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Electronic excitation energies of molecules in solution: State specific and linear response methods for nonequilibrium continuum solvation models

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We present a formal comparison between the two different approaches to the calculation of electronic excitation energies of molecules in solution within the continuum solvation model framework, taking also into account nonequilibrium effects. These two approaches, one based on the explicit evaluation of the excited state wave function of the solute and the other based on the linear response theory, are here proven to give formally different expressions for the excitation energies even when exact eigenstates are considered. Calculations performed for some illustrative examples show that this formal difference has sensible effects on absolute solvatochromic shifts (i.e., with respect to gas phase) while it has small effects on relative (i.e., nonpolar to polar solvent) solvatochromic shifts. © 2005 American Institute of Physics. [DOI: 10.1063/1.1867373]

I. INTRODUCTION

Absorption and emission of photons by molecules in solution due to an electronic excitation/deexcitation are processes that involve the whole solute-solvent system. Actually all phenomena of molecular origin taking place in condensed phase systems have a holistic character which represents a challenge for a correct quantum-mechanical (QM) description. In this work we limit ourselves to a description of electronic excitation/deexcitation processes treated by using a continuum solvation model.¹ We are aware that the same phenomena can be treated with discrete semiclassical solvent models,^{2,3} but the simplicity of the continuum models allows, in our opinion, to better examine the essential aspects of the problem we are considering.

The quantum mechanical (QM) solvation models belong to the class of implicit focused models⁴ where the solvent is treated as a dielectric medium and the solute-solvent electrostatic interaction is expressed in term of the dielectric permittivity of the solvent. In the basic continuum models, the solvent is completely equilibrated with the charge distribution of the solute, (i.e., equilibrium solvation) and the medium is described in terms of its static permittivity. The description of fast vertical electronic processes requires an extension of the basic model (nonequilibrium solvation scheme), which considers a partition of the solvent response into two components, fast and slow. The former is related to the dielectric constant at optical frequencies and the latter is

related to both the static and the optical dielectric constant. Different semiclassical schemes^{5–10} have been proposed to evaluate solvatochromic shifts (i.e., the excitation energy difference between gas phase and solution for a given solute) from the properties of the gas-phase molecule. These different schemes exploit the Onsager's solvation model,¹¹ enclosing the solute in a spherical cavity built in the continuous dielectric representing the solvent and considering the solute as a polarizable dipole. The solvatochromic shifts are finally given in terms of the ground and excited state dipoles and polarizabilities of the solute considered in gas-phase, and of the static and optical dielectric constant of the solvent.

Within the QM continuum solvation framework, as in the case of isolated molecules, it is practice to compute the excitation energies with two different approaches: the state-specific (SS) method and the linear-response (LR) method. The former has a long tradition,^{12–27} starting from the pioneering paper by Yomosa in 1974,¹² and it is related to the classical theory of the solvatochromic effects; the latter has been introduced few years ago in connection with the development of the linear-response theory for continuum solvation models,^{28–36} but earlier works by Ruiz-Lopez and Rinaldi (using the random phase approximation) should be also mentioned.³⁷ The state-specific method solves the nonlinear Schrödinger equation for the states of interest (ground and excited states) and postulates that the transition energies are differences between the corresponding values of the free-energy functional and the basic energetic quantity of the QM continuum models. The linear-response approach instead determines directly the excitation energies, defined as singularities of the frequency-dependent linear-response functions of

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the solvated molecule in the ground state, avoiding explicit calculation of the excited state wave functions.

The increasing use of the LR method to calculate excitation energies of molecules in solution calls for a comparison of this method with the historically accepted SS approach beyond the mere observation that when applied to the same system they usually give somewhat different numerical results. While it has been demonstrated that for isolated molecules the SS and LR methods are equivalent³⁸ (in the limit of the exact solution of the corresponding equations), a formal comparison for molecules described by QM continuum models is still lacking, mainly because of the nonlinear nature of the effective solute Hamiltonian. The present paper is devoted to fill this gap by presenting a direct connection between the two methods. The problems related to the nonlinearity of the effective Hamiltonian are dealt with a proper perturbative analysis. We remark that here the focus is on vertical excitation energies only: the other properties of the excited state are not discussed.

The paper is organized as follows: in Sec. II we present a theoretical framework in which the state-specific and the linear-response approaches are compared in a coherent way. In Sec. III we discuss, on the basis of this theoretical analysis, the numerical outcomes of the state-specific and linear-response approaches in actual calculations, respectively, at the (configuration interaction) single (CIS) and Tamm-Dancoff approximation (TDA) level, for the excitation energies of molecular solutes described with the polarizable continuum model (PCM).³⁹ Section IV with conclusions and comments ends the paper.

II. THEORY

A. State-specific theory for solutes in excited states

The aim of this section is to develop a Rayleigh-Schrödinger perturbation theory of the nonlinear Schrödinger equation for excited electronic states of a molecular solute. This perturbation theory may be considered as a generalization of the approach by Angyan, who studied the solvation energy and the static-response properties for a solute in the ground state.⁴⁰

The stationary states (ground and excited states) Ψ_i of a solute are obtained as solutions of the nonlinear and time-independent Schrödinger equation:

$$H_M(\Psi_i)|\Psi_i\rangle = E_i|\Psi_i\rangle \quad \text{with} \quad H_M(\Psi_i) = H_M^{\text{vac}} + V(\Psi_i), \quad (1)$$

where H_M^{vac} is the Hamiltonian of the isolated molecule M and $V(\Psi_i)$ is a nonlinear operator that describes the interaction of the solute with the solvent having the general form

$$V(\Psi_i) = A\langle\Psi_i|B|\Psi_i\rangle. \quad (2)$$

In the case of the continuum model we are using, namely, PCM, A corresponds to the molecular electrostatic potential operator \hat{V} , while B corresponds to the apparent charge operator \hat{Q} , which describes the polarization of the solvent, under the electrostatic potential generated by the solute M , in

terms of an apparent surface distribution which spreads on the surface of the cavity hosting M .

The stationary states which solve Eq. (1) make stationary the free-energy functional $G(\Psi_i)$ defined as

$$G(\Psi_i) = \langle\Psi_i|H_M(\Psi_i)|\Psi_i\rangle - \frac{1}{2}\langle\Psi_i|V(\Psi_i)|\Psi_i\rangle. \quad (3)$$

It represents the free energy of the whole solute-solvent system with respect to a reference state in which the solvent medium is unperturbed and the particles composing M (nuclei and electrons) are not interacting and do not have kinetic energy. To simplify the notation, in the following we shall use i instead of the complete symbol Ψ_i .

The free energy of the electronic excited states with respect to that of the electronic ground state is called electronic excitation energy, and it is defined as

$$\Delta G_{0i} = G(i) - G(0). \quad (4)$$

The excitation energies given by Eq. (4) implicitly refer to a situation in which the solvent is able to instantaneously readjust to the solute wave function change upon excitation (from $|0\rangle$ to $|i\rangle$), since they are obtained as differences of equilibrium free energies. For this reason they are sometimes called *equilibrium* excitation energies. However, a model that takes into account the solvent incapability of immediately achieving a complete equilibrium with the solute excited state has been proven more suitable to reproduce the experimental findings.^{14,41} [Thus, in the following, we shall present our derivation for the equilibrium model (which gives simpler formulas) and the necessary refinements for the nonequilibrium situation are then given in Sec. II B.

In order to solve the nonlinear Schrödinger equation (1) for the excited states of a solute, we use a perturbative scheme that we limit to the first order for the sake of simplicity. The zeroth-order Hamiltonian is given by $H_M(0) = H_M^{\text{vac}} + V(0)$ and we assume that the solutions of the Schrödinger equation corresponding to such Hamiltonian are known:

$$H_M(0)|i^{(0)}\rangle = E_i^{(0)}|i^{(0)}\rangle, \quad (5)$$

where $|i^{(0)}\rangle$ is the i th electronic states obtained in presence of the (fixed) reaction field due to the ground state $[V(0)]$. In the following we shall use $|0\rangle$ to denote the ground state.

