Solvent-Induced Shift of Spectral Lines in Polar-Polarizable Solvents

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Abstract

Solvent-induced shift of optical transition lines is traditionally described by the Lippert-McRae equation given in terms of the Onsager theory for dipole solvation. It splits the overall shift into the equilibrium solvation by induced dipoles and the reaction field by the permanent dipoles in equilibrium with the chromophore in the ground state. We have reconsidered this classical problem from the perspective of microscopic solvation theories. A microscopic solvation functional is derived and continuum solvation is consistently introduced by taking the limit of zero wavevector in the reciprocal-space solvation susceptibility functions. We show that the phenomenological expression for the reaction field of permanent dipoles in the Lippert-McRae equation is not consistent with the microscopic theory. The main deficiency of the Lippert-McRae equation equation is the use of additivity of the response by permanent and induced dipoles of the liquid. An alternative closed-form equation for the spectral shift is derived. Its continuum limit allows a new, non-additive functionality for the solvent-induced shift in terms of the high-frequency and static dielectric constants. The main qualitative outcome of the theory is a significantly weaker dependence of the spectral shift on the polarizability of the solvent than predicted by the Lippert-McRae formula.

Introduction

The free energy of solvation of a solute particle placed in a liquid can often be calculated in the linear response approximation. This implies that the free energy is quadratic in the solute-solvent interaction energy, with the proportionality constant α^{solv} identified as the solvation susceptibility. In the case of polar, both dipolar and non-dipolar, liquids, the main part of the solute-solvent interaction energy comes from electrostatic interactions. It can be written as a general expansion in the multipole moments of the liquid molecules, but the first non-vanishing multipole, the dipole moment, dominates for polar liquids.[1] The free energy of solvation is then written as the integral of the electric field of the solute charges (vacuum field) $\mathbf{E}_0$ with the dipolar polarization density $\mathbf{P}_{\text{eq}}$ in equilibrium with this field[2,3]

$$F = -\tfrac{1}{2} \int_\Omega \mathbf{E}_0 \cdot \mathbf{P}_{\text{eq}} \, d\mathbf{r} \qquad (1)$$

The integral is taken over the volume Ω occupied by the liquid. The solvation susceptibility α^{solv} connects, in this formalism, the equilibrium polarization with the external field, $\mathbf{P}_{\text{eq}} = \alpha^{\text{solv}} \mathbf{E}_0$. This linear relation, which had given name to the linear response approximation, makes the solvation energy a quadratic functional of the field of external charges

$$F = -\tfrac{1}{2} \alpha^{\text{solv}} \int_\Omega \mathbf{E}_0 \cdot \mathbf{E}_0 \, d\mathbf{r} \qquad (2)$$

It is important to realize that in contrast to the dielectric susceptibility of a bulk material, which is a material property, the solvation susceptibility depends on both the shape of the repulsive core of the solute and the distribution of the solute charge. This dependence comes not in the form of the dependence on the strength of the electric field, which is already included in the integral of $\mathbf{E}_0 \cdot \mathbf{E}_0$, but as an entangled combination of the symmetry of the charge distribution and the solute shape.

Two famous examples can be brought to illustrate this point, solvation of a spherical ion in the Born solvation model[4] and solvation of a spherical dipole in the Onsager model.[5] One has

$$\alpha^L = (4\pi)^{-1}(1 - \epsilon^{-1}) \qquad (3)$$

in the former and

$$\alpha_d = \frac{3}{4\pi} g(\epsilon), \quad g(\epsilon) = \frac{\epsilon - 1}{2\epsilon + 1} \qquad (4)$$

in the latter. In both cases, ϵ is the dielectric constant of the bulk. The superscript "L" assigns the Born solvation susceptibility to the longitudinal response, as explained below. The subscript "d" in eq 4 refers to the spherical dipole configuration. Both equations are derived as solutions of the dielectric boundary value problem[3] in which the solute carves a spherical cavity in the continuum dielectric characterized by the dielectric constant ϵ.

Spectroscopy is the most reliable experimental tool to measure solvation on the microscopic length-scale,[6] but theoretical interpretation of the spectral shift is not free from ambiguity. The problem is fairly straightforward in basic terms. Absorption of a photon of radiation changes the elec-

trostatic interaction of the solute with the medium. The spectral shift is a result of the solute-solvent interaction being different in the ground and excited states. It is composed of two parts characterized by drastically different time-scales. The polarization of the electronic shells of the molecules occurs on the time-scale of electronic motion. The contribution of this fast subsystem, following adiabatically the optical excitation, to the spectral shift is given by the difference of free energies of electronic solvation (solvation by the polarized electronic shells of the solvent molecules) in the excited and ground states, ΔF_e. At the opposite timescale limit, the nuclei of the solvent are frozen during the transition (Franck-Condon principle). The contribution of the nuclear coordinates to the spectral shift comes from the difference in energies, in contrast to the difference in free energies for the electronic component, of the excited-state and ground-state solutes interacting with the frozen nuclei. This basic physics, involving two drastically different time-scales, can be expressed by the equation for the spectral shift[7–9]

$$\hbar\Delta\omega = \Delta F_e + \langle\Delta E_n\rangle_1 \qquad (5)$$

where $\Delta E_n = E_2(\Gamma_n) - E_1(\Gamma_n)$ is the difference in the interaction energies of the solute with the nuclear degrees of freedom in an instantaneous nuclear configuration Γ_n and labels 1 and 2 denote the ground and excited states, respectively. The ensemble average $\langle\dots\rangle_1$ accounts for the fact that solutes in a macroscopic experiment are distributed according to the equilibrium statistics consistent with the ground state (subscript "1") at the time of light absorption. Equation 5 applies to the shift of the emission line upon the replacement $1 \to 2$ in the statistical average; the statistical distribution of the medium is in equilibrium with the exited state of the chromophore in this case.

While the meaning of the electronic free energy ΔF_e is unambiguous and can be determined according to the rules specified by eqs 1 and 2, the nuclear part is harder to define. Various approaches to assign this component of the shift have been debated in the literature[10–13] and the problem is far from solved. The main difficulty seems to arise from attempts to separate nuclear (slow) from electronic (fast) components in terms of the frequency-dependent dielectric spectroscopy,[14] where this separation is also not clearly defined. Here, we address the problem from the viewpoint of micro-

scopic liquid state theories and consistently introduce the splitting into the electronic and nuclear polarization in terms of correlated fluctuations of the induced (fast) and permanent (slow) dipoles in the liquid.

Historically, the first approach to treat the nuclear part of the shift was proposed by Lippert[7] and McRae,[8] who both assumed that $\langle\Delta E_n\rangle_1$ can be associated with the nuclear reaction field R_{n1} acting on the solute dipole changing with electronic transition,

$$\langle\Delta E_n\rangle_1 = -\Delta m R_{n1} \qquad (6)$$

where $\Delta m = m_2 - m_1$, m_2 and m_1 are the solute dipole moments in the excited and ground states, respectively.

This idea, while obviously correct in the dipolar approximation for the solute, shifts the problem of defining the nuclear response to the nuclear reaction field R_{n1}. The resolution of this problem was suggested empirically along the same lines as used in dielectric spectroscopy. The real part of the frequency-dependent dielectric function $\epsilon'(\omega)$ typically shows a sequence of drops $\Delta\epsilon_j$ (dielectric decrements) corresponding to separate relaxation processes in the liquid with the relaxation times τ_j.[14–16] Adding up all $\Delta\epsilon_j$ then yields $\epsilon - 1$.

