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A state-specific polarizable continuum model time dependent density functional theory method for excited state calculations in solution

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An effective state specific (SS) model for the inclusion of solvent effects in time dependent density functional theory (TD-DFT) computations of excited electronic states has been developed and coded in the framework of the so-called polarizable continuum model (PCM). Different relaxation time regimes can be treated thus giving access to a number of different spectroscopic properties together with solvent relaxation energies of paramount relevance in electron transfer processes. SS and conventional linear response (LR) models have been compared for two benchmark systems (coumarin 153 and formaldehyde in different solvents) and in the limiting simple case of a dipolar solute embedded in a spherical cavity. The results point out the complementarity of LR and SS approaches and the advantages of the latter model especially for polar solvents. The favorable scaling properties of PCM-TD-DFT models in both SS and LR variants and their availability in effective quantum mechanical codes pave the route for the computation of reliable spectroscopic properties of large molecules of technological and/or biological interest in their natural environments. © 2006 American Institute of Physics. [DOI: [10.1063/1.2222364](https://doi.org/10.1063/1.2222364)]

I. INTRODUCTION

A deeper understanding of the static and dynamic properties of excited electronic states is fundamental for a number of processes of technological or biological interest, ranging from photonics to vision.¹ All these fields are receiving significant benefits from the ongoing integration between experimental and computational studies. This is favored from the experimental point of view by the development of increasingly accurate techniques for the detection and characterization of short-lived species² and from the computational point of view by the development of new theoretical methods for the study of excited states³ and by the availability of new hardware and software allowing for the treatment of large molecules of chemical interest. Of course, the usefulness of computational methods would be quite limited if environmental effects could not be taken into the proper account since most of the above mentioned processes occur indeed in solution. As a consequence even a qualitative agreement with experiments requires the use of a suitable solvation model.

From this point of view, the so-called polarizable continuum model (PCM) has been shown to provide a reliable description of solvent effects on both ground and excited state properties.⁴ Several studies indicate that PCM is fully adequate to describe the spectroscopic properties in apolar and polar/nonhydrogen bonding solvents, while the explicit

inclusion of a small number of solvent molecules of the cybotactic region is sufficient for an accurate treatment of hydrogen bonding solvents.⁵

The application of PCM to excited electronic states leads to a fairly complex theoretical problem, since the solvent reaction field couples the ground state density with the density correction and the orbital relaxation arising from the electronic transition. More in general this is also true for those post-self-consistent-field (SCF) methods that are used to include the electron correlation effects in the ground state energy and density: MP2, configuration interaction (CI), coupled clusters (CC), etc. The solvent reaction field should be variationally determined together with all the other parameters in the method [molecular orbital (MO) coefficients, CI coefficients, excitation amplitudes, etc.], but this leads to a highly nonlinear problem since all those parameters do depend on the solvent reaction field. It is thus possible to envision different approaches to the problem of post-SCF self-consistent reaction field (SCRf) with PCM. At a first level of approximation, solvent effects can be introduced simply through polarization of the SCF molecular orbitals: the reaction field is thus self-consistent with the SCF density, and the polarized orbitals are simply used to compute the post-SCF density correction, which does not alter the reaction field. This is the approach used, for example, with MP2 (Ref. 6) or CC (Ref. 7) methods.

Other approaches to achieve self-consistency between the post-SCF/excited state density and the solvent reaction

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field have also been explored,^{8,9} but their practical application has been hampered by the high computational cost, with the noteworthy exception of PCM/complete active space self-consistent field^{10,11} (CASSCF) in which a fully variational formulation of solvent effect on the excited state properties is achieved, by efficiently solving a different effective Schrödinger equation for each state of interest.

A number of computational approaches to the study of excited electronic states exploit the linear response (LR) formalism, which avoids the calculation of the exact excited state electron density in favor of a direct determination of the excitation energies. In these methods the polarized SCF orbitals are still used, but an additional PCM correction is introduced which typically depends on the ground to excited state transition density.^{12,13} Additional corrections to the PCM-LR treatment have been recently proposed, employing a perturbative approach based on the knowledge of the excited state density *in vacuo*.¹⁴ The most popular LR methods are random phase approximation (RPA), the Tamm-Dancoff approximation (TDA), which corresponds to the configuration interaction with singles (CIS), when based on the Hartree-Fock (HF) wave function,¹⁵ and all the methods rooted in the time dependent density functional theory (TD-DFT).¹⁶ Among them, TD-DFT recently received considerable attention, since it emerged as a very effective tool for the study of excited states.¹⁷ As a matter of fact, when coupled to suitable density functionals, TD-DFT often represents the best compromise between accuracy and computational cost for describing the excited state behavior in medium/large size molecules, reaching an accuracy comparable to that of the most sophisticated (but exceedingly expensive) post-Hartree-Fock methods in most cases (e.g., valence excitations of organic and metallo-organic systems).¹⁸ Furthermore, significant steps to overcome the “traditional” deficiencies of TD-DFT (for example, the treatment of long range electron transfer or of transitions with substantial contribution from double excitations) have been made.^{19,20} PCM TD-DFT has been successfully applied to the study of the spectroscopic behavior of several chemical systems in solution.²¹ Additionally analytical first derivatives have been recently implemented, allowing for effective excited state geometry optimizations.²²

In two recent papers, Cammi *et al.*²³ and Corni *et al.*²⁴ have shown that the PCM LR approach is intrinsically different from its state-specific (SS) counterpart, analyzing the outcome of CIS-PCM calculations, for which a strict comparison between SS and LR results is more straightforward. CIS method can be considered indeed either as a standard CI or as a linear response method based on the Tamm-Dancoff approximation (*vide supra*): *in vacuo* these two points of view lead to the same equations.