The perturbed Schrödinger equation for a generic state $|i\rangle$ reads

$$\{H_M(0) + \lambda[V(i) - V(0)]\}|i\rangle = E|i\rangle, \quad (6)$$

where we have introduced the perturbation parameter λ to proceed to the separation of the various perturbation orders. The parameter λ gauges the switch from the reaction field of the ground state ($\lambda=0$) to that which is proper for the excited state i ($\lambda=1$). The free-energy functional $G^\lambda(i)$ whose stationarity yields Eq. (6) is

$$G^\lambda(i) = \langle i|H_M(0) + \lambda[V(i) - V(0)]|i\rangle - \frac{1}{2}\lambda[\langle i|V(i)|i\rangle - \langle 0|V(0)|0\rangle] - \frac{1}{2}\langle 0|V(0)|0\rangle. \quad (7)$$

The solution of Eq. (6) is obtained in terms of the following power series:

$$E = E^{(0)} + \lambda E^{(1)} + \lambda E^{(2)} + \dots, \quad (8)$$

$$|i\rangle = |i^{(0)}\rangle + \lambda|i^{(1)}\rangle + \dots \quad (9)$$

We remark that due to the nonlinear nature of the interaction operator $V(i)$, it must be expanded in a power series as well:

$$V(i) = V^{(0)}(i) + \lambda V^{(1)}(i) + \dots, \quad (10)$$

where

$$V^{(0)}(i) = \hat{\mathbf{V}} \cdot \langle i^{(0)} | \hat{\mathbf{Q}} | i^{(0)} \rangle = V(i^{(0)}), \quad (11)$$

$$V^{(1)}(i) = 2\hat{\mathbf{V}} \cdot \langle i^{(0)} | \hat{\mathbf{Q}} | i^{(1)} \rangle. \quad (12)$$

Let us introduce the series (8)–(10) into Eq. (6) and separate the various perturbative orders. At zeroth order, we have (as expected)

$$H_M(0)|i^{(0)}\rangle = E_i^{(0)}|i^{(0)}\rangle. \quad (13)$$

The first-order equation for the wave function is given by

$$H_M^{\text{vac}}|i^{(1)}\rangle + [V(i^{(0)}) - V(0)]|i^{(0)}\rangle = E_i^{(0)}|i^{(1)}\rangle + E^{(1)}|i^{(0)}\rangle. \quad (14)$$

By projecting this equation on $|i^{(0)}\rangle$, we obtain the first-order correction to the energy

$$\langle i^{(0)} | V(i^{(0)}) - V(0) | i^{(0)} \rangle = E^{(1)}. \quad (15)$$

Since we are only interested here in the excitation energies at the first order, we omit the expression for $|i^{(1)}\rangle$. The energy corrected to the first order, E_i^I is thus given by:

$$E_i^I = E_i^{(0)} + E_i^{(1)} = \langle i^{(0)} | H_M(0) | i^{(0)} \rangle + \langle i^{(0)} | V(i^{(0)}) - V(0) | i^{(0)} \rangle, \quad (16)$$

and exploiting the definition of $H_M(0) = H_M^{\text{vac}} + V(0)$ we have

$$E_i^I = \langle i^{(0)} | H_M^{\text{vac}} | i^{(0)} \rangle + \langle i^{(0)} | V(i^{(0)}) | i^{(0)} \rangle. \quad (17)$$

The physical meaning of this equation is clear: the energy corrected to the first order corresponds to the energy of the solute in the unperturbed state $|i^{(0)}\rangle$ subjected to the reaction field due to the charge density associated with the zeroth-order wave function $|i^{(0)}\rangle$ itself.

Now, we pass to consider the first-order correction to the Gibbs free energy given by Eq. (7). By introducing the power series of the wave function and of the nonlinear interaction term, we obtain the following zeroth- and first-order expressions:

$$G^{(0)}(i) = \langle i^{(0)} | H_M(0) | i^{(0)} \rangle - \frac{1}{2} \langle 0 | V(0) | 0 \rangle, \quad (18)$$

$$G^{(1)}(i) = \langle i^{(0)} | [V(i^{(0)}) - V(0)] | i^{(0)} \rangle - \frac{1}{2} \langle i^{(0)} | V(i^{(0)}) | i^{(0)} \rangle + \frac{1}{2} \langle 0 | V(0) | 0 \rangle. \quad (19)$$

The Gibbs free energy for the excited state $|i\rangle$ corrected to the first order $G^I(i)$, is then given by

$$G^I(i) = G^{(0)}(i) + G^{(1)}(i) = E_i^{(0)} + \frac{1}{2} \langle i^{(0)} | V(i^{(0)}) | i^{(0)} \rangle - \langle i^{(0)} | V(0) | i^{(0)} \rangle. \quad (20)$$

We can now evaluate the excitation energy corrected to the first order, i.e., $\Delta G_{0i}^I = G^I(i) - G(0)$:

$$\Delta G_{0i}^I = \Delta E_{0i}^{(0)} + \frac{1}{2} [\langle i^{(0)} | V(i^{(0)}) | i^{(0)} \rangle + \langle 0 | V(0) | 0 \rangle] - \langle i^{(0)} | V(0) | i^{(0)} \rangle, \quad (21)$$

where we have defined $\Delta E_{0i}^{(0)} = E_i^{(0)} - E_0^{(0)}$. This equation has a clear physical meaning: The first term ($\Delta E_{0i}^{(0)}$) represents the zeroth-order excitation energy that corresponds to the electronic transition $|0\rangle \rightarrow |i^{(0)}\rangle$ in the presence of the fixed reaction field of the ground state, $V(0)$; the remaining terms describe the effects due to the swap of this ground-state reaction potential $V(0)$ with the new reaction potential $V(i^{(0)})$ produced by the (unperturbed) excited state $|i^{(0)}\rangle$.

Equation (21) may be rewritten, in a more explicit form, in terms of the solvations operators $\hat{\mathbf{V}}$ and $\hat{\mathbf{Q}}$ previously defined:

$$\Delta G_{0i}^I = \Delta E_{0i}^{(0)} + \frac{1}{2} [\langle i^{(0)} | \hat{\mathbf{V}} | i^{(0)} \rangle - \langle 0 | \hat{\mathbf{V}} | 0 \rangle] \cdot [\langle i^{(0)} | \hat{\mathbf{Q}} | i^{(0)} \rangle - \langle 0 | \hat{\mathbf{Q}} | 0 \rangle]. \quad (22)$$

Equation (22) can be interpreted as the quantum-mechanical version of the classical theories of the solvent effect on the electronic transition. As will be shown in the Appendix, this connection is more evident if we apply Eq. (21) to the simplified solvations model of a dipolar solute in a spherical cavity.

B. Nonequilibrium effects

A nonequilibrium formulation of the perturbative theory presented so far can be obtained by starting with the proper nonequilibrium quantities. In particular, we have to introduce a nonequilibrium free energy:

$$G^{\text{neq}}(i, 0) = \langle i | H_M^{\text{vac}} | i \rangle + \frac{1}{2} \langle i | V_d(i) | i \rangle + \langle i | V_{in}(0) | i \rangle - \frac{1}{2} \langle 0 | V_{in}(0) | 0 \rangle \\ = \langle i | H_M^{\text{vac}} + V(0) | i \rangle + \frac{1}{2} \langle i | V_d(i) | i \rangle - \langle i | V_d(0) | i \rangle - \frac{1}{2} \langle 0 | V_{in}(0) | 0 \rangle, \quad (23)$$

where $G^{\text{neq}}(i, 0)$ is the free energy of a system in which the slow degrees of freedom of the solvent are equilibrated with the solute wave function $|0\rangle$ while the fast degrees of freedom are in equilibrium with the slow ones and with the solute wave function $|i\rangle$. The adjective “slow” and “fast” here mean “slower than” or “at least as fast as” the phenomenon under study (a vertical electronic excitation in the present case). Following this solvent response partition, the solute-solvent interaction operator $V(\Psi)$ has been divided into an inertial part $V_{in}(\Psi)$ and a dynamic part $V_d(\Psi)$ [i.e., $V(\Psi) = V_{in}(\Psi) + V_d(\Psi)$]. Details on the PCM form of $G^{\text{neq}}(i, 0)$, $V_d(i)$, and $V_{in}(i)$ are given in Ref. 42. By applying the stationary condition (with respect to i) to the functional in Eq. (23), a nonequilibrium nonlinear Schrödinger equation is obtained:

$$[H_M^{\text{vac}} + V_{in}(0) + V_d(i)]|i\rangle = E_i^{\text{neq}}|i\rangle. \quad (24)$$

Again, we would like to solve perturbatively such an equation by using the same zeroth-order wave functions as given in Eq. (5). By introducing the perturbation parameter λ , we obtain

$$\{H_M^{\text{vac}} + V(0) + \lambda[V_d(i) - V_d(0)]\}|i\rangle = E_i^{\text{neq}}|i\rangle, \quad (25)$$

where the zeroth-order Hamiltonian is again $H_M(0) = H_M^{\text{vac}} + V(0)$. The perturbative nonequilibrium free energy is

$$\begin{aligned} G^{\text{neq},\lambda}(i,0) &= \langle i|H_M^{\text{vac}} + V(0) + \lambda[V_d(i) - V_d(0)]|i\rangle \\ &\quad - \frac{1}{2}\lambda[\langle i|V_d(i)|i\rangle - \langle 0|V_d(0)|0\rangle] \\ &\quad - \frac{1}{2}\langle 0|V(0)|0\rangle. \end{aligned} \quad (26)$$

Equation (25) can be obtained by imposing that the functional in Eq. (26) is stationary (with respect to i). By developing energies and wave functions in power series of λ , as done for the equilibrium case, it is possible to obtain the nonequilibrium excitation energy corrected to the first order [$\Delta G_{0i}^{\text{neq},\text{I}} = G^{\text{neq},\text{I}}(i,0) - G(0)$]:

$$\begin{aligned} \Delta G_{0i}^{\text{neq},\text{I}} &= \Delta E_{0i}^{(0)} + \frac{1}{2}[\langle i^{(0)}|\hat{\mathbf{V}}|i^{(0)}\rangle - \langle 0|\hat{\mathbf{V}}|0\rangle][\langle i^{(0)}|\hat{\mathbf{Q}}_d|i^{(0)}\rangle \\ &\quad - \langle 0|\hat{\mathbf{Q}}_d|0\rangle], \end{aligned} \quad (27)$$

where $\hat{\mathbf{Q}}_d$ is the apparent charge operator obtained by considering only the dynamic response of the solvent. In the following section, we shall derive an expression corresponding to $\Delta G_{0i}^{\text{neq},\text{I}}$ in the alternative framework of the response theory for molecules in solution.