The additivity concept of the dielectric frequency analysis[14,16,17] was extended in the Lippert-McRae theory to the reaction field such that the total reaction field is given as a sum of the nuclear and electronic components, $R = R_n + R_e$. Adopting this additivity scheme does not solve the problem since neither R nor R_n are defined here. One typically makes the next approximation that the total reaction field R can be associated with the static dielectric constant ϵ and R_e is associated with the high-frequency dielectric constant ϵ_∞. Within this framework, one gets for for the nuclear reaction field in the ground state

$$R_{n1} = \frac{2m_1}{R_0^3}\left[g(\epsilon) - g(\epsilon_\infty)\right] \qquad (7)$$

where R_0 is the radius of the spherical solute and ϵ_∞ is commonly associated with the refractive index n_D, $\epsilon_\infty = n_D^2$. Combining these ideas, one gets for the spectral shift

$$\hbar\Delta\omega = \Delta F_e - \frac{2\Delta m m_1}{R_0^3}\left[g(\epsilon) - g(\epsilon_\infty)\right] \qquad (8)$$

and

$$\Delta F_e = -\frac{m_2^2 - m_1^2}{R_0^3} g(\epsilon_\infty) \tag{9}$$

As mentioned above, the extension to emission transitions is achieved by replacing $m_1 \to m_2$ in eq 8.

While the sequence of steps leading to eq 8 seems plausible within the framework of analyzing the polarization of macroscopic materials in a uniform external field, as is done in dielectric experiments, its extension to the boundary value problem of solvation is fundamentally questionable. The general argument against this approach is non-additivity of interfacial polarization entering the boundary value problem.[3] It is hard to expect that different processes contributing to the polarization of the interface will add up in the electrical field acting on the solute dipole. In what follows we indeed show that the additivity assumption $R_n = R - R_e$ is inconsistent with a number of theoretical approaches aiming at describing the interfacial polarization.

Even the standard polarization functionals circulating in the theory of electronic transitions in polarizable media do not support the additivity of the nuclear and electronic components in the reaction field. As we show below, the functionals proposed by Pekar[18,19] and Marcus[20–22] to describe charge-transfer transitions in polar media lead, after an amendment to the dipolar response, to the replacement of $g(\epsilon) - g(\epsilon_\infty)$ in the Lippert-McRae equation 7 with a function $g(\epsilon, \epsilon_\infty)$, which does not allow additivity of the static and electronic polarization components

$$g(\epsilon_\infty, \epsilon) = \frac{\epsilon - \epsilon_\infty}{2\epsilon_\infty \epsilon + 1} \tag{10}$$

The lack of additivity in the function describing nuclear dipole moments is in fact consistent with the Fröhlich-Onsager-Kirkwood framework for the dielectric constant of polar liquids,[23] where such additivity also does not appear. For instance, the Kirkwood-Fröhlich equation establishes the connection between the liquid dielectric constant and the fluctuations of the permanent dipoles in the liquid[23,24]

$$\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} = g_K y \tag{11}$$

Here, g_K is the Kirkwood factor and $y = (4\pi/9)\beta\rho m^2$ is the polarity parameter of dielectric theories[25,26] given in terms of the molecular gas-phase dipole moment m (permanent dipole) and the number density ρ; $\beta = 1/(k_B T)$ is the inverse temperature. It is clear from this equation that the total and high-frequency dielectric constants are quite entangled in the response defining the variance of the permanent dipole of the liquid on the right-hand side of the equation.

While eq 10 gives the first warning that the Lippert-McRae framework might be incorrect, further examination of the problem shows that the Pekar-Marcus functionals do not provide the correct picture either. It turns out that the Marcus functional[20–22] involves an oversimplified description of the interaction between the permanent and induced dipoles in the liquid. We therefore replace this functional, derived in the limit of a continuum dielectric, with a microscopic functional. This theory is given in terms of the microscopic reciprocal-space polarization density $\tilde{\mathbf{P}}(\mathbf{k})$, instead of the polarization density $\mathbf{P}(\mathbf{r})$ of the dielectric theories. Correspondingly, the susceptibilities of dielectric models are replaced in the microscopic theory by nonlocal susceptibility functions depending on the wavevector k.[25] The transition to the continuum limit is achieved by extrapolating the microscopic susceptibilities to zero wavevector, $k \to 0$. The result is an alternative formula for the nuclear reaction field given in terms of the following function

$$g_m(\epsilon_\infty, \epsilon) = \frac{\epsilon_\infty^2 + 2}{3}\left(\frac{\epsilon_\infty + 2}{3\epsilon_\infty}\right)^2 \frac{(\epsilon - 1)(\epsilon - \epsilon_\infty)}{2\epsilon^2 - \epsilon\epsilon_\infty - \epsilon_\infty} \tag{12}$$

This novel function, derived in more detail below, shows a significantly reduced alteration of the nuclear reaction field with changing ϵ_∞ compared to both the Lippert-McRae function $g(\epsilon) - g(\epsilon_\infty)$ and the Pekar-Marcus result in eq 10. The low sensitivity of the nuclear reaction field to ϵ_∞ or, alternatively, to the solvent polarizability is in general agreement with numerical simulations of dipolar solutes in polarizable liquids[27] (see below).

Polarization Functionals

In order to proceed to a microscopic theory of the spectral shift, one has to define the instantaneous energies $E_i(\Gamma_n)$ $(i = 1, 2)$ involved in the spectroscopic transitions and forming the instantaneous energy gap ΔE_n in eq 5. Those are obtained by assuming that the electronic degrees of freedom of the solvent follow adiabatically the changes in the electronic distribution of the solute. In terms of

the separation of time scales, this condition implies that the excitation frequencies ω_s of the solvent are much higher than the absorption/emission frequency of the chromophore $\omega_{\text{abs/em}}$. In other words, the spectrum is measured in the transparency window of the solvent.[18] This condition is mathematically expressed[28] by the requirement that the energies $E_i(\Gamma_n)$ are obtained by tracing out the electronic degrees of freedom of the solvent from the entire Hamiltonian of the system H_i

$$e^{-\beta E_i} = \text{Tr}_{s,e}\left[e^{-\beta H_i} \right] \tag{13}$$

We use the term "energies" or "instantaneous energies" when referring to E_i as a shorthand term for what should properly be called the partial free energies.[28] Electronic excitations of the bath caused by thermal agitation are allowed in the trace taken in eq 13 and the resulting E_i are generally functions of temperature.

More specifically, the problem is typically set up by specifying a nonequilibrium functional depending on two collective coordinates: the fast electronic polarization $\mathbf{P}_e$ and the slow nuclear polarization $\mathbf{P}_n$. In the Born-Oppenheimer approximation, the trace above is represented by taking the functional integral over the electronic polarization field $\mathbf{P}_e$ and the corresponding conjugate momentum $\mathbf{\Pi}_e$[28]

$$e^{-\beta E_i} = \int \mathcal{D}\mathbf{P}_e \mathcal{D}\mathbf{\Pi}_e e^{-\beta F_i[\mathbf{P}_n, \mathbf{P}_e]} \tag{14}$$

Macroscopic functionals

Two formulations for the functional of the continuum macroscopic fields $\mathbf{P}_e$ and $\mathbf{P}_n$, Pekar and Marcus, have been advanced in the literature. The earlier formulation by Pekar[18,19] considers two uncorrelated fields $\mathbf{P}_e$ and $\mathbf{P}_n$ interacting with the field of the external charges $\mathbf{E}_{0i}$

$$F_i[\mathbf{P}_n, \mathbf{P}_e] = \sum_\gamma \frac{1}{2\alpha_{ee}^\gamma} \mathbf{P}_e^\gamma * \mathbf{P}_e^\gamma$$
$$+ \sum_\gamma \frac{1}{2\alpha_{nn}^\gamma} \mathbf{P}_n^\gamma * \mathbf{P}_n^\gamma - \sum_\gamma \mathbf{P}^\gamma * \mathbf{E}_{0i}^\gamma \tag{15}$$

where

$$\mathbf{P}^\gamma = \mathbf{P}_e^\gamma + \mathbf{P}_n^\gamma \tag{16}$$

is the total polarization field density. Index $\gamma = L, T$ specifies either the longitudinal (L) or transverse (T) component of the field. According to the Helmholtz theorem,[3] any vector field $\mathbf{F}$ can be split into the longitudinal (irrotational) and transverse (solenoidal) components. They are orthogonal by producing zero of their scalar product integrated over the entire space, $\int \mathbf{F}^L \cdot \mathbf{F}^T d\mathbf{r} = 0$. Because of this orthogonality, there is no cross (L-T) components in the integrals in eq 15, where we use the shorthand notation

$$\mathbf{F} * \mathbf{G} = \int_\Omega \mathbf{F} \cdot \mathbf{G} \ d\mathbf{r} \tag{17}$$

