbf{x}, \mathbf{X}) = E_0^B(\mathbf{X}) + E_{\text{rep}}^{SB}(\mathbf{x}, \mathbf{X}) + E_{\text{disp}}^{SB}(\mathbf{x}, \mathbf{X}). \quad (3.62)$$

Note that $E^B(\mathbf{x}, \mathbf{X})$ can be simply the classical potential energy function, used in computer simulations.

The solvent configuration is defined by the positions of the center of mass \mathbf{r} of the molecules and by the corresponding Euler angles Ω , which define the orientation of each molecule. The shorthand notation \mathbf{X} means the ensemble of the positional and orientational coordinates for the solute and the solvent: $\mathbf{X} = \{X^S, X^1, X^2, \dots\}$, where $\mathbf{X} = (\mathbf{r}, \Omega)$.

The configurational partition function of the canonical ensemble at some fixed solute internal nuclear coordinates

$$Z(\mathbf{x}) = \int d\mathbf{X} \exp[-\beta \mathcal{E}(\mathbf{x}, \mathbf{X})] \quad (3.63)$$

cannot be factorized into terms comprising only the solute electronic wave function and only solvent nuclear terms, since the solute electronic wave function depends parametrically on \mathbf{X} . In effect, $\psi^S(\mathbf{x}, \mathbf{X})$, the solute electronic wave function, minimizes the solute-solvent total energy at a given solvent configuration \mathbf{X} .

One can avoid the separate optimization of the solute electronic wave function for each solvent configuration by introducing a *mean field approximation*, based on the following Ansatz:

$$\mathcal{E}_{MF}(\mathbf{x}, \mathbf{X}) = E^B(\mathbf{x}, \mathbf{X}) + \langle \Upsilon(\mathbf{x}) | \hat{H}^S(\mathbf{x}) + \hat{V}_r^B(\mathbf{X}) + \frac{1}{2} \hat{\Pi}_r^B(\mathbf{X}) | \Upsilon(\mathbf{x}) \rangle. \quad (3.64)$$

The mean field solute electronic wave function $\Upsilon(\mathbf{x})$ does not depend on the solvent configurations \mathbf{X} . Since $\psi^S(\mathbf{x}, \mathbf{X})$ was the optimal electronic wave function for each solvent nuclear configuration, the energy \mathcal{E}_{MF} calculated with $\Upsilon(\mathbf{x})$ is necessarily higher than (or at best equal to) $\mathcal{E}(\mathbf{x}, \mathbf{X})$ at a given solvent configuration. This implies that \mathcal{E}_{MF} is a strict upper bound of the potential energy in a given configuration:

$$\mathcal{E}(\mathbf{x}, \mathbf{X}) \leq \mathcal{E}_{MF}(\mathbf{x}, \mathbf{X}). \quad (3.65)$$

Using relationship (3.65), a variation principle is obtained for the approximate free energy:

$$-\beta \ln \int d\mathbf{X} \exp[-\beta \mathcal{E}(\mathbf{x}, \mathbf{X})] \leq -\beta \ln \int d\mathbf{X} \exp[-\beta \mathcal{E}_{MF}(\mathbf{x}, \mathbf{X})], \quad (3.66)$$

$$F(\mathbf{x}) \leq F_{MF}(\mathbf{x}). \quad (3.67)$$

The mean field partition function at fixed solute coordinates $Z_{MF}(\mathbf{x})$ can be simplified by using that \hat{H}^S and $\Upsilon(\mathbf{x})$ do not depend on the solvent coordinates \mathbf{X} :

$$\begin{aligned} Z_{MF}(\mathbf{x}) &= \exp[-\beta F_0^B(\mathbf{x})] \\ &\times \exp[-\beta \langle \Upsilon(\mathbf{x}) | \hat{H}^S(\mathbf{x}) | \Upsilon(\mathbf{x}) \rangle] \\ &\times \left\langle \exp[-\beta \langle \Upsilon(\mathbf{x}) | \hat{\rho}_r^S | \Upsilon(\mathbf{x}) \rangle \{V_r^B(\mathbf{x}, \mathbf{X}) + \frac{1}{2} \Pi_r^B(\mathbf{x}, \mathbf{X})\}] \right\rangle_B. \end{aligned} \quad (3.68)$$

