

## Electronic excitation energies of molecules in solution within continuum solvation models: Investigating the discrepancy between state-specific and linear-response methods

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Citation: [The Journal of Chemical Physics](#) **123**, 134512 (2005); doi: 10.1063/1.2039077

View online: <http://dx.doi.org/10.1063/1.2039077>

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# Electronic excitation energies of molecules in solution within continuum solvation models: Investigating the discrepancy between state-specific and linear-response methods

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(Received 18 May 2005; accepted 27 July 2005; published online 6 October 2005)

In a recent article [R. Cammi, S. Corni, B. Mennucci, and J. Tomasi, *J. Chem. Phys.* **122**, 104513 (2005)], we demonstrated that the state-specific (SS) and the linear-response (LR) approaches, two different ways to calculate solute excitation energies in the framework of quantum-mechanical continuum models of solvation, give different excitation energy expressions. In particular, they differ in the terms related to the electronic response of the solvent. In the present work, we further investigate this difference by comparing the excitation energy expressions of SS and LR with those obtained through a simple model for solute-solvent systems that bypasses one of the basic assumptions of continuum solvation models, i.e., the use of a single Hartree product of a solute and a solvent wave function to describe the total solute-solvent wave function. In particular, we consider the total solute-solvent wave function as a linear combination of the four products of two solute states and two solvent electronic states. To maximize the comparability with quantum-mechanical continuum model the resulting excitation energy expression is recast in terms of response functions of the solvent and quantities proper for the solvated molecule. The comparison of the presented expressions with the LR and SS ones enlightens the physical meaning of the terms included or neglected by these approaches and shows that SS agrees with the results of the four-level model, while LR includes a term classified as dispersion in previous treatments and neglects another related to electrostatic. A discussion on the possible origin of the LR flaw is finally given. © 2005 American Institute of Physics. [DOI: [10.1063/1.2039077](https://doi.org/10.1063/1.2039077)]

## I. INTRODUCTION

In a recent paper,<sup>1</sup> we have performed a formal comparison of two different strategies to compute excitation energies of a solute in the framework of quantum-mechanical (QM) continuum models of solvation.<sup>2,3</sup> Such models represent the solvent as a continuum dielectric with a cavity that hosts the solute described at a quantum mechanical level. An effective solute Hamiltonian, characterized by a nonlinear potential term that takes into account the polarization interaction with the solvent, is used. The two strategies examined in Ref. 1 were the state-specific (SS) method<sup>4–19</sup> and the linear-response (LR) method.<sup>20–28</sup> The former solves the effective nonlinear Schrödinger equation for the states of interest (the ground and the excited states) and assumes that the excitation energies are differences between the corresponding values of the total solute-solvent free energy. The latter determines the excitation energies as poles of the frequency-dependent linear-response functions of the solute in the

ground state described by the effective Hamiltonian, avoiding the explicit calculation of the excited-state wave function.

The main conclusion of the mentioned paper, from the formal point of view, was that even in the limit of exact states the SS and the LR methods applied to molecules in solution give different expressions for the excitation energy. In particular, while the inertial response of the solvent is accounted for in the same way in both approaches, the terms related to the fast solvent degrees of freedom (i.e., those able to instantaneously readjust to the ground-to-excited-state solute transition) are different. In that paper, we anticipated that the origin of the LR-SS difference lies on basic assumptions of the QM continuum models, i.e., the Hartree partition of the overall (solute+solvent) state and the use of a single Hartree product.<sup>29</sup> The application of the two approaches to the effective nonlinear Schrödinger equation for the solute resulting from these assumptions gives the different terms noted in Ref. 1.

The aim of the present paper is to clarify the origin of the discrepancy in the SS and LR expressions of the solute excitation energy by comparing them with the results of a

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simple formal model for the solute-solvent system that assumes the Hartree partition (thus neglecting the electron exchange Pauli effects) but uses more than a single function to describe the solute+solvent system. Such a model will be kept as simple as possible to clarify the meaning of the various terms and their relation with usual continuum-model quantities. The model can be seen as a simplified group function<sup>30,31</sup> approach to the problem of excitation energies in solution, one group being the solute and the other being the solvent. Briefly, we shall consider a two-level model for the states of the solute and a two-level model for the electronic states of the solvent, giving origin to an overall four-fold space for the solute-solvent states. A peculiarity of our model is that we explicitly try to maximize the comparability with QM continuum models, and for this reason the properties of the molecule *in solution* will be used. This is to be contrasted with the use of properties for the *gas-phase* molecule, which have generally been exploited by previous semiclassical treatments of solvatochromic shifts (such as, e.g., in Refs. 32–34).

The paper is organized as follows: in Sec. II the basics of the exploited theoretical model will be given; in Sec. III the model will be applied to the study of the ground state (energy and wave function), creating the connection with the basic quantities used in QM continuum models; then, in Sec. IV we shall work out the expression of the excitation energy in the framework of the four-level model; and in Sec. V we shall compare it with the expressions from SS and LR. Finally, in Sec. VI a summary of the paper will be given.

## II. A FOUR-LEVEL MODEL FOR THE SOLUTE-SOLVENT SYSTEM: DEFINITIONS AND THERMAL AVERAGING

Let us consider two interacting systems having two levels each. Let us call the first system the *solute* and the second system the *solvent*. We assume the Born-Oppenheimer approximation for the solvent (it is not necessary to assume it for the solute). The Hamiltonian of the isolated solute is called  $H^M$  and the electronic one of the isolated solvent is  $H^S$ . The two possible electronic states of the solvent, when the interaction with the solute is switched off, are  $|A'(Q)\rangle$  and  $|B'(Q)\rangle$ ,  $A'$  being the electronic ground state.  $Q$  represents the nuclear solvent coordinates (the nuclei will be considered as classical particles). The corresponding energies are:

$$E'_A(Q) = \langle A'(Q) | H^S | A'(Q) \rangle, \quad (1)$$

$$E'_B(Q) = \langle B'(Q) | H^S | B'(Q) \rangle. \quad (2)$$

We remark that the states  $|A'(Q)\rangle$  and  $|B'(Q)\rangle$  represent, in our model, macroscopic states of the solvent, i.e., states that may be delocalized on several solvent molecules. Coherently,  $Q$  groups the coordinates of all the solvent molecules.

For the solute system, we shall consider a generic bidimensional basis made by the states  $|0\rangle$  and  $|1\rangle$ . We shall define  $E_0 = H^M_{00} = \langle 0 | H^M | 0 \rangle$ ,  $E_1 = H^M_{11} = \langle 1 | H^M | 1 \rangle$ , and  $H_{01} = \langle 0 | H^M | 1 \rangle = \langle 1 | H^M | 0 \rangle$ , with  $E_0 \leq E_1$ .