The solvation susceptibilities α_{ab}^γ, $a, b = e, n$ in Pekar's functional in eq 15 are designed to produce the polarization of the liquid surrounding the solute $\mathbf{P}_{ia}^\gamma$ in equilibrium with the vacuum electric field of the solute charges

$$\mathbf{P}_{ia}^\gamma = \alpha_{aa}^\gamma \mathbf{E}_{0i}^\gamma \tag{18}$$

As is well known from the standard dielectric boundary value problem, the equilibrium polarization is a complex function of the boundary conditions projecting both the shape of the solute cavity and the symmetry of the field (typically expressed through the expansion in rotational invariants[3]) on the solvation susceptibility. The dielectric boundary conditions are set in terms of the dielectric constant of the material. In other words, a connection is sought between the solvation susceptibilities α_{ab}^γ and dielectric susceptibilities χ_{ab}^γ reported by the dielectric experiment. The separate electronic and nuclear susceptibilities are established based on their corresponding dielectric relaxation peaks.

Not sufficiently appreciated in the literature is the fact that the standard plane capacitor dielectric experiment reports the zero-frequency transverse susceptibility[25,29]

$$\chi^T = \frac{\epsilon - 1}{4\pi} = \frac{\beta}{\Omega} \lim_{\mathbf{k} \to 0} \langle |\tilde{\mathbf{P}}_e^T + \tilde{\mathbf{P}}_n^T|^2 \rangle \tag{19}$$

where $\tilde{\mathbf{P}}_e(\mathbf{k})$ and $\tilde{\mathbf{P}}_n(\mathbf{k})$ are the reciprocal-space polarization fields. The electronic component of the transverse susceptibility is separated experimentally by applying the alternating voltage with a sufficiently high frequency, at which all nuclear motions of the bulk dielectric are dynamically frozen. This requires frequencies in the optical part of the spectrum, and the high-frequency dielectric constant is associated with the optical refractive index, $\epsilon_\infty = n_D^2$. The high-frequency dielectric increment $\Delta \epsilon_M$, that is, the excess of the dielectric

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constant over the lowest possible value of unity, is associated with the transverse susceptibility $\chi_e^T = (\epsilon_\infty - 1)/(4\pi)$. One then assumes that the sequence of all remaining dielectric increments $\Delta\epsilon_j$, $j = 1, \ldots, M - 1$ has to be associated with various nuclear modes of the liquid projecting on its dipole moment. Assuming that all those nuclear modes are uncorrelated from the electronic induced molecular dipoles, one defines the nuclear transverse susceptibility χ_n^T by subtracting χ_e^T from χ^T

$$\chi_n^T = (\epsilon - \epsilon_\infty)/(4\pi) \qquad (20)$$

The longitudinal response of a dielectric can be measured by changing the charge at the capacitor plates, instead of the voltage in the standard setup.[23] The result of such an experimental setup is the dielectric modulus $1/\epsilon$, instead of the dielectric constant.[14] One correspondingly obtains a set of longitudinal dielectric susceptibilities: $\chi_e^L = (\epsilon_\infty - 1)/(4\pi\epsilon_\infty)$, $\chi^L = (\epsilon - 1)/(4\pi\epsilon)$, and

$$\chi_n^L = (\epsilon - \epsilon_\infty)/(4\pi\epsilon\epsilon_\infty) \qquad (21)$$

This set of susceptibilities is also based on the additivity assumption, that is, the absence of any cross-correlations between the electronic and nuclear dipoles, now extended from the transverse to the longitudinal dielectric response.

The sequence of severe simplifications outlined here was introduced in the original Pekar formulation[19] to treat the problem of polaron mobility in ionic crystals and was then transferred to the problem of electronic transitions in molecular systems with little or no modification. Before proceeding to improving the theory, it is useful to specify these assumptions: (i) the neglect of the transverse polarization of the dielectric and (ii) the neglect of the interaction (coupling) between the electronic and nuclear polarization fields. The connection between the solvation susceptibilities and dielectric susceptibilities is especially simple in the Pekar formalism

$$\alpha_{aa}^\gamma = \chi_{aa}^\gamma \qquad (22)$$

and

$$\alpha_{ab} \to \infty, \quad a \neq b \qquad (23)$$

The first approximation implies that only the longitudinal field projections $\mathbf{P}_e^L$ and $\mathbf{P}_n^L$ are included in the polarization functional. The restriction of the polarization fields to the longitudinal components limits the ability of the theory to connect to the standard dielectric boundary problem.[3]

The theory produces incorrect solvation susceptibilities for all distributions of the solute charge except for the special case of a spherical ion. The Pekar functional thus yields the Born susceptibility in eq 3, but is not capable of producing the Onsager susceptibility in eq 4. Both longitudinal and transverse dielectric susceptibilities are combined together in the dielectric boundary value problem to allow more complex functions of the dielectric constant than the one appearing in the Born equation.

A correct continuum form of α_{aa}^γ in eq 15 can be produced by either requiring eq 18 to be consistent with the dielectric boundary value problem or as the continuum $k \to 0$ limit of solvation susceptibilities produced by microscopic liquid-state theories. The latter route is based on the solution achieved in ref 30 for solvation of a spherical dipole. It suggests the following modification of α_{aa}^γ compared to the simplistic form in eq 22

$$\alpha_{aa} = \alpha_{aa}^L = \alpha_{aa}^T = \frac{3\chi_a^L \chi_a^T}{\chi_a^L + 2\chi_a^T} \qquad (24)$$

Connecting to eq 4, this relation implies $\alpha_d = \alpha_{aa}$.

Once the solvation susceptibilities α_{aa}^γ are defined, one can follow the sequence of standard steps to obtain the spectral shift. The first step is to ingrate out the electronic polarization field $\mathbf{P}_e$. Integrating the Gaussian functional in eq 14 is equivalent to minimizing $F[\mathbf{P}_e, \mathbf{P}_n]$ with respect to $\mathbf{P}_e$. Since the electronic and nuclear polarization fields are uncorrelated, one obtains for the instantaneous energy (partial free energy) depending on the fluctuating field $\mathbf{P}_n$

$$E_i[\mathbf{P}_n] = F_{e,i} + \sum_\gamma \frac{1}{2\alpha_{nn}^\gamma} \mathbf{P}_n^\gamma * \mathbf{P}_n^\gamma - \sum_\gamma \mathbf{P}_n^\gamma * \mathbf{E}_{0i}^\gamma \qquad (25)$$

Here, the free energy of electronic solvation is

$$F_{e,i} = -\frac{\alpha_{ee}}{2} \sum_\gamma \mathbf{E}_{0i}^\gamma * \mathbf{E}_{0i}^\gamma = -\frac{\alpha_{ee}}{2} \mathbf{E}_{0i} * \mathbf{E}_{0i} \qquad (26)$$

where we have dropped the projection label since the susceptibilities α_{ee}^γ are equal per eq 24.

