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A comparison between state-specific and linear-response formalisms for the calculation of vertical electronic transition energy in solution with the CCSD-PCM method

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The calculation of vertical electronic transition energies of molecular systems in solution with accurate quantum mechanical methods requires the use of approximate and yet reliable models to describe the effect of the solvent on the electronic structure of the solute. The polarizable continuum model (PCM) of solvation represents a computationally efficient way to describe this effect, especially when combined with coupled cluster (CC) methods. Two formalisms are available to compute transition energies within the PCM framework: State-Specific (SS) and Linear-Response (LR). The former provides a more complete account of the solute-solvent polarization in the excited states, while the latter is computationally very efficient (i.e., comparable to gas phase) and transition properties are well defined. In this work, I review the theory for the two formalisms within CC theory with a focus on their computational requirements, and present the first implementation of the LR-PCM formalism with the coupled cluster singles and doubles method (CCSD). Transition energies computed with LR- and SS-CCSD-PCM are presented, as well as a comparison between solvation models in the LR approach. The numerical results show that the two formalisms provide different absolute values of transition energy, but similar relative solvatochromic shifts (from nonpolar to polar solvents). The LR formalism may then be used to explore the solvent effect on multiple states and evaluate transition probabilities, while the SS formalism may be used to refine the description of specific states and for the exploration of excited state potential energy surfaces of solvated systems. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4816482>]

I. INTRODUCTION

The importance of the effect of the environment on molecular electronic excitations cannot be overstated. When quantum mechanical (QM) methods are used to describe the chromophore, however, the inclusion of such effects requires the introduction of some approximations due to the unmanageable computational cost associated with a full QM treatment of the entire system. The typical example of “environment” surrounding a molecule (or supramolecular aggregate) is a solvent, which requires the consideration of a large number of explicit molecules in order to reproduce bulk effects. Additionally, even when a relatively small number of explicit solvent molecules is introduced to describe microsolvation interactions, the computational cost quickly becomes unbearable if highly accurate QM methods are used, as those offered by coupled cluster theory (CC).¹

The models that introduce an approximate description of the solvent can be divided in two large families: explicit and implicit models. The former maintain an atomistic representation of the solvent molecules, often described as classical polarizable forces fields where the parameterization may be based on experimental or theoretical data. These models have the ability of describing direct solute-solvent interactions such as hydrogen bonds, but require a large number of solvent configurations (and corresponding QM calculations) to achieve

statistical averaging. Implicit models, on the other hand, describe the solvent as a continuum, polarizable medium that implicitly provides the solvent configuration averaging. Conversely, the drawback is the inability to account for specific solute-solvent interactions. A vast amount of work has been devoted to the development of these models, and a complete account is beyond the scope of this paper.^{2,3} Possibly, the best balance between a realistic solvent description and low computational cost is in the combination of these two approaches, and several examples are already available in the literature.⁴

One of the most popular continuum solvation models is the polarizable continuum model (PCM) originally developed by Tomasi and co-workers.^{2,5,6} PCM describes the solvent as a polarizable dielectric characterized by the macroscopic dielectric constant, ϵ . A cavity of molecular shape hosts the solute, and is usually built as a series of interlocking spheres centered on the solute nuclei. The solvent polarization is represented by an apparent surface charge spread on the cavity surface. In the computational practice, the surface charge is discretized in finite elements and the PCM integral operators are replaced by their matrix representation. Modern implementations of the various flavors of PCM are very efficient,⁶⁻¹³ and typically only increase the computational cost of self-consistent field methods (SCF), like those developed in Kohn-Sham density functional theory (DFT), by less than 20%. More recently, the coupling of PCM with CC wave functions has been proposed by Cammi,¹⁴ although, a similar development was presented by Christiansen and

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co-workers^{15–17} on a related solvation model named dielectric continuum (DC). Despite the difference in solvation models, the ensuing “solvated” CC equations are the same. Contrary to SCF methods, CC-PCM is considerably more expensive than gas phase CC since the correlation solvent term couples the T and Λ amplitudes, which are the CC excitation and deexcitation operators (the latter is derived in CC gradient theory),^{1,18–20} respectively.

The study of vertical electronic transitions introduces two further complications for continuum models. The first is the description of the “nonequilibrium” solvation regime.² This is related to the different response time of the electron and nuclear/orientational motions in the solvent molecules (of the order of 10^{-15} s and 10^{-12} s, respectively) to changes in the solute charge distribution. When a fast change in the solute electronic density occurs, such as in a vertical transition, a nonequilibrium state is created where only the solvent electrons are considered fast enough to respond to this change while the solvent molecules can be considered frozen in the configuration in equilibrium with the initial solute charge density. In PCM, a nonequilibrium regime is modeled by separating the solvent response in two contributions: a *dynamic* part, which is equilibrated with the new solute density and that depends on the square of the refractive index of the medium (i.e., the optical dielectric constant, ϵ_∞), and an *inertial* part, which is frozen in the initial equilibrium condition and depends on the both dielectric constants (ϵ and ϵ_∞).^{2,21–23}