The state space of the overall system (the *liquid solu-*

*tion*) is spanned by the tensor product vectors  $|0A'\rangle (=|0\rangle \otimes |A'\rangle)$ ,  $|0B'\rangle$ ,  $|1A'\rangle$ , and  $|1B'\rangle$ . The interaction  $W$  between the two systems is an operator that acts in the tensor product space. In particular, we shall assume a product form for  $W$ :

$$W = -\mu F, \quad (3)$$

where  $\mu$  acts only on the solute states and  $F$  acts only on the solvent state. We have chosen symbols that are reminiscent of a particularly simple model for solute-solvent interactions (dipolar solute in a spherical cavity continuum model), since this makes easier to follow the physics behind the manipulations that we shall perform in this work. However, the same symbols can be interpreted in a general way, encompassing other more advanced continuum models such as the polarizable continuum model (PCM).<sup>35</sup> To shorten the notation, we shall define the following matrix elements for the  $\mu$  and  $F$  operators:

$$\mu_{00} = \langle 0 | \mu | 0 \rangle,$$

$$\mu_{11} = \langle 1 | \mu | 1 \rangle,$$

$$\mu_{01} = \langle 0 | \mu | 1 \rangle = \langle 1 | \mu | 0 \rangle,$$

$$F'_{AB}(Q) = \langle A'(Q) | F | B'(Q) \rangle = \langle B'(Q) | F | A'(Q) \rangle,$$

$$F'_{AA}(Q) = \langle A'(Q) | F | A'(Q) \rangle,$$

$$F'_{BB}(Q) = \langle B'(Q) | F | B'(Q) \rangle. \quad (4)$$

To correctly take into account the several almost degenerate nuclear configurations of the solvent, we shall perform a thermal averaging over  $Q$ . In the spirit of QM continuum models, we will use a total Hamiltonian  $H^{\text{tot}} (= H^M + H^S + W)$  with the matrix element already averaged over  $Q$ .<sup>36</sup> In particular, to define the  $Q$  thermal distribution we assume that the solvent is held in the unpolarized  $A'$  electronic state, but the interaction with the solute in the pure state  $|0\rangle$  is turned on. We use such a distribution for all the matrix elements since our final goal is to calculate *vertical* excitation energies, i.e., excitation energies with the nuclear position fixed during the excitation. Actually, as we shall discuss later on, the electronic state of the solvent is perturbed by the solute. However, since we limit ourselves to the linear response of the solvent, the nuclear and the electronic degrees of freedom of the solvent can be considered as decoupled. A generic matrix element of  $H^{\text{tot}}$  can be written as  $\langle i\alpha(Q) | H^{\text{tot}} | j\beta(Q) \rangle$ , where  $i$  and  $j$  run over the solute states (i.e.,  $i=0, 1$ ) and  $\alpha(Q)$  and  $\beta(Q)$  refer to the solvent states (i.e.,  $\alpha(Q) = A'(Q)$ ,  $\beta(Q) = B'(Q)$ ). The value of such a matrix element is

$$\langle i\alpha(Q) | H^{\text{tot}} | j\beta(Q) \rangle = H^M_{ij} \delta_{\alpha\beta} + \delta_{ij} \delta_{\alpha\beta} E'_\alpha(Q) - \mu_{ij} F'_{\alpha\beta}(Q). \quad (5)$$

By using the procedure described in Appendix A the thermally averaged matrix elements of  $H^{\text{tot}}$  are given by

$$H^{\text{tot}}_{i\alpha,j\beta} = H^M_{ij} \delta_{\alpha\beta} + \delta_{\alpha\beta} (\delta_{ij} E'_\alpha - \mu_{ij} g_n \mu_{00}) - (1 - \delta_{\alpha\beta}) \mu_{ij} F'_{\alpha\beta}, \quad (6)$$

where  $g_n$  is the static nuclear response function of the sol-

vent, while  $E'_\alpha$  and  $F'_{\alpha\beta}$  are the mean values of  $E'_\alpha(Q)$  and  $F'_{\alpha\beta}(Q)$  for the *unpolarized* solvent.

The exact energies and states of the interacting systems can, in principle, be found by diagonalizing the Hamiltonian matrix  $\mathbf{H}'_{\text{tot}}$  of the overall system, whose elements are those given in Eq. (6). This matrix can be blocked as in the following equation:

$$\mathbf{H}'_{\text{tot}} = \begin{pmatrix} \mathbf{H}'_{00} & \mathbf{H}'_{01} \\ \mathbf{H}'_{10} & \mathbf{H}'_{11} \end{pmatrix}, \quad (7)$$

where  $\mathbf{H}'_{00}$  is the block diagonal acting on the subspace  $\{|0A'\rangle, |0B'\rangle\}$ ,  $\mathbf{H}'_{11}$  is the block diagonal acting on the subspace  $\{|1A'\rangle, |1B'\rangle\}$ , and  $\mathbf{H}'_{01}, \mathbf{H}'_{10}$  are the off-diagonal blocks.

Our aim is to compare continuum-model-like excitation energies of the solute (as found, e.g., in Ref. 1) with the exact eigenenergy differences of this minimal model. To this end, a direct diagonalization of  $\mathbf{H}'_{\text{tot}}$  is not the most convenient way. We shall instead introduce the usual assumptions made in continuum models, and then, by looking at the overall Hamiltonian of the total solute-solvent system under these assumptions, we can check what terms we have neglected. Such a procedure is applied in Sec. III to the ground state, and in Sec. IV to the excited state.

In the following, we shall always disregard terms that are more than second order in the solute-solvent interaction  $W$ . This is basically the usual assumption of linearity in the electrostatic solvent response.

### III. GROUND STATE OF THE FOUR-LEVEL MODEL

#### A. A continuum-like approximation

Let us now focus on the ground state of the overall system. We start by making a continuum-like approximation; i.e., we assume that the ground state of the solute-solvent system is a single Hartree product given by the ground state of the solute in solution times a polarized state of the solvent. In particular, we now specialize the definition of  $|0\rangle$  (it was a generic solute state in Sec. II), assuming that  $|0\rangle$  is the ground state of the solute in the presence of the solvent in a continuum-model sense; i.e., it solves the nonlinear effective Schrödinger equation defined in the framework of continuum models [see Eq. (B2) in Appendix B]. Thus, the overall ground state will be  $|0A\rangle$ , with  $|A\rangle = c_a|A'\rangle + c_b|B'\rangle$ . Assuming  $|0A\rangle$  as the ground state implies to also assume that the diagonal block  $\mathbf{H}'_{00}$  of the total Hamiltonian is decoupled to the rest of the Hamiltonian, i.e.,  $\mathbf{H}'_{01} = \mathbf{H}'_{10} = 0$  since the total system ground-state wave function is spanned only by  $|0A'\rangle$  and  $|0B'\rangle$ . In particular,  $\mathbf{H}'_{00}$  reads as:

$$\mathbf{H}'_{00} = \begin{pmatrix} E_0 + E'_A - g_n\mu_{00}^2 & -\mu_{00}F'_{AB} \\ -\mu_{00}F'_{AB} & E_0 + E'_B - g_n\mu_{00}^2 \end{pmatrix}. \quad (8)$$