For the field of the spherical dipole ($\hat{\mathbf{r}} = \mathbf{r}/r$)

$$\mathbf{E}_{0i} = \mathbf{m}_i \cdot (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{1})\, r^{-3} \qquad (27)$$

one obtains $\mathbf{E}_{0i} * \mathbf{E}_{0i} = (8\pi/3)(m_i^2/R_0^3)$. The Onsager equation then follows for the solvation free

energy

$$F_{e,i} = -\frac{m_i^2}{R_0^3} g(\epsilon_\infty) \qquad (28)$$

The spectral shift immediately follows from eqs 5, 6, and 25 as

$$\hbar\Delta\omega = \Delta F_e - \sum_\gamma \Delta\mathbf{E}_0^\gamma * \mathbf{P}_{n1}^\gamma \qquad (29)$$

where $\Delta\mathbf{E}_0^\gamma = \mathbf{E}_{02}^\gamma - \mathbf{E}_{01}^\gamma$ and the equilibrium ground-state polarization density is $\mathbf{P}_{n1}^\gamma = \alpha_{nn}^\gamma \mathbf{E}_{01}^\gamma$. We therefore obtain from eqs 24 and 29

$$\hbar\Delta\omega = \Delta F_e - \frac{2\Delta m m_1}{R_0^3} g(\epsilon_\infty, \epsilon) \qquad (30)$$

where ΔF_e is given by eq 9, but, in contrast to eq 8, the nuclear response function is not represented as the difference of the corresponding total and electronic solvation susceptibilities. We obtain eq 10 instead.

The electronic and nuclear polarization fields are uncoupled in the Pekar functional, which is reflected by the infinite values of the cross susceptibilities α_{ab} in eq 23. This is not a physically justified starting point. It is clear that induced and permanent dipoles interact in a polar-polarizable liquid and this physical reality needs be reflected in the functional, at least at the outset. The quadratic functional can of course be diagonalized to eliminate the cross terms, but the physical interactions in the liquid should enter the resulting diagonal susceptibilities. This is achieved below in terms of microscopic nonlocal susceptibilities. Before turning to the full microscopic description, we first briefly discuss the distinctions between the Pekar and Marcus[20,21] functionals.

The Marcus[20,21] functional, and some alternative formulations proposed in the literature,[11,22,31] accounts for the interactions between the induced and permanent dipoles in the liquid in the form of the Coulomb dipole-dipole potential. While this interaction term eliminates the assumption of non-interacting fields of the Pekar functional, the polarization fields involved still carry the longitudinal symmetry. Therefore, the coupling between the electronic and nuclear polarization fields is accounted for in these functionals as the Coulomb interactions between the corresponding longitudinal vector fields.[22,32] This description is inconsistent with the microscopic functional discussed below in two critical aspects: (i) the transverse components of the polarization fields are coupled as well and,

more importantly, (ii) the Coulomb interaction is insufficient to correctly account for the coupling between the polarization fields. The reason for the latter is that coarse graining the microscopic polarization into a polarization field $\mathbf{P}_{e,n}$ "dresses" the Coulomb interaction with correlations arising from the local liquid structure, thus significantly modifying the corresponding cross susceptibilities. One needs a consistent microscopic theory to derive such "dressed" susceptibilities.

Returning back to the Marcus functional, one can represent its different forms suggested in the literature[11,22,31] by putting the solvation susceptibilities in the matrix $(A^\gamma)_{ab} = \alpha_{ab}^\gamma$. The result is the following concise form

$$F_i[\mathbf{P}_e, \mathbf{P}_n] = \tfrac{1}{2} \sum_\gamma \sum_{a,b} A_{ab}^\gamma \mathbf{P}_a^\gamma * \mathbf{P}_b^\gamma - \sum_\gamma \mathbf{P}^\gamma * \mathbf{E}_{0i}^\gamma. \qquad (31)$$

The longitudinal matrix $\mathbf{A}^L$ contains off-diagonal matrix elements describing Coulomb interaction between $\mathbf{P}_e$ and $\mathbf{P}_n$

$$\mathbf{A}^L = \begin{pmatrix} \alpha_{ee}^{-1} & (4\pi)^{-1} \\ (4\pi)^{-1} & \alpha_{nn}^{-1} \end{pmatrix} \qquad (32)$$

The diagonal susceptibilities α_{ee} and α_{nn} consistent with the dipolar solvation are given by eq 24. The matrix $\mathbf{A}^T$ is diagonal, with the same elements on the diagonal as in the matrix $\mathbf{A}^L$ and zeros for the off-diagonal elements.

Repeating the same steps as above for the spectral shift, we again arrive at eqs 10 and 30. The conclusion of this procedure is that both the Pekar and the Marcus functionals produce identical expressions for the spectral shift.[12] The result is however distinct from the Lippert-McRae equation (eq 8). We now turn to the nonlocal formulation of the problem in terms of reciprocal space susceptibilities $\alpha_{ab}^\gamma(k)$. These susceptibilities can be either directly calculated from computer simulations of polar-polarizable fluids or calculated from parameterization schemes based on analytic functions[33] produced by solutions of integral equations for dipolar liquids.[34]

Microscopic formulation

Microscopic functionals for solvation problems are formulated based on the corresponding functionals for the homogeneous polar liquids accounting for microscopic correlations between the liquid molecules. Several routes can be taken to arrive

at the Gaussian functional in terms of reciprocal-space continuous fields[30,35,36] $\tilde{\mathbf{P}}_e(\mathbf{k})$ and $\tilde{\mathbf{P}}_n(\mathbf{k})$. A significant point regarding all such constructs was made by Chandler,[36] who emphasized that the repulsive core of the solute renormalizes the standard Gaussian functionals in ways that cannot by introduced by adding the repulsion potential to the functional.

The role of repulsions is to introduce a part of the direct space excluded from the reach of fluctuations.[37] This is a fundamentally nonlinear perturbation of the liquid. If such an excluded manifold is consistently introduced in the construction of the Gaussian functional, its Gaussian form can still be maintained, in a certain approximation, but the Gaussian susceptibility entering the quadratic term of the functional is renormalized in a way analogous to introducing boundary conditions into the corresponding equations of motion. In application to polar solvation, this perspective clearly shows that the standard Pekar and Marcus functionals are only approximations to the real solvation problem.[38] They do not take into account the combination of the symmetry imposed by the shape of the solute and its specific charge distribution and are capable of producing only Born-like solvation susceptibilities (eq 3).

A full solution for the problem of renormalizing the Gaussian nonlocal susceptibility by the repulsive core of the solute leads to significant technical difficulties rooted in the inhomogeneous character of the problem. The scalar susceptibility α^{solv} in Eq. 2 is generalized to a second rank tensor $\boldsymbol{\alpha}^{\mathrm{solv}}(\mathbf{r}', \mathbf{r}'')$ such that the solvation energy is a convolution of vacuum fields with the susceptibility function

$$F = -\tfrac{1}{2}\mathbf{E}_0 * \boldsymbol{\alpha}^{\mathrm{solv}} * \mathbf{E}_0 \qquad (33)$$

While it is in principle possible to obtain a general solution for $\tilde{\boldsymbol{\alpha}}(\mathbf{k}', \mathbf{k}'')$ in reciprocal space,[39] calculation of the 6D integral in eq 33 is computationally challenging. Fortunately, an exact closed-form solution, avoiding such integrals, can be obtained for a spherical dipole.[30] This analytical form for the microscopic solvation susceptibility is used here to calculate the nuclear response entering the spectral shift. This application, and eq 12 following from it, is a novel result of this study. Our main focus is on how reliable is the additivity concept incorporated in the Lippert-McRae approach when confronted with exact solutions based on microscopic liquid-state theories. The fact that this formula (eq 7)

contradicts both the Pekar and Marcus functionals suggests the need for an alternative solution.