The SS route should, in principle, lead to a more reliable and accurate determination of the variation of the solvation free energy associated with the change in the electron density upon excitation.

Actually, there are indications that the LR and SS approaches differ also in another significant aspect, i.e., the treatment of nonequilibrium solvent effects. Electron excitation is indeed an intrinsically dynamic process and thus it is

important that the characteristic times of solvent degrees of freedom are taken into account. Two extreme time regimes can be identified:^{25,26} (i) the nonequilibrium regime, in which only solvent electronic polarization (fast degree of freedom) is in equilibrium with the excited state electron density of the solute, while the slow solvent degrees of freedom remain equilibrated with the ground state electron density; (ii) the fully equilibrated regime, where all the solvent degrees of freedom are in equilibrium with the electron density of the state of interest. In the framework of continuum solvation models the two situations are ruled by two different dielectric constants. In the nonequilibrium case, the reaction field due to the fast solvent degrees of freedom depends on the dielectric constant at optical frequency (ϵ_{opt} , usually related to the square of the solvent refractive index n , $\epsilon_{\text{opt}}=n^2$). Equilibrium solvation is instead ruled by the static dielectric constant (ϵ).

In this respect a comparison among the results of the studies published so far^{10,12,25} suggests that, when applied to similar systems, LR (PCM-TD/DFT) and SS (PCM-CASSCF) calculations provide different estimates of the difference between the equilibrium and nonequilibrium solvation energies (in the following we label this quantity as λ). This latter is a critical quantity for many fundamental dynamical processes, such as, just to make an example, inter- and intramolecular electron transfers.²⁷

On the ground of the above considerations, it is clear that obtaining a state specific PCM TD-DFT method would be highly desirable. In the first part of the present paper we thus present the first application of a state specific iterative version of the PCM/TD-DFT method. Next, both LR and SS PCM/TD-DFT methods are applied to the study of the spectroscopic behavior in solution of two representative systems, namely, coumarin 153 (hereafter C153) and formaldehyde, paying special attention to the treatment of equilibrium/nonequilibrium solvation effects.

II. THEORETICAL METHODOLOGY

In the PCM the solvent is described as a homogeneous dielectric, which is polarized by the solute. The latter is placed in a cavity within the solvent medium (built as the envelope of spheres centered on the solute atoms) and the proper electrostatic problem at the cavity surface is solved using a boundary element approach.⁴

The resulting reaction field contribution to the solute free energy (G) can be expressed as

$$G = \frac{1}{2} \mathbf{V}^\dagger \mathbf{q}, \quad (1)$$

where vector \mathbf{V} collects the values of the solute's electrostatic potential and \mathbf{q} are the apparent surface charges placed at the center of the surface *tesserae* (i.e., the small tiles which the cavity surface is finely subdivided in), where also \mathbf{V} is computed.

These charges are the solution of the PCM linear system, and different models for their determination have been devised. In the latest version of the method^{4(d),24} they depend on the solute's electrostatic potential and, thus, on its density, through a general relationship of the form

$$\mathbf{q} = -\mathbf{D}\mathbf{V}, \quad (2)$$

where the square matrix \mathbf{D} is the inverse of the matrix defining the PCM linear system and is related to cavity geometrical parameters and to the solvent dielectric constant ϵ .

Let us now first briefly recall the LR implementation of PCM/TD-DFT calculation.¹² To this aim, it is useful to introduce an alternative formulation of the solute solvent interaction energy,

$$G = \frac{1}{2} \int_{\Gamma} \int_{\Gamma} \mathbf{V}(\mathbf{s}) \mathcal{Q}(\mathbf{s}', \mathbf{s}) \mathbf{V}(\mathbf{s}') ds ds', \quad (3)$$

introducing the response operator (\mathcal{Q}) (Ref. 28) connecting the solute electrostatic potential (\mathbf{V}) in different points (\mathbf{s}, \mathbf{s}') of the cavity surface, while Γ indicates that the integration is extended to the cavity surface. Even if a detailed discussion on the properties of the operator \mathcal{Q} is outside the scope of the present paper and it can be found elsewhere,^{12,28} it is useful to briefly recall that

$$\mathcal{Q}(\mathbf{s}, \mathbf{s}') = \frac{1}{2} [\tilde{\mathcal{Q}}(\mathbf{s}, \mathbf{s}') + \tilde{\mathcal{Q}}(\mathbf{s}', \mathbf{s})], \quad (4)$$

and that the operator $\tilde{\mathcal{Q}}(\mathbf{s}', \mathbf{s})$ is the kernel of $\hat{T}^{-1}\hat{\mathcal{R}}$. Operators \hat{T} and $\hat{\mathcal{R}}$ relate the effective solvation charge density to the solute electrostatic potential and depend on the dielectric constant of the solvent and on the shape of the cavity.

