CCSD-PCM: Improving upon the reference reaction field approximation at no cost

Marco Caricato

Articles you may be interested in

Electrostatics of proteins in dielectric solvent continua. II. Hamiltonian reaction field dynamics
J. Chem. Phys. 140, 104103 (2014); 10.1063/1.4867281

Implementation of the CCSD-PCM linear response function for frequency dependent properties in solution:
Application to polarizability and specific rotation
J. Chem. Phys. 139, 114103 (2013); 10.1063/1.4821087

A comparison between state-specific and linear-response formalisms for the calculation of vertical electronic
transition energy in solution with the CCSD-PCM method
J. Chem. Phys. 139, 044116 (2013); 10.1063/1.4816482

Improving upon CCSD(T): Λ CCSD (T) . II. Stationary formulation and derivatives
J. Chem. Phys. 128, 044111 (2008); 10.1063/1.2830237

Improving upon CCSD(T): Λ CCSD (T) . I. Potential energy surfaces
J. Chem. Phys. 128, 044110 (2008); 10.1063/1.2830236

CCSD-PCM: Improving upon the reference reaction field approximation at no cost

Marco Caricato[a)]

Gaussian, Inc., 340 Quinnipiac St. Bldg. 40, Wallingford, Connecticut 06492, USA

The combination of the coupled cluster (CC) method with the polarizable continuum model (PCM) of solvation requires a much larger computational effort than gas phase CC calculations, since the PCM contribution depends nonlinearly on the CC reduced density: perturbation theory energy and density (PTED) scheme. An approximation can be introduced that neglects the "correlation" PCM contribution and only considers the "reference" PCM contribution to the free energy: PTE scheme. The PTE scheme is a computationally efficient strategy, since the cost is comparable to gas phase CC, but the difference in the free energy with respect to the PTED scheme can be significant. In this work, two intermediate approximations are presented, PTE(S) and PTES (where S stands for singles), which retain the computational efficiency of the PTE scheme while reducing the energy gap with the PTED scheme. PTE(S) only introduces an energy correction to the PTE free energy, while PTES introduces explicit PCM terms in the iterative solution of the CC equations. PTE(S) improves the PTE free energy, although such correction is small. PTES recovers 50%–80% of the PTE-PTED difference and represents a promising approach to perform calculations in solution of CC quality at a cost comparable to gas phase CC. The expressions for the CC-PTE(S) and -PTES wave functions, free energy, and free energy analytical gradients are presented, and the methods are tested with numerical examples. © *2011 American Institute of Physics*. [doi:10.1063/1.3624373]

I. INTRODUCTION

Single reference coupled cluster (CC) theory[1,2] represents one of the most successful and widely used approaches to study properties of isolated molecules. The exponential *ansatz* for the cluster expansion recovers most of the dynamical electron correlation even for truncated excitation expansions. Also, approximated CC methods are size consistent and can be systematically improved. A limitation of the theory is its computational cost, which makes it routinely affordable only for medium size molecules.

When the system of interest is in solution, the issue of computational cost becomes even more significant. A number of approaches have been proposed to introduce the solvent effect in an approximate way in CC calculations.[3–13] Among these, the approach of Cammi[11] is particularly appealing. It is based on the polarizable continuum model of solvation (PCM),[14,15] where the solvent is represented as a polarizable dielectric characterized by its dielectric constant. A cavity of molecular shape hosts the solute, and the solvent polarization is modeled as an apparent surface charge on the cavity surface. The electrostatic solute-solvent interaction is introduced in the solute Hamiltonian as an interaction operator, so that solute and solvent mutually polarize. PCM is computationally very efficient and is usually able to properly describe the solvent effect as long as there is no direct interaction between the solvent molecules and the solute (for instance, strong hydrogen bonds).