C. Exact linear-response theory for molecules in solution

In this section, we present a formal theory for the determination of the poles of the linear-response functions for exact states of molecules in solution. These poles, as said in the Introduction, define the linear-response excitation energies of the solute, and the final aim of the section is to derive the expression of the linear-response excitation energies correct at the first order, to compare with the corresponding expression (27) obtained by the state-specific theory discussed in the preceding section.

Let us consider a molecular solute under a time-dependent perturbation (e.g., an electromagnetic field). The molecular solute is described by the time-dependent effective Hamiltonian

$$H_M(\Psi) = H_M^{\text{vac}} + W(t) + V(\Psi), \quad (28)$$

where H_M^{vac} is the Hamiltonian of the isolated systems, $V(\Psi)$ describes the interaction with the solvent medium and depends on the solute wave function Ψ , and $W(t)$ represents the interaction with the external perturbation, which we consider applied adiabatically so that $W(t)$ vanishes at $(t=-\infty)$.

The time evolution of the system is completely determined by the nonlinear time-dependent Schrödinger equation (atomic units are used here)

$$H_M(\Psi)|\Psi\rangle = i\frac{\partial}{\partial t}|\Psi\rangle. \quad (29)$$

This equation can be obtained by using a generalized variational Frenkel's principle^{43,44}

$$\delta\langle\tilde{\Psi}|\hat{G} - i\frac{\partial}{\partial t}|\tilde{\Psi}\rangle = 0, \quad \frac{\partial}{\partial t}\langle\delta\tilde{\Psi}|\tilde{\Psi}\rangle = 0, \quad (30)$$

where we have used the “phase isolated” form of the approximated wave function $|\tilde{\Psi}\rangle$ and \hat{G} is the free energy operator:

$$\hat{G} = \hat{H}_M(\tilde{\Psi}) - \frac{1}{2}V(\tilde{\Psi}). \quad (31)$$

Denoting $|\tilde{0}\rangle$ the perturbed time-dependent exact wave function, we can write

$$|\tilde{0}\rangle = e^{i\mathbf{T}\cdot\boldsymbol{\alpha}(t)}|0\rangle. \quad (32)$$

Here $|0\rangle$ is the exact ground-state wave function of the molecular solute immediately before the switching-on of the time-dependent perturbation and $e^{i\mathbf{T}\cdot\boldsymbol{\alpha}(t)}$ is a unitary operator which generates the evolution of the molecular state. \mathbf{T} is a row vector of operators,

$$\mathbf{T} = (\mathbf{R}^\dagger, \mathbf{R}), \quad (33)$$

where \mathbf{R}^\dagger and \mathbf{R} collect excitation and deexcitation operators:

$$R_n^\dagger = |n^{(0)}\rangle\langle 0|, \quad R_n = |0\rangle\langle n^{(0)}|, \quad (34)$$

where $|n^{(0)}\rangle$ denotes a basis for the orthogonal complement space to the ground state $|0\rangle$, chosen to be composed by the eigenstates of $H_M(0) = H_M^{\text{vac}} + V(0)$. Thus, the states $|n^{(0)}\rangle$ represent the electronic excited states in the presence of the ground-state reaction field, and correspond to the state already defined in Eq. (5) of the preceding section. In Eq. (32), $\boldsymbol{\alpha}(t)$ is the column vector collecting the time-dependent amplitudes $\alpha_n(t)$ and $\alpha_{-n}(t)$ which multiply the operators R_n^\dagger and R_n , respectively.

Introducing this parametrization of the wave function, the Frenkel variational principle [Eq. (30)] gives an equation for the evolution of the amplitudes $\boldsymbol{\alpha}(t)$. The solution of such a response equation for the exact states of the molecular solute can be given by a perturbative power expansion of the excitation amplitudes $\boldsymbol{\alpha}(\boldsymbol{\alpha} = \boldsymbol{\alpha}^1 + \boldsymbol{\alpha}^2 + \dots)$ with respect to the perturbation $W(t)$. The linear-response equation is obtained by keeping only the first-order terms. Such equation can be expressed as follows:

$$iS_{jl}^{[2]}\dot{\alpha}_i^1(t) - G_{jl}^{[2]}\alpha_i^1(t) = -iW_j^{[1]}, \quad (35)$$

where

$$S_{jl}^{[2]} = \text{sgn}(l)\delta_{jl}, \quad (36)$$

$$W_j^{[1]} = \langle j^{(0)}|W(t)|0\rangle, \quad (37)$$

and $G_{jl}^{[2]}$ are elements of the free-energy matrix that will be discussed later on.

By Fourier transforming Eq. (35) we obtain

$$i(-i\omega + \epsilon)S_{jl}^{[2]}\alpha_i^1(\omega) - G_{jl}^{[2]}\alpha_i^1(\omega) = -iW_j^{\omega[1]}. \quad (38)$$

In matricial form we can write

$$[\mathbf{G}^{[2]} - (\omega + i\epsilon)\mathbf{S}^{[2]}]\boldsymbol{\alpha}^1(\omega) = i\mathbf{W}^{\omega[1]}, \quad (39)$$

whose formal solution is given by

$$\alpha^1(\omega) = [\mathbf{G}^{[2]} - (\omega + i\epsilon)\mathbf{S}^{[2]}]^{-1} i\mathbf{W}^{\omega[1]}. \quad (40)$$

In the linear-response approach the excitation energies of the solute are defined as poles ω_j of the linear-response amplitudes $\alpha^1(\omega)$, and from the previous equation it follows that they are given as eigenvalues of the generalized Hermitian eigenvalue problem

$$\mathbf{G}^{[2]}\beta_j = \omega_j \mathbf{S}^{[2]}\beta_j. \quad (41)$$

In the PCM nonequilibrium framework, the free-energy matrix $\mathbf{G}^{[2]}$ has elements given by

$$G_{jl}^{[2]} = E_{jl}^{[2]} + \mathbf{v}_{jl}^{[2]} \cdot \mathbf{q}(0) + \mathbf{v}_j^{[1]} \cdot \mathbf{q}_l^{d[1]}, \quad (42)$$

where

$$E_{jl}^{[2]} = \langle j^{(0)} | H_M^{\text{vac}} | l^{(0)} \rangle - \delta_{jl} \langle 0 | H_M^{\text{vac}} | 0 \rangle,$$

$$\mathbf{v}_{jl}^{[2]} = \langle j^{(0)} | \hat{\mathbf{V}} | l^{(0)} \rangle - \delta_{jl} \langle 0 | \hat{\mathbf{V}} | 0 \rangle,$$

$$\mathbf{v}_j^{[1]} = \langle j^{(0)} | \hat{\mathbf{V}} | 0 \rangle,$$

$$\mathbf{q}_l^{d[1]} = \langle l^{(0)} | \hat{\mathbf{Q}}_d | 0 \rangle, \quad (43)$$

and $\mathbf{q}(0)$ is a vector collecting the apparent charges induced by the total charge density of the solute (electrons and nuclei) in the ground state, which can be formally written as $\mathbf{q}(0) = \langle 0 | \hat{\mathbf{Q}} | 0 \rangle$.