It has been shown¹² that the PCM contribution to the time dependent Kohn-Sham equation depends on the term $\delta\phi(\mathbf{s}', \omega)$,

$$\delta\phi(\mathbf{s}', \omega) = \int_{\mathbf{R}^3} \frac{\delta\rho^{\text{el}}(\mathbf{r}', \omega)}{|\mathbf{s}' - \mathbf{r}'|} d\mathbf{r}', \quad (5)$$

that formally corresponds to an electrostatic potential computed using the electron density variation ($\delta\rho^{\text{el}}$) associated with the electronic transition in place of a specific electron density (ρ^{el}). The contribution from the PCM operator is then defined as

$$v^{\text{PCM}}[\delta\rho^{\text{el}}](\mathbf{r}) = \int_{\Gamma} \int_{\Gamma} \delta\phi(\mathbf{s}', \omega) \mathcal{Q}(\epsilon_{\text{opt}}; \mathbf{s}', \mathbf{s}) \frac{1}{|\mathbf{s} - \mathbf{r}|} ds ds', \quad (6)$$

if only the fast solvation degrees of freedom are equilibrated with the excited state density of the solute, and

$$v^{\text{PCM}}[\delta\rho^{\text{el}}](\mathbf{r}) = \int_{\Gamma} \int_{\Gamma} \delta\phi(\mathbf{s}', \omega) \mathcal{Q}(\epsilon; \mathbf{s}', \mathbf{s}) \frac{1}{|\mathbf{s} - \mathbf{r}|} ds ds', \quad (7)$$

when treating equilibrium solvation.

In the nonequilibrium case, the PCM response matrix \mathcal{Q} depends on the dielectric constant at optical frequency (ϵ_{opt}), whereas in the equilibrium case it depends on ϵ .

In the presence of the solvent, the coupling matrix elements ($K_{st,uv}^0$ for an isolated system) entering the solution of the time dependent Kohn-Shan equations thus become

$$K_{st,uv} = K_{st,uv}^0 + \int_{\Gamma} \int_{\Gamma} \phi_{st}(\mathbf{s}') \mathcal{Q}(\epsilon_{\text{opt}}; \mathbf{s}', \mathbf{s}) \phi_{uv}(\mathbf{s}) ds' ds, \quad (8)$$

$$\phi_{st}(\mathbf{s}) = - \int_{\mathbf{R}^3} \psi_s^*(\mathbf{r}) \frac{1}{|\mathbf{s} - \mathbf{r}|} \psi_t(\mathbf{r}) d\mathbf{r}, \quad (9)$$

in the case of nonequilibrium solvation and

$$K_{st,uv} = K_{st,uv}^0 + \int_{\Gamma} \int_{\Gamma} \phi_{st}(\mathbf{s}') \mathcal{Q}(\epsilon; \mathbf{s}', \mathbf{s}) \phi_{uv}(\mathbf{s}) ds' ds, \quad (10)$$

for equilibrium solvation.

We can now introduce the SS implementation of PCM/TD-DFT. In SS methods the excited state equilibrium ($\mathcal{G}_{\text{eq}}(2)$) free energy in solution thus explicitly depends on the excited state (2) density.

$$\mathcal{G}_{\text{eq}}^{(2)} = \frac{1}{2} \sum_i q_i^{(2)} V_{i,p}^{(2)} = \frac{1}{2} \sum_i q_{i,f}^{(2)} V_{i,p}^{(2)} + \frac{1}{2} \sum_i q_{i,s}^{(2)} V_{i,p}^{(2)}. \quad (11)$$

The nonequilibrium ($\mathcal{G}_{\text{neq}}^{(2)}$) free energy in solution also involves an explicit dependence on the density of the ground state (1),

$$\begin{aligned} \mathcal{G}_{\text{neq}}^{(2)} = & \frac{1}{2} \sum_i q_{i,f}^{(2)} V_{i,p}^{(2)} + \left(\sum_i q_{i,s}^{(1)} V_{i,p}^{(2)} - \frac{1}{2} \sum_i q_{i,s}^{(1)} V_{i,p}^{(1)} \right) \\ & + \frac{1}{2} \left(\sum_i q_{i,s}^{(1)} V_{i,f}^{(2)} - \sum_i q_{i,s}^{(1)} V_{i,f}^{(1)} \right). \end{aligned} \quad (12)$$

In the above equations q_f/q_s and V_f/V_s are the polarization charges and the corresponding potential relative to the “fast” and “slow” solvent degrees of freedom. $V_p^{(n)}$ is instead the potential generated by the density of the state (n).