In his extension of PCM to CC theory, called PCM-PTED (perturbation theory energy and density) scheme for histori-

cal reasons,[16,17] Cammi separates the solvent interaction with the reference function from the "correlation" interaction. The latter depends on the CC reduced one particle density matrix (1PDM). To compute the reduced 1PDM, the auxiliary Λ vector from CC gradient theory is necessary,[1,2,18,19] and this makes the calculation of the PCM-PTED free energy computationally expensive compared to a gas phase energy calculation. This is somewhat mitigated in property calculations, for example in geometry optimizations, since the 1PDM is required even in the gas phase. However, the mutual polarization between solute and solvent requires several PCM macroiterations; thus, several evaluations of the 1PDM for each free energy calculation, until convergence is reached.

An approximation can be introduced, where the "correlation" interaction is neglected: PTE scheme.[11,16,17] In this approach, the CC wave function and the Λ vector are decoupled as in the gas phase, and the solute-solvent polarization is only introduced through the polarization of the molecular orbitals (MOs). The PTE scheme is computationally equivalent to gas phase CC, since the extra work in the reference wave function calculation is negligible compared to the CC part. The implementation and testing of the PTE and PTED schemes[13,20] showed that while the difference between the two approaches can be minor for small systems, it increases for larger systems and can become significant.

By re-examining the CC-PCM-PTED equations, I have realized that two intermediate approximations between the PTE and PTED schemes can be invoked. These approximations, called PTE(S) and PTES, only consider the part of the reduced 1PDM that does not depend on the Λ vector, that is the single CC amplitudes (the "S" stands for singles).

---
a)Electronic mail: marco@gaussian.com.

Therefore, in the PTE(S) and PTES schemes, the CC equations are decoupled from the Λ equations as for PTE. In PTE(S), the correlation contribution is introduced as an energy correction to the PTE free energy, while in PTES, explicit PCM terms enter the iterative solution of the CC equations. Both PTE(S) and PTES are still computationally equivalent to CC-PCM-PTE, since the extra work for the PCM terms is negligible.

In this paper, I introduce the expressions for the free energy in the CC-PCM-PTE(S) and -PTES schemes and the free energy analytical gradients. Numerical tests are also presented, in order to assess the efficacy of the two approaches. These tests show that both schemes reduce the difference between PTE and PTED. The improvement of PTE(S) is usually small, while PTES is able to recover 50%–80% of the "correlation" PCM contribution. Thus, PTES represents an efficient approach to perform CC calculations in solution at a computational cost comparable to the gas phase CC.

This paper is organized as follows. The theory is described in Sec. II. The numerical tests are presented and discussed in Sec. III, and Sec. IV contains concluding remarks.

II. THEORY

A review of the theory and implementation of the family of polarizable continuum models of solvation can be found in the available literature,[14, 15, 21–25] and will not be repeated here. Additionally, I will follow the notation introduced by Cammi[11] for consistency in the PCM expressions and refer the interested reader to Ref. 11 for more details.

The CC-PCM-PTED free energy functional is[11, 26, 37]

$$G(\Lambda, T) = \langle \Phi^0|(1 + \Lambda)e^{-T} H_0 e^T|\Phi^0\rangle$$
$$+ \frac{1}{2}\bar{\mathbf{V}}(\Lambda, T) \cdot \bar{\mathbf{Q}}(\Lambda, T), \quad (1)$$

where H_0 is the molecular Hamiltonian, Φ^0 is the reference function (usually the Hartree-Fock wave function, HF), T is the excitation operator, and Λ is the Z vector from gradient theory.[18, 19] $\bar{\mathbf{Q}}(\Lambda, T)$ and $\bar{\mathbf{V}}(\Lambda, T)$ are the PCM reaction field and solute electrostatic potential on the cavity surface, respectively,[11]

$$\bar{\mathbf{Q}}(\Lambda, T) = \langle \Phi^0|(1 + \Lambda)e^{-T} \mathbf{Q} e^T|\Phi^0\rangle, \quad (2)$$

$$\bar{\mathbf{V}}(\Lambda, T) = \langle \Phi^0|(1 + \Lambda)e^{-T} \mathbf{V} e^T|\Phi^0\rangle. \quad (3)$$

Since both depend on the total (frozen orbitals) CC density, the reaction field couples the T and Λ equations, in contrast to the *gas phase* case where Λ is not required for the calculation of the energy. The scalar product in the PCM term indicates that the reaction field and the potential on the cavity surface are discretized in surface elements, and the bold font is used to indicate that these are vectors of dimension equal to the number of surface elements.[27]