Solving to second order in  $W$ , we found for the ground-state

energy  $E_g$  and the solvent polarized states  $|A\rangle$  and  $|B\rangle$ :

$$E_g = E_0 + E'_A - \mu_{00} \frac{F'_{AB}F'_{AB}}{E'_B - E'_A} \mu_{00} - g_n\mu_{00}^2, \quad (9)$$

$$|A\rangle = |A'\rangle \left( 1 - \frac{\mu_{00}^2 F'^2_{AB}}{2(E'_B - E'_A)^2} \right) + |B'\rangle \frac{\mu_{00}F'_{AB}}{E'_B - E'_A}, \quad (10)$$

$$|B\rangle = |B'\rangle \left( 1 - \frac{\mu_{00}^2 F'^2_{AB}}{2(E'_B - E'_A)^2} \right) - |A'\rangle \frac{\mu_{00}F'_{AB}}{E'_B - E'_A}. \quad (11)$$

The linear-response function  $g_e$  that characterizes the electronic solvent response to the solute distribution of charge is that giving the variation of the  $F$  expectation value (averaged over the nuclear coordinate set  $Q$ ) as a function of the solute  $\mu$ . Such a function can be defined through perturbation theory as

$$g_e = 2 \frac{F'_{AB}F'_{AB}}{E'_B - E'_A}. \quad (12)$$

Thus,

$$E_g = E_0 + E'_A - \frac{1}{2}g_e\mu_{00}^2 - g_n\mu_{00}^2. \quad (13)$$

Once the energy needed to polarize the classical degrees of freedom of the solvent ( $+1/2g_n\mu_{00}^2$ ) is taken into account, Eq. (13) is what is found in continuum models for the ground-state free energy (for electronic degrees of freedom, excited states are, at room temperature, several  $k_B T$ 's higher in energy than is the ground state, thus our solvation energies for the ground state simply coincide with solvation free energies). In addition, we remark that  $(g_n + g_e)\mu_{00} = g\mu_{00}$  is what would be called *reaction field* in the framework of continuum models.  $g$  is the total (nuclear plus electronic) response function of the solvent.

We have thus seen that if a single Hartree product for the ground state is used, its energy obtained within the four-level model corresponds to the continuum-model result. In Sec. III B, we shall go beyond the single Hartree product assumption and treat the exact (in the four-level model framework) calculation of the ground-state energy.

#### B. Beyond the single Hartree product approximation: The dynamic correlation between solute and solvent

In Sec. III A, we assumed that the ground state could be written as a single Hartree product  $|0A\rangle$ . Now, we may write the overall Hamiltonian and check what the continuum-model-like assumptions mean in terms of neglected matrix elements. In order to be the ground state,  $|0A\rangle$  should be the lowest-energy eigenstate of  $\mathbf{H}'_{\text{tot}}$ , thus all the nonzero off-diagonal matrix elements involving  $|0A\rangle$  in the overall Hamiltonian are quantities neglected by continuum models. In the analysis that follows, instead of using the unpolarized solvent states  $|A'\rangle$  and  $|B'\rangle$ , we introduce the polarized ones,



$|A\rangle$  and  $|B\rangle$ . With this choice, the polarization of the solvent induced by the solute ground state is directly taken into account in the Hamiltonian, making the other effects more

clearly visible. The matrix  $\mathbf{H}^{\text{tot}}$  representing the total Hamiltonian in the basis that exploits the polarized solvent states  $\{|0A\rangle, |0B\rangle, |1A\rangle, |1B\rangle\}$  is<sup>37</sup>

$$\begin{pmatrix}
 |0A\rangle & |0B\rangle & |1A\rangle & |1B\rangle \\
 \hline
 E_0 + E'_A - \frac{1}{2}g\mu_{00}^2 & 0 & 0 & -\mu_{01}F'_{AB} \\
 0 & E_0 + E'_B + \frac{1}{2}g\mu_{00}^2 - g_n\mu_{00}^2 & -\mu_{01}F'_{AB} & H_{01} + \mu_{01}(g_e - g_n)\mu_{00} \\
 0 & -\mu_{01}F'_{AB} & E_1 + E'_A + \frac{1}{2}g\mu_{00}^2 - \mu_{11}g\mu_{00} & -(\mu_{11} - \mu_{00})F'_{AB} \\
 -\mu_{01}F'_{AB} & H_{01} + \mu_{01}(g_e - g_n)\mu_{00} & -(\mu_{11} - \mu_{00})F'_{AB} & E_1 + E'_B - \frac{1}{2}(g_e - g_n)\mu_{00}^2 + \mu_{11}(g_e - g_n)\mu_{00}
 \end{pmatrix}. \quad (14)$$

In particular, we note that the off-diagonal matrix element  $\langle 0A | H^{\text{tot}} | 1A \rangle$  is null as proved in Appendix B. In other terms, by using the continuum-like assumptions, we effectively decoupled the state  $|0A\rangle$  from  $|0B\rangle$  and  $|1A\rangle$ . However, the state  $|0A\rangle$  is still coupled with  $|1B\rangle$ , through the off-diagonal term  $-\mu_{01}F'_{AB}$ . Here we come to an interesting point: the ground state that we obtain by diagonalizing  $\mathbf{H}^{\text{tot}}$  is a mix of  $|0A\rangle$  (the continuum-model-like ground state of the system) and  $|1B\rangle$ . The real ground state is thus an entangled state, which cannot be represented as a tensor (Hartree) product of a solvent and a solute state. For this reason, we could call  $-\mu_{01}F'_{AB}$  the *entanglement term*. Another way to interpret the effects of such a term is to note that it creates simultaneous intersubsystem double excitations (the solute is promoted from  $|0\rangle$  to  $|1\rangle$  and the solvent from  $|A\rangle$  to  $|B\rangle$ ). Thus, it represents a *dynamical correlation* between the solute and the solvent. Obviously, a model that pretends to have as the ground state of the system a tensor product of one polarized solute state and one polarized solvent state inevitably neglects such term.