We here propose an effective approach to the solution of the nonlinear problem of determining the polarization charges corresponding to excited state density based on a self-consistent iterative procedure. Starting from a TD-DFT calculation *in vacuo* a first approximation to the state specific reaction field is computed using the electron density of the state of interest by solving Eq. (2). In the next step, a TD-DFT calculation is performed in the presence of this first set of polarization charges, providing an updated excited state density and, consequently, a new set of polarization charges. This iterative procedure continues until convergence on the reaction field is achieved.

The final equilibrium and nonequilibrium energies of the state of interest are easily obtained by adding the corrections obtained by Eq. (11) or Eq. (12) to the excited state energy provided by the TD calculation. It is important to remind that, since solvent effect is already included in the ground state calculation used as starting point for the TD calculation, it is necessary to subtract the contribution to the solvation energy coming from the SCF density.

A. Computational details

In the DFT and TD-DFT calculations¹⁶ the PBE0 (Ref. 29) functional has been used. Despite the absence of adjust-

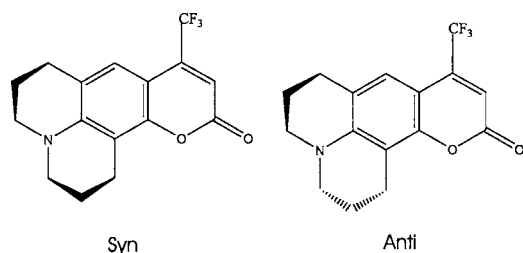


FIG. 1. Schematic drawing of the two conformers of C153.

able parameters, when employed in TD-DFT calculations, PBE0 (TD-PBE0) has already provided excitation spectra in very good agreement with the available experimental results.^{21,30,31} Ground state geometry optimizations have been performed with the standard 6-31G(*d*) basis set, and excitation energies have been refined by using the larger 6-31+G(*d,p*) and 6-311+G(2*d*,2*p*) basis sets. Bulk solvent effects on the ground and the excited states have been taken into account by means of the latest developments²⁸ of PCM.⁴

In equilibrium condition standard static dielectric constants at 298 K have been used, namely, 78.39 (water), 46.7 [dimethyl sulfoxide (DMSO)], and 2.023 (cyclohexane). The optical dielectric constants used in the nonequilibrium calculations are instead 1.776 (water), 2.179 (DMSO), and 2.028 (cyclohexane), respectively. The united atom topological model (UATM) has been used for building the molecular cavity, defining the cavity radii according to the united atom for Hartree-Fock (UAHF) model.³²

All the calculations have been performed by using a development version of the GAUSSIAN package.³³

III. RESULTS

A. Coumarin 153

C153 (see Fig. 1) is one of the most used “molecular probes” of crucial dynamical aspects of solvation. In this molecule the $S_0 \rightarrow S_1$ transition has a $\pi \rightarrow \pi^*$ character, and it essentially corresponds to a highest occupied molecular orbital (HOMO) \rightarrow lowest unoccupied molecular orbital (LUMO) transition (see Fig. 2).

However, while the HOMO is delocalized on the whole molecule, with significant contribution by the π orbitals of the “central” benzenic ring and of the nitrogen atom, the LUMO is mainly localized on the “quinonelike” terminal ring with significant contribution of the π^* orbital of the carbonyl group. As a consequence the $S_0 \rightarrow S_1$ transition has a partial intramolecular charge transfer character (from the nitrogen atom to the carbonyl group), and S_1 has a partial zwitterionic character (with the nitrogen atom and the oxygen of the carbonyl group bearing formal positive and negative charges, respectively). This results in a significant solvent shift of this transition, which, coupled to the molecular rigidity, makes C153 an ideal tool for investigating the different solvation rates by time resolved spectroscopic techniques.^{34–36}

Two conformers (*syn* and *anti*) with comparable stabilities are possible for C153 (see Fig. 1): in the gas phase the *syn* conformer is more stable by only ≈ 0.014 eV (PBE0/

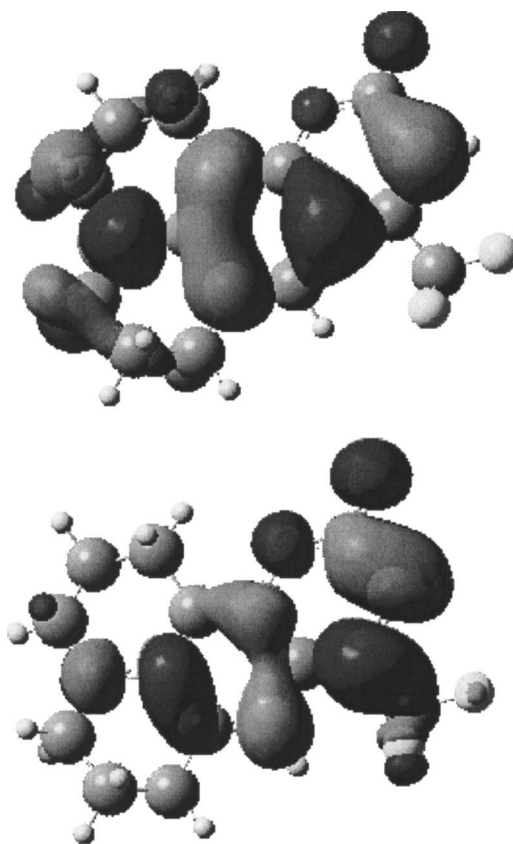


FIG. 2. Schematic drawing of the HOMO (upper) and the LUMO (lower) of C153.