As said at the beginning of this section, the poles ω_j correspond, in the framework of the response theory, to the excitation ($j > 0$) and deexcitation ($j < 0$) energies. The excitation energy expression given in the preceding section [Eq. (27)], which is obtained by explicitly considering the excited state wave functions, is correct only to the first order in the change of the reaction field from the ground to the actual state. To coherently compare these excitation energies with ω_j , we have to find out ω_j^I , i.e., the value of ω_j to the first order in the change of the reaction field in passing from $|0\rangle$ to the exact time-dependent wave function $|\tilde{0}\rangle$. To this end, we have to introduce the perturbation parameter λ in Eq. (41) in a consistent way with the explicit state treatment, Eq. (25). $\mathbf{G}^{[2]}$, given in Eq. (42), is the sum of three terms: it is easy to show that these three terms correspond one by one to the three terms of the Hamiltonian appearing in Eq. (25). This is obvious for the first terms, related to H_M^{vac} in both cases. The second term should be related to the static reaction field obtained for the ground state. Indeed, by rearranging the second term of Eq. (42) and exploiting the definition of the $\hat{\mathbf{V}}$ and $\hat{\mathbf{Q}}$ operators, we obtain

$$\mathbf{v}_{jl}^{[2]} \cdot \mathbf{q}(0) = \langle j^{(0)} | V(0) | l^{(0)} \rangle - \delta_{jl} \langle 0 | V(0) | 0 \rangle, \quad (44)$$

which makes clear the correspondence with $V(0)$ in Eq. (25). Finally, the dynamic response of the solvent appears explicitly only in the third term for both equations. In conclusion, the perturbation parameter λ should be introduced in Eq. (41) as follows:

$$[\mathbf{G}^{[2],(0)} + \lambda \mathbf{v}^{[1]} \mathbf{q}^{d[1]}] \beta_j = \omega_j \mathbf{S}^{[2]} \beta_j, \quad (45)$$

where

$$G_{jl}^{[2],(0)} = E_{jl}^{[2]} + \mathbf{v}_{jl}^{[2]} \cdot \mathbf{q}(0). \quad (46)$$

The same conclusion obtained by this heuristic argument could be reached by a more rigorous (but also more cumbersome) approach, in which the perturbation parameter λ is introduced from the very beginning in the Frenkel variational principle, and Eq. (45) is then rederived via the same procedure that leads to Eq. (41) from the unperturbed Frenkel principle equation.

Since we have chosen the vectors $|n^{(0)}\rangle$ to be eigenstate of $H_M(0) = H_M^{\text{vac}} + V(0)$, $\mathbf{G}^{[2],(0)}$ is actually diagonal with

$$G_{ij}^{[2],(0)} = \delta_{ij} (E_i^{(0)} - E_0^{(0)}) = \delta_{ij} \Delta E_{0i}^{(0)}, \quad (47)$$

where $\Delta E_{0i}^{(0)}$ is exactly the same quantity that appeared in the preceding section. To find ω_j^I , we have to insert into Eq. (45) the developments in λ -power series of ω_j and β_j and separate the various orders. The equations to the zeroth- and first-order read

$$\mathbf{G}^{[2],(0)} \beta_j^{(0)} = \omega_j^{(0)} \mathbf{S}^{[2]} \beta_j^{(0)}, \quad (48)$$

$$\mathbf{G}^{[2],(0)} \beta_j^{(1)} + [\mathbf{v}^{[1]} \mathbf{q}^{d[1]}] \beta_j^{(0)} = \omega_j^{(0)} \mathbf{S}^{[2]} \beta_j^{(1)} + \omega_j^{(1)} \mathbf{S}^{[2]} \beta_j^{(0)}, \quad (49)$$

$\mathbf{v}^{[1]} \mathbf{q}^{d[1]}$ in Eq. (49) and in the following are meant to be as evaluated by zeroth-order wave functions (this is not explicitly indicated in the symbols in order to keep the notation light). From Eq. (48) and taking into account the diagonal form of $\mathbf{G}^{[2],(0)}$ we obtain for $\omega_j^{(0)}$ and $\beta_j^{(0)}$,

$$\omega_j^{(0)} = \text{sgn}(j) \Delta E_{0j}^{(0)},$$

$$[\beta_j^{(0)}]_i = \delta_{ij}. \quad (50)$$

If we now multiply Eq. (49) from the left by $\beta_j^{(0)}$, we obtain the expression for $\omega_j^{(1)}$

$$\omega_j^{(1)} = \text{sgn}(j) \mathbf{v}_j^{[1]} \mathbf{q}_j^{d[1]}. \quad (51)$$

Thus,

$$\omega_j^I = \omega_j^{(0)} + \omega_j^{(1)} = \text{sgn}(j) (\Delta E_{0j}^{(0)} + \mathbf{v}_j^{[1]} \mathbf{q}_j^{d[1]}). \quad (52)$$

The physical meaning of this equation is as follows: the first term ($\Delta E_{0j}^{(0)}$) represents the exact excitation energy in the presence of the fixed reaction field of the ground state. The second term ($\mathbf{v}_j^{[1]} \mathbf{q}_j^{d[1]}$) takes care of the effects of the coupling between the electronic excitation and the reaction field, in the linear-response scheme. Such a term corresponds to the interaction energy between the transition density and the reaction field due to the transition density itself. Equation (52) can be rewritten in a more explicit form, by introducing the $\hat{\mathbf{V}}$ and $\hat{\mathbf{Q}}_d$ operators:

$$\omega_j^I = \text{sgn}(j) (\Delta E_{0j}^{(0)} + \langle j^{(0)} | \hat{\mathbf{V}} | 0 \rangle \cdot \langle 0 | \hat{\mathbf{Q}}_d | j^{(0)} \rangle) \quad (53)$$

In the following section we shall compare the results obtained from the LR and SS approaches.

D. Formal comparison between LR and SS

It is now possible to meaningfully compare the excitation energies obtained with the explicit determination of the

excited state wave functions $\Delta G_{0i}^{\text{neq},I}$ in Eq. (27) and those given by the response theory, ω_j^I (with $j > 0$) in Eq. (53). By comparing the two expressions, we note that they are formally and physically different. In Eq. (27), the explicit solvent term (that beyond $\Delta E_{0j}^{(0)}$) depends on expectation values over the ground and the (unperturbed) excited states of the operators $\hat{\mathbf{V}}$ and $\hat{\mathbf{Q}}_d$, while in Eq. (53) only transition matrix elements of such operators appear.

The difference between the two approaches can be clarified by interpreting the excitation in solution as a two-step process: in the first step, the molecule (that was in its ground state in equilibrium with the solvent) is excited to the state i , characterized by the wave function $|i^{(0)}\rangle$ in presence of the reaction field $V(0)$, i.e., the whole solvent polarization is frozen to the value proper for the solute ground state. The energy change related to this process is $\Delta E_{0i}^{(0)}$. No differences between the response and the explicit state theories are found at this point. In the second step of the excitation procedure, the fast degrees of freedom of the solvent rearrange to equilibrate with the charge density of the solute excited state (note that in our first-order theory the excited solute wave function does not relax during this step, remaining $|i^{(0)}\rangle$). The difference between the linear response and the explicit state theories rises in this step since the energy variation accompanying the relaxation of the fast solvent degrees is given by $\frac{1}{2}[\langle i^{(0)}|\hat{\mathbf{V}}|i^{(0)}\rangle - \langle 0|\hat{\mathbf{V}}|0\rangle][\langle i^{(0)}|\hat{\mathbf{Q}}_d|i^{(0)}\rangle - \langle 0|\hat{\mathbf{Q}}_d|0\rangle]$ for the explicit state theory, while it is not explicitly accounted for in the linear-response framework. On the contrary, the linear response accounts for a dynamical correction to the excited state energy so that it is related to the response of the solvent to the density of charge of the solute oscillating at the Bohr frequency. Such a term is given by $\langle i^{(0)}|\hat{\mathbf{V}}|0\rangle\langle 0|\hat{\mathbf{Q}}_d|i^{(0)}\rangle$.

The origin of this LR-SS difference lies on basic assumptions of QM continuum models, i.e., the Hartree partition of the overall solute-solvent state and the use of a single Hartree product for the overall state,^{1,45–49} as revealed by a preliminary analysis⁵⁰ based on a group function approach.^{3,51,52} When these approximations are made, the linear Schrödinger equation for the overall system is replaced by two nonlinear effective equations, one for the solute and the other for the solvent, both involving a self-consistent interaction term. Continuum models neglect the explicit consideration of the solvent degrees of freedom, thus the nonlinear effective equation for the solvent is actually not solved; the effects of the solvent are instead taken into account by a classical description of its response in the self-consistent term appearing in the solute effective equation. The application of the SS and the LR approaches to the solute self-consistent problem gives the different dynamical terms obtained above in Eqs. (27) and (53). On the contrary, when only the Hartree partition is assumed (i.e., the overall state is not assumed to be a single Hartree product, taking into account, in other terms, the dynamical correlation between the two subsystems) the overall system can be described by a single linear Schrödinger equation, giving the same excitation energies for both approaches. This preliminary analysis (not too different from the perturbation theories of solvent effects derived by, e.g., McRae⁷ and Liptay⁹ seems

to relate the different dynamical terms of the two methods to different physical origins: the SS term takes into account the capability of the fast degrees of freedom of the solvent to follow self-consistently the solute excitation; the LR term is a consequence of the dynamical solute-solvent correlation, i.e., it is related to the response of the solvent to the charge density of the solute oscillating at the Bohr frequency. Remarkably, it appears that such a term remains buried in what has been classified as dispersion energy in the semiclassical treatments by McRae and Liptay. Thus, when the dispersion contribution is added to the electrostatic SS result, the transition matrix element term of the LR approach is recovered. The contrary is not true: the present formulation of the LR approach does not take into account the SS-like dynamical term.