If the entanglement term is taken into account, the actual lowest-energy eigenstate ( $|GS\rangle$ ) of  $\mathbf{H}^{\text{tot}}$  (at the first order in  $W$ ) is

$$|GS\rangle = |0A\rangle + |1B\rangle \frac{\mu_{01}F'_{AB}}{E'_B - E'_A + E_1 - E_0} \quad (15)$$

and the corresponding eigenvalue (at the second order in  $W$ ) is

$$E_g^{\text{ent}} = E_0 + E'_A - \frac{1}{2}g\mu_{00}^2 - \frac{\mu_{01}F'_{AB}F'_{AB}\mu_{01}}{E'_B - E'_A + E_1 - E_0}. \quad (16)$$

The last term of this expression can be rearranged as shown in Appendix C to give the expression

$$E_g^{\text{ent}} = E_0 + E'_A - \frac{1}{2}g\mu_{00}^2 - \frac{1}{2\pi} \int_0^\infty d\omega g_e(i\omega) \alpha(i\omega), \quad (17)$$

where  $\alpha(i\omega)$  is a frequency-dependent response function (evaluated at the imaginary frequency  $i\omega$ ) for the solute in solution, coincident with the usual ground-state dipole-dipole polarizability if we assume that  $\mu$  is the dipole moment operator, and  $g_e(i\omega)$  is the frequency-dependent generalization of the solute electronic response function  $g_e$ .

The physical meaning of the last term in Eq. (17) should be now more clear: the quantum fluctuation of the solute density of charge induces an instantaneous electronic polarization of the solvent that originates a reaction field acting back on the solute. Even if the fluctuations and the consequent reaction field average to zero, the resulting interaction energy has a nonzero average since field and fluctuations are correlated. In conclusion, the last term represents the *dispersion* interaction energy between the solute and the solvent.<sup>38</sup> We also note that since in the present paper the nuclear modes of the solvent are treated classically, they do not directly contribute to the dispersion interaction.

#### IV. THE EXCITED-STATE ENERGY FOR THE FOUR-LEVEL MODEL

In this section, our aim is to obtain an expression for the solute excitation energy that accounts for all the effects of the solute-solvent interaction in the framework of the minimal model. This expression will then be used in Sec. V as a benchmark for the solute excitation energy expressions obtained with the continuum approaches of Ref. 1. As for the

ground state, we shall proceed toward the complete excitation energy through a series of approximated intermediate expressions.

### A. Frozen solvent approximation

First, let us consider the state  $|1A\rangle$ . This is not a true eigenstate of  $H^{\text{tot}}$ , however, we can define an excitation energy to this state by exploiting its energy expectation value. In  $|1A\rangle$ , the state of the solvent is the same as in the ground state; i.e., the electron solvent polarization is frozen during the excitation (we recall that also the nuclear polarization is frozen, since we assumed for all the solvent states a nuclear coordinate distribution fixed to that equilibrated with the solute ground state). The expectation value of the energy in this state is  $E_1 + E'_A + (1/2)g\mu_{00}^2 - \mu_{11}g\mu_{00}$ ; i.e., the excitation energy from  $|0A\rangle$  to  $|1A\rangle$ , computed as a difference of expectation value, is

$$\Delta E_{01}^{(0)} = E_1 - E_0 + \mu_{00}g(\mu_{00} - \mu_{11}). \quad (18)$$

Noting that  $E_1 - E_0$  is what we called  $\Delta E_{01}^{\text{vac}}$  for SS and LR in Ref. 1, we find that the present  $\Delta E_{01}^{(0)}$  is exactly equal to  $\Delta E_{01}^{(0)}$  defined for the SS and LR methods in Ref. 1 (we remind the reader that  $\Delta E_{01}^{(0)}$  was found to be equal in the two approaches).  $\Delta E_{01}^{(0)}$  has the meaning of excitation energy at a fixed total reaction field.

### B. Polarizable solvent approximation

Let us proceed further. The energy expectation value obtained for  $|1A\rangle$  is to be compared with the eigenenergy of the true solute-solvent excited state obtained by diagonalizing  $\mathbf{H}^{\text{tot}}$  at the second order in  $W$ . To have an excitation energy expression comparable with those given in Ref. 1, we will neglect in such a diagonalization the terms that would mix the solute excited state  $|1\rangle$  with  $|0\rangle$ . In Ref. 1 this approximation followed from the perturbation approach we used; here, we have to explicitly introduce it. Moreover, we also neglect, for the moment, the entanglement term (i.e.,  $\langle 1A|H^{\text{tot}}|0B\rangle$ ). Such assumptions correspond to diagonalize only the  $\mathbf{H}_{11}^{\text{tot}}$  diagonal block, which represents  $H^{\text{tot}}$  restricted to the  $\{|1A\rangle, |1B\rangle\}$  subspace. In other terms, the excited state is represented by a single Hartree product  $|1A''\rangle$ . Within this framework, the excited-state energy is

$$E_{\text{ex}} = E_1 + E'_A + \frac{1}{2}g\mu_{00}^2 - \mu_{11}g\mu_{00} - \frac{1}{2}g_e(\mu_{00} - \mu_{11})^2. \quad (19)$$

Thus

$$\Delta E_{01} = \Delta E_{01}^{(0)} - \frac{1}{2}g_e(\mu_{00} - \mu_{11})^2. \quad (20)$$

The last term appears due to the coupling of  $|1A\rangle$  with  $|1B\rangle$ , i.e., to the changes in the electronic solvent polarization to adapt to the solute excited state. The solute state is not changed simply because we explicitly forced it not to change. In fact, due to the remix of  $|A\rangle$  and  $|B\rangle$  during the  $\mathbf{H}_{11}^{\text{tot}}$  diagonalization leading to Eq. (19), the states  $|1A\rangle$  and  $|1B\rangle$  are replaced by the new states  $|1A''\rangle$  and  $|1B''\rangle$ . While the off-diagonal element  $\langle 0A|H^{\text{tot}}|1A\rangle = H_{01} - \mu_{01}g\mu_{00}$  was null due to the choice of  $|0\rangle$  and  $|1\rangle$ , the new off-diagonal element responsible for the  $|0\rangle$ - $|1\rangle$  mixing becomes

$\langle 0A|H^{\text{tot}}|1A''\rangle = H_{01} - \mu_{01}g\mu_{00} + (1/2)\mu_{01}g_e(\mu_{00} - \mu_{11})$ , which is not null any longer. Thus, since  $\langle 0A|H^{\text{tot}}|1A''\rangle$  is not zero, there should be a remix of  $|0\rangle$  and  $|1\rangle$  to give a new excited state  $|1'\rangle$  different from  $|1\rangle$  and thus nonorthogonal to  $|0\rangle$  (a typical feature of continuum models coming from the hidden tensor-product structure of the Hilbert space of the total system).