By introducing the normal-product form of an operator[2]

$$X_N = X - \langle \Phi^0|X|\Phi^0\rangle = X - \bar{X}^0. \quad (4)$$

Equation (1) can be rewritten as

$$G(\Lambda, T) = G^0 + \langle \Phi^0|(1 + \Lambda)e^{-T} H_{0N}^{\text{PCM}} e^T|\Phi^0\rangle$$

$$+ \frac{1}{2}\bar{\mathbf{V}}_N(\Lambda, T) \cdot \bar{\mathbf{Q}}_N(\Lambda, T), \quad (5)$$

where G^0 is the reference free energy:

$$G^0 = \langle \Phi^0|H_0|\Phi^0\rangle + \frac{1}{2}\bar{\mathbf{V}}^0 \cdot \bar{\mathbf{Q}}^0, \quad (6)$$

and H_{0N}^{PCM} contains the PCM operator with the reference reaction field

$$H_{0N}^{\text{PCM}} = H_{0N} + \mathbf{V}_N \cdot \bar{\mathbf{Q}}^0. \quad (7)$$

In Eq. (5) as in Eq. (1), the coupling between the T and Λ equations is due to the PCM term since both $\bar{\mathbf{V}}_N$ and $\bar{\mathbf{Q}}_N$ depend on T and Λ.

In the PTE approximation, the $1/2 \bar{\mathbf{V}}_N \cdot \bar{\mathbf{Q}}_N$ term in Eq. (5) is neglected. Therefore, the coupling between the T and Λ equations is eliminated. The CC-PTE equations for the T and Λ amplitudes (t and λ, respectively) are formally identical to those for the gas phase, and the solvent effect is introduced only through the polarized MOs and orbital energies. The PTE model is computationally equivalent to a gas phase calculation, since the extra work introduced by PCM in the computation of Φ^0 and G^0 is negligible compared to the solution of the CC equations.

However, expanding the $1/2 \bar{\mathbf{V}}_N \cdot \bar{\mathbf{Q}}_N$ term

$$\frac{1}{2}\bar{\mathbf{V}}_N(\Lambda, T) \cdot \bar{\mathbf{Q}}_N(\Lambda, T) = \frac{1}{2}\langle \Phi^0|(1 + \Lambda)e^{-T}\mathbf{V}_N e^T|\Phi^0\rangle \cdot \langle \Phi^0|(1 + \Lambda)e^{-T}\mathbf{Q}_N e^T|\Phi^0\rangle$$

$$= \frac{1}{2}\langle \Phi^0|e^{-T}\mathbf{V}_N e^T|\Phi^0\rangle \cdot \langle \Phi^0|e^{-T}\mathbf{Q}_N e^T|\Phi^0\rangle + \frac{1}{2}\langle \Phi^0|\Lambda e^{-T}\mathbf{V}_N e^T|\Phi^0\rangle \cdot \langle \Phi^0|e^{-T}\mathbf{Q}_N e^T|\Phi^0\rangle$$

$$+ \frac{1}{2}\langle \Phi^0|e^{-T}\mathbf{V}_N e^T|\Phi^0\rangle \cdot \langle \Phi^0|\Lambda e^{-T}\mathbf{Q}_N e^T|\Phi^0\rangle + \frac{1}{2}\langle \Phi^0|\Lambda e^{-T}\mathbf{V}_N e^T|\Phi^0\rangle \cdot \langle \Phi^0|\Lambda e^{-T}\mathbf{Q}_N e^T|\Phi^0\rangle, \quad (8)$$

one notices that the T/Λ coupling is only due to the last term. Therefore, the two approximations that are the focus of this work are based on the neglect of this term.