The second issue is the difference between state-specific (SS) and linear-response (LR) formalisms, which is the topic of this work in the framework of coupled cluster theory. In the SS formalism,^{21,24} the ground and excited state energy and wave function are computed, and the transition energy is calculated as the difference between the energy of the two states. In the LR formalism,^{25,26} transition energies are obtained directly as the poles of the linear response function. Both approaches provide the same final expressions for transition energies when applied to isolated molecules, also in the context of CC theory.^{27,28} They differ, however, when a continuum model is added to the picture even for exact states. The origin of this discrepancy was formally analyzed in details in two papers by Cammi *et al.*²² and Corni *et al.*²³ for a generic wave function. References 22 and 23 show that the difference is due to the basic assumption of continuum models, i.e., the Hartree partition of the solute-solvent state,²⁹ which leads to different expressions for the transition energy when the SS and LR formalisms are applied. They also show that, in the nonequilibrium regime, the SS formalism accounts for the mutual relaxation between the solute electronic density and the dynamic part of the solvent response, which is neglected in the LR expressions. The latter contains, on the other hand, a term that has been classified as a solute-solvent dispersion interaction.³⁰ Such term is neglected in the SS formalism consistently with the electrostatic approximation, and can be recovered when dispersion models are included in PCM. Conversely, care must be applied when using the LR formalism with models than include dispersion effects to avoid double counting. Finally, Refs. 22 and 23 show that both SS and LR formalisms include the same inertial solvent response. The SS formalism thus contains a more complete description

of the electrostatic solute-solvent interaction in the excited state. However, it is also more computationally demanding. To reduce the gap between the two formalisms, a corrected LR (cLR)³¹ approach was proposed in the context of time-dependent DFT (TDDFT).

In this work, I revisit the SS and LR solvation formalisms explicitly in the context of the CC-PCM approach. Both formalisms were already derived in detail elsewhere.^{15,32–35} Here I review the main expressions and focus on the comparison of the correlation and excited state PCM terms between the two approaches, and discuss the computational implications in detail. Numerical tests are then presented that compare their relative performance with the coupled cluster singles and doubles (CCSD) method.¹ This work examines the large difference in computational cost between the two formalisms in the framework of CC theory, and the numerical tests aim to answer the critical question of whether the LR formalism can be effectively used to compute transition energies. To the best of my knowledge, this is the first implementation of the LR-PCM approach within CC theory.

The paper is organized as follows. The theoretical and computational analysis of the SS- and LR-CCSD-PCM formalisms is carried out in Sec. II. Numerical results are presented in Sec. III for the two approaches. A direct comparison between LR- and SS-CCSD-PCM is presented in Sec. III A, where solvatochromic shifts are computed and compared to experimental data. Transition properties are also computed with the LR-CCSD-PCM method, and results are compared in Sec. III B with an approximate definition of the linear response residues that does not include the response of the T amplitudes. A discussion of the results and concluding remarks is presented in Sec. IV.

II. THEORY

In this section, I review the theory for the SS and LR formalisms for the calculation of vertical transition energies and properties within the framework of coupled cluster theory combined with PCM. A detail account of both formalisms can be found elsewhere, and only the final expressions are considered here.^{15,32–35} No detail about the various flavors of PCM^{2,5–13,36} and the solution of the corresponding equations is discussed here since the PCM terms that enter the CC equations take the same form for all of the versions. Although nonequilibrium solvation^{2,15,21–23,34} is essential to reproduce experimental transition energies and is used in the calculations reported in Sec. III, it also makes the formalism more cumbersome. Therefore, the expressions in the following are those for the equilibrium solvation regime where ϵ is used everywhere.

Both formalisms share the same expression for the ground state free energy, which can be written as a functional of the CC amplitudes:^{14,37}

$$G_0^{PTED} = G_{ref} + \langle \Phi_0 | (1 + \Lambda) e^{-T} H_N^{PCM} e^T | \Phi_0 \rangle + \frac{1}{2} \bar{\mathbf{V}}_N \cdot \bar{\mathbf{Q}}_N, \quad (1)$$

where \mathbf{V} is the electrostatic potential generated by the solute on the cavity surface and \mathbf{Q} is the dielectric response (i.e., the PCM charges), and the bold font indicates a vector containing the finite-element discretization of both quantities. PTED stands for “perturbation theory energy and density,” and refers to the original derivation of the solvent effect in correlated wave functions through perturbation theory.^{38,39} This scheme will be assumed through the rest of the work and the label omitted. Φ_0 is the reference wave function, usually Hartree-Fock (HF), G_{ref} is the corresponding free energy, and the subscript N refers to the normal-product form of the operator. The Hamiltonian in Eq. (1) includes the PCM term with the reference charges \mathbf{Q}_0 :

$$H_N^{PCM} = H_N + \mathbf{V}_N \cdot \overline{\mathbf{Q}}_0. \quad (2)$$

The overbar indicates the expectation value of the charge operator \mathbf{Q} , i.e., the trace of the operator with a suitable one-particle density matrix (1PDM). In Eq. (2), \mathbf{Q}_0 is obtained as the trace of the charge operator with the reference density matrix. The correlation charges $\overline{\mathbf{Q}}_N$ are computed as the trace of the same charge operator with the correlation 1PDM:

$$\gamma_{pq}^0 = \langle \Phi_0 | (1 + \Lambda) e^{-T} \{p^\dagger q\} e^T | \Phi_0 \rangle \quad (3)$$

where p, q are generic molecular orbitals (MOs). The ground state free energy in Eq. (1) is computed by minimizing the functional with respect to the T and Λ amplitudes. In fact, since the PCM term in Eq. (1) is quadratic in T and Λ , both sets of amplitudes are necessary, contrary to the gas phase where only the T amplitudes are required to evaluate the energy.