Since the main issue discussed here is the nuclear solvent response, we leave aside the complete formulation of the problem in terms of the electronic and nuclear polarization fields and turn directly to the functional $E_i[\tilde{\mathbf{P}}_n]$ of the nuclear polarization. The other term entering eq 8 is the electronic solvation free energy ΔF_e. It can be calculated by applying different levels of the theory, but the physical meaning of this term is well defined and will not be discussed any further.

The instantaneous energy $E_i[\tilde{\mathbf{P}}_n]$ as a functional of the reciprocal space nuclear polarization field $\tilde{\mathbf{P}}_n$ is formulated in terms of the dipolar susceptibility $\chi_{nn}^{\gamma}(k)$ and the screening function $q^{\gamma}(k)$. The expression for $E_i[\tilde{\mathbf{P}}_n]$ has the form[33,39]

$$\begin{aligned} E_i[\tilde{\mathbf{P}}_n] = F_{e,i} + \tfrac{1}{2}\sum_{\gamma,\mathbf{k}}(\chi_{nn}^{\gamma})^{-1}\tilde{\mathbf{P}}_n^{\gamma}\cdot\tilde{\mathbf{P}}_n^{\gamma} \\ - \sum_{\gamma,\mathbf{k}}q^{\gamma}(k)\tilde{\mathbf{P}}_n^{\gamma}\cdot\tilde{\mathbf{E}}_0^{\gamma} \end{aligned} \qquad (34)$$

The nonlocal nuclear susceptibility

$$\chi_{nn}^{\gamma}(k) = \alpha_{nn}^{\gamma}(k)\left(1 - \frac{\alpha_{ee}^{\gamma}(k)\alpha_{nn}^{\gamma}(k)}{\alpha_{en}^{\gamma}(k)^2}\right)^{-1} \qquad (35)$$

is defined in terms of nonlocal functions $\alpha_{ab}^{\gamma}(k)$ forming the L and T 2×2 matrices $\mathbf{A}^{\gamma}$ in the functional $F_i[\tilde{\mathbf{P}}_e, \tilde{\mathbf{P}}_n]$. The susceptibility function $\chi_{nn}^{\gamma}(k)$ appears in the form given by eq 35 after minimizing the functional $F_i[\tilde{\mathbf{P}}_e, \tilde{\mathbf{P}}_n]$ in terms of the electronic polarization field $\tilde{\mathbf{P}}_e$. Note that the cross component, $\propto \tilde{\mathbf{P}}_e * \tilde{\mathbf{P}}_n$, which is present already in the longitudinal term of the continuum Marcus functional (eqs 31 and 32), is what requires a separate susceptibility function $\chi_{nn}(k)$. One obtains $\chi_{nn}^{\gamma} = \alpha_{nn}^{\gamma}$ when $\alpha_{en}^{\gamma} \to \infty$, which is the assumption adopted in the Pekar functional (eqs 15 and 23). We use here the shorthand notation α_{ab}^{γ} and χ_{nn}^{γ} for the $k = 0$ values of the corresponding nonlocal susceptibilities.

The nuclear solvation susceptibilities $\chi_{nn}^{\gamma}(k)$ can be also related to nonlocal susceptibilities of the bulk solvent $\chi_n^{\gamma}(k)$. This connection is analogous to the connection established between the solvation susceptibilities and dielectric susceptibilities in the dielectric boundary value problem, with the exception that the nonlocal susceptibilities $\chi_n^{\gamma}(k)$ reflect microscopic correlations of dipoles in the liquid. The $k \to 0$ limit of these functions connect them

to dielectric susceptibilities of the dielectric experiment. The solution of this problem for a spherical dipole is given by the following relations[30]

$$
\begin{aligned}
\chi_{nn}^{L}(k) &= \frac{3\chi_{n}^{T}}{\chi_{n}^{L} + 2\chi_{n}^{T}}\chi_{n}^{L}(k) \\
\chi_{nn}^{T}(k) &= \frac{3\chi_{n}^{L}}{\chi_{n}^{L} + 2\chi_{n}^{T}}\chi_{n}^{T}(k)
\end{aligned}
\tag{36}
$$

where, as in eq 24, $\chi_{n}^{\gamma} = \chi_{n}^{\gamma}(0)$. However, in contrast to the continuum functionals discussed above, with the susceptibilities given by eqs 20 and 21, we have the following $k = 0$ values in eq 36

$$
\begin{aligned}
\chi_{n}^{L} &= \frac{\epsilon - 1}{4\pi\epsilon} \\
\chi_{n}^{T} &= \frac{\epsilon - \epsilon_{\infty}}{4\pi\epsilon_{\infty}}
\end{aligned}
\tag{37}
$$

These functional forms are consistent with numerical simulations of polarizable liquids.[33]

The nonlocal susceptibilities $\chi_{n}^{\gamma}(k) \propto S_{n}^{\gamma}(k)$ are defined through the orientational structure factors $S_{n}^{\gamma}(k)$ describing longitudinal and transverse orientational fluctuations of the permanent dipoles in bulk polar liquid.[30,40,41] Analytic forms for these functions have been recently developed on the basis of computer simulations of polar-polarizable fluids.[33] These functions are parametrized based on the solution of the mean-spherical approximation for dipolar hard spheres.[34] However, due to rather generic properties of polar interactions, these reparametrized functionalities are capable of reproducing dipolar fluctuations in molecular liquids as produced by molecular simulations.[33,41] They are listed in the Supporting Information for completeness.

Finally, the nonlocal functions $q^{\gamma}(k)$ in eq 34 represent screening of the vacuum electric field of the solute by the induced dipoles in the solvent, which are in equilibrium with both that field and the instantaneous nuclear polarization of the liquid $\mathbf{P}_{n}$. This procedure of establishing the equilibrium field $\mathbf{P}_{ie}^{L}$ is known in the literature as the Marcus partitioning,[13] in contrast to the Pekar partitioning for which the equilibrium polarization is in equilibrium with the vacuum field only. Mathematically, the screening arises from the cross susceptibility $\alpha_{en}^{\gamma}(k)$ in the polarization functional, which couples the electronic and nuclear polarization fields. Since this coupling is eliminated in the Pekar functional, $q^{\gamma} = q^{\gamma}(0) = 1$ in that case. The continuum Marcus functional yields[22] $q^{L} = \epsilon_{\infty}^{-1}$ and $q^{T} = 1$.

Both the longitudinal and transverse projections of $q^{\gamma}(k)$ in principle depend on the wavevector k in the microscopic model. However, the results of numerical simulations suggest that this dependence is very weak and can be usually neglected.[33] One arrives at simple approximate forms for these screening functions[33,42] consistent with Lorenz screening in dielectrics[24]

$$
\begin{aligned}
q^{L} &= \frac{\epsilon_{\infty} + 2}{3\epsilon_{\infty}} \\
q^{T} &= \frac{\epsilon_{\infty} + 2}{3}
\end{aligned}
\tag{38}
$$

Equation 38 is obtained under the same assumptions about the correlations between the induced dipoles in the polarizable liquid as those leading to the Clausius-Mossotti equation for ϵ_{∞}.[25] While these forms are consistent with simulations,[33] more accurate summation of diagrams appearing in the multi-particle theories of induced polarization[43] might lead to improved screening functions.

Once all k-dependent susceptibilities and screening factors in eq 34 have been specified, one can proceed to establishing the microscopic expression for the nuclear spectral shift. It follows immediately from the Gaussian form of the polarization functional in eq 34

$$
\langle \Delta E_{n} \rangle_{1} = -\sum_{\gamma, \mathbf{k}} (q^{\gamma})^{2}\chi_{nn}^{\gamma}(k)\mathrm{Re}\left[\Delta\tilde{\mathbf{E}}_{0}^{\gamma} \cdot \tilde{\mathbf{E}}_{01}^{\gamma}\right] \tag{39}
$$

The $k \to 0$ limit taken in $\chi_{nn}^{\gamma}(k)$ allows us to establish the continuum limit in this expression. This limit turns out to be distinct from what we obtained above for the Marcus and Pekar functionals since both the screening functions and the $k \to 0$ nuclear susceptibilities χ_{n}^{γ} (eq 37) are somewhat different from those used in those functionals (eqs 20 and 21). The result is a new continuum limit for the nuclear shift of the spectral line in eq 30, with the polarity function given by eq 12.