In the following, I implicitly assume that the reaction field is computed by using the symmetric version of the PCM

equations, either for the integral equation formalism PCM (IEF-PCM)[21, 22, 25] or the conductor-like PCM,[23, 24] so that the following relations apply:

$$\frac{\partial}{\partial \xi}\left(\frac{1}{2}\bar{\mathbf{V}}(\xi) \cdot \bar{\mathbf{Q}}(\xi)\right) = \bar{\mathbf{V}}^\xi(\xi) \cdot \bar{\mathbf{Q}}(\xi), \quad (9)$$

$$\frac{1}{2}\bar{\mathbf{V}}(\xi_1)\cdot\bar{\mathbf{Q}}(\xi_2)=\frac{1}{2}\bar{\mathbf{V}}(\xi_2)\cdot\bar{\mathbf{Q}}(\xi_1), \qquad (10)$$

where the parameter ξ refers to the T or Λ amplitudes.

A. PTE(S) scheme

In this approximation, all $\mathbf{V}_N \cdot \mathbf{Q}_N$ terms that depend on Λ are neglected (last three terms in Eq. (8)). Thus, the PTE(S) free energy functional is

$$G^{\text{PTE(S)}} = G^0 + \langle \Phi^0|(1+\Lambda)e^{-T}H_{0N}^{\text{PCM}}e^T|\Phi^0\rangle$$
$$+ \frac{1}{2}\bar{\mathbf{V}}_N(T)\cdot\bar{\mathbf{Q}}_N(T), \qquad (11)$$

where I introduced the notation

$$\bar{\mathbf{Q}}_N(T) = \langle \Phi^0|e^{-T}\mathbf{Q}_N e^T|\Phi^0\rangle, \qquad (12)$$

to outline that the apparent surface charges only depend on the T amplitudes. Another way to view this approximation is to consider that the correlation reaction field is only determined by that part of the CC reduced 1PDM (γ_{pq} in Table I of Ref. 11) that does not depend on the Λ amplitudes

$$\gamma_{pq} \simeq t_i^a. \qquad (13)$$

Here and in the following, the usual notation is used for the MO labels: $ijk\ldots$ for occupied MOs, $abc\ldots$ for virtual MOs, and $pqr\ldots$ for generic MOs, and Einstein's convention for the summation over common indexes is used.

Imposing the stationarity of $G^{\text{PTE(S)}}$ with respect to variations of the Λ amplitudes, one obtains the equations for t

$$\frac{\partial G^{\text{PTE(S)}}}{\partial \lambda} = \langle \Phi|e^{-T}H_{0N}^{\text{PCM}}e^T|\Phi^0\rangle = 0$$
$$\equiv \frac{\partial G^{\text{PTE}}}{\partial \lambda}, \qquad (14)$$

where Φ is an excited determinant with respect to the reference wave function. It is understood that there is a set of equations for each order of excitations.

Since the $\bar{\mathbf{V}}_N(T)\cdot\bar{\mathbf{Q}}_N(T)$ energy term in Eq. (11) does not depend on Λ, it does not contribute to the T equations, and the PTE(S) T equations are equivalent to the PTE equations. Once Eq. (14) is solved, Eq. (11) reduces to

$$G^{\text{PTE(S)}} = G^0 + \langle \Phi^0|e^{-T}H_{0N}^{\text{PCM}}e^T|\Phi^0\rangle$$
$$+ \frac{1}{2}\bar{\mathbf{V}}_N(T)\cdot\bar{\mathbf{Q}}_N(T). \qquad (15)$$

Hence, in the PTE(S) approximation, the correlation PCM contribution is only a correction to the PTE free energy and

can be computed after solving the T equations:

$$\frac{1}{2}\langle \Phi^0|e^{-T}\mathbf{V}_N e^T|\Phi^0\rangle \cdot \langle \Phi^0|e^{-T}\mathbf{Q}_N e^T|\Phi^0\rangle$$
$$= \frac{1}{2}t_i^a \mathbf{v}_{ia}\bar{\mathbf{Q}}_N(T). \qquad (16)$$

B. PTES scheme

In the PTES scheme, only the last term in Eq. (8) is neglected. The free energy functional thus becomes

$$G^{\text{PTES}} = G^0 + \langle \Phi^0|(1+\Lambda)e^{-T}H_{0N}^{\text{PCM}}e^T|\Phi^0\rangle$$
$$+ \bar{\mathbf{V}}_N(\Lambda, T)\cdot\bar{\mathbf{Q}}_N(T)$$
$$- \frac{1}{2}\bar{\mathbf{V}}_N(T)\cdot\bar{\mathbf{Q}}_N(T), \qquad (17)$$

where I used the relation in Eq. (10) to rearrange the remaining terms.