The reference PCM term in Eq. (2) is implicitly contained in the (diagonal) Fock operator, i.e., the orbital energies, and does not give rise to explicit terms in the CC equations. One could make a different choice and evaluate the reference wave function in gas phase and include the entire PCM contribution in the CC part, as done by Christiansen and Mikkelsen.^{15,16} However, a “solvated” reference wave function is preferable because the largest solvent contribution to the polarization of the solute wave function comes from the polarization of the orbitals, which are variationally optimized through a SCF scheme. Additionally, this allows the definition of approximations in the correlation solvation that greatly reduce the computational cost of the calculation.^{14,32–34,37,40} The SCF is decoupled from the CC part of the calculation as for gas phase CC (unless Brueckner orbitals are employed,⁴¹ but this is not considered here) both for ground and excited states.

In gas phase, the SS approach is known as equation of motion CC (EOM-CC).^{1,19,20,28} For isolated molecules, EOM- and LR-CCSD^{27,42,43} provide the same values of transition energies, obtained as eigenvalues of the similarity transformed Hamiltonian operator (called Jacobian matrix in the LR literature), $e^{-T} H_N e^T$.^{1,19,20,27,28,42,43} The similarity transformation makes the dressed Hamiltonian non-Hermitian, thus left- and right-hand eigenvectors are different and both are required for the evaluation of transition properties. These eigenvectors are obtained with separate (partial⁴⁴) diagonalizations of the matrix form of the operator and its transpose, and excitation energies for multiple electronic states can be computed in a single calculation. Transition properties in the

EOM formalism as suggested by Stanton and Bartlett²⁸ are computed without the inclusion of the T amplitude response (frozen- T approximation). This response is included in the LR formalism^{20,27,43} and requires the solution of another linear system of equations to evaluate perturbation-free amplitudes (similar to the ground state Λ amplitudes from gradient theory). These two approaches are only equivalent when the complete set of excitations is included in the T operator, for instance, EOM-CCSD and LR-CCSD provide the same value of transition properties for a two-electron system. For larger systems, only the LR approach provides size-intensive transition properties, but the numerical difference between the two is negligible unless a large number of electrons (hundreds) is correlated.⁴⁵

When the solvent effect is introduced through a continuum model like PCM, the SS and LR formalisms diverge also for transition energies. Furthermore, the LR function for CC wave functions as derived by Christiansen and Mikkelsen for the DC model,¹⁵ and rederived more recently by Cammi for PCM,³⁵ neglects a solvent contribution that is quadratic in the perturbed Λ amplitudes and would couple the left and right eigenvectors of the similarity transformed Hamiltonian. As shown below, this quadratic dependence is maintained in the SS approach where both left and right eigenvectors are necessary for the evaluation of the energy.

The starting point for the formulation of the SS-CCSD-PCM solvation approach is the free energy functional for the K th excited state:

$$G_K = G_{ref} + \langle \Phi_0 | L_K [e^{-T_K} H_N^{PCM} e^{T_K}, R_K] | \Phi_0 \rangle + \langle \Phi_0 | (1 + \Lambda_K) e^{-T_K} H_N^{PCM} e^{T_K} | \Phi_0 \rangle + \omega_K (1 - \langle \Phi_0 | L_K R_K | \Phi_0 \rangle) + \frac{1}{2} \overline{\mathbf{V}}_N^K \cdot \overline{\mathbf{Q}}_N^K, \quad (4)$$

where $\omega_K, L_K,$ and R_K are the similarity transformed Hamiltonian K th eigenvalue, left and right eigenvectors, respectively. The charges $\overline{\mathbf{Q}}_N^K$ are computed as the trace of the charge operator with the K th state 1PDM:

$$\gamma_{pq}^K = \langle \Phi_0 | L_K [e^{-T} \{p^\dagger q\} e^T, R_K] | \Phi_0 \rangle + \langle \Phi_0 | (1 + \Lambda_K) e^{-T} \{p^\dagger q\} e^T | \Phi_0 \rangle. \quad (5)$$

G_K is obtained by minimizing the functional in Eq. (4) with respect to the $T_K, R_K, L_K,$ and Λ_K amplitudes. The subscript K for the T operator indicates that also the T amplitudes are state specific, since the correlation PCM term in Eq. (4) depends quadratically on the density γ^K in Eq. (5).^{33,34} In other words, the equations for $T_K, R_K, L_K,$ and Λ_K are coupled by the solvent term.