### C. Excited-state energy including dynamic correlation terms

When entanglement terms are not neglected, we obtain the following excited state energy:<sup>39</sup>

$$E_{\text{ex}}^{\text{ent}} = E_1 + E'_A + \frac{1}{2}g\mu_{00}^2 - \mu_{11}g\mu_{00} - \frac{1}{2}g_e(\mu_{00} - \mu_{11})^2 - \frac{\mu_{01}F'_{AB}F'_{AB}\mu_{01}}{E'_B - E'_A + E_0 - E_1}. \quad (21)$$

By following the procedure described in Appendix D, it is possible to reformulate Eq. (21) to obtain

$$E_{\text{ex}}^{\text{ent}} = E_1 + E'_A + \frac{1}{2}g\mu_{00}^2 - \mu_{11}g\mu_{00} - \frac{1}{2}g_e(\mu_{00} - \mu_{11})^2 - g_e^d\mu_{01}^2 - \frac{1}{2\pi} \int_0^\infty d\omega g_e(i\omega)\alpha_{\text{ex}}(i\omega), \quad (22)$$

where  $\alpha_{\text{ex}}(i\omega)$  is the excited state analogous to  $\alpha(i\omega)$  and  $g_e^d = g_e(\omega = E_1 - E_0)$  is the frequency-dependent solvent electronic response function evaluated at the solute excitation energy. It is worth remarking a possible problem in the nomenclature of the new terms that appear in Eq. (22) [new with respect to Eq. (19)]. In analogy with the ground-state expression [Eq. (17)], one would be tempted to call the last term,  $-1/2\pi \int_0^\infty d\omega g_e(i\omega)\alpha_{\text{ex}}(i\omega)$ , the dispersion interaction in the excited state. In this picture, the new term  $-g_e^d\mu_{01}^2$  can be interpreted as an interaction with a different physical origin. The transition dipole of the molecule oscillating at the Bohr frequency induces an oscillating polarization in the solvent which creates a (in-phase) reaction field on the molecule; this field gives a nonzero, on the average, interaction with the transition dipole itself. On the contrary, the sum of the two new terms as a whole may be considered as originated by dispersion interactions. For example, the semiclassical derivations by McRae<sup>32</sup> and Liptay<sup>33</sup> and the quantum-mechanical model of Röscher and Zerner<sup>40</sup> implicitly assumed this second point of view, and also recently the sum of the two terms has been classified as a van der Waals term.<sup>41</sup> These two pictures obviously lead to different definitions of

electrostatic excitation energies: in the first picture, the term  $-g_e^d \mu_{01}^2$  is part of such an excitation energy; in the second picture it is not. We shall come back to this point in Sec. V dedicated to the comparison of the results for the four-level model with those for the SS and LR approaches. In view of such a comparison, we give here the complete expression of the excitation energy shift (at a fixed solute excited state):

$$\Delta E_{01}^{\text{ent}} = \Delta E_{01}^{(0)} - \frac{1}{2} g_e (\mu_{00} - \mu_{11})^2 - g_e^d \mu_{01}^2 - \frac{1}{2\pi} \int_0^\infty d\omega g_e(i\omega) [\alpha_{\text{ex}}(i\omega) - \alpha(i\omega)]. \quad (23)$$

We end this section with a short digression on the difference between  $g_e$  and  $g_e^d$ , both appearing in Eq. (23). In computational continuum-model practice,  $g_e$  and  $g_e^d$  are assumed to be equal and they are calculated in the same way, i.e., by using the dielectric constant of the solvent at optical frequencies (often at the sodium *D*-line frequency). Strictly speaking,  $g_e^d$  should be taken at the solute excitation frequency and should not contain contributions from the solvent nuclear polarization (which, however, are negligible at optical frequencies);<sup>42</sup>  $g_e$  represents the *static* electronic solvent response function, and the value of  $g_e^d$  for optical frequencies should be extrapolated back to  $\omega=0$ . However, when the exploited dielectric constant is taken at an optical frequency much smaller than the solvent excitation energies (as usually done), the corrections due to the  $\omega=0$  extrapolation are very likely negligible. Remarkably, while  $g_e^d$  may have an imaginary part [giving origin, e.g., to a finite lifetime for the solute excited state (see Ref. 43)],  $g_e$  must be purely real.

## V. EXCITATION ENERGIES WITHIN LR AND SS APPROACHES IN CONTINUUM MODELS: A COMPARISON WITH THE FOUR-LEVEL MODEL RESULTS

In Sec. IV, we worked out the expression for the solute excitation energy in the framework of the four-level model, i.e., Eq. (23). We need that expression to achieve the original goal of the present article, i.e., to compare the results for the model presented here with the results obtained with the SS and LR treatments in Ref. 1. The analysis of these approaches we made in Ref. 1 was limited to the electrostatic contribution; other terms, such as dispersion, were not explicitly included.

- (a) State-specific (SS) approach. The expression found for the solute excitation energy in Ref. 1, translated into the notation of the present article is

$$\Delta E_{01}^{\text{SS}} = \Delta E_{01}^{(0)} - \frac{1}{2} g_e (\mu_{00} - \mu_{11})^2. \quad (24)$$

The electronic term  $-(1/2)g_e(\mu_{00}-\mu_{11})^2$  is present both in the four-level model results [Eq. (23)] and in the state-specific calculation [Eq. (24)]. In particular, the  $\Delta E_{01}^{\text{SS}}$  expression fully coincides with Eq. (20), i.e., the four-level model result obtained by neglecting the

entanglement terms. The term  $-g_e^d \mu_{01}^2$  is instead not present in the SS excitation energy expression. We remark that  $-g_e^d \mu_{01}^2$ , in the light of the discussion reported in Sec. IV, can be considered part of the dispersion interactions in the excited state, as implicitly assumed, for example, in Liptay and McRae analyses. Since  $\Delta E_{01}^{\text{SS}}$  is intended to be purely electrostatic in origin, the lack of such a term is justified.

- (b) Linear-response (LR) approach. In the LR approach, we found the excitation energy expression to be

$$\Delta E_{01}^{\text{LR}} = \Delta E_{01}^{(0)} - g_e^d \mu_{01}^2. \quad (25)$$

Thus, the term  $(1/2)g_e(\mu_{00}-\mu_{11})^2$  is not taken into account. In other words, LR neglects the relaxation of the solvent electronic degrees of freedom to adapt to the solute excited state. On the contrary,  $-g_e^d \mu_{01}^2$  is explicitly present, even though in the derivation of LR dispersion was not explicitly included.

We would like to remark again that the  $\Delta E_{01}^{(0)}$  (the excitation energy at a fixed reaction field) is common to the present four-level model and to the SS and the LR approaches.