6-311+G(2*d*,2*p*)/PBE0/6-31G(*d*) calculations), but in DMSO solution the two conformers are nearly isoenergetic. Since *syn*- and *anti*-C153 are present in solution in comparable amounts, we investigated the ground and first excited electronic states of both isomers by using SS and LR approaches (see Table I).

Inspection of Table I confirms that, as already shown, TD-DFT calculations can provide good estimates of the vertical excitation energies (VEE) of the $S_0 \rightarrow S_1$ transition in C153.³⁷ On this respect it is worth of noting that in C153 both HOMO and LUMO are delocalized on the entire molecule, and TD-DFT does thus not suffer from the deficiencies often exhibited in the treatment of electron transfer transitions between molecular orbital pairs with vanishingly small overlap.¹⁹

The VEE predicted by TD-PBE0/6-311+G(2*d*,2*p*) calculations in the gas phase is indeed ≈ 0.25 eV lower than the maximum of the absorption band recorded in apolar solvents. However, a comparison between LR-PCM/TD-PBE0/6-31G(*d*) VEE obtained in cyclohexane and the results obtained in the gas phase at the same level of theory shows that the inclusion of bulk solvent effects would decrease the VEE by ≈ 0.15 eV.

LR-nonequilibrium PCM computations in DMSO provide a good estimate of solvent shift with respect to the gas phase, even if the computed value (≈ 0.25 eV) is confirmed³⁸ to be underestimated with respect to the experimental one (0.43 eV).³⁵ LR-PCM calculations underestimate also the VEE solvent shift between cyclohexane and DMSO (0.11 eV

TABLE I. Vertical excitation energy (in eV) of the $S_0 \rightarrow S_1$ transition of coumarin C153 calculated, according to different solvation models, by PCM/TD-PBE0/6-31G(d) calculations on PCM/PBE0/6-31G(d) geometries optimized in the condensed phase. Experimental absorption maxima (in eV): 3.22 (cyclohexane), 2.94 (DMSO), and 3.37 (gas phase) (Ref. 35).

	<i>Anti</i>		<i>Syn</i>	
	Gas phase			
6-31G(<i>d</i>)	3.492		3.497	
6-31+G(<i>d</i> , <i>p</i>)	3.390		3.382	
6-311+G(2 <i>d</i> ,2 <i>p</i>)	3.364		3.368	
	Cyclohexane	DMSO	Cyclohexane	DMSO
	Linear response			
Nonequilibrium	3.354(0.454)	3.238(0.4619)	3.360(0.441)	3.244(0.450)
μ_0/μ_1	8.4/14.6	10.1/16.0	8.02/14.3	9.64/15.7
Equilibrium	3.354(0.454)	3.140(0.6039)	3.360(0.441)	3.148(0.589)
μ_0/μ_1	8.4/14.6	10.1/17.2	8.02/14.3	9.64/16.9
	State specific			
Nonequilibrium	3.240(0.359)	3.029(0.359)	3.242(0.348)	3.034(0.349)
μ_0/μ_1	8.4/14.5	10.1/15.9	8.02/14.3	9.64/15.6
Equilibrium	3.240(0.359)	2.907(0.353)	3.242(0.348)	2.904(0.343)
μ_0/μ_1	8.4/14.5	10.1/16.7	8.02/14.3	9.64/16.4

versus an experimental value of 0.28 eV), whereas the equilibrium result (0.2 eV) is closer to the experimental value.

Although the general trends obtained by LR and the SS approaches are similar, some remarkable differences are apparent, leading to a much better agreement of SS results with the experimental values. SS calculations provide indeed non-equilibrium VEE significantly smaller than their LR counterparts by ≈ 0.1 and ≈ 0.2 eV in cyclohexane and in DMSO, respectively. As a consequence, the computed SS gas phase \rightarrow DMSO and cyclohexane \rightarrow DMSO solvent shifts are 0.46 and 0.21 eV, respectively, in remarkable agreement with the experimental results.

Time resolved fluorescence experiments allow estimating dynamical equilibrium/non-equilibrium solvation effects, and provide values of 0.24 and -0.008 eV for λ in DMSO and cyclohexane, respectively.

The λ values provided by PCM computations are consistent with the experimental estimates, especially considering that they refer to the absorption, and not to the emission, process. The λ computed by SS calculations in DMSO is indeed 0.12 eV, 0.025 larger than that obtained by LR calculations. Both approaches agree in predicting a negative, though very small, λ value in cyclohexane.

The last difference between SS and LR calculations concerns the intensity of the $S_0 \rightarrow S_1$ transition. LR calculations predict indeed that when solvent is fully equilibrated the transition is noticeably more intense than in non-equilibrium conditions, whereas this result is not confirmed by SS calculations.