In the SS scheme, excitation energies are not simply given by the eigenvalues ω_K as in gas phase, and must be computed as the difference between the free energy of the excited and the ground states, in Eqs. (1) and (4), respectively.^{33,34} The evaluation of transition energies with this approach is rather computationally expensive compared to gas phase. Therefore, a number of approximate schemes have been proposed that decouple the ground state part of the calculation from the excited state part and do not require the solution of the Λ_K equations similar to gas phase (although, all of the

approximate schemes are still state-specific, thus only one excited state at a time can be considered).^{33,34} A limitation of the SS approach is that transition properties are not well defined because the ground and excited states are no longer orthogonal.

In the nonequilibrium regime, the $\overline{\mathbf{Q}}_N^K$ are replaced by

$$\overline{\mathbf{Q}}_N^K \rightarrow \overline{\mathbf{Q}}_{N,in}^0 + \overline{\mathbf{Q}}_{N,dyn}^K, \quad (6)$$

where $\overline{\mathbf{Q}}_{N,in}^0$ are the inertial part of the ground state correlation charges in Eq. (1) and remain fixed during the excited state calculation. The dynamic charges $\overline{\mathbf{Q}}_{N,dyn}^K$ are computed with the excited state density in Eq. (5) and ε_∞ . For polar solvents, the inertial charges represent that largest part of the solvent response since $\varepsilon \gg \varepsilon_\infty$.

The explicit PCM terms in Eq. (4), however, only add a negligible overhead over the “gas phase” terms since they can be rolled into other already necessary intermediates.³³ The evaluation of the excited state charges $\overline{\mathbf{Q}}_N^K$ scales as $O(N^5)$ for CCSD (where N is the size of the basis set) since this is the work necessary to evaluate to density γ^K in Eq. (5). Thus, the computational cost for the evaluation of transition energies in the SS approach is due to two factors: (i) both ground and excited states calculations need to be performed separately as the transition energy is computed as the difference between the state energies; (ii) the SS approach couples all the amplitudes equations.^{33,34}

In the LR formalism, transition energies are obtained as poles of the linear response function (i.e., through the diagonalization of the non-Hermitian CC-PCM Jacobian).^{15,35} When the PCM term quadratic in the perturbed Λ amplitudes is neglected,^{15,35} transition energies can be obtained by diagonalization from either side, although, both eigenvectors are still needed to evaluate transition properties. Therefore, transition energies towards multiple states can be computed at once as in gas phase.

The explicit PCM terms in the right-hand and left-hand diagonalization are, respectively,

$$\begin{aligned} & \langle \Phi_n | [e^{-T} \mathbf{V}_N e^T, R_K] | \Phi_0 \rangle \cdot \overline{\mathbf{Q}}_N \\ & + \langle \Phi_n | e^{-T} \mathbf{V}_N e^T | \Phi_0 \rangle \cdot \overline{\mathbf{Q}}_N^R, \end{aligned} \quad (7)$$

$$\begin{aligned} & \langle \Phi_0 | L_K [e^{-T} \mathbf{V}_N e^T, \tau_m] | \Phi_0 \rangle \cdot \overline{\mathbf{Q}}_N \\ & + \langle \Phi_0 | (1 + \Lambda) [e^{-T} \mathbf{V}_N e^T, \tau_m] | \Phi_0 \rangle \cdot \overline{\mathbf{Q}}_N^L. \end{aligned} \quad (8)$$

The charges $\overline{\mathbf{Q}}_N^R$ are computed as the trace of the charge operator with the (frozen- T) left transition density γ_{pq}^{0K} , while the charges $\overline{\mathbf{Q}}_N^L$ are computed as the trace of the charge operator with the right transition density γ_{pq}^{K0} :

$$\begin{aligned} \gamma_{pq}^{0K} &= \langle \Phi_0 | (1 + \Lambda) [e^{-T} \{p, q\} e^T, R_K] | \Phi_0 \rangle, \\ \gamma_{pq}^{K0} &= \langle \Phi_0 | L_K e^{-T} \{p, q\} e^T | \Phi_0 \rangle. \end{aligned} \quad (9)$$

The explicit PCM contribution to the eigenvalue equations in the LR formalism is at the heart of the difference with the SS formalism. In the latter, the PCM charges $\overline{\mathbf{Q}}_N^K$ are

computed with the excited state 1PDM, while in LR the PCM contribution is given as a sum of the ground state and transition charges: $\overline{\mathbf{Q}}_N + \overline{\mathbf{Q}}_N^R$ in Eq. (7) and $\overline{\mathbf{Q}}_N + \overline{\mathbf{Q}}_N^L$ in Eq. (8), respectively. In a nonequilibrium calculation, the transition charges $\overline{\mathbf{Q}}_N^R$ and $\overline{\mathbf{Q}}_N^L$ are computed by using ε_∞ instead of ε .^{15,35} Comparing the SS nonequilibrium eigenvalue equations (with the nonequilibrium solvation charges in Eq. (6)) and the LR nonequilibrium eigenvalue equations, (7) and (8), it is evident that the inertial part of the solvent response is the same in the two formalisms, as shown for a general wave function in Refs. 22 and 23.