The T amplitudes are again computed by imposing the stationarity of G^{PTES} with respect to changes in λ

$$\frac{\partial G^{\text{PTES}}}{\partial \lambda} = \langle \Phi|e^{-T}H_{0N}^{\text{PCM}}e^T|\Phi^0\rangle$$
$$+ \langle \Phi|e^{-T}\mathbf{V}_N e^T|\Phi^0\rangle \cdot \bar{\mathbf{Q}}_N(T) = 0. \qquad (18)$$

Note that the PTES T equations in Eq. (18) are formally identical to the PTED equations[11] with the substitution $\bar{\mathbf{Q}}_N(\Lambda, T) \to \bar{\mathbf{Q}}_N(T)$.

Also in this approximation, the T equations are decoupled from the Λ equations since there is no explicit dependence on Λ in Eq. (18). Contrary to the PTE(S) scheme, here correlation PCM terms explicitly appear in the iterative solution of the CC equations. However, the computational cost of such terms is negligible. In fact, the most expensive PCM terms in Eq. (18), which formally scale as $\mathcal{O}(N^5)$ for CC singles and doubles[11] (CCSD, where N is the number of basis functions) can be folded in intermediates that are common to the gas phase equations, so that no extra $\mathcal{O}(N^5)$ work is actually performed. Hence, the cost of each iteration in the PTES scheme is still computationally equivalent to that of a gas phase CC calculation.

When the T amplitudes are computed by solving Eq. (18), G^{PTES} in Eq. (17) reduces to

$$G^{\text{PTES}} = G^0 + \langle \Phi^0|e^{-T}H_{0N}^{\text{PCM}}e^T|\Phi^0\rangle$$
$$+ \frac{1}{2}\bar{\mathbf{V}}_N(T)\cdot\bar{\mathbf{Q}}_N(T), \qquad (19)$$

which is formally equivalent to $G^{\text{PTE(S)}}$ in Eq. (15).

C. Analytical free energy gradients

The derivation of the analytical gradients of the PTE(S) and PTES free energy functionals closely follows Cammi's derivation for the PTED scheme[11] and need not be repeated here. PCM only adds a few extra terms to the gas phase CC analytical energy gradient expressions, which can be found in Refs. 18 and 19. Consequently, here I report only the different expressions for the PTE(S) and PTES terms compared to PTED.

The calculation of the analytical gradients of the free energy functional requires the evaluation of the Λ vector, for both the PTE(S) and PTES schemes. In either case, the equations for the λ amplitudes can be obtained by imposing the stationarity of the free energy functionals, Eqs. (11) and (17), with respect to variations of t. For PTE(S), one has

$$
\begin{aligned}
\frac{\partial G^{\text{PTE(S)}}}{\partial t} &= \langle \Phi^0 | [\Lambda, e^{-T} H_{0N}^{\text{PCM}} e^T] | \Phi \rangle \\
&+ \langle \Phi^0 | e^{-T} H_{0N}^{\text{PCM}} e^T | \tilde{\Phi} \rangle \langle \tilde{\Phi} | \Lambda | \Phi \rangle \\
&+ \langle \Phi^0 | e^{-T} H_{0N}^{\text{PCM}} e^T | \Phi \rangle \\
&+ \langle \Phi^0 | e^{-T} \mathbf{V}_N e^T | \Phi \rangle \cdot \bar{\mathbf{Q}}_N(T) = 0. \quad (20)
\end{aligned}
$$

Equation (20) is formally equivalent to the PTE Λ equations[11] except for the constant term

$$
\langle \Phi^0 | e^{-T} \mathbf{V}_N e^T | \Phi \rangle \cdot \bar{\mathbf{Q}}_N(T) = \mathbf{v}_{ia} \cdot \bar{\mathbf{Q}}_N(T), \quad (21)
$$

which only appears in the singles amplitudes equations.