In the following section we exploit our theoretical results, represented by Eqs. (27) and (53), to analyze and rationalize the numerical difference between the two methods of evaluation of excitation energies.

III. NUMERICAL RESULTS

In order to numerically quantify the differences between the state-specific and linear-response methods of calculation of the excitation energy, it would be useful to exploit a computational method giving the same value for $\omega_i^{(0)}$ and $\Delta E_{0i}^{(0)}$, as it would be in the case of exact state solutions. The simplest, yet meaningful, possibility is to revert to the (CIS) method. In fact, this method can be obtained from two points of view: one is to consider the method as a standard CI, in which the wave function of the excited state is constructed by single excitations from the HF determinant [in this case Eq. (4) applies]; the other is to consider CIS as the result of the Tamm–Dancoff approximation applied to the linear-response equation based on the HF wave function [in this case, Eq. (41) applies]. The two ways of looking at the CIS method give the same equations *in vacuo*, but differ for molecules in solution due to the form of the explicit solvent term.

In this section, we shall examine excitation energies calculated with the CIS method, by describing the solvent with PCM and introducing its effects in the two alternative ways discussed above. In particular, we shall refer to the LR and SS excitation energy to distinguish between them. We remark that excitation energies will be computed using standard nonperturbative expressions developed in PCM framework for the SS and the LR methods, while the first-order expressions given above [i.e., Eqs. (27) and (53)] will be used to give a rational of the numerical outcomes.

A. Computational details

Three different molecules have been considered in the calculations: acrolein (A), methylenecyclopropene (MCP), and paranitroaniline (PNA). For A, the first two excited states ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, respectively) have been studied, while for MCP and PNA only the first excited state ($\pi \rightarrow \pi^*$ for both molecules) has been studied. We have selected two representative solvents: one polar (acetonitrile) and one characterized by a low polarity (dioxane). This combination

TABLE I. Excitation energies and dipole moments for the three different molecules and the two solvents under study. Energies ($\Delta E^{\text{LR}} \equiv \omega_j$, $\Delta E^{\text{SS}} \equiv \Delta G_{0j}^{\text{neq}}$) are given in eV and dipole moments in debye.

	Acetonitrile				Dioxane			
	A		MCP	PNA	A		MCP	PNA
	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
$\Delta\mu_{0i}$	4.169	2.296	7.051	7.847	4.188	2.157	7.279	^a
μ_{0i}	0.000	5.412	1.754	7.440	0.000	5.690	1.777	6.393
ΔE_{gas}	4.357	6.965	5.642	5.014	4.357	6.965	5.642	5.014
ΔE^0	4.650	6.830	5.890	4.607	4.467	6.914	5.754	4.835
ΔE^{LR}	4.646	6.601	5.845	4.457	4.462	6.631	5.697	4.666
ΔE^{SS}	4.568	6.798	5.701	4.510	4.373	6.877	5.506	4.696

^a $\Delta\mu_{0i}$ could not be determined because of difficulties in converging.

of chromophores and solvents has been chosen as a significant sample over a range of electronic excitation of different nature and in different environments.

The geometry of the molecules has been optimized for each solvent by using the B3LYP hybrid functional. For the geometry optimizations a 6-31G(d,p) basis set has been used while for the calculation of properties a Dunning double ζ basis set with additional $d(0.2)$ function for C,N,O, has been used (the number in parentheses is the exponents of the extra function). The sphere radii used to build the molecular cavity were 1.9 for CH_n ($n=1,2,3$), 1.7 for other C, 1.52 for O, 1.6 for N, and 1.2 for H when bonded to N, all multiplied by a cavity size factor of 1.2. The LR-CIS calculations of the transition energies ($\Delta E^{\text{LR}} \equiv \omega_{0i}$) and dipole (μ_{0i}), and have been done with GAUSSIAN03,⁵³ while for the SS-CIS calculation of the excitation energies ($\Delta E^{\text{SS}} \equiv \Delta G_{0i}^{\text{neq}}$) and dipole moment of excited states (μ_{ii}) has been performed using a local version of GAMESS.⁵⁴ The cavity tessellation parameters have been chosen to give the same tessellation with both programs. The zeroth-order energy ΔE^0 (which is equal for LR and SS in the CIS framework) has been found by switching off the explicit reaction field contribution in the CIS equations solved by GAUSSIAN03.

B. Comparison of the LR and SS excitation energies

We have collected the excitation energies calculated for the three molecules and the two solvents under study in Table I.

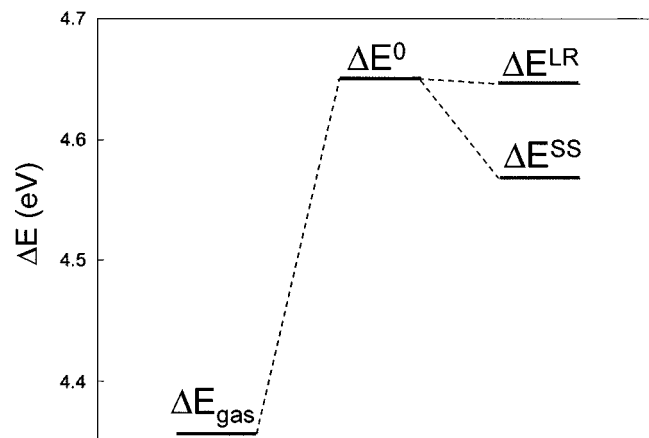
Graphical representation of the results in acetonitrile are also given in Figs. 1–4. In each figure, the gas-phase excitation energy ΔE_{gas} , the zeroth-order excitation energy ΔE^0 (that, at the CIS level, is the same for LR and SS), and the LR and SS, excitation energies (ΔE^{LR} and ΔE^{SS} , respectively) are reported.

The analysis of the results will be done at two levels: in Sec. III B 1, we shall show that these results confirm the theoretical predictions that we have made in the preceding section on the basis of the perturbative approach. To do this, we shall refer to the simplified model presented in the Appendix, which has the advantage of exploiting quantities such as transition dipole moment or difference of dipole expectation values that are routinely calculated in most quantum-chemistry packages, and we shall show that by

comparing the magnitude of the calculated $2|\vec{\mu}_{0i}|$ with $|\vec{\mu}_{ii} - \vec{\mu}_{00}|$ (the molecular quantities that determine the explicit solvent contributions in the first-order spherical model), one can predict the relative order of the LR and SS excitation energies. Then, in Sec. III B 2, we shall focus on the magnitude of the computed differences between the LR and the SS approaches, to verify if the discrepancies predicted by the theory are only a formal problem (i.e., the numerical differences are always negligible) or if they have an impact on the calculations. As we shall see, the two ways of including solvent effects give different numerical results, but such differences are not large if relative shifts between different solvents are of interest.

1. Correlation of the excitation energy with the molecular dipoles

What we would like to discuss now is the relation between the relative order of the LR and SS excitation energies in Figs. 1–4 and the dipole moments (differences of dipoles and transition dipoles) of the various excitations considered. On the basis of the simplified version of our theory, presented in the Appendix, the state-specific and linear-response excitation energies of a dipolar solute in a spherical cavity, should be related, at the first order, by the following simple relation:

FIG. 1. Excitation energies for the acroleine $n \rightarrow \pi^*$ transition in acetonitrile.

ΔE^0 is using
PCM orbitals from
SCF.

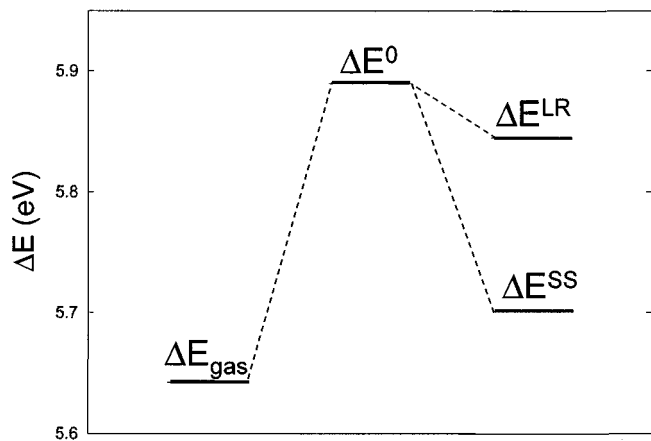


FIG. 2. Excitation energies for the methylenecyclopropene $\pi \rightarrow \pi^*$ transition in acetonitrile.