Ground to excited state transition properties (e.g., oscillator or rotatory strengths) can be computed in the LR approach by evaluating the residues of the response function. This requires the solution of another linear system of equations to obtain the amplitudes for the deexcitation operator M_K . The explicit PCM terms in these equations are

$$\begin{aligned} & \langle \Phi_0 | (1 + \Lambda) [e^{-T} \mathbf{V}_N e^T, R_K], \tau_n | \Phi_0 \rangle \cdot \overline{\mathbf{Q}}_N \\ & + \langle \Phi_0 | M_K [e^{-T} \mathbf{V}_N^{PCM} e^T, \tau_n] | \Phi_0 \rangle \cdot \overline{\mathbf{Q}}_N \\ & + \langle \Phi_0 | (1 + \Lambda) [e^{-T} \mathbf{V}_N e^T, \tau_n] | \Phi_0 \rangle \cdot (\overline{\mathbf{Q}}_N^R + \overline{\mathbf{Q}}_N^M), \end{aligned} \quad (10)$$

where the charges $\overline{\mathbf{Q}}_N^M$ are computed as the trace of the charge operator and the γ^{K0} 1PDM in Eq. (9) with M_K instead of L_K .

The additional computational cost of the explicit PCM terms in Eqs. (7) and (8) is larger than the corresponding SS equations. The terms that contain $\overline{\mathbf{Q}}_N$ are formally the same as the $\overline{\mathbf{Q}}_N^K$ terms for SS, except that the ground state correlation charges are now used. Hence, they can use the same code. As discussed above, the work introduced by these terms is negligible, especially considering that the $\overline{\mathbf{Q}}_N$ charges do not vary during the diagonalization iterations. On the other hand, the terms that depend on $\overline{\mathbf{Q}}_N^R$ and $\overline{\mathbf{Q}}_N^L$ in Eqs. (7) and (8) are new. The evaluation of $\overline{\mathbf{Q}}_N^R$ and $\overline{\mathbf{Q}}_N^L$ also scales as $O(N^5)$ since this is the scaling for the evaluation of the transition density matrices in Eq. (9). If an iterative diagonalization procedure⁴⁴ is used to obtain few eigenvalues of the Jacobian matrix, as it is usually the case for CCSD, a set of charges needs to be computed for each new trial vector used in the subspace expansion. This is opposite to the SS case, where only one set of $\overline{\mathbf{Q}}_N^K$ charges is computed every few iterations. The explicit $\overline{\mathbf{Q}}_N^R$ and $\overline{\mathbf{Q}}_N^L$ terms in Eq. (9) are available in the supplementary material.⁴⁶ These terms add more $O(N^5)$ work.

In summary, the SS approach requires little work in terms of explicit PCM contributions and negligible extra contractions with CC amplitudes are required. However, the amplitudes equations are all coupled, one excited state at a time can be considered, and the ground and excited states calculations need to be carried out separately. On the other hand, in the LR approach, the T - Λ , R_K , and L_K equations are clearly decoupled, multiple excited states can be computed simultaneously, and transition properties are well defined. The downside is that extra $O(N^5)$ work is added for each state at each diagonalization iteration, although, the scaling of a CCSD gas phase calculation is already $O(N^6)$. Therefore, in general, the

LR approach is computationally significantly less demanding than SS.

Both formalisms were implemented in a development version of the GAUSSIAN suite of programs for restricted and unrestricted wave functions, and making use of Abelian point group symmetry.⁴⁷

III. RESULTS

This section reports numerical examples that compare the performance of the CCSD-PCM method with the SS and LR formalisms on a series of small molecules against experimental data of vertical excitation energies in gas phase and in solution. Also, oscillator strengths are presented to compare the calculation of transition properties with full LR formula and the frozen- T approximation,²⁸ which provides considerable savings in computational time if many electronic states are investigated. A comparison of PCM and the DC model is reported in the supplementary material.⁴⁶ These results show that the LR-CCSD-PCM method performs better than the DC model as the latter seems to suffer from escaped charge issues and provide unphysical values of solvatochromic shifts. IEF-PCM, on the other hand, handles the same issue robustly.⁴⁸ The water example also shows the importance of the cavity shape, as the value of the transition energy varies considerably passing from a spherical cavity to one that follows the molecular shape.

The symmetric version of the integral equation formalism flavor of PCM (IEFPCM)^{6,12} is used throughout. The cavity is built as a series of interlocking spheres located on the atomic nuclei with the solvation model D (SMD).⁴⁹ These radii were parameterized to reproduce values of solvation free energy computed with the B3LYP⁵⁰ hybrid functional and, in my experience, work well also for CC methods.^{33,34,37,40,41,51} The nonequilibrium regime is used for all calculations. The aug-cc-pVDZ basis set⁵² is used throughout, and all geometries are optimized in the corresponding medium at CCSD level. The optimized geometries can be found in the supplementary material.⁴⁶

The comparison with experiment will mostly focus on trends since a bare PCM solvation may not be sufficient to describe specific solute-solvent interactions (such as strong hydrogen bonds in protic solvents) or non-electrostatic interactions in low polar solvents. Additionally, the assignment of vertical excitation energies in solution is accompanied with a larger uncertainty compared to gas phase data due to broadening of the absorption bands. In general, the calculations in solution are expected to provide less accurate results than those in gas phase since the approximation in the description of the environment is larger.