The Λ equations for PTES are

$$
\begin{aligned}
\frac{\partial G^{\text{PTES}}}{\partial t} &= \langle \Phi^0 | [\Lambda, e^{-T} H_{0N}^{\text{PCM}} e^T] | \Phi \rangle \\
&+ \langle \Phi^0 | [\Lambda, e^{-T} \mathbf{V}_N e^T] | \Phi \rangle \cdot \bar{\mathbf{Q}}_N(T) \\
&+ \big(\langle \Phi^0 | e^{-T} H_{0N}^{\text{PCM}} e^T | \tilde{\Phi} \rangle \\
&+ \langle \Phi^0 | e^{-T} \mathbf{V}_N e^T | \tilde{\Phi} \rangle \cdot \bar{\mathbf{Q}}_N(T) \big) \langle \tilde{\Phi} | \Lambda | \Phi \rangle \\
&+ \langle \Phi^0 | e^{-T} H_{0N}^{\text{PCM}} e^T | \Phi \rangle \\
&+ \langle \Phi^0 | e^{-T} \mathbf{V}_N e^T | \Phi \rangle \cdot \bar{\mathbf{Q}}_N(\Lambda, T) = 0. \quad (22)
\end{aligned}
$$

Equation (22) is very similar to the Λ equations for PTED,[11] with the substitution $\bar{\mathbf{Q}}_N(\Lambda, T) \to \bar{\mathbf{Q}}_N(T)$ for all of the PCM terms except the last one. For the explicit expressions of the PTED Λ equations for CCSD, see Table IV in Ref. 11 and note 18 in Ref. 13.

The charges $\bar{\mathbf{Q}}_N(T)$ do not change during the iterative solution of Eqs. (20) and (22), but the $\bar{\mathbf{Q}}_N(\Lambda, T)$ in Eq. (22) do. This does not add a significant amount of work compared to the PTE case, since the evaluation of $\bar{\mathbf{Q}}_N(\Lambda, T)$ requires the 1PDM, which is relatively inexpensive to compute. For instance, for CCSD the evaluation of the 1PDM scales as $\mathcal{O}(N^5)$, while the evaluation of the leading terms in the Λ equations scales as $\mathcal{O}(N^6)$.

Once the Λ vector is computed, there are few extra terms that must be added to the gas phase CC energy gradient expressions. The following are the terms that differ between the PTE(S)/PTES schemes and PTED.[11] The PTE(S) skeleton terms are

$$
\text{PTE(S):} \left(\frac{1}{2} \bar{\mathbf{V}}_N(T) \cdot \bar{\mathbf{Q}}_N(T) \right)^{[\alpha]} = t_i^a v_{ia}^{[\alpha]} \cdot \bar{\mathbf{Q}}_N(T), \quad (23)
$$

while for PTES they are

$$
\begin{aligned}
\text{PTES:} \ & \left(\bar{\mathbf{V}}_N(\Lambda, T) \cdot \bar{\mathbf{Q}}_N(T) - \frac{1}{2} \bar{\mathbf{V}}_N(T) \cdot \bar{\mathbf{Q}}_N(T) \right)^{[\alpha]} \\
&= \left(\gamma_{pq} v_{pq}^{[\alpha]} - t_i^a v_{ia}^{[\alpha]} \right) \cdot \bar{\mathbf{Q}}_N(T) + t_i^a v_{ia}^{[\alpha]} \cdot \bar{\mathbf{Q}}_N(\Lambda, T).
\end{aligned}
$$
$$(24)$$