We have found that the excitation energy obtained from our minimal model contains more terms than what given by both LR and SS. In particular, these two methods include different subsets of the total number of terms. However, there is an important difference between the two methods: the SS approach is, in a sense, aware of the terms that it is neglecting (it considers them as due to the dispersion interaction), and they can be inserted explicitly when needed. By contrast, the present formulation of the LR approach really lacks one term  $[(1/2)g_e(\mu_{00}-\mu_{11})^2]$  and includes another one  $(-g_e^d \mu_{01}^2)$  that appears to be part of the dispersion contribution in the treatments of some authors (such as McRae and Liptay). Thus, when dispersion terms are added to the LR results, care must be taken not to include  $-g_e^d \mu_{01}^2$  twice.

It is worth mentioning that when the LR and the SS approaches are applied not to the effective solute Schrödinger equation of the QM continuum models but to the minimal model presented here, they give the same results (the proof is trivial). Thus, the origin of the LR flaw must be related to the use of a single Hartree product and to the effective equation that the solute part of such a product satisfies. In particular, we believe that the problem lies in the incapability of the nonlinear effective solute Hamiltonian of QM continuum models to correctly describe energy expectation values of mixed solute states, i.e., states that are not stationary. Since in a perturbation approach (such as the LR treatment) the perturbed state can be seen as a linear combination of zeroth-order states, the inability of the effective Hamiltonian approach to treat mixed states causes a wrong repartition of the solvent terms among the various perturbation orders. Let us show these points. To avoid complications arising from the entanglement terms, we assume  $\mu_{01}=0$ . This

also means [See Eq. (B1)] that  $H_{01}=0$ ; i.e., the ground state in solution is equal to the ground state in gas phase. In addition, since we already know that the LR problem regards

only the electronic solvent polarization terms, let us assume that  $g_n=0$ . Thus, the total Hamiltonian of the four-level system is reduced to

$$\begin{pmatrix} |0A\rangle & |0B\rangle & |1A\rangle & |1B\rangle \\ E_0 + E'_A - \frac{1}{2}g_e\mu_{00}^2 & 0 & 0 & 0 \\ 0 & E_0 + E'_B + \frac{1}{2}g_e\mu_{00}^2 & 0 & 0 \\ 0 & 0 & E_1 + E'_A + \frac{1}{2}g_e\mu_{00}^2 - \mu_{11}g_e\mu_{00} & -(\mu_{11} - \mu_{00})F'_{AB} \\ 0 & 0 & -(\mu_{11} - \mu_{00})F'_{AB} & E_1 + E'_B - \frac{1}{2}g_e\mu_{00}^2 + \mu_{11}g_e\mu_{00} \end{pmatrix}. \quad (26)$$

In this case the exact ground state of the system is a single Hartree product ( $|0A\rangle$ ), and it corresponds to what is predicted by the QM continuum-model approach. From the structure of the total Hamiltonian in Eq. (26), it appears that also the excited state corresponding to a solute excitation can be formulated as a single Hartree product, since during the diagonalization of  $H^{\text{tot}}$ ,  $|1A\rangle$  mixes only with  $|1B\rangle$  to give the states  $|1A''\rangle$  and  $|1B''\rangle$ . By performing such a diagonalization, we bring the total Hamiltonian to the form

$$\begin{pmatrix} |0A\rangle & |0B\rangle & |1A''\rangle & |1B''\rangle \\ E_0 + E'_A - \frac{1}{2}g_e\mu_{00}^2 & 0 & 0 & 0 \\ 0 & E_0 + E'_B + \frac{1}{2}g_e\mu_{00}^2 & 0 & 0 \\ 0 & 0 & E_1 + E'_A - \frac{1}{2}g_e\mu_{11}^2 & 0 \\ 0 & 0 & 0 & E_1 + E'_B + \frac{1}{2}g_e\mu_{11}^2 \end{pmatrix}. \quad (27)$$

It is easy to verify that the energy eigenvectors corresponding to  $|0A\rangle$  and  $|1A''\rangle$  in Eq. (27) are equal (up to the unperturbed solvent energy  $E'_A$ ) to the free-energy results from the free-energy functional  $\mathcal{G}[|s\rangle]$  defined in QM continuum model as

$$\mathcal{G}[|s\rangle] = \langle s | H^M - \hat{\mu}g_e\mu_{ss} | s \rangle - \frac{1}{2}\langle s | -\hat{\mu}g_e\mu_{ss} | s \rangle, \quad (28)$$

when  $|s\rangle=|0\rangle$ ,  $|s\rangle=|1\rangle$ . It is also clear that the nonlinear effective Schrödinger equation obtained from the stationarity of  $\mathcal{G}$  is solved by the states  $|0\rangle$  and  $|1\rangle$ . In summary, for what regards eigenenergies and eigenstates, the QM continuum approach gives the same results as the complete four-level system. Let us consider now a mixed state of the overall system, called  $|T\rangle$  and defined as  $|T\rangle=c_0|0A\rangle+c_1|1A''\rangle$ , with  $c_0^2+c_1^2=1$ . The exact expectation value of the overall energy

of the system obtained by the total Hamiltonian is simply

$$E_T = \langle T | H^{\text{tot}} | T \rangle = E'_A + c_0^2E_0 + c_1^2E_1 - \frac{1}{2}g_e(c_0^2\mu_{00}^2 + c_1^2\mu_{11}^2). \quad (29)$$

On the contrary, when we calculate  $\mathcal{G}[|s_T\rangle]$  for  $|s_T\rangle=c_0|0\rangle+c_1|1\rangle$  (i.e., when we keep in the solute state the same degree of linear mixing as in  $|T\rangle$ ), the result is clearly different:

$$\begin{aligned} \mathcal{G}[|s_T\rangle] &= c_0^2E_0 + c_1^2E_1 - \frac{1}{2}g_e(c_0^4\mu_{00}^2 + c_1^4\mu_{11}^2 \\ &\quad + 2c_0^2c_1^2\mu_{00}\mu_{11}). \end{aligned} \quad (30)$$

Thus it is not generally true that for a generic state  $|s_T\rangle$ ,  $\mathcal{G}[|s_T\rangle]$  coincides with the overall system energy. Thus, when a perturbed ground-state function is introduced in  $\mathcal{G}[|s_T\rangle]$  (as done in the LR approach), there are no warranties



that the corresponding perturbed free energy corresponds to the correct total system energy. In other terms,  $\mathcal{G}[|s_T\rangle]$  works well for stationary states, but it does not interpolate correctly between them. By comparing Eqs. (29) and (30), one finds that changes in energy due to a mixing of the ground state with excited states appear at a higher order in the effective equation approach than in the complete four-level system. For example, if we choose  $c_0$  and  $c_1$  to make  $|T\rangle$  and  $|s_T\rangle$  perturbed ground states (i.e.,  $c_0 \approx 1$  and  $c_1 \ll 1$ ,  $|T\rangle = |0A\rangle + c_1|1A''\rangle$ ,  $|s_T\rangle = |0\rangle + c_1|1\rangle$ ), we find that  $(1/2)g_e\mu_{11}^2$  is multiplied by  $c_1^4$  in the free energy of Eq. (30), while it is multiplied by  $c_1^2$  in the expectation energy of the four-level model [Eq. (29)]. This proves that a perturbation approach based on the effective nonlinear Hamiltonian has an incorrect repartition of the electronic solvent terms among the various perturbation orders. The pole of the linear-response functions will thus lack some solvent terms, since they are accounted for in higher orders. The inadequacy of the effective nonlinear Hamiltonian approach to describe mixed states have been previously noted by other authors.<sup>44</sup>