Using eq 39, the final expression for the nuclear component of the spectral shift is

$$
\langle \Delta E_{n} \rangle_{1} = -\frac{2\Delta m m_{1}}{R_{1}^{3}}\frac{g_{m}(\epsilon_{\infty}, \epsilon)}{\epsilon_{\infty}^{2} + 2}\left[\epsilon_{\infty}^{2}J^{T} + 2J^{L}\right] \tag{40}
$$

where $g_{m}(\epsilon_{\infty}, \epsilon)$ is given by eq 12,

$$
J^{\gamma} = \frac{6R_{1}}{\pi}\int_{0}^{\infty} j_{1}(kR_{1})^{2}(\chi_{n}^{\gamma}(k)/\chi_{n}^{\gamma})dk \tag{41}
$$

and $j_{\ell}(x)$ is the spherical Bessel function of order
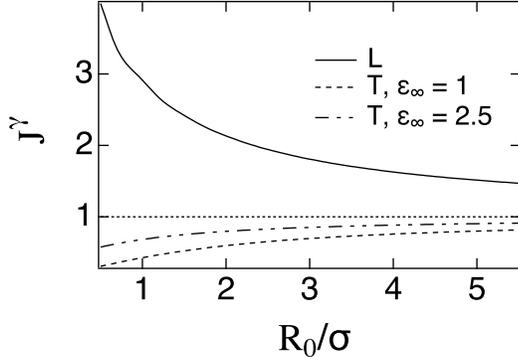
9

ℓ.[44]

Figure 1: Integrals J^γ from eq 41 for $\gamma = \{L, T\}$ vs the ratio of the solute radius R_0 to the solvent diameter σ. J^L does not depend on ϵ_∞, J^T is shown for $\epsilon_\infty = 1$ (dashed line) and $\epsilon_\infty = 2.5$ (dash-dotted line); $\epsilon = 78$. The dotted line indicates the continuum limit $J^\gamma = 1$. The functional form of the nonlocal susceptibilities $\chi_n^\gamma(k)$ is provided in the Supporting Information.

Note that when the finite size of the solvent molecules is specified by their effective diameter σ, the effective radius of the solute becomes the radius of the solvent-excluded sphere, $R_1 = R_0 + \sigma/2$. The continuum limit is achieved mathematically in eqs 40 and 41 by shrinking the solvent size to zero, $\sigma \to 0$, and, correspondingly, assuming $\chi_n^\gamma(k) \to \chi_n^\gamma$. One obtains $J^\gamma = 1$ for the integrals in eq 41 and the continuum result with $g_m(\epsilon_\infty, \epsilon)$ from eq 12. In physical systems, the continuum limit is reached with increasing the solute size to the limit $R_0/\sigma \gg 1$. However, this limit is not reached for the typical molecular sizes of optical dyes, $R_0/\sigma \simeq 1$, and the deviation of J^γ from the continuum result $J^\gamma = 1$ remains substantial (Figure 1).

Figure 2 presents illustrative calculations of the nuclear spectral shift $\langle \Delta E_n \rangle_1$ following from different theories discussed here. The nuclear shift is calculated by changing ϵ_∞ while keeping ϵ constant. This is not a fully realistic approximation when applied to real polar liquids since ϵ should generally increase when the polarizability of the liquid increases at the constant value of the permanent dipole moment.[26] However, at the typical situation of $\epsilon \gg \epsilon_\infty$ the sensitivity of the final result to the changes in ϵ is not significant. The results shown in Figure 2 are meant to illustrate the main point of our analysis, which is a significant difference in
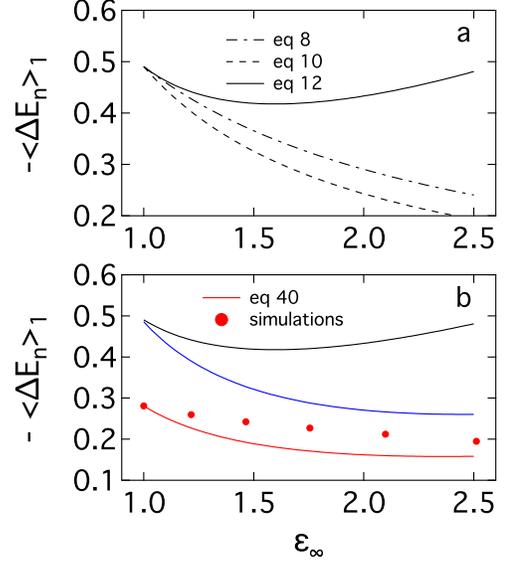

Figure 2: Normalized nuclear spectral shift $-R_0^3 \langle \Delta E_n \rangle_1 / (2\Delta m m_1)$ vs ϵ_∞. (a) The result of the Lippert-McRae formula (eq 8, dash-dotted line), of the Pekar-Marcus functional (eq 10, dashed line), and of the continuum limit of our calculations (eq 12, solid black lines, reproduced in both panels for comparison with other results). (b) The solid red line refers to the result of calculating k-integrals with the nonlocal susceptibilities in eqs 40 and 41 at $R_0/\sigma = 0.9$ and $R_1 = R_0 + \sigma/2 = 1.4\sigma$. The blue line denotes the same calculation performed with $R_1 = 1.2\sigma$. The static dielectric constant is not varied and is set at the value of water $\epsilon = 78$ and the polarity parameter is $y = 3.86$. The points refer to the results of Monte Carlo simulations of a spherical dipole in a solvent of dipolar polarizable spheres ($R_0/\sigma = 0.9$).[27] The simulation results are scaled to make them consistent with the k-integration (the red line) at $\epsilon_\infty = 1$.

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the sensitivity of $\langle \Delta E_n \rangle_1$ to changes in ϵ_∞ between our present analysis and the classical theories.

The calculations shown in Figure 2a were done for a water-like solvent with $\epsilon = 78$ and varied ϵ_∞. The nuclear dipolar susceptibility following from the Pekar and Marcus functionals (eq 10, dashed line) produces a somewhat stronger dependence of the nuclear shift on ϵ_∞ than the standard Lippert-McRae approximation[7,8] (eq 8, dash-dotted line). A significantly different result is obtained in the continuum limit of the microscopic parametrization of the liquid susceptibility functions given by eq 12.[33] There is a very weak variation of the nuclear spectral shift, with a shallow minimum. Given the typical range of ϵ_∞ available to experiment, this minimum can hardly be observed. One can therefore conclude that for any practical purposes the microscopic parametrization of the polarization functional (eq 34) produces no detectable dependence of the nuclear shift on ϵ_∞ in the continuum limit $R_0/\sigma \gg 1$. We discuss next how reliable this continuum limit is in application to typical molecular chromophores, but first note that approximations pertinent to the derivation of the Clausius-Mossotti equation[25] were applied in deriving the screening functions in eq 38. The range of ϵ_∞ values should not be extended much beyond that used in Figure 2 without a more rigorous calculations of the corresponding screening functions.

The results of microscopic calculations based on integrating the nonlocal susceptibilities in eqs 40 and 41 are shown in Figure 2b. These calculations require some additional parameters (see Supporting Information for more detail). Since the nuclear susceptibility functions of the bulk solvent $\chi_n^\gamma(k)$ depend on $k\sigma$, one has to specify the ratio of the solute size to the solvent diameter, R_0/σ. In addition, the $k \to \infty$ asymptote $\chi_n^\gamma(\infty)$ is equal to $3y/(4\pi)$, where $y = (4\pi/9)\beta\rho m^2$ is the standard polarity parameter of dielectric theories[24,26] (ρ is the number density, m is the dipole moment, and $\beta = 1/(k_B T)$ is the inverse temperature). The results of microscopic calculations with $R_0/\sigma = 0.9$ and $y = 3.86$ (taken for SWM4-DP[45] water) are shown by the solid red line in Figure 2b.