$$\frac{\Delta E^0 - \Delta E^{\text{LR}}}{\Delta E^0 - \Delta E^{\text{SS}}} = \frac{2\mu_{0i}^2}{\Delta\mu_{0i}^2}, \quad (54)$$

where $\Delta\mu_{0i} = |\mu_{ii} - \mu_{00}|$ and $0 \rightarrow i$ is the electronic transition under study. Equation (54) implies that if two-times of the square of the transition moment $2\mu_{0i}^2$ is larger than the square of the variation of the dipole moments $\Delta\mu_{0i}^2$, then $\Delta E^0 - \Delta E^{\text{LR}}$ is larger than $\Delta E^0 - \Delta E^{\text{SS}}$, i.e., ΔE^{LR} is smaller than ΔE^{SS} . Obviously we cannot expect that such a relation (based on a first-order perturbation theory, a spherical cavity, and a dipolar coupling only between the solute and the reaction field) is exactly fulfilled by the PCM computed values. However, it is reasonable to suppose that the relative magnitude of ΔE^{LR} and ΔE^{SS} correlates with $2\mu_{0i}^2$ and $\Delta\mu_{0i}^2$. By ordering the four transitions under study from that with the largest $2\mu_{0i}^2/\Delta\mu_{0i}^2$ to that with the smallest $2\mu_{0i}^2/\Delta\mu_{0i}^2$, we obtain $A(n \rightarrow \pi^*) > \text{MCP}(\pi \rightarrow \pi^*) > \text{PNA}(\pi \rightarrow \pi^*) > A(\pi \rightarrow \pi^*)$, which is also the order we have chosen for Figs. 1–4. As it can be easily seen by passing from Fig. 1 and 4, the relative magnitude of the LR and SS excitation energies indeed follows (qualitatively) the prediction based on $2\mu_{0i}^2$ and $\Delta\mu_{0i}^2$. To make the comparison clearer, we have grouped in a single figure, Fig. 5, the differences $\Delta E^{\text{LR}} - \Delta E^{\text{SS}}$ for the four transitions under study (in acetonitrile). In conclusion, what

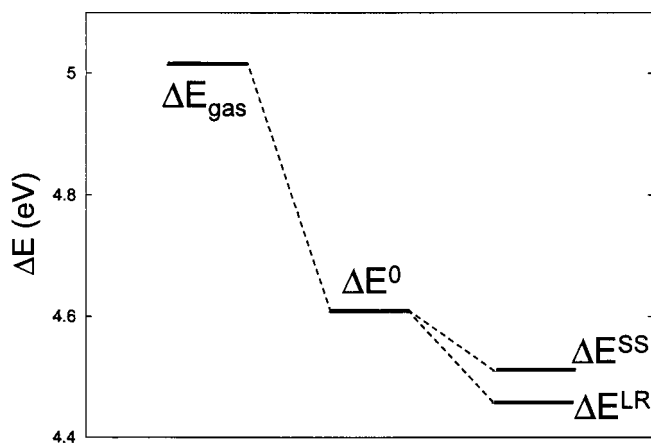


FIG. 3. Excitation energies for the parinitroaniline $\pi \rightarrow \pi^*$ transition in acetonitrile.

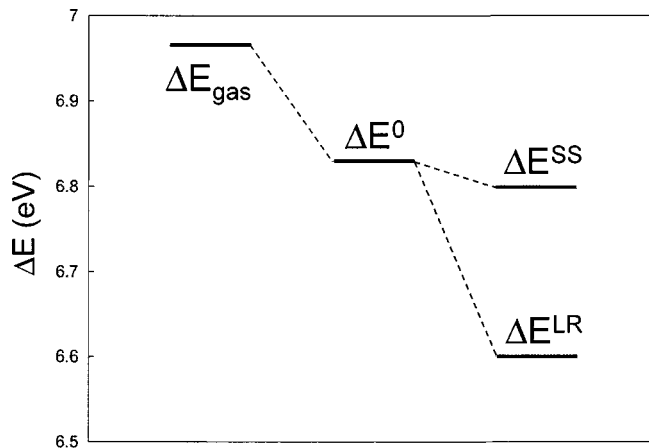


FIG. 4. Excitation energies for the acroleine $\pi \rightarrow \pi^*$ transition in acetonitrile.

we found is what we expected, i.e., if $\Delta\mu_{0i}^2$ is larger than $2\mu_{0i}^2$, the SS excitation energy is smaller than the LR one and vice versa. This is a criterion that can be used if only LR or SS results are available, and one would like to make qualitative considerations on the results obtainable with the other approach.⁵⁵

2. Solvatochromic shifts

Now we consider the magnitude of the differences between the excitation energies calculated within the SS and LR approaches. In calculations for molecules in solution one is often interested in solvatochromic shifts. Strictly speaking, the solvatochromic shifts is the difference between the excitation energy in a given solvent and in the gas phase.⁵⁶ We shall refer to these as *absolute* solvatochromic shifts. However, often the gas-phase value is replaced by the value measured in a nonpolar solvent. These *relative* solvatochromic shifts are more easy to be experimentally determined than the absolute shifts. Moreover, the calculation-experiment comparison for these shifts is usually more meaningful because nonelectrostatic solvation effects (not included in our calculations) are similar for polar and nonpolar solvents, thus

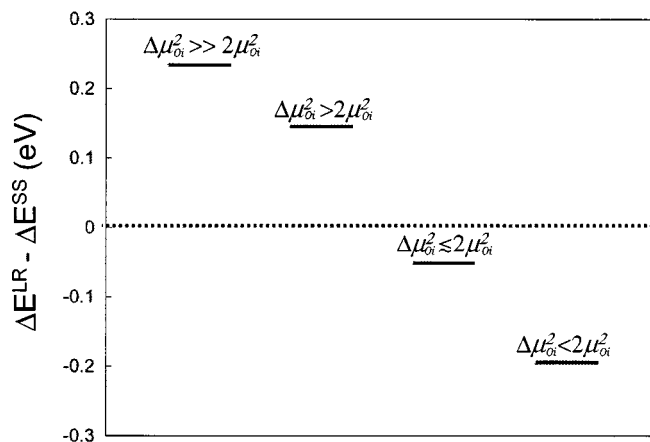


FIG. 5. Comparison of linear-response (LR) and state-specific (SS) excitation energies for the four transitions under study in acetonitrile. The order of the transitions (from left to right) is $A(n \rightarrow \pi^*)$, $\text{MCP}(\pi \rightarrow \pi^*)$, $\text{PNA}(\pi \rightarrow \pi^*)$, and $A(\pi \rightarrow \pi^*)$.

TABLE II. Solvatochromic shifts ($\Delta E^{\text{LR/SS}} - \Delta E_{\text{gas}}$) and shift differences between the two approaches ($\Delta E^{\text{LR}} - \Delta E^{\text{SS}}$) for the three molecules and the two solvents under study. Values in meV.

	Acetonitrile				Dioxane			
	A		MCP	PNA	A		MCP	PNA
	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
$\Delta E^{\text{LR}} - \Delta E_{\text{gas}}$	289	-864	203	-557	105	-334	55	-348
$\Delta E^{\text{SS}} - \Delta E_{\text{gas}}$	211	-167	59	-504	16	-88	-136	-318
$\Delta E^{\text{LR}} - \Delta E^{\text{SS}}$	78	-197	144	-53	89	-246	191	-30

they mostly cancel out for relative shifts. In any case, we shall examine both definitions of shifts.

Let us begin with the absolute solvatochromic shifts. These quantities are reported in Table II for the different excitations under study, in acetonitrile and dioxane.

As it is evident, the differences between the two approaches are usually comparable with the magnitude of absolute solvatochromic shifts (with the exception of the PNA transition). In at least one case [MCP($\pi \rightarrow \pi^*$) in dioxane], there is not only a quantitative difference between the shifts, but even a qualitative difference, since LR predicts a blue solvatochromism while SS predicts a redshift. Now we discuss the effects of the solvent polarity on the absolute solvatochromic shifts. We consider only the two extreme cases (extreme in terms of $2\mu_{0i}^2/\Delta\mu_{0i}^2$), i.e., the A($n \rightarrow \pi^*$) and the A($\pi \rightarrow \pi^*$) transitions. Figure 6 shows the excitation energies for these transitions in dioxane and in acetonitrile. As it can be seen, the main difference in passing from acetonitrile to dioxane is a shift of ΔE^0 , ΔE^{LR} , and ΔE^{SS} , which reduces the solvatochromic shift (note that the dotted line in the figure represents the gas-phase excitation energy). The shift is similar, but not exactly equal, for the LR and SS excitation energies (the difference is more evident for the A($\pi \rightarrow \pi^*$) transition). In particular, in dioxane the absolute differences $|\Delta E^{\text{LR}} - \Delta E^{\text{SS}}|$ are larger than in acetonitrile for all the transitions considered, as seen from the last row of Table II. Such a finding depends on two effects. Let us consider the simplified spherical cavity model, for which $|\Delta E^{\text{LR}} - \Delta E^{\text{SS}}| = |g(R, \epsilon_{\text{opt}})(\mu_{0i}^2 - 1/2\Delta\mu_{0i}^2)|$. Both a change of the optical di-

electric constant [that affects $g(R, \epsilon_{\text{opt}})$] and a change of the dipoles μ_{0i} and $\Delta\mu_{0i}$ will modify $|\Delta E^{\text{LR}} - \Delta E^{\text{SS}}|$. In passing from acetonitrile to dioxane, $g(R, \epsilon_{\text{opt}})$ increases since $\epsilon_{\text{opt}}(\text{dioxane}) > \epsilon_{\text{opt}}(\text{acetonitrile})$, while the dipoles μ_{0i} and $\Delta\mu_{0i}$ increase or decrease, always by small amounts (see Table I). For the four considered transitions, the former effect prevails on the latter, and the solvatochromic shift differences $|\Delta E^{\text{LR}} - \Delta E^{\text{SS}}|$ are larger in dioxane.