This expression has been obtained by multiplying and dividing eq. (3.63) with the partition function of the reference solvent state

$$\exp[-\beta F_0^B(\mathbf{x})] = \int d\mathbf{X} \exp[-\beta E^B(\mathbf{x}, \mathbf{X})], \quad (3.69)$$

where the following notation has been introduced for the statistical mean with respect to the reference state of the solvent:

$$\langle \dots \rangle_B = \frac{\int dX \dots \exp[-\beta E^B(\mathbf{x}, X)]}{\int dX \exp[-\beta E^B(\mathbf{x}, X)]} \quad (3.70)$$

It should be pointed out again that $E^B(\mathbf{x}, X)$ includes the solute–solvent repulsion potential, therefore this reference state corresponds to the solvent where the solute cavity has already been prepared.

An explicit expression of the free energy can be obtained by expanding the statistical mean of the exponential expression in eq. (3.68) in cumulant series [93]. An analogue of the usual linear reaction field expression can be obtained by truncating the cumulant expansion at the second order:

$$F_{MF}(\mathbf{x}) = F_0^B(\mathbf{x}) + \langle \Upsilon(\mathbf{x}) | \hat{H}^S | \Upsilon(\mathbf{x}) \rangle + \langle \Upsilon(\mathbf{x}) | \hat{\rho}_r^S | \Upsilon(\mathbf{x}) \rangle \langle V_r^B \rangle \\ + \frac{1}{2} \langle \Upsilon(\mathbf{x}) | \hat{\rho}_r^S | \Upsilon(\mathbf{x}) \rangle [\langle \mathbf{G}_{r,r'}^{B,el} \rangle_B + \langle \mathbf{G}_{r,r'}^{B,or} \rangle_B] \langle \Upsilon(\mathbf{x}) | \hat{\rho}_r^S | \Upsilon(\mathbf{x}) \rangle. \quad (3.71)$$

This relationship defines the linear response approximation to the solute free-energy potential surface $F_{MF}(\mathbf{x})$ as a sum of different contributions, namely the free energy of the solvent reference state, the solute energy associated with the mean field wave function, the interaction energy of the solute with the mean field of the solvent and the solute–solvent reaction field energy. This latter quantity consists of two contributions: the electronic and the orientational ones.

The orientational reaction potential response function is the classical limit of the corresponding static linear response function (see [93, pp. 147–50]):

$$\langle \mathbf{G}_{r,r'}^{B,or} \rangle_B = \beta [\langle V_r^B V_{r'}^B \rangle_B - \langle V_r^B \rangle_B \langle V_{r'}^B \rangle_B]. \quad (3.72)$$

This takes into account the coupling of the charge density of the solute molecule with the structure of the solvent: the solute field aligns in competition with the thermal movements the neighboring solvent molecules. The other quantity $\langle \mathbf{G}_{r,r'}^{B,el} \rangle_B$ is the statistical average of the electronic reaction potential response function, which has been defined in eq. (3.18), taken at different solvent configurations. This describes the deformation of the electronic density of the solvent molecules under the effect of the solute field.

3.3.2. Solute-only statistical mean field Schrödinger equation

The optimal mean field solute wave function Υ can be found by the quantum chemical variation method, as outlined in the introduction. The following nonlinear Schrödinger equation is obtained:

$$\{\hat{H}^S + \hat{\rho}_r^S \langle V_r^B \rangle_B + \hat{\rho}_r^S [\langle \mathbf{G}_{r,r'}^{B,el} \rangle_B + \langle \mathbf{G}_{r,r'}^{B,or} \rangle_B] \langle \Upsilon | \hat{\rho}_r^S | \Upsilon \rangle\} \Upsilon = E \Upsilon. \quad (3.73)$$

The derivation of such “statistically significant” Schrödinger equations has been discussed earlier by Tapia [2] and Yomosa [94].