The spectral shift from microscopic calculations is somewhat lower than in the continuum limit, which is a consequence of increasing the solute radius from the van der Waals radius R_0 to the radius of the solvent-excluded sphere $R_1 = R_0 + \sigma/2$. The effective radius of the solute, considered as an adjustable parameter, typically falls between these two limiting values. A consistent route to the effective solute radius is provided by liquid-state perturbation theories, which result in the following definition of the effective radius R_eff for the problem of dipolar solvation[46]

$$R_\text{eff}^{-3} = 3 \int_0^\infty g_{0s}(r)(dr/r^4) \qquad (42)$$

This definition is based on the solute-solvent radial pair distribution function $g_{0s}(r)$ and typically results in $R_0 < R_\text{eff} < R_1$. Indeed, replacing $R_1/\sigma = 1.4$ with $R_\text{eff}/\sigma = 1.2$ in the microscopic calculations shown in Figure 2b ($R_0/\sigma = 0.9$) results in an upward increase of the spectral shift to its continuum value at $\epsilon_\infty = 1$. However, the dependence on ϵ_∞ is somewhat stronger with this choice of the radius than for the continuum result (cf. blue and black lines in Figure 2b). This is caused by the deviation of the integrals J^γ from their continuum limit $J^\gamma = 1$ in this range of solute sizes (Figure 1). This calculation thus demonstrates that the dependence of the spectral shift on ϵ_∞ slightly changes with the solute size, but never reaches the steepness of the Lippert-McRae and Pekar-Marcus predictions.

In order to further illustrate the consistency of our results with other available evidence, we also show the results of numerical Monte Carlo simulations of a spherical dipolar solute in a set of polar polarizable fluids with constant permanent dipole and varying polarizability[27] (the dielectric constant increased in simulations with increasing ϵ_∞, in contrast to our present calculations where it was held constant). The simulations refer not to the spectral shift, but to the reorganization energy, which is half of the Stokes shift[47] (difference between the absorption and emission spectral maxima). Note that the electronic part of the spectral shift ΔF_e cancels out in the Stokes shift and the reorganization energy physically represents the nuclear response of the solvent when the linear response approximation is applied. The points in Figure 2 are arbitrarily scaled to coincide with the microscopic calculation at $\epsilon_\infty = 1$. This qualitative comparison indicates that the weak dependence of the nuclear response on ϵ_∞, consistent with our present calculations, also follows from numerical simulations.

Discussion and Conclusions

The main goal of our analysis is to scrutinize the additivity assumption introduced by Lippert[7] and McRae[8] to calculate the nuclear reaction field acting on the chromophore's dipole moment in optical transitions. This concept originates from the empirically established additivity of the transverse dielectric response of bulk materials obtained experimentally by modulating voltage in the plane capacitor dielectric experiments. In such measurements, dielectric decrements $\Delta\epsilon_j$ arising from dynamic processes characterized by relaxation times τ_j add up to $\epsilon - 1$, where ϵ is the total static dielectric constant. The additivity concept breaks down already for the longitudinal response, such as shown in the Born susceptibility in eq 3. It is clear from eq 3 that additivity of $\epsilon = \sum_j \Delta\epsilon_j$ does not project to additivity of α^L. However, explicit calculations and computer simulations[33] show that one can still construct the longitudinal nuclear response by subtracting $\alpha_{ee}^L = \chi_e^L$ from $\alpha^L = \chi^L$ in eq 3. This subtraction yields the famous Pekar factor responsible for the solvent effect in continuum models of nuclear solvation.[19,20] This success is, however, limited to a single solvation configuration, the spherical ion. Being a very special case, solvation of a spherical ion does not expose the difficulties encountered with a general case of nonspherical molecules carrying a complex distribution of charge.

The situation with the additivity hypothesis becomes more entangled for solutes of complex shape and charge distribution. We have studied here the case of dipole solvation, which is the main target in spectral shift calculations. From a more fundamental perspective, the advantage of this special case is that it, on the one hand, exposes the difficulties encountered with charge distributions requiring both longitudinal and transverse solvent responses and, on the other hand, allows exact solutions for the microscopic solvation susceptibilities.[30] We have taken full advantage of this latter opportunity to show that the electronic and nuclear solvation susceptibilities, such as given by eq 24, are complex functions of the corresponding longitudinal and transverse dielectric susceptibilities. This complex form does produce, in its continuum limit, the Onsager expression for the electronic component of the shift, ΔF_e, in eq 8. However, the mixing of the static, ϵ, and electronic, ϵ_∞, dielectric constants in the nuclear solvation susceptibility leads to the functionality which does not allow the additivity suggested by the Lippert-McRae formula (eq 8). We conclude that the Lippert-McRae equation is only an *ad hoc* guess.

The physical reason behind the failure of the additivity assumption is the actual physical interactions between the permanent and induced dipoles in the liquid through long-range Coulomb interactions and local structural correlations. These interactions only implicitly, through the susceptibilities, are taken into account in the Pekar functional and are represented by Coulomb interactions in the Marcus functional. Both representations are inconsistent with the liquid-state theories and simulations. The correct result can be obtained as the continuum $k \to 0$ limit of microscopic models and simulations.[33] This approach has allowed us to build the effective nuclear susceptibility functions $\chi_{nn}^\gamma(k)$ (eq 35), which incorporate the cross induced-permanent dipolar correlations in its longitudinal and transverse components ($\gamma = L, T$).[33] The cross correlations are also responsible for the appearance of the screening functions $q^\gamma(k)$ in the microscopic functional (eq 34). Those are found to satisfy the Lorentz form given by eq 38. The combination of $\chi_{nn}^\gamma(k)$ and q^γ leads to the solvent effect on the nuclear spectral shift described in its continuum limit by $g(\epsilon_\infty, \epsilon)$ in eq 12, where two dielectric constants, ϵ_∞ and ϵ, enter a complex functional form quite distinct from the Lippert-McRae function. Overall, the dependence of the nuclear spectral shift on ϵ_∞ is much weaker than predicted by the classical theories employed in the field.

Supporting Information Available: Derivation of equations used in the text and parametrization of the nonlocal solvent susceptibilities. This material is available free of charge via the Internet at `http://pubs.acs.org/`.

References

(1) Gray, C. G.; Gubbins, K. E. *Theory of Molecular Liquids*; Clarendon Press: Oxford, 1984.

(2) Landau, L. D.; Lifshitz, E. M. *Electrodynam-*

ics of Continuous Media; Pergamon: Oxford, 1984.

(3) Jackson, J. D. *Classical Electrodynamics*; Wiley: New York, 1999.

(4) Born, M. Volumen und Hydratationswärme der Ionen. *Z. Phys.* **1920**, *1*, 45–48.

(5) Onsager, L. Electric Moments of Molecules in Liquids. *J. Am. Chem. Soc.* **1936**, *58*, 1486–1493.

(6) Reichardt, C. Solvatochromic Dyes as Solvent Polarity Indicators. *Chem. Rev.* **1994**, *94*, 2319–2358.

(7) E. Lippert, Spectroscopische Bestimmung des Dipolmomentes Aromatischer Verbindungen im Ersten Angeregten Singulettzustand. *Z. Electrochem.* **1957**, *61*, 962–975.

(8) McRae, E. G. Theory of Solvent Effects on Molecular Electronic Spectra. Frequency Shifts. *J. Phys. Chem.* **1957**, *61*, 562–572.