A. Excitation energy

In this section, the SS and LR approaches are compared between each other and against experiment for four small molecules (water, acrolein, methylenecyclopropene (MCP), and acetone) in various solvents.

TABLE I. H₂O excitation energy and solvatochromic shift (eV) in gas and in water.

	Gas		Water		Shift	
	1B ₁	2A ₁	1B ₁	2A ₁	1B ₁	2A ₁
Expt. ⁵³	7.4	9.7	8.2	9.9	0.8	0.2
LR	7.41	9.84	7.95	10.23	0.54	0.39
SS	7.41	9.84	7.77	10.10	0.36	0.26

For the first system, water, two transitions in gas and in water solution ($\epsilon = 78.36$ and $\epsilon_\infty = 1.778$) are considered since experimental values are available.⁵³ The data are reported in Table I. The transition energies in gas phase are rather well reproduced. The solvatochromic shifts, on the other hand, are less accurate: too small for the first transition, and too large for the second. However, considering that liquid water is one of the most challenging scenarios for an electrostatic continuum model, the experimental trends are quite well reproduced. For the first transition, which has a large shift of 0.8 eV, LR seems to provide a better agreement with experiment. However, large blue shifts indicate a much larger stabilization of the ground state than the excited state upon interaction with the solvent. Such stabilization is not completely recovered by a bare PCM approach due to the missing effect of the hydrogen bond network, and may change the transition energy considerably. The shift in the second transition is significantly smaller, indicating a more similar solvation arrangement in the ground and excited states. This may correspond to a better error cancellation in the theoretical description of ground and excited state solvation. For this transition, the SS approach provides a better agreement with the experimental results. Note that the DC model provides the wrong sign for the solvatochromic shift for these transitions:²⁶ -0.49 eV and -3.30 eV, respectively, as shown in Table IV in the supplementary material.⁴⁶ PCM with the same one-sphere cavity used in Ref. 26 provides shifts of 0.28 eV and -0.04 eV, which indicate that basis set, geometry, and cavity have a large influence on this property.

The second molecule is acrolein, for which experimental excitation energies are available in gas, cyclohexane ($\epsilon = 2.02$ and $\epsilon_\infty = 2.035$) and water. The data are collected in Table II. This molecule is interesting because the solvent effect is opposite for the first two transitions, leading to a positive relative solvatochromic shift (from nonpolar to polar solvent) for the first transition and a negative one for the second transition, and similar in magnitude. The geometries for the calculations are taken from Refs. 33 and 34 and were optimized at CCSD(-PCM) level in the corresponding medium. The SS data are also taken from Ref. 34. The gas phase calculations reproduce rather well the experimental transition energy for the first state, which is overestimated by 0.17 eV. On the other hand, the second excitation energy is overestimated by almost 0.4 eV. This is probably due to vibronic effects, neglected in the calculations, since this $\pi \rightarrow \pi^*$ transition leads to a torsion around the central C-C bond. Table II also reports cyclohexane-gas (C-G), water-gas (W-G), and water-cyclohexane (W-C) shifts. Both LR and SS approaches

TABLE II. Vertical absorption energy and solvatochromic shift (eV) of acrolein in gas (G), water (W), and cyclohexane (C).

	Gas	CycloH	Water	Shift (C-G)	Shift (W-G)	Shift (W-C)
$n \rightarrow \pi^*, A''$						
Expt.	3.71 ^a	3.71 ^b	3.94 ^c	0.00	+0.23	+0.23
LR	3.88	3.91	4.10	+0.03	+0.22	+0.19
SS	3.88	3.87	4.05	-0.01	+0.17	+0.18
$\pi \rightarrow \pi^*, A'$						
Expt.	6.41 ^a	6.11 ^b	5.90 ^d	-0.30	-0.51	-0.21
LR	6.80	6.55	6.39	-0.25	-0.41	-0.16
SS	6.80	6.71	6.54	-0.09	-0.26	-0.17

^aReference 54.^bReference 55.^cReference 56.^dReference 57.

reproduce the W-C shifts rather satisfactorily. The W-G and C-G shifts seem to be better reproduced with the LR formalism, especially the large ones for the second transition. However, the W-C shift is better suited for a comparison between calculations and experiment because of better error cancellation in the calculations. For instance, nonelectrostatic solute-solvent interactions are neglected for both solvents and the error may partially cancel out, while no such effects exist in the gas phase and solvent-gas shifts may be more unbalanced. The importance of nonelectrostatic interactions is evident when comparing experimental absolute values of transition energy in gas and cyclohexane for the second transition, which differ by 0.3 eV, contrary to the general wisdom that low-polar solvents are basically equivalent to gas phase. Note that the SS transition energies are smaller than those computed with the LR formalism for the first transition, but the trend is opposite for the second transition. This is consistent with previous results and is due to relative differences between transition and state electric dipole moments.^{22,23}