The mean field wave function Υ plays the role of a “variational parameter” and cannot be interpreted as the representation of the electronic structure of a particular solute molecule in the presence of a solvent. The physical significance of Υ can be realized by considering the average value of an arbitrary operator \hat{A} , associated with the solute subsystem:

$$\langle \hat{A} \rangle = \frac{\int dX \langle \psi(x, X) | \hat{A} | \psi(x, X) \rangle \exp[-\beta \mathcal{E}(x, X)]}{\int dX \exp[-\beta \mathcal{E}(x, X)]}. \quad (3.74)$$

In the mean field approximation, this average can be directly evaluated as a quantum chemical expectation value taken with the Υ wave function:

$$\langle \hat{A} \rangle_{MF} = \langle \Upsilon | \hat{A} | \Upsilon \rangle. \quad (3.75)$$

This error of the mean field approximation with respect to the exact value can be estimated as

$$\begin{aligned} \Delta \langle \hat{A} \rangle &= \langle \hat{A} \rangle - \langle \hat{A} \rangle_{MF} \\ &= \frac{\int dX \{ \langle \psi(x, X) | \hat{A} | \psi(x, X) \rangle - \langle \Upsilon | \hat{A} | \Upsilon \rangle \} \exp[-\beta \mathcal{E}(x, X)]}{\int dX \exp[-\beta \mathcal{E}(x, X)]}. \end{aligned} \quad (3.76)$$

The error may be different for different physical quantities. One can anticipate a reasonable behavior as far as the mean field average reproduces correctly the expectation values associated with low-energy solvent configurations.

To our best knowledge, the statistical mechanical calculation of $\langle G_{r,r'}^{B,or} \rangle_B$ has not been attempted up to now for direct use in quantum chemical solvent effect calculations. Nevertheless, this would create an interesting link with the popular dielectric models.

In a certain sense, various continuum dielectric models can be regarded as approximations to the statistical mechanical mean field theory, replacing reaction potential response functions by their classical electrostatic counterpart. The previous analysis may give some hints to point out the limitations of the mean field model in general and the problems with the interpretation of the corresponding solute electronic wave functions.

4. Embedding in replicates of the subsystem

A special case of the solute–solvent model system is when the total system consists of two or more replicates, i.e. strictly identical subunits related to each other by appropriate symmetry operations. This can occur, for example, for some specific symmetrical configurations of dimers or oligomers of small molecules, and also this is the case for molecular crystals.

4.1. SYMMETRICAL DIMER

Let us consider first the simplest model, which consists of only two identical subsystems, related by a general symmetry operation \hat{Q} . Remaining in the framework of the mean field model, described by eqs. (3.8), the subsystem wave functions can be obtained by a self-consistent procedure. First the subsystem wave function should be optimized in the field of the fixed partner, then the partner charge density should be updated by using the symmetry operation relating the two subsystems and the new subsystem wave function is obtained in the modified field of the partner. These steps can be repeated until convergence.

Such an iterative scheme can be cast in more compact form if we introduce the symmetry relationships directly into eqs. (3.8):

$$|\psi^B\rangle = \hat{Q} |\psi^S\rangle, \quad (4.1)$$

where \hat{Q} is a symmetry operator $\{U|q\}$, including a real orthogonal rotation matrix U and a translation vector q . The effect of \hat{Q} on a function $\chi(\mathbf{r})$ (e.g. an atomic orbital) is

$$\hat{Q}\chi(\mathbf{r}) = \chi[U^{-1}(\mathbf{r} - \mathbf{q})]. \quad (4.2)$$

The effective equation for the monomer S reads as

$$\left\{ \hat{H}^S + \int d^3 r d^3 r' \hat{\rho}(\mathbf{r}) T(\mathbf{r}, \mathbf{r}') \langle \psi | \hat{Q}^\dagger \hat{\rho}(\mathbf{r}') \hat{Q} | \psi \rangle \right\} | \psi \rangle = E | \psi \rangle, \quad (4.3)$$

which can be written in an equivalent form by shifting the effect of the symmetry operation to the Coulomb interaction kernel:

$$\left\{ \hat{H} + \int d^3 r d^3 r' \hat{\rho}(\mathbf{r}) T(\mathbf{r}, U\mathbf{r}' + \mathbf{q}) \langle \psi | \hat{\rho}(\mathbf{r}') | \psi \rangle \right\} = E | \psi \rangle. \quad (4.4)$$

A similar equation can be written for the monomer B as well.