The recent advances in PCM/TD-DFT theory²² allow one to calculate the changes on the first order density matrix associated with the electronic transition and, thus, to evaluate first order properties such as the dipole moment, employing both LR and SS approaches (see Table I). Both LR and SS

calculations predict that $S_0 \rightarrow S_1$ transition leads to an increase of the dipole moment by ≈ 6 D, in good agreement with experimental estimates.

B. Formaldehyde

In the next step of our analysis we have investigated the lowest energy $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of formaldehyde in aqueous solution (see Table II). Let us recall, first of all, that the purpose of the present paper is to compare the results delivered by two different approaches in the calculation of bulk solvent effects, and not to obtain the most accurate estimate of experimental solvent shifts. It is indeed important to remind that, in order to quantitatively reproduce the experimental blueshift in aqueous solution, hydrogen bond interactions with first solvation shell molecules have to be explicitly taken into account.¹⁰

Confirming previous computational results, the lowest energy $n \rightarrow \pi^*$ transition corresponds to the HOMO \rightarrow LUMO excitation; it is dipole forbidden, falls at ≈ 4 eV, and produces the first singlet excited state S_1 . The excited state dipole moment is smaller than that of the ground state, giving account of the experimental solvent blueshift. This result is confirmed by both SS and LR calculations. However, the former method provides larger VEE and solvent blueshift.

The lowest energy $\pi \rightarrow \pi^*$ transition corresponds to the HOMO-1 \rightarrow LUMO transition. In agreement with previous computational results it is peaked around 9.5 eV and, though not being very intense, exhibits a non-negligible oscillator strength. In analogy with the $n \rightarrow \pi^*$ transition examined above, it is blueshifted in aqueous solution with respect to the gas phase, according to both LR and SS approaches, in line with this smaller dipole moment. We indeed remind that the effect of the solute solvent dispersion interaction on the

TABLE II. Vertical excitation energy (in eV) of the two lowest energy $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of formaldehyde calculated in aqueous solution, according to different solvation models, by PCM/TD-PBE0/6-311++G(d,p) calculations on PCM/PBE0/6-31G(d) optimized geometries. Oscillator strengths in parentheses and excited state dipole moments (in debye) in *italics*.

	Nonequilibrium solvation	Equilibrium solvation	Solvent shift	λ (cm ⁻¹)
6-31G(d) ^a				
$n \rightarrow \pi^*$				
LR	4.1397(0.00)2.02	4.1313(0.00)1.92	524	68
SS	4.1744(0.00)1.99	4.0919(0.00)1.92	803	665
$\pi \rightarrow \pi^*$				
LR	10.0187(0.09)1.24	9.9298(0.13)1.15	858	717
SS	10.1551(0.07)1.07	10.0477(0.06)0.83	1958	866
6-311++G(d,p) ^b				
$n \rightarrow \pi^*$				
LR	4.0420(0.00)2.10	4.0307(0.00)1.92	800	91
SS	4.0983(0.00)2.04	3.9802(0.00)1.90	1254	953
$\pi \rightarrow \pi^*$				
LR	9.4862(0.13)1.31	9.3636(0.17)0.93	345	989
SS	9.5850(0.10)1.31	9.4616(0.09)1.15	1142	995

^aGround state dipole moment=2.6632 D; gas phase excitation energy: $n \rightarrow \pi^*$ =4.0748 eV and $\pi \rightarrow \pi^*$ =9.9123 eV.

^bGround state dipole moment=3.0314 D; gas phase excitation energy: $n \rightarrow \pi^*$ =3.9428 eV; and $\pi \rightarrow \pi^*$ =9.4434 eV.

VEE (Ref. 10) is not included in the present treatment. Also for this transition the solvent blueshift computed by SS method is significantly larger than that obtained at the LR level.

SS and LR approaches provide also different estimates of λ , even if both methods predict that λ is larger for the $\pi \rightarrow \pi^*$ transition. In particular, the values provided by SS calculations for both transitions are similar, whereas LR calculations predict that λ is remarkably larger for the most intense transition, being close to zero for the $n \rightarrow \pi^*$ dark state. In this respect, it is worth of noting that CAS(4/3)/6-31G(d) calculations on acetone predict that λ associated with the lowest energy $n \rightarrow \pi^*$ transition is ≈ 400 cm⁻¹,¹⁰ in qualitative agreement with the SS result. In order to assess the reliability of SS and LR computations, it is useful to compute the free energy in solution of the lowest energy triplet state of formaldehyde (T_1). The electronic configuration of this state involves half filled HOMO and LUMO molecular orbitals and thus its electron density is expected to be very similar to that of S_1 (arising from the HOMO \rightarrow LUMO transition). PCM/PBE0/6-31G(d) calculations indicate that the equilibrium solvation energy of T_1 is ≈ 300 cm⁻¹ smaller than that of S_0 , in good agreement with the equilibrium solvent shift predicted by SS computations (≈ 230 cm⁻¹). Furthermore, LR/PCM/TD-PBE0 calculations predict that λ associated with the $S_0 \rightarrow T_1$ transition is vanishingly small, while their SS counterparts provide results similar to that obtained for the $S_0 \rightarrow S_1$ transition.