Experimental data for MCP in n-pentane and methanol are available.⁵⁸ MCP also has solvatochromic shifts between polar and nonpolar solvents that are opposite in sign between the two lowest transitions: the shift for the first transition is large and positive, 0.48 eV, while the shift for the second transition is small and negative, -0.12 eV. The experimental and calculated data for this molecule are reported in Table III ($\epsilon = 32.61$ and $\epsilon_\infty = 1.766$ for methanol, and $\epsilon = 1.84$ and $\epsilon_\infty = 1.843$ for n-pentane). The table also reports n-pentane-gas (P-G), methanol-gas (M-G), and methanol-n-pentane (M-P) shifts. The geometry and the SS values are taken from Refs. 33 and 34. The calculations with both SS and LR formalisms give quite similar M-P shifts for both transitions. The first one is about half of the experimental value, which is reasonable considering the simplicity of the solvation model used. As for the second transition both theoretical approaches basically show a very small solvent effect. As for acrolein, the SS transition energies are smaller than those with the LR formalism for the first transition, and the opposite occurs for the second one. Also, the change in sign for the P-G shift in the first transition is consistent with previous results.^{22,23}

TABLE III. Vertical absorption energy and solvatochromic shift (eV) for MCP in gas (G), methanol (M), and n-pentane (P).

	Gas	n-Pentane	Methanol	Shift (P-G)	Shift (M-G)	Shift (M-P)
$\pi \rightarrow \pi^*, B_2$						
Expt. ⁵⁸		4.01	4.49			+0.48
LR	4.48	4.55	4.75	+0.07	+0.27	+0.20
SS	4.48	4.43	4.64	-0.05	+0.16	+0.21
$\pi \rightarrow \pi^*, A_1$						
Expt. ⁵⁸		6.02	5.90			-0.12
LR	6.15	6.02	6.01	-0.13	-0.14	-0.01
SS	6.15	6.10	6.10	-0.05	-0.05	0.00

The last system is acetone, for which the $n \rightarrow \pi^*$ transition is considered and its solvatochromic shifts in cyclohexane and water. There is a variety of experimental data available for this molecule that differ considerably. For instance, the value of the transition energy in gas phase varies from 4.37 eV²¹ to 4.48 eV.⁵⁹ For consistency, here I report the data from Reichardt's book.⁵⁹ The experimental and theoretical results are collected in Table IV. The gas phase value computed at this level of theory agrees rather well with experiment. The cyclohexane to gas shift (C-G) has the opposite sign for both LR and SS, an indication that nonelectrostatic interactions (neglected in the calculation) play an important role. The water to gas (W-G) shift is well reproduced by both approaches. The water to cyclohexane shift (W-C) is also in reasonable agreement with experiment with both approaches, and LR is closer to experiment. However, consider that the calculated W-C shift is probably underestimated since explicit hydrogen-bond interactions should significantly increase the blueshift in water.

B. Transition properties

In this section, results for oscillator strengths computed with the complete LR formalism and with the frozen- T approach suggested by Stanton and Bartlett²⁸ are presented. The goal is to assess whether the latter approximation provides good estimates of the LR transition properties as in gas phase.⁴⁵ Only oscillator strengths are considered because the molecules in this work do not show an electronic circular dichroism spectrum due to their symmetry. Nonetheless, rotatory strengths can be computed with the current implementation of the LR-CCSD-PCM method in GAUSSIAN.

TABLE IV. Vertical absorption energy and solvatochromic shift (eV) for acetone in gas (G), cyclohexane (C), and water (W) for the lowest $n \rightarrow \pi^*$ transition (A_2).

	Gas	Shift (C-G)	Shift (W-G)	Shift (W-C)
Expt. ⁵⁹	4.48	-0.05	+0.21	+0.26
LR	4.46	+0.03	+0.19	+0.22
SS	4.46	+0.01	+0.17	+0.18

TABLE V. Transition energy (eV) and oscillator strengths for the molecules treated in Sec. III A. All calculations are performed with the LR-PCM formalism. Oscillator strengths are computed with the full LR formula (f) and the frozen- T approximation (f_T).

	ΔE	f_T	f		ΔE	f_T	f
Water in water							
B_1	7.95	0.077	0.078				
A_2	9.73	0.000	0.000				
A_1	10.23	0.122	0.124				
B_1	11.06	0.000	0.000				
A_1	11.63	0.000	0.000				
B_2	12.05	0.011	0.011				
A_2	12.64	0.000	0.000				
B_2	14.00	0.174	0.177				
Acrolein							
Water				Cyclohexane			
A''	4.10	0.000	0.000	A''	3.91	0.000	0.000
A'	6.39	0.549	0.554	A'	6.55	0.510	0.515
A'	7.23	0.016	0.016	A'	7.00	0.061	0.061
A''	7.48	0.000	0.000	A''	7.20	0.000	0.000
MCP							
Methanol				n-Pentane			
B_2	4.75	0.017	0.017	B_2	4.55	0.017	0.017
B_1	5.44	0.022	0.022	B_1	5.38	0.011	0.011
A_1	6.01	0.387	0.393	A_2	5.97	0.000	0.000
A_2	6.15	0.000	0.000	B_1	5.99	0.036	0.036
B_1	6.21	0.033	0.033	A_1	6.02	0.370	0.377
A_2	6.82	0.000	0.000	A_2	6.62	0.000	0.000
A_1	7.57	0.149	0.151	A_1	7.51	0.156	0.159
B_2	8.20	0.013	0.013	B_2	8.18	0.022	0.022
Acetone							
Water				Cyclohexane			
A_2	4.65	0.000	0.000	A_2	4.49	0.000	0.000
B_2	6.81	0.047	0.047	B_2	6.43	0.040	0.040
A_1	7.85	0.011	0.011	A_1	7.47	0.001	0.001
B_2	7.88	0.001	0.001	A_2	7.48	0.000	0.000
A_2	7.95	0.000	0.000	B_2	7.55	0.005	0.005
A_1	8.60	0.188	0.190	A_1	8.21	0.099	0.100
B_1	9.01	0.019	0.019	B_1	8.54	0.019	0.019
B_1	9.22	0.002	0.002	B_1	9.22	0.005	0.005