Let us now pass to examine the relative (nonpolar to polar) solvatochromic shifts. The acetonitrile-dioxane shifts obtained by the LR and SS methods are compared in Table III.

The LR-SS difference for polar to nonpolar shifts are much smaller than the absolute shifts discussed before. For three out of four cases, the difference ranges between 6% and 28%, and only in the fourth case ($\pi \rightarrow \pi^*$ transition of acrolein), the differences between the two approaches are as large as the value of the shift. Note, however, that such a shift is quite small (-30 or -79 meV, depending on the method). We also remark that both the LR and the SS give the same sign for the shifts, i.e., there are no cases in which LR and SS give a *qualitative* difference. Why the LR-SS difference for relative shifts is smaller than for absolute shifts? As we have pointed out in the Theory, the excitation energy difference between the two approaches originates only by the different role of the dynamic response of the solvent in the two methods. **Since the optical dielectric constants of acetonitrile and dioxane are not too different (1.76 and 2.2, respectively), the dynamic response contribution to the relative solvatochromic shifts tends to cancel out for both the LR and the SS approach.** In other terms, the relative solvatochromic shifts are dominated by the inertial response of the solvent, which would give exactly the same shift in both approaches. Note that all the usual solvents have quite similar dynamic responses. Thus, we expect that the difference between LR and SS relative shifts are always quite small, due to the argument presented above.

3. Comparison with experimental data

In this section, we compare the calculated relative shifts with the experimental one. The intrinsic level of our calculations (CIS) is, in general, not very high. However, recently it has been shown that for MCP, CIS gives fairly good results for the energy transition considered in the present paper.⁵⁷ For the A transitions, the gas-phase excitation energies reported in Table I are within 0.5 eV of the MR-CISD+Q results obtained in Ref. 27. In any case, the most meaningful

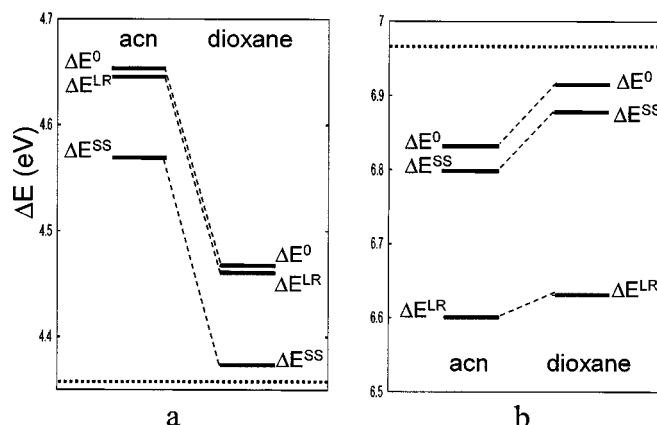


FIG. 6. Comparison between excitation energies obtained in acetonitrile and in dioxane. (a) Results for the A($n \rightarrow \pi^*$) transition, (b) Results for the A($\pi \rightarrow \pi^*$) transition. The dotted line indicates the computed gas-phase excitation energy.

TABLE III. Acetonitrile-dioxane shifts of the excitation energies ($\Delta\Delta^{\text{LR/SS}} = \Delta E_{\text{acn}}^{\text{LR/SS}} - \Delta E_{\text{diox}}^{\text{LR/SS}}$) and shift differences between the two approaches ($\Delta\Delta^{\text{LR}} - \Delta\Delta^{\text{SS}}$) for the three molecules under study. Values in meV.

	A		MCP	PNA
	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
$\Delta\Delta^{\text{Exp}^a}$	230	-60	480	-80
$\Delta\Delta^{\text{LR}}$	184	-30	148	-209
$\Delta\Delta^{\text{SS}}$	195	-79	195	-186
$\Delta\Delta^{\text{LR}} - \Delta\Delta^{\text{SS}}$	-11	49	-47	-23

^aExperimental values for polar to apolar solvatochromic shift. Reference 58 for A (water to hexane), Ref. 59 for MCP (methanol to n-pentane, -78 °C), and Ref. 60 for PNA (acetonitrile to dioxane).

way to compare with experiments is to consider solvatochromic shifts and not absolute energies. In fact, the errors intrinsic in the level of calculation tend to cancel out when energy differences (like solvatochromic shifts) are taken. The experimental values for the polar to nonpolar solvatochromic shifts are reported in Table III. For all the considered transitions, the sign of the calculated shift agrees with the experimental one. In the case of two A transitions, also the magnitude of the shift is satisfactory. For the MCP and PNA transitions, the calculation underestimates and overestimates, respectively, the experimental shifts. We remark, however, that the experimental values for MCP are obtained at a low temperature (-78 °C), where it is not clear how well a continuum description based on a single, isotropic dielectric constant can work. As a general comment, we remark that the discrepancies between calculations and experiments are always comparable or even larger than the LR-SS ones. This means that, at least for the considered transitions, it is not possible to clearly rate the two approaches in comparison with the experimental data.

IV. CONCLUSIONS

In this paper we have presented a formal and a numerical analysis of the differences between two widely used approaches to the calculation of excitation energies of molecules in solution. From the formal point of view, we have derived *comparable* expressions for the excitation energies in the framework of the two different approaches by exploiting perturbation developments having the same zeroth-order quantities and the same perturbation parameter. The theoretical analysis has permitted to work out analytical expressions for the excitation energies that highlighted the intrinsic differences between the two methods: in the SS approach a part of the solvatochromic shift is related to differences of expectation values, while in the LR approach it relates to transition matrix elements. By using a nonequilibrium approach in both frameworks, we have also established that these intrinsic differences are related only to the interaction of the solute with the *fast* response of the solvent medium.

A preliminary analysis based on the group function approach⁵⁰ relates the presence of different terms to the application of the SS and LR schemes to the self-consistent equations obtained when a single Hartree product is used to represent the overall solute-solvent state (the use of such product is one of the basis of continuum models). Following

this analysis, the terms that differ in the SS and in the LR approaches are related to different physical origins: the SS term takes into account the capability of a part of the solvent degrees of freedom to follow the changes in the solute wavefunction upon excitation. Such a term is not accounted for by LR. LR, instead, accounts for a dynamical correction to the excited state energy so that it is related to the response of the solvent to the charge density of the solute oscillating at the Bohr frequency. From the analysis of the semiclassical derivation reported, e.g., by McRae⁷ and Liptay⁹ it appears that such a term belongs to what has been classified as dispersion energy in these treatments. Thus, when the electrostatic SS solvatochromic shifts is supplemented with the (coherently calculated) dispersion contribution, the transition dipole dependent term of LR is recovered.

From this discussion, it appears that while the SS treatment of solvatochromic shifts can be made complete by adding suitable dispersion terms, the present LR treatment is really unable to account for the term related to the relaxation of the fast solvent polarization. In addition, when the dispersion contribution is added to the LR value, care must be taken not to account twice the transition dipole dependent term.

Such a discussion, focused on the differences between the two methods, should not eclipse an important similarity between SS and LR. It has to be stressed again that the solvatochromic contribution related to the inertial response of the solvent is described in the same way by the two approaches. Such a contribution represents the main part of relative solvatochromic shifts, which are thus described equally well by the SS and the LR approaches (for what regards the solvation model).

The numerical analysis, put forward for some illustrative cases, has confirmed the predictions of the theory presented in this paper. We have seen that the formal differences between the two approaches have also some practical consequences. In particular, we found non-negligible differences between the two approaches for absolute solvatochromic shifts, while quite small discrepancies were found for relative (polar to nonpolar) shifts.