(9) Suppan, P. Solvatochromic Shifts: The Influence of the Medium on the Energy of Electronic States. *J. Photochem. Photobiol. A* **1990**, *50*, 293–330.

(10) Brady, J. E.; Carr, P. W. An Analysis of Dielectric Models of Solvatochromism. *J. Phys. Chem.* **1985**, *89*, 5759–5766.

(11) Aguilar, M. A.; Olivares del Valle, F. J.; Tomasi, J. Nonequilibrium Solvation: An *Ab Initio* Quantum-Mechanical Method in the Continuum Cavity Model Approximation. *J. Chem. Phys.* **1993**, *98*, 7375–7384.

(12) Aguilar, M. A. Separation of the Electric Polarization into Fast and Slow Components: A Comparison of Two Partition Schemes. *J. Phys. Chem. A* **2001**, *105*, 10393–10396.

(13) Cossi, M.; Barone, V. Separation between Fast and Slow Polarizations in Continuum Solvation Models. *J. Phys. Chem. A* **2000**, *104*, 10614–10622.

(14) Richert, R. Supercooled Liquids and Glasses by Dielectric Relaxation Spectroscopy. *Adv. Chem. Phys.* **2015**, *156*, 101–195.

(15) Böttcher, C. J. F. *Theory of Electric Polarization*; Elsevier, 1973; Vol. 2.

(16) Tielrooij, K.-J.; Hunger, J.; Buchner, R.; Bonn, M.; Bakker, H. J. Influence of Concentration and Temperature on the Dynamics of Water in the Hydrophobic Hydration Shell of Tetramethylurea. *J. Am. Chem. Soc.* **2010**, *1332*, 15671–15678.

(17) Cametti, C.; Marchetti, S.; Gambi, C. M. C.; Onori, G. Dielectric Relaxation Spectroscopy of Lysozyme Aqueous Solutions: Analysis of the delta-Dispersion and the Contribution of the Hydration Water. *J. Phys. Chem. B* **2011**, *115*, 7144–7153.

(18) Pekar, S. I. Local Quantum States of Electrons in an Ideal Ion Crystal. *JETP* **1946**, *16*, 341–348.

(19) Pekar, S. I. *Research in Electron Theory of Crystals*; USAEC: Washington, D.C., 1963.

(20) Marcus, R. A. Electrostatic Free Energy and Other Properties of States Having Nonequilibrium Polarization. I. *J. Chem. Phys.* **1956**, *24*, 979–989.

(21) Marcus, R. A. Free-Energy of Nonequilibrium Polarization Systems .4. A Formalism Based on the Nonequilibrium Dielectric Displacement. *J. Phys. Chem.* **1994**, *98*, 7170–7174.

(22) Lee, S.; Hynes, J. T. Solution Reaction Path Hamiltonian for Reactions in Polar Solvents. I. Formulation. *J. Chem. Phys.* **1988**, *88*, 6853–6862.

(23) Fröhlich, H. *Theory of Dielectrics*; Oxford University Press: Oxford, 1958.

(24) Böttcher, C. J. F. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1973; Vol. 1.

(25) Madden, P.; Kivelson, D. A Consistent Molecular Treatment of Dielectric Phenomena. *Adv. Chem. Phys.* **1984**, *56*, 467–566.

(26) Stell, G.; Patey, G. N.; Høye, J. S. Dielectric Constants of Fluid Models: Statistical Mechanical Theory and its Quantitative Implementation. *Adv. Chem. Phys.* **1981**, *48*, 183–328.

(27) Gupta, S.; Matyushov, D. V. Solvent and Solute Polarizability Effects on the Reorganization Energy of Electron Transfer. *J. Phys. Chem. A* **2004**, *108*, 2087–2096.

(28) Matyushov, D. V.; Ladanyi, B. M. Dispersion Solute-Solvent Coupling in Electron Transfer Reactions. I. Effective Potential. *J. Chem. Phys.* **1998**, *108*, 6362–6377.

(29) Kivelson, D.; Friedman, H. Longitudinal Dielectric Relaxation. *J. Phys. Chem.* **1989**, *93*, 7026–7031.

(30) Matyushov, D. V. Dipole Solvation in Dielectrics. *J. Chem. Phys.* **2004**, *120*, 1375–1382.

(31) Kim, H. J.; Hynes, J. T. Equilibrium and Nonequilibrium Solvation and Solute Electronic Structure. III. Quantum Theory. *J. Chem. Phys.* **1992**, *96*, 5088–5110.

(32) Felderhof, B. U. Fluctuations of Polarization and Magnetization in Dielectric and Magnetic Media. *J. Chem. Phys.* **1977**, *67*, 493–500.

(33) Dinpajooh, M.; Newton, M. D.; Matyushov, D. V. Free Energy Functionals for Polarization Fluctuations: Pekar Factor Revisited. *J. Chem. Phys.* **2017**, *145*, 064504 (1-18).

(34) Wertheim, M. S. Exact Solution of the Mean Spherical Model for Fluids of Hard Spheres with Permanent Electric Dipole Moments. *J. Chem. Phys.* **1971**, *55*, 4291–4298.

(35) Chandra, A.; Bagchi, B. Microscopic Free Energy Functional for Polarization Fluctuations: Generalization of Marcus–Felderhof Expression. *J. Chem. Phys.* **1991**, *94*, 2258–2261.

(36) Chandler, D. Gaussian Field Model of Fluids with an Application to Polymeric Fluids. *Phys. Rev. E* **1993**, *48*, 2898–2905.

(37) Li, H.; Kardar, M. Fluctuation-Induced Forces Between Manifolds Immersed in Correlated Fluids. *Phys. Rev. A* **1992**, *46*, 6490–6500.

(38) Song, X.; Chandler, D.; Marcus, R. A. Gaussian Field Model of Dielectric Solvation Dynamics. *J. Phys. Chem.* **1996**, *100*, 11954–11959.

(39) Matyushov, D. V. Solvent Reorganization Energy of Electron Transfer in Polar Solvents. *J. Chem. Phys.* **2004**, *120*, 7532–7556.

(40) Fonseca, T.; Ladanyi, B. M. Wave Vector Dependent Static Dielectric Properties of Associated Liquids: Methanol. *J. Chem. Phys.* **1990**, *11*, 8148–8155.

(41) Milischuk, A. A.; Matyushov, D. V.; Newton, M. D. Activation Entropy of Electron Transfer Reactions. *Chem. Phys.* **2006**, *324*, 172–194.

(42) Matyushov, D. V. Reorganization Energy of Electron Transfer in Polar Liquids: Dependence on the Reactant Size, Temperature, and Pressure. *Chem. Phys.* **1993**, *174*, 199–218.

(43) Wertheim, M. S. Theory of Polar Fluids – V. Thermodynamics and Thermodynamic Perturbation Theory. *Mol. Phys.* **1979**, *37*, 83–94.

(44) Abramowitz, M., Stegun, I. A., Eds. *Handbook of Mathematical Functions*; Dover: New York, 1972.

(45) Lamoureux, G.; Harder, E.; Vorobyov, I. V.; Roux, B.; MacKerell, A. D., Jr. A Polarizable Model of Water for Molecular Dynamics Simulations of Biomolecules. *Chem. Phys. Lett.* **2006**, *418*, 245–249.

(46) Matyushov, D. V.; Ladanyi, B. M. A Perturbation Theory and Simulations of the Dipole Solvation Thermodynamics: Dipolar Hard Spheres. *J. Chem. Phys.* **1999**, *110*, 994–1009.

(47) Reynolds, L.; Gardecki, J. A.; Frankland, S. J. V.; Maroncelli, M. Dipole Solvation in Nondipolar Solvents: Experimental Studies of Reorganization Energies and Solvation Dynamics. *J. Phys. Chem.* **1996**, *100*, 10337–10354.

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