The eigenvalues E^S and E^B of the effective equations for the monomers contain both the total interaction energy with the other partner. Therefore, the meaningful quantity $\mathcal{E}/2$, the total energy per monomer, can be obtained by subtracting the superfluous interaction energy:

$$\mathcal{E}/2 = E - \frac{1}{2} \int d^3 r d^3 r' \langle \psi | \hat{\rho}(\mathbf{r}) | \psi \rangle T(\mathbf{r}, U\mathbf{r}' + \mathbf{q}) \langle \psi | \hat{\rho}(\mathbf{r}') | \psi \rangle. \quad (4.5)$$

This relationship is formally analogous to (3.24). Nevertheless, the origin of the factor of 1/2 is different in the two cases. In the model of identical subsystems, no linear response hypothesis was invoked. The factor of 1/2 appears simply to avoid double counting of the interaction energy of the monomers.

In spite of the strong formal similarity of the above equations with those derived for the polarizable environment, the essential difference is that eq. (4.4)

provides for an exact solution of the mean field equations (there is no first-order perturbational approximation).

4.2. REPLICATES IN ORDERED PHASE: THE SCMP MODEL

The iterative procedure, making use of the symmetry relationship of the subunits, is particularly well-adapted for the description of the local electronic structure of molecular crystals. Several calculations appeared in the literature, where the subunit wave function was optimized in the Madelung potential of the whole crystal [37,95–101]. In these works, the fractional Mulliken charges obtained from the subunit wave functions were used to evaluate the Madelung potential. The iterations were carried out until convergence in the Madelung potential, whence the name of the method: “self-consistent Madelung potential” (SCMP) approach. Recently, this scheme has been reformulated in terms of a nonlinear Schrödinger equation [37]. The effective Schrödinger equation for the subunit is:

$$\left\{ \hat{H} + \hat{\rho}_r \mathbf{G}_{r,r'}^{Mad} \langle \psi | \hat{\rho}_{r'} | \psi \rangle \right\} | \psi \rangle = E | \psi \rangle. \quad (4.6)$$

Here, $\mathbf{G}_{r,r'}^{Mad}$ stands for the lattice sum:

$$\mathbf{G}_{r,r'}^{Mad} = \sum_i \sum_q T(r, U^i r' + q) \quad (4.7)$$

and the summations run over the i space group operations and the q lattice translations.

The self-consistent Madelung potential model has been implemented in a similar atomic multipolar scheme as the generalized SCRF theory. The only difference is in the calculation of the effective interaction kernel tensors, which are defined as successive derivatives of the partial Madelung sums

$$\mathbf{G}^{ab} = \sum_i \sum_q T(a, U^i \mathbf{b} + q). \quad (4.8)$$

For higher-order tensors, one should take into account properly the $U_{\alpha\beta}^i$ rotation matrices associated with the space group operations:

$$\begin{aligned} \mathbf{G}_{\alpha}^{ab} &= \nabla_{\alpha}^a \sum_i \sum_q T(a, U^i \mathbf{b} + q) = \sum_i \sum_q T_{\alpha}(a, U^i \mathbf{b} + q), \\ \mathbf{G}_{\alpha}^{ba} &= -\nabla_{\alpha}^b \sum_i \sum_q T(a, U^i \mathbf{b} + q) = \sum_i \sum_q U_{\alpha\beta}^i T_{\beta}(a, U^i \mathbf{b} + q), \\ \mathbf{G}_{\alpha\beta}^{ab} &= -\nabla_{\alpha}^a \nabla_{\beta}^b \sum_i \sum_q T(a, U^i \mathbf{b} + q) = \sum_i \sum_q U_{\beta\gamma}^i T_{\alpha\gamma}(a, U^i \mathbf{b} + q). \end{aligned}$$

The lattice sums can be most conveniently calculated by the standard Ewald summation method [102,103].