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APPENDIX: EXCITATION ENERGIES FOR A DIPOLAR SOLUTE IN A SPHERICAL CAVITY

When studying a physical phenomenon with a quite complex model, it is often convenient to consider a simpler case, for which the derived equations become more transparent and easier to understand. Let us suppose that the cavity hosting the solute is spherical and that the solute interacts with the solvent only through its dipole moment, disregarding effects due to higher multipole moments. Within these assumptions, the solute-solvent interaction operator $V(\Psi)$ defined in Eq. (2) reads

$$V(\Psi) = -\vec{\mu} \cdot g(R, \epsilon) \langle \Psi | \vec{\mu} | \Psi \rangle, \quad (\text{A1})$$

where $\vec{\mu}$ is the dipole moment operator and $g(R, \epsilon)$ is the well-known reaction field factor (depending on the cavity radius R and the solvent dielectric constant ϵ) given by

$$g(R, \epsilon) = \frac{2(\epsilon - 1)}{R^3(2\epsilon + 1)}. \quad (\text{A2})$$

The dynamic equivalent of the operator $V(\Psi)$, called $V_d(\Psi)$, is simply

$$V_d(\Psi) = -\vec{\mu} \cdot g(R, \epsilon_{\text{opt}}) \langle \Psi | \vec{\mu} | \Psi \rangle, \quad (\text{A3})$$

where ϵ_{opt} is the optical dielectric constant of the solvent. In the following, we shall abbreviate $g(R, \epsilon_{\text{opt}})$ with g_d . It is easy to recognize that the form of Eq. (A3) corresponds to define the operators A and B_d [see Eq. (2)] as

$$A = \vec{\mu}, \quad B_d = -g_d \vec{\mu}. \quad (\text{A4})$$

Let us now rewrite the expression for the excitation energy obtained from the explicit consideration of the excited states in the nonequilibrium framework [Eq. (27)] in terms of V_d as given in Eq. (A3):

$$\Delta G_{0i}^{\text{neq}, \text{I}} = \Delta E_{0i}^{(0)} - \frac{1}{2} (\langle i^{(0)} | \vec{\mu} | i^{(0)} \rangle - \langle 0 | \vec{\mu} | 0 \rangle) \cdot (g_d \langle i^{(0)} | \vec{\mu} | i^{(0)} \rangle - g_d \langle 0 | \vec{\mu} | 0 \rangle) = \Delta E_{0i}^{(0)} - \frac{1}{2} g_d (\vec{\mu}_{ii}' - \vec{\mu}_{00})^2. \quad (\text{A5})$$

In Eq. (A5) we have introduced the shorthand notation $\vec{\mu}_{ij} = \langle i^{(0)} | \vec{\mu} | j^{(0)} \rangle$. We recall that $\Delta E_{0i}^{(0)}$ is the vertical excitation internal energy computed by considering that the solvent response does not change in the excitation. In this simple model, the explicit effects of the solvent (i.e., those beyond the changes in wave functions due to the ground-state reaction field) are represented by the simple term appearing in the right-hand side of Eq. (A5), $(g_d/2)(\vec{\mu}_{ii}' - \vec{\mu}_{00})^2$. Thus, the explicit effects depend on the difference between the expectation values of the dipole moment in the ground and in the excited state.

Let us now turn to the response theory treatment. As we have already outlined above, the point in which the response theory and the excited state treatment differ is the explicit contribution of the solvent to the excited state. In other words, $\Delta E_{0i}^{(0)}$ and $\omega_i^{(0)}$ have an equivalent role in the two treatments, and, for exact states, they are indeed equal [see Eq. (50)]. We have seen that the explicit contribution to ω_i^1 (the energy of the excitation to the state n in the linear-response formalism, at the first order in the solute-solvent interaction) is given by $\langle i^{(0)} | \hat{\mathbf{V}} | 0 \rangle \langle 0 | \hat{\mathbf{Q}}_d | i^{(0)} \rangle$ (i.e., $\langle i^{(0)} | A | 0 \rangle \times \langle 0 | B_d | i^{(0)} \rangle$ within the general notation). By assuming for A

and B_d the expressions given in Eq. (A4), which are proper for a spherical cavity and a dipolar solute, such an explicit solvent term reads

$$\langle i^{(0)} | A_d | 0 \rangle \langle 0 | B_d | i^{(0)} \rangle = -g_d |\vec{\mu}_{0i}|^2. \quad (\text{A6})$$

In other words, while the explicit solvent contribution in Eq. (A5) depends on the variation of the dipole moment between the ground and the excited state, in the linear-response formalism the solvent term depends on the transition dipole moment between the two states. Thus, the linear-response excitation energy ω_i^1 to be compared with $\Delta G_{0i}^{\text{neq}, \text{I}}$ in Eq. (A5) is

$$\omega_i^1 = \omega_i^{(0)} - g_d |\vec{\mu}_{0i}|^2. \quad (\text{A7})$$

As said in the Introduction, different semiclassical expressions have been worked out for solvatochromic shifts. Although our aim is not to give a new expression of such kind since we rely on a quantum-chemistry description of the solute, a comparison with the existing expressions can be interesting. The semiclassical expression more widely used in the interpretation of experimental data seems to be that by McRae.⁷ For the electrostatic component of the shift (the only one we are considering in the present paper), such an expression is (translated to our notation)

$$\Delta G_{0i}^{\text{McRae}} = \Delta E_{0i}^{\text{vac}} - \frac{1}{2} g_d [(\vec{\mu}_{ii}^{\text{vac}})^2 - (\vec{\mu}_{00}^{\text{vac}})^2] - \left[\frac{2(\epsilon - 1)}{R^3(\epsilon + 1)} - \frac{2(\epsilon_{\text{opt}} - 1)}{R^3(\epsilon_{\text{opt}} + 1)} \right] \vec{\mu}_{00}^{\text{vac}} \cdot (\vec{\mu}_{ii}^{\text{vac}} - \vec{\mu}_{00}^{\text{vac}}) + \text{DPOL}, \quad (\text{A8})$$

where the quantities proper for the isolated molecule have the superscript vac. In Eq. (A8), DPOL refers to terms related to changes in the molecular polarizability upon excitation, which are not accounted for in our first-order LR and SS theories. For this reason, we shall not consider DPOL anymore. The fractions involving dielectric constants in Eq. (A8) resemble the definition of g and g_d [Eq. (A2)], but the denominators are different. By looking at the McRae's derivation, such denominators depend on an approximate way of introducing the effects on the solute dipole moment of the ground-state reaction field. In our derivation, the effects of the ground-state reaction field are implicitly accounted for by the use of the solute dipole moment in solution. When the difference between solute dipole moments in gas-phase and in solution is neglected, Eq. (A8) becomes

$$\Delta G_{0i}^{\text{McRae}} = \Delta E_{0i}^{\text{vac}} - \frac{1}{2} g_d (\vec{\mu}_{ii}^2 - \vec{\mu}_{00}^2) - (g - g_d) \vec{\mu}_{00} \cdot (\vec{\mu}_{ii} - \vec{\mu}_{00}). \quad (\text{A9})$$

The same equation (under the same approximations) can be derived by starting from the work by Liptay.^{9,56} In order to compare our expressions with Eq. (A9), we have to make explicit $\Delta E_{0i}^{(0)}$ in Eqs. (A5) and (A7). In particular, we found that

$$\Delta E_{0i}^{(0)} = \Delta E_{0i}^{\text{vac}'} - g\vec{\mu}_{00} \cdot (\vec{\mu}_{ii} - \vec{\mu}_{00}), \quad (\text{A10})$$

where $\Delta E_{0i}^{\text{vac}'}$ is the excitation energy in gas phase, but computed with the states as in solution. By exploiting Eq. (A10), for SS we obtain

$$\begin{aligned} \Delta G_{0i} &= \Delta E_{0i}^{\text{vac}'} - g\vec{\mu}_{00} \cdot (\vec{\mu}_{ii} - \vec{\mu}_{00}) - \frac{1}{2}g_d(\vec{\mu}_{ii} - \vec{\mu}_{00})^2 \\ &= \Delta E_{0i}^{\text{vac}'} - \frac{1}{2}g_d(\vec{\mu}_{ii}^2 - \vec{\mu}_{00}^2) - (g - g_d)\vec{\mu}_{00} \cdot (\vec{\mu}_{ii} - \vec{\mu}_{00}), \end{aligned} \quad (\text{A11})$$

which is equal to the McRae-like equation (A9) when the differences between solute state in gas phase and in solution are neglected. Thus, as expected, our SS treatment basically becomes equivalent to the semiclassical one when an Onsager model is used. Instead, the LR solvatochromic shift does not reduce to Eq. (A9), which does not account for any terms involving transition dipoles.

Another equation that has been proposed in the literature for solvatochromic shift is that given by Karelson and Zerner,¹⁶ who adopted a QM description of the solute within the Onsager continuum model. In Ref. 16(b), different expressions can be found, depending on the form of the solvent interaction term in the solute Fock equations (called models A and B) and the kind of electronic relaxation considered. The equation that should be compared with ours is the Eq. (26a) of that work, which is (translated to our notation)

$$\Delta G_{0i}^{\text{KZ}} = \Delta E_{0i}^{(0)} + \frac{1}{2}g\vec{\mu}_{00} \cdot (\vec{\mu}_{ii} - \vec{\mu}_{00}) + \frac{1}{2}g_d\vec{\mu}_{ii} \cdot (\vec{\mu}_{00} - \vec{\mu}_{ii}). \quad (\text{A12})$$

When the term $\Delta E_{0i}^{(0)}$ in Eq. (A12) is made explicit as in Eq. (A10), the resulting Karelson–Zerner expression for the solvatochromic shift differs both from ours and from Eq. (A9). In any case, Eq. (A12) does not contain any explicit solute transition dipole terms.

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