Finally, it is worth of mentioning that SS calculations predict that the intensity of the $\pi \rightarrow \pi^*$ transition is significantly larger in equilibrium conditions, confirming the results obtained on C153.

IV. DISCUSSION

In the preceding section we have shown that the values of the nonequilibrium VEE and λ provided by SS and LR implementations of PCM-TD-DFT are different. Those discrepancies can be profitably discussed in the framework of a previous study by Cammi *et al.* where the authors show that, to the first order, nonequilibrium excitation energy in solution ΔG^{01} can be decomposed into two terms.²³ Both in the SS and in the LR approach, the zeroth-order contribution corresponds to the electronic transition in the presence of the solvent reaction field of the ground state. The second contribution arises from the equilibration of the solvent degrees of freedom to the excited state charge density of the solute. It is explicitly taken into account in the SS approach by the term

$$\frac{1}{2}[\langle 1|\hat{V}|1\rangle - \langle 0|\hat{V}|0\rangle][\langle 1|\hat{Q}_d|1\rangle - \langle 0|\hat{Q}_d|0\rangle], \quad (13)$$

where \hat{V} is the molecular electrostatic potential operator and \hat{Q}_d is the apparent charge operator obtained when considering only the fast response of the solvent.

In the LR approach the above contribution is not taken into account. It is instead present a “dynamical correction” term, due to the response of the solvent to the solute charge density oscillating at the Bohr frequency,³⁹

$$\langle 1|\hat{V}|0\rangle \cdot \langle 0|\hat{Q}_d|1\rangle. \quad (14)$$

From a physical point of view this term corresponds to the interaction energy between the transition density and the corresponding reaction field.

In order to better understand the physical meaning of the above equation Cammi *et al.*²³ calculated the SS and LR

excitation energies provided by CIS method in the limiting simple case of a dipolar solute embedded in a spherical cavity.⁴⁰

We follow the same strategy in order to further investigate the differences of the two approaches for TD-DFT PCM, focusing our attention on the calculation of λ .

Starting our analysis from the SS approach, the equilibrium solvation energies of the ground ($|0\rangle$) and the excited state ($|1\rangle$) are, respectively,

$$\Delta G^{\text{eq}} = -\frac{1}{2}g(\epsilon)\mu_1^2, \quad (15)$$

$$\Delta G_0^{\text{eq}} = -\frac{1}{2}g(\epsilon)\mu_0^2, \quad (16)$$

where μ_0 and μ_1 are the ground and the excited state dipole moment, respectively. $g(\epsilon)$ is the factor relating the dielectric reaction field to the field generated by the dipole within the cavity. In our simple case it is given by

$$g(\epsilon) = \frac{2(\epsilon - 1)}{(2\epsilon + 1)} \frac{1}{r^3}, \quad (17)$$

where r is the cavity radius and ϵ is the static dielectric constant. When treating nonequilibrium solvation this term depends on $g(\epsilon_{\text{opt}})$. In the simple case we are examining it is possible to show that the nonequilibrium solvation free energy is

$$\Delta G_1^{\text{neq}} = -\frac{1}{2}g(\epsilon)\mu_0^2 - g(\epsilon)\mu_0(\mu_1 - \mu_0) - \frac{1}{2}g(\epsilon_{\text{opt}})(\mu_1 - \mu_0)^2. \quad (18)$$

Nonequilibrium solvent shift can then be obtained by subtracting Eqs. (15) and (18),

$$\Delta G_1^{\text{neq}} - \Delta G_0^{\text{eq}} = -g(\epsilon)\mu_0(\mu_1 - \mu_0) - \frac{1}{2}g(\epsilon_{\text{opt}})(\mu_1 - \mu_0)^2. \quad (19)$$

This term is due to the sum of two contributions, depending on the difference and on the square of the difference between the excited and the ground state dipole moment, respectively.

For what concerns the LR approach, the nonequilibrium first order correction to the zeroth-order excitation energy is

$$\Delta\omega'^{\text{neq}} = -g(\epsilon_{\text{opt}})|\mu_{01}^{\text{tr}}|^2. \quad (20)$$

The correction to the excited state solvation energy in the LR approach is thus proportional to the transition dipole moment between the two states (μ_{01}^{tr}).

On this basis it is possible to explain the difference in the solvent shift predicted by LR and SS approaches. As previously suggested, their relative behavior depends on the ratio between the transition dipole moment and the variation of dipole moment associated with a given transition. For very weak transitions (e.g., $n \rightarrow \pi^*$ in formaldehyde) we can expect that the excited state stability is underestimated by the LR approach.

The opposite occurs for the first $\pi \rightarrow \pi^*$ transition of formaldehyde that is not very intense and does not involve a large variation in the dipole moment. In both the above cases the difference between the two approaches is quite significant, being of the same order of magnitude as the total solvent shift. In C153 we are in the presence of a bright transi-

tion involving a large dipole moment shift: in this case both approaches give quite similar solvatochromic shifts. In DMSO the difference between the LR and SS results is 0.035 eV, i.e., $\approx 10\%$ of the total solvent shift with respect to the gas phase.