4.3. REPLICATES IN DISORDERED PHASE

Although the instantaneous environment of each molecule in a liquid depends on the actual configuration \mathbf{X} , in the mean field approximation pure molecular liquids also can be considered as collections of replicates.

The mean field model implies here that the configuration-dependent electronic wave function of a molecule $\psi(\mathbf{x}, \mathbf{X})$ has been replaced by the mean field wave function $\Upsilon(\mathbf{x})$. The total potential energy of an N -molecule model of the liquid can be written:

$$E_{MF}(\mathbf{x}, \mathbf{X}) = E^0(\mathbf{x}, \mathbf{X}) + N\langle \Upsilon(\mathbf{x}) | \hat{H}(\mathbf{x}) + \frac{1}{2} \hat{\rho}_r^1(\mathbf{x}) V_r(\mathbf{X}, \Upsilon) | \Upsilon(\mathbf{x}) \rangle. \quad (4.10)$$

$E^0(\mathbf{x}, \mathbf{X})$ denotes the potential energy of a reference liquid, with electrostatic interactions excluded. Although this choice may seem somewhat artificial, it should be kept in mind that the structure of molecular liquids is essentially determined by the repulsive interactions. This simple Van der Waals model can always be improved by adding the interaction energy due to a reference charge distribution in $E^0(\mathbf{x}, \mathbf{X})$ and renormalizing H , the monomer Hamiltonian, accordingly. $V_r(\mathbf{X}, \Upsilon)$ is the electrostatic potential in a given configuration calculated with the electronic density of the mean field wave function Υ . Here, we can use that the mean field charge distribution of each individual molecule is the same. The charge distribution of the k th molecule can be generated by a translation \mathbf{r}^k and a rotation $U(\Omega)$ of the center of mass, therefore one can write

$$V_r(\mathbf{X}, \Upsilon) = \sum_{k \neq 1} T(\mathbf{r}, U(\Omega^k) \mathbf{r}' + \mathbf{r}^k) \langle \Upsilon | \hat{\rho}(\mathbf{r}') | \Upsilon \rangle. \quad (4.11)$$

Following an analogous procedure as in the previous section, the free energy of the pure liquid in the mean field approximation turns out to be

$$F_{MF} = F^0 - \beta \ln \langle \exp[-\beta N \langle \Upsilon(\mathbf{x}) | \hat{H} + \frac{1}{2} \hat{\rho}_r V_r(\mathbf{X}, \Upsilon) | \Upsilon(\mathbf{x}) \rangle] \rangle_0, \quad (4.12)$$

where the statistical mean $\langle \dots \rangle_0$ is taken on the reference state of the liquid, corresponding to the energy E^0 . Truncating the cumulant expansion of the mean of the exponential at the *first order*, i.e. neglecting the structural implications of the electrostatic corrections, the free energy is approximately:

$$F_{MF} = F^0 + N \langle \Upsilon(\mathbf{x}) | \hat{H} + \frac{1}{2} \hat{\rho}_r \langle V_r(\mathbf{X}, \Upsilon) \rangle_0 | \Upsilon(\mathbf{x}) \rangle. \quad (4.13)$$

The average potential can be expressed as:

$$\begin{aligned} & \langle V_r(\mathbf{X}, \Upsilon) \rangle_0 \\ &= \int d^3 r' \left\langle \sum_{k \neq 1} T(\mathbf{r}, U(\Omega_k) \mathbf{r}' + \mathbf{q}_k) \langle \Upsilon | \hat{\rho}_r^1 | \Upsilon \rangle \right\rangle_0 \\ &= \int d^3 r' \mathbf{G}^{liq}(\mathbf{r}, \mathbf{r}') \langle \Upsilon | \hat{\rho}_r^1 | \Upsilon \rangle. \end{aligned} \quad (4.14)$$