Above, we have outlined a detailed analysis of the problems for the present LR approach. This analysis can be taken as the starting point to elaborate strategies to correct the LR results. However, we remark, as we have already done in Ref. 1, that the LR-SS difference regards only the electronic (i.e., fast) response of the solvent, while the nuclear response (responsible for the largest part of the relative solvatochromic shift) is described at the same level in the two approaches. Thus, for most applications the LR-SS excitation energy difference, caused by the reasons discussed in the present article, is negligible in comparison with other factors. For example, we have to recall that the LR and SS approaches applied to the QM methods used in real-life computations give different results even for molecules in gas phase (because of the inevitably approximated nature of the solute wave function).

## VI. SUMMARY

In this paper, a simple model for solutions based on Hartree partition has been presented and connected with advanced QM continuum models for solvation. We have shown how useful such a minimalist approach can be to interpret results from advanced continuum models, made complex by the nonlinear nature of the involved equations. In particular,

the expression of the excitation energies of the solute in solution has been worked out and compared with the LR and SS ones. Such analysis has highlighted some important facts:

- The nuclear part of the solvent response is taken into account at the same level in the LR and the SS approaches. This level coincides with what we found for the minimal model studied in the present article.
- When the dynamical correlations between the solute and the solvent are neglected, the results of the model coincide with the SS excitation energies, while the LR result lacks the term related to the rearrangement of the electronic solvent degrees of freedom to adapt to the solute wave function in the excited state.
- The dynamical term present in the LR expression comes from the response of the solvent to the density of charge of the solute oscillating at the Bohr frequency. Such a term, being originated by the dynamical solute-solvent interactions might be classified as a part of dispersion, and indeed it was implicitly classified in such a way in previous works.<sup>32,33,40</sup> Thus, when the dispersion contribution (with the meaning just explained) is added to the SS result, the excitation energy of the four-level model is recovered. This is not generally true for LR.
- When the LR and the SS approaches are applied to the four-level model, without reverting to a single Hartree product wave function, they trivially give the same excitation energy expression.
- The incapability of the present LR formulation to take into account the electronic relaxation term has been related to the inadequacy of the nonlinear solute effective Hamiltonian defined in QM continuum models to describe mixed (i.e., nonstationary) solute states.

## APPENDIX A: THERMAL AVERAGING OF THE MATRIX ELEMENTS OF THE TOTAL HAMILTONIAN

In this appendix, we compute the thermal average of  $\langle i\alpha(Q)|H^{\text{tot}}|j\beta(Q)\rangle$  in Eq. (5) over the chosen  $Q$  distribution (that proper for the solvent in the  $A'$  state interacting with the solute in the pure state  $|0\rangle$ ). The averaged matrix element will be indicated as  $\langle\langle i\alpha|H^{\text{tot}}|j\beta\rangle\rangle_{\text{int}}$ . Its expression is

$$\langle\langle i\alpha|H^{\text{tot}}|j\beta\rangle\rangle_{\text{int}} = H_{ij}^M \delta_{\alpha\beta} + \frac{\int dQ e^{-(E'_A(Q) - \mu_{00}F'_{AA}(Q))/k_B T} [\delta_{ij} \delta_{\alpha\beta} E'_\alpha(Q) - \mu_{ij} F'_{\alpha\beta}(Q)]}{\int dQ e^{-(E'_A(Q) - \mu_{00}F'_{AA}(Q))/k_B T}} \quad (\text{A1})$$

Taking only the terms that may contribute to the system energy until the second order in the solute-solvent interaction, we find

$$\langle\langle i\alpha|H^{\text{tot}}|j\beta\rangle\rangle_{\text{int}} = H_{ij}^M \delta_{\alpha\beta} + \delta_{\alpha\beta} \left( \delta_{ij} \langle E'_\alpha \rangle_{\text{iso}} - \mu_{ij} \frac{\langle F'_{\alpha\alpha} F'_{AA} \rangle_{\text{iso}}}{k_B T} \mu_{00} \right) - (1 - \delta_{\alpha\beta}) \mu_{ij} \langle F'_{\alpha\beta} \rangle_{\text{iso}}, \quad (\text{A2})$$

where  $\langle \dots \rangle_{\text{iso}}$  means that the thermal average is to be taken

over the distribution proper for the *isolated* solvent in the pure ground state  $A'$ :

$$\langle \cdots \rangle_{\text{iso}} = \frac{\int dQ e^{-E'_A(Q)/k_B T} [\cdots]}{\int dQ e^{-E'_A(Q)/k_B T}}. \quad (\text{A3})$$

In Eq. (A2), we have used  $\langle F'_{AA} \rangle_{\text{iso}} = \langle F'_{BB} \rangle_{\text{iso}} = 0$ , which corresponds to assumption that the isolated solvent does not have a net polarization. To simplify the notation, in the following we shall use  $E'_A$  and  $E'_B$  to indicate  $\langle E'_A \rangle_{\text{iso}}$  and  $\langle E'_B \rangle_{\text{iso}}$  respectively. Similarly,  $F'_{AB} = F'_{BA}$  will indicate  $\langle F'_{\alpha\beta} \rangle_{\text{iso}}$  with  $\alpha \neq \beta$ .  $\langle F'_{\alpha\alpha} F'_{AA} \rangle_{\text{iso}} / k_B T$  plays the role of a static nuclear response function of the solvent, and we shall call it  $g_n^\alpha$ . Such identification is basically the fluctuation-dissipation theorem<sup>45</sup> for the specific case under study. Since the considered solute-solvent interaction is electrostatic in origin,  $g_n^\alpha$  is related to the nuclear part of the solvent dielectric constant. In the following we shall use for  $B'$  the same nuclear response function  $g_n^B$  used for  $A'$ , i.e.,  $g_n^B = g_n^A = g_n = \langle F'_{AA} F'_{AA} \rangle_{\text{iso}} / k_B T$ . Such an assumption, while simplifying the intermediate formulas, does not affect the final expressions of the quantities we are interested in.

By using the definitions given above, the (thermally averaged) matrix element of  $H^{\text{tot}}$  is finally given by Eq. (6).