In order to compute λ in the framework of the SS approach it is useful to rearrange expression (18) by adding and subtracting $\frac{1}{2}g(\epsilon)\mu_1^2$.

$$\Delta G_1^{\text{neq}} = -\frac{1}{2}g(\epsilon)\mu_1^2 + \frac{1}{2}[g(\epsilon) - g(\epsilon_{\text{opt}})](\mu_1 - \mu_0)^2. \quad (21)$$

Comparison between Eqs. (16) and (21) shows that

$$\lambda = [g(\epsilon) - g(\epsilon_{\text{opt}})](\mu_1 - \mu_0)^2, \quad (22)$$

λ is thus proportional to the square of the dipole moment shift associated with the electronic transition. Furthermore it is vanishing when $\epsilon_{\text{opt}} \approx \epsilon$ as it happens in nonpolar solvents such as cyclohexane.

In the LR approach the only difference between the equilibrium and the nonequilibrium case is the substitution of ϵ_{opt} with ϵ [see Eqs. (8) and (10)]. Therefore, the corresponding equilibrium excitation energy and λ are

$$\Delta\omega'^{\text{eq}} = -g(\epsilon)|\mu_{01}^{\text{tr}}|^2, \quad (23)$$

$$\lambda = -[g(\epsilon) - g(\epsilon_{\text{opt}})]|\mu_{01}^{\text{tr}}|^2. \quad (24)$$

On the ground of Eq. (24) we can thus expect that an increase of the transition dipole moment leads to a remarkable stabilization of the excited state. As a matter of fact we have seen (both for C153 and formaldehyde) that in the LR framework bright transitions are much stronger with fully equilibrated solvent. On the contrary solvent equilibration does not affect the transition intensity in the SS approach. In this latter case ΔG^{eq} is not influenced by the transition dipole moment.

The above relationships can explain also why in the LR approach λ is much larger for bright transitions, being instead vanishingly small for dark transitions. This effect accounts for the “unphysical” $\lambda=0$ value predicted by LR PCM calculations for the $S_0 \rightarrow T_1$ transitions in formaldehyde, that is spin forbidden and thus is characterized by a vanishing oscillator strength.

V. CONCLUDING REMARKS

In this paper we have presented the first state specific version of PCM/TD-DFT calculations, and its comparison with the “traditional” one, based on a linear response formalism. Both approaches have been applied to the study of low energy transitions of C153 and formaldehyde in different solvents and their results have been interpreted and generalized by employing a simple dipolar solvation model.

On the balance, our results indicate that SS version of PCM/TD-DFT provides more reliable results than its LR counterpart. In fact, the solvent shifts computed for C153 by SS computations are closer to the experimental ones than those obtained at the LR level. Furthermore, when applied to formaldehyde, SS computations provide estimates in qualitative agreement with PCM/CAS calculations and do not exhibit some counterintuitive features shown by LR calculations in the treatment of the dipole forbidden transitions.

SS approach is expected to be more accurate especially in polar solvents, where the effect of the variation of the dipole moment associated with electronic transition should be significant. This term is explicitly taken into account by SS calculations, whereas it is absent in LR calculations. As a consequence there are some processes in which LR results should be considered with a lot of caution and the SS approach is strongly recommended. A typical example is the calculation of the equilibrium solvation energy (and, thus, of λ) in long range electron transfer processes. These transitions are indeed usually characterized by small oscillator strengths and large variations of the dipole moment. The SS implementation we present could thus provide an useful method for the study of several static and dynamic aspects of solvation. It shares the same remarkable features of accuracy and low computational cost of the LR model, so that it can be applied to the study of excited states for systems of biochemical or technological interest. Furthermore, these features are coupled with the reliability of state specific methods for the treatment of critical properties like, e.g., the solvent reorganization energy.

On the other hand, our results confirm that the LR version of PCM/TD-DFT is able to provide qualitatively correct estimates of vertical excitation energies, as indicated, after all, by the good agreement usually found between its results and experimental absorption spectra. Actually, LR and SS approaches have been shown to be identical at the zeroth order, related to the interaction with the slow solvation degrees of freedom.²³ This contribution usually provides the main part of solvatochromic shifts. Furthermore the first order correction is proportional in LR to the transition dipole moment, a term that should be considered dependent on the dispersion energy in a semiclassical framework. There are several processes, namely, those involving a “not very polar” solute in an apolar solvent, in which this contribution is expected to be the most relevant one. It cannot be excluded that in such cases the LR approach could provide more accurate results than SS calculations.

Let us finally point out that solvation dynamics is a complex phenomenon, and many aspects cannot be treated in the framework of pure continuum models, but require the inclusion of some explicit solvent molecules. While a detailed treatment of nonequilibrium solvent effects in this framework is outside the scope of the present paper, previous experience shows that very effective discrete-continuum models can be employed since, thanks to the reliable description of bulk effects afforded by the PCM, the number of needed explicit water molecules is very small.

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