The effective interaction function for the molecular liquid $\mathbf{G}^{liq}(\mathbf{r}, \mathbf{r}')$ can be expressed with the angular pair correlation function of the liquid $g(\mathbf{r}, \Omega)$:

$$\mathbf{G}^{liq}(\mathbf{r}, \mathbf{r}') = \rho N \int d^3 \mathbf{r} d^3 \Omega g(\mathbf{r}, \Omega) T(\mathbf{r}, U(\Omega) \mathbf{r}' + \mathbf{r}). \quad (4.15)$$

There are relatively few works on the direct utilization of statistically mechanically calculated pair correlation functions in quantum chemical solvent effect calculations. Sesé and coworkers [104–107] did some systematic studies on the influence of the liquid phase on molecular electronic structure at the CNDO/2 level. In the spirit of the ZDO approximation, atom–atom pair distribution functions were used exclusively in setting up the effective potential. This model corresponds to an atomic point charge representation of the molecular charge distribution and the following effective interaction kernel is obtained for the atom pair a, b :

$$\mathbf{G}^{ab} = 4\pi\rho N \int d r (g_{ab}(r) - 1)r. \quad (4.16)$$

Generalization to higher atomic multipole moments would be necessary for the reasonable implementation of the method with ab initio wave functions.

5. Summary of effective interaction kernels

Let us summarize the main results of the previous sections by recapitulating the most important expressions for the reaction potential response function derived for different cases. Our aim was to stress formal analogies of various approaches, which treat solvent effects by effective quantum chemical Hamiltonian methods and underline the basic features of the corresponding physical model.

As has already been emphasized, only *average reaction field* models were considered and direct reaction field theories [108], whose validity seems to be questionable [109], were excluded from the present review.

Some of the models are not complete without the specification of the solvent mean field, but it is not our main concern here, and we refer to the specific sections for more information.

Spherical cavity

$$\mathbf{G}(\mathbf{r}, \mathbf{r}') = \sum_{n=0}^{\infty} \sum_{m=-n}^n f_n R_{nm}(\mathbf{r}) R_{nm}(\mathbf{r}'). \quad (5.1)$$

Ellipsoidal cavity

$$\mathbf{G}(\mathbf{r}, \mathbf{r}') = \sum_{lm} \sum_{l'm'} f_{lm, l'm'} R_{lm}(\mathbf{r}) R_{l'm'}(\mathbf{r}'). \quad (5.2)$$

Cavity of general shape

$$\mathbf{G}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_{ij} \{T(\mathbf{r}, s_i) S_{ij} \bar{\omega}(s_j, \mathbf{r}') + T(\mathbf{r}', s_i) S_{ij} \bar{\omega}(s_j, \mathbf{r})\}. \quad (5.3)$$

Discrete model with fixed configuration

$$\begin{aligned} \mathbf{G}(\mathbf{r}, \mathbf{r}') &= -T(\mathbf{r}, \mathbf{r}'') C^B(\mathbf{r}'', \mathbf{r}''') T(\mathbf{r}', \mathbf{r}''') \\ &\approx \sum_{ij} T_\alpha(\mathbf{r}, \mathbf{r}_i) A_{\alpha\beta}(\mathbf{r}_i, \mathbf{r}_j) T_\beta(\mathbf{r}_j, \mathbf{r}'). \end{aligned} \quad (5.4)$$

Orientalional polarization in solvent mean field

$$\mathbf{G}(\mathbf{r}, \mathbf{r}') = \beta [\langle V^B(\mathbf{r}) V^B(\mathbf{r}') \rangle_B - \langle V^B(\mathbf{r}) \rangle_B \langle V^B(\mathbf{r}') \rangle_B]. \quad (5.5)$$