## APPENDIX B: GROUND STATE AND EFFECTIVE SCHRÖDINGER EQUATION

In this appendix we shall prove that when  $|0\rangle$  satisfies the nonlinear effective Schrödinger equation exploited by continuum models, then  $\langle 0A | H^{\text{tot}} | 1A \rangle = H_{01} - \mu_{01} g \mu_{00} = 0$ . Let us introduce the nonlinear effective Schrödinger equation of continuum models for the ground state of a generic solute:

$$[H^M - \hat{\mu} g \mu_{s_1 s_1}] |s_1\rangle = E'_{s_1} |s_1\rangle, \quad (\text{B1})$$

where  $s_1$  is the solute ground state. Note the structure of the effective Hamiltonian: it is the sum of  $H$  in vacuo ( $H^M$ ) plus the interaction  $(-\hat{\mu} g \mu_{s_1 s_1})$  with the reaction field induced by the ground state ( $g \mu_{s_1 s_1}$ ). We assumed that  $|0\rangle$  is the solute ground state in the continuum-model sense; that is, we assumed  $|s_1\rangle = |0\rangle$ . Equation (B1) thus becomes

$$[H^M - \hat{\mu} g \mu_{00}] |0\rangle = E'_0 |0\rangle, \quad E'_0 = E_0 - g \mu_{00}^2. \quad (\text{B2})$$

Taking the Hermitian conjugate of such an equation and projecting it from the right on  $|1\rangle$ , we find that:

$$\langle 0 | [H^M - \hat{\mu} g \mu_{00}] | 1 \rangle = 0 \quad (\text{B3})$$

which can be rewritten as

$$H_{01} - \mu_{01} g \mu_{00} = 0. \quad (\text{B4})$$

That is what we wanted to prove.

## APPENDIX C: REARRANGEMENT OF THE LAST TERM IN EQ. (16)

Here we shall discuss how the last term in Eq. (16), related to dynamical solute-solvent correlations, can be re-

cast in terms of frequency-dependent response functions of the solvent and the solute. We make use of the integral transformation:

$$\frac{1}{x+y} = \frac{2}{\pi} \int_0^\infty d\omega \frac{x}{x^2 + \omega^2} \frac{y}{y^2 + \omega^2} \quad (\text{C1})$$

that holds for  $x, y > 0$ . By applying such a relation to the last term of Eq. (16), we obtain:

$$\frac{\mu_{01} F'_{AB} F'_{AB} \mu_{01}}{(E'_B - E'_A + E_1 - E_0)} = \int_0^\infty \frac{d\omega}{2\pi} \left( \frac{2(E'_B - E'_A) F'_{AB} F'_{AB}}{(E'_B - E'_A)^2 + \omega^2} \right) \times \left( \frac{2(E_1 - E_0) \mu_{01} \mu_{01}}{(E_1 - E_0)^2 + \omega^2} \right) \quad (\text{C2})$$

In the right-hand side of Eq. (C2) it is easy to recognize the product of two dynamical “polarizability” evaluated at the imaginary frequency  $i\omega$ : one,  $2(E'_B - E'_A) F'_{AB} F'_{AB} / [(E'_B - E'_A)^2 + \omega^2]$ , is the time-dependent generalization of the electronic solvent response function  $g_e$ ; the other,  $2(E_1 - E_0) \mu_{01} \mu_{01} / [(E_1 - E_0)^2 + \omega^2]$ , is the frequency-dependent response function for the solute in solution, coincident with the usual dipole-dipole polarizability if we assume that  $\mu$  is the dipole moment operator. We shall call this solute response function  $\alpha(i\omega)$ . By inserting these definitions in Eq. (C2), the last term of  $E_g^{\text{ent}}$  is eventually rewritten as in Eq. (17).

## APPENDIX D: REARRANGEMENT OF EQ. (21)

In this appendix, we show how to recast the last term of Eq. (21) in order to obtain Eq. (22). Note that we cannot directly transform the last term of Eq. (21) as done for Eq. (16) in Appendix C. In fact, we have at the denominator  $E_0 - E_1$  which is negative, and the integral transformation does not hold. However, we can still relate such term to a continuum-like quantity, the dynamic electronic solvent response function  $g_e(\omega)$ . Such a function is defined as

$$g_e(\omega) = \frac{F'_{AB} F'_{AB}}{E'_B - E'_A + \omega} + \frac{F'_{AB} F'_{AB}}{E'_B - E'_A - \omega}. \quad (\text{D1})$$

Thus,  $g_e(\omega = E_1 - E_0) \equiv g_e^d$  is

$$g_e^d = \frac{F'_{AB} F'_{AB}}{E'_B - E'_A + E_1 - E_0} + \frac{F'_{AB} F'_{AB}}{E'_B - E'_A + E_0 - E_1}. \quad (\text{D2})$$

The second term in the right-hand side of Eq. (D2), multiplied by  $\mu_{01}^2$ , is already present in the excited-state energy of Eq. (21). We thus add and subtract to that energy the term  $(\mu_{01} F'_{AB} F'_{AB} \mu_{01}) / (E'_B - E'_A + E_1 - E_0)$  to obtain

$$E_{\text{ex}}^{\text{ent}} = E_1 + E'_A + \frac{1}{2} g \mu_{00}^2 - \mu_{11} g \mu_{00} - \frac{1}{2} g_e(\mu_{00} - \mu_{11})^2 - g_e^d \mu_{01}^2 + \frac{\mu_{01} F'_{AB} F'_{AB} \mu_{01}}{E'_B - E'_A + E_1 - E_0}. \quad (\text{D3})$$

The last term can now be reformulated by using the integral relation Eq. (C1), leading to the same relation as in Eq. (C2). This time, however, the solute polarizability at the frequency  $i\omega$ , called  $\alpha_{\text{ex}}(i\omega)$ , is not given by  $2(E_1 - E_0) \mu_{01} \mu_{01} / [(E_1 - E_0)^2 + \omega^2]$  but by  $2(E_0 - E_1) \mu_{01} \mu_{01} / [(E_1 - E_0)^2 + \omega^2]$ . Taking

this into account, we finally found Eq. (22). Let us make a brief remark regarding  $\alpha_{\text{ex}}(i\omega)$ . Our simple two-level model for the solute gives  $\alpha_{\text{ex}}(i\omega) = -\alpha(i\omega)$ . The manipulation reported in this appendix seems to exploit this relation, which obviously is not true for solutes with more than two levels. However, the other levels of the solute represent excited states with respect to  $|1\rangle$ , and to take them into account in Eq. (22) we can exploit the same procedure used for the ground-state energy in Appendix C. Thus, even if the deexcitation to the state  $|0\rangle$  and the excitations to the states  $|N\rangle$  with  $N > 1$  follow different routes in the algebra, they finally recombine to give exactly the same form as in Eq. (22).

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