Table V collects the excitation energy and oscillator strength for the lowest two states of each irrep for the same test molecules studied in Sec. III A. The results in the table indicate that the frozen- T (f_T values) is a reasonable approximation for the computation of transition properties, similar to gas phase. The approximate values are within 2% of the full values when bright states are considered as, for instance, the highest B_2 state of water, the lowest A' state of acrolein, the lowest A_1 state of MCP, and the second A_1 state of acetone. This is true independently of large changes in magnitude of the oscillator strength when changing solvent, as for the second A_1 state of acetone, which passes from 0.1899 in water to 0.1001 in cyclohexane. The quality of the results with the approximate scheme is bound to decrease by increasing the size of the system due to the lack of size intensity. However, this is likely to follow the same trend as in gas phase, where a large number of electrons need to be correlated before this effect is relevant.⁴⁵ As for the size of systems that are routinely treatable at the moment with CC methods, other sources of

error (such as basis set incompleteness) are likely to be more relevant.

IV. DISCUSSION AND CONCLUSIONS

This work reports a comparison between the state-specific and linear-response solvation formalisms for the calculation of vertical electronic absorption energy with the CCSD-PCM method. The SS formalism couples the equations for the T_K , R_K , L_K , and Λ_K equations, and only allows the calculation of the energy of one excited state at a time. Additionally, transition energies are computed as the difference between the ground and excited state energies from two separate calculations. The LR approach, on the other hand, decouples the ground and excited state part of the calculation and, in the approximation proposed in Refs. 15 and 35, decouples the left- and right-hand diagonalization of the non-Hermitian CC Jacobian. In this respect, the LR approach is rather close to a gas phase calculation in computational cost as only extra $O(N^5)$ work is added to the CCSD equations, which already scale as $O(N^6)$. A series of approximations has been proposed to reduce the cost of the SS approach, which decouple the T equations from the excited state part of the calculation and do not require the solution of the Λ_K equations (unless analytic energy gradients are computed).³²⁻³⁴ These approximations greatly reduce the cost of the calculation, and allow the calculation of excitation energies in one step. However, they still have the limitation that only one excited state at a time can be computed. Note that such approximations can also be applied to the ground state⁴⁰ and a linear response function can be derived, but this is beyond the scope of this work.

Section III reports test calculations that compare the LR and SS formalisms against experimental data, and calculations of oscillator strengths computed with the full LR approach and an approximate scheme. The comparison with experiment in Sec. III A for four small to medium size molecules (water, acrolein, MCP, and acetone) in polar and low-polar solvents shows that such a crude solvation model is already able to provide the correct experimental trends of solvatochromic shifts. The LR and SS formalisms perform similarly in many cases, providing polar to low-polar solvent shifts close in magnitude, although, the absolute values of solvation energies may vary considerably, as shown in Tables I–III. The SS transition energy can be higher or lower than that computed with LR, depending on the relative magnitude of the transition dipole and of the difference in electric dipole between the ground and excited states,^{22,23} as shown by the two transitions of acrolein and MCP in Tables II and III. The solvent-gas shifts are better reproduced by the LR formalism in some cases (the first transition for water in Table I, and the second transition of acrolein in Table II). However, this may be attributed to unbalanced approximations between the gas phase and solution calculations (and in possible uncertainties in the experimental data).

The comparison between the complete LR definition of transition moments and the frozen- T approximation for the calculation of oscillator strengths, reported in Sec. III B, shows that the latter can be successfully used to compute transition properties of small/medium size molecules, as in gas

phase. The non-size intensivity of transition properties in the approximate scheme provides increasing errors when the size of the system increases, but this is probably a smaller source of errors than, for instance, the choice of solvation model and cavity shape.

In conclusion, the LR formalism represents a computationally efficient approach to account for electrostatic effects of the solvent on transition energies when applied in the context of coupled cluster theory, especially since many states can be computed at once and its cost is comparable to that of gas phase. Also, it allows for the calculation of transition properties. The more physically complete and more computationally demanding SS formalism, on the other hand, can be used for refining the value of the transition energy when a specific state is of interest. This approach may be more appropriate for the investigation of excited state potential energy surfaces where a complete account of the mutual solute-solvent polarization is more important. The LR-PCM solvation formalism can also be used to compute frequency-dependent properties such as molecular polarizabilities and specific rotation in solution, which will be presented in a separate work.

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