Self-consistent Madelung potential

$$\mathbf{G}(\mathbf{r}, \mathbf{r}') = \sum_i \sum_q T(\mathbf{r}, U^i \mathbf{r}' + \mathbf{q}). \quad (5.6)$$

Pure liquid in the mean field approximation

$$\mathbf{G}(\mathbf{r}, \mathbf{r}') = \rho N \int d^3 \mathbf{r} d^3 \mathbf{\Omega} g(\mathbf{r}, \mathbf{\Omega}) T(\mathbf{r}, U(\mathbf{\Omega}) \mathbf{r}' + \mathbf{r}). \quad (5.7)$$

Although the above list is not exhaustive, it shows quite well the variety of reaction potential response functions (or effective interaction kernels), which are the basic ingredients of the average reaction field type solvent effect theories.

Many of these relationships have already been used in the literature, either in the above form or in their approximate version. One exception is the reaction potential response function for orientational polarization, which could be calculated from statistical mechanical simulation as a correlation function of the solvent mean potential. This would provide an interesting test of the validity of dielectric continuum models.

There are further possibilities, suggested by the previous analysis, which are worth exploring in the future, namely the systematic application of distributed multipole approximation for the reaction potential operator. Work in this direction is in progress.

6. List of symbols

\mathbf{A}	: nonlocal many-body dipole polarizability matrix;
$\alpha, \beta, \gamma, \dots$: x, y, x Cartesian components;
$\alpha_{r,p}^i$: nonlocal polarizability of the i th solvent molecule;
$A_{r,p}^{ij}$: many-body polarizability of a collection of solvent molecules;
$C_{r'',r'''}^B$: charge density reponse function of the total solvent system;
$\chi_\mu(\mathbf{r})$: atomic orbital;
$C_{nm}(\omega)$: modified spherical harmonic ($\omega = \theta, \phi$);
$\Delta E^B(0 \rightarrow b)$: excitation energy;
$\Delta \langle \hat{\rho}_r^B \rangle$: polarization charge density;
E	: exact total energy of the solute–solvent system;
\mathcal{E}	: total energy of the solute–solvent system in Hartree approximation;
E_0^B	: solvent energy;
E_0^i	: solvent monomer energies;
$E^B(\mathbf{x}, \mathbf{X})$: unperturbed solvent energy;
$\mathcal{E}_{MF}(\mathbf{x}, \mathbf{X})$: energy calculated with mean field solute wave function;
E_k^S	: k th eigenvalue of the solute-only Schrödinger equation;
ϵ	: dielectric constant (relative permittivity);
$\delta(\mathbf{r})$: three-dimensional delta function;
$F(\mathbf{x})$: free energy;
$f_n(\epsilon, a)$: reaction potential factor in the spherical cavity model;
$\mathbf{G}_{r,r'}^B$: reaction potential response function;
$g(\mathbf{r}^1, \mathbf{r}^2, \Omega^1, \Omega^2)$: angular pair distribution function;
\hat{H}	: total Hamiltonian of the solute–solvent system
\hat{H}^B	: solvent Hamiltonian;
\hat{H}^i	: Hamiltonian of the i th solvent molecule;
\hat{H}^S	: solute Hamiltonian;
\hat{H}^{SB}	: solute–solvent interaction Hamiltonian;
$J(\psi, \mathbf{X})$: energy functional;
μ_α^a	: atomic dipole moment component;
$\langle \hat{O} \rangle_X$: normalized expectation value of operator \hat{O} ;
$\hat{\Pi}^B$: reaction potential operator;
$\Pi_r^B(\mathbf{x}, \mathbf{X})$: reaction potential function;
$P_{\mu\nu}$: first-order density matrix;
$P_n(\cos \gamma_{ij})$: Legendre polynomial of order n ;
Ψ	: total wave function;

ψ^S	: solute wave function;
ϕ_b^B	: unperturbed solvent wave function;
ψ^B	: solvent wave function;
ϕ^i	: unperturbed wave function of the i th solvent molecule;
ψ^S	: solute wave function;
\hat{Q}	: symmetry operator;
q_L	: translation part of the \hat{Q} symmetry operator;
\hat{Q}_{LM}	: ellipsoidal multipole moment functions;
Q_{nm}^a	: atomic multipole (spherical harmonics) moment component;
\hat{R}_0^B	: reduced resolvent associated with B ;
$R_{nm}(\mathbf{r})$: regular spherical harmonic;
$\hat{\rho}^X(\mathbf{r})$: total charge density operator of subsystem X ;
$S_{r,q}^{ij}$: screening function of the solvent;
S	: matrix representation of the solvent screening function;
$S_{(a)\mu\rho}^{-1}$: inverse of the atomic block of the overlap matrix;
$T(\mathbf{r}, \mathbf{r}')$: Coulomb interaction kernel;
U	: rotation part of the \hat{Q} symmetry operator;
$Y(\mathbf{x})$: mean field solute wave function;
\hat{V}^B	: potential operator of the unperturbed solvent charge density;
V_r^B	: permanent potential of the solvent charge density;
\hat{V}_k^S	: solute potential operator;
X	: solvent configurational coordinates;
\mathbf{x}	: solute internal coordinates;
$\xi_{\alpha\beta\dots\nu}^{(n)}$: traceless Cartesian multipole moments;
$Y_{nm}(\omega)$: spherical harmonics;
$Z(\mathbf{x})$: canonical partition function.

Appendix A: Equivalent charge densities

The general expressions for electrostatic interactions can be conveniently written in terms of a continuous charge density $\rho(\mathbf{r})$. In computational applications, it is often more convenient to replace continuous distributions by a set of point multipoles. Then one has, for example, a discrete point charge distribution:

$$\rho(\mathbf{r}) = \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i),$$

a discrete point dipole distribution:

$$\mathbf{P}(\mathbf{r}) = \sum_i \mathbf{m}_i \delta(\mathbf{r} - \mathbf{r}_i),$$

and higher multipolar distributions.

It is possible to have a shorthand formalism, valid for all the discrete multipolar distributions by introducing the concept of *equivalent charge density* [49; 48, pp. 60–61]. This quantity can replace formally the continuous charge density in the appropriate formulae and thus one can avoid complications with the handling of special cases of multipolar distributions.

Let us consider the electrostatic potential $V(\mathbf{r})$ of a set of traceless Cartesian multipole moments $\xi_{\alpha\beta\dots\nu}^{(n)a}$ situated in points \mathbf{a} :

$$V(\mathbf{r}) = \sum_a \sum_n \frac{(-1)^n}{(2n-1)!!} \xi_{\alpha\beta\dots\nu}^{(n)a} \nabla_\alpha \nabla_\beta \dots \nabla_\nu \frac{1}{|\mathbf{a} - \mathbf{r}|}. \quad (\text{A.1})$$

Applying the Laplacian to both sides of this expression of the potential, using the Laplace equation

$$\Delta V(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \quad (\text{A.2})$$

and the relation

$$-\Delta \frac{1}{|\mathbf{a} - \mathbf{r}|} = 4\pi\delta(\mathbf{a} - \mathbf{r}), \quad (\text{A.3})$$

the following general expression is obtained for the equivalent charge density:

$$\rho(\mathbf{r}) = \sum_a \sum_n \frac{(-1)^n}{(2n-1)!!} \xi_{\alpha\beta\dots\nu}^{(n)a} \nabla_\alpha \nabla_\beta \dots \nabla_\nu \delta(\mathbf{a} - \mathbf{r}). \quad (\text{A.4})$$

The explicit expression of the equivalent charge density with the first few traceless Cartesian multipole moments [110] is given by:

$$\rho(\mathbf{r}) = \sum_a \{Q^a - \mu_\alpha^a \nabla_\alpha^a + \frac{1}{2} \Theta_{\alpha\beta}^a \nabla_\alpha^a \nabla_\beta^a + \dots\} \delta(\mathbf{a} - \mathbf{r}). \quad (\text{A.5})$$

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