The remaining terms that need be added to the gas phase CC expressions are (following the notation in Table VI of Ref. 11 and note 18 in Ref. 13)

$$
\text{PTE(S):} \ I'_{km} = -\frac{1}{2} t_k^c \mathbf{v}_{cm} \cdot \bar{\mathbf{Q}}_N(T),
$$

$$
I'_{ea} = -\frac{1}{2} t_j^e \mathbf{v}_{ja} \cdot \bar{\mathbf{Q}}_N(T),
$$

$$
I'_{em} = -\frac{1}{2} t_j^e \mathbf{v}_{jm} \cdot \bar{\mathbf{Q}}_N(T),
$$

$$
I'_{me} = \frac{1}{2} t_m^c \mathbf{v}_{ce} \cdot \bar{\mathbf{Q}}_N(T). \quad (25)
$$

$$
\begin{aligned}
\text{PTES:} \ I'_{km} &= -\gamma_{kq} \mathbf{v}_{qm} \cdot \bar{\mathbf{Q}}_N(T) - \frac{1}{2} t_k^c \mathbf{v}_{mc} \cdot \bar{\mathbf{Q}}_N(\Lambda, T) \\
&+ \frac{1}{2} t_k^c \mathbf{v}_{mc} \cdot \bar{\mathbf{Q}}_N(T),
\end{aligned}
$$

$$
\begin{aligned}
I'_{ea} &= -\gamma_{eq} \mathbf{v}_{qa} \cdot \bar{\mathbf{Q}}_N(T) - \frac{1}{2} t_j^e \mathbf{v}_{ja} \cdot \bar{\mathbf{Q}}_N(\Lambda, T) \\
&+ \frac{1}{2} t_j^e \mathbf{v}_{ja} \cdot \bar{\mathbf{Q}}_N(T),
\end{aligned}
$$

$$
\begin{aligned}
I'_{em} &= -\gamma_{eq} \mathbf{v}_{qm} \cdot \bar{\mathbf{Q}}_N(T) - \frac{1}{2} t_j^e \mathbf{v}_{jm} \cdot \bar{\mathbf{Q}}_N(\Lambda, T) \\
&+ \frac{1}{2} t_j^e \mathbf{v}_{jm} \cdot \bar{\mathbf{Q}}_N(T),
\end{aligned}
$$

$$
\begin{aligned}
I'_{me} &= \gamma_{mq} \mathbf{v}_{qe} \cdot \bar{\mathbf{Q}}_N(T) + \frac{1}{2} t_m^c \mathbf{v}_{ce} \cdot \bar{\mathbf{Q}}_N(\Lambda, T) \\
&- \frac{1}{2} t_m^c \mathbf{v}_{ce} \cdot \bar{\mathbf{Q}}_N(T). \quad (26)
\end{aligned}
$$

As in the case of the PTED scheme, the work added by the PTE(S) and PTES PCM terms to the gas phase CC gradient terms is also negligible.

III. RESULTS

The PTE(S) and PTES methods described in Secs. I and II were implemented for the CCSD method in a development version of the Gaussian suite of programs.[28] The implementation includes the restricted closed shell and the unrestricted wave function and makes use of Abelian point group symmetry.[19]

In this section, I present a series of tests that compare the performance of the PTE(S) and PTES schemes with PTE and PTED. The tests include solvation free energies, defined as the difference between the free energy in solution and the gas phase energy, for five organic molecules in water: pyridine, aniline, phenol, p-bromophenol, and chlorobenzene. For this molecules, convergence and timing are also discussed. Another example is the interaction energy of a stacked uracil dimer in water. The last test case is a dihydrogen complex of Fe$^+$ in tetrahydrofuran (THF). The PCM cavity is built from interlocking spheres centered on each nucleus and using the universal force field (UFF) radii.[29] The symmetric version of IEF-PCM[25] is used, and Scalmani and Frisch's continuous surface charge scheme[27] is employed.

TABLE I. Solvation free energy (kcal/mol) for five organic molecules in water with the IEF-PCM method.

	PTE	PTE(S)	PTES	PTED
Pyridine	−4.73	−4.74	−4.77	−4.80
Aniline	−5.32	−5.32	−5.35	−5.38
Phenol	−5.79	−5.79	−5.82	−5.85
p-Br-phenol	−6.29	−6.30	−6.33	−6.36
Cl-benzene	−2.50	−2.51	−2.53	−2.57

For the five organic molecules, the 6-31+G(d,p) basis set is used, and the geometries are optimized at the corresponding level of theory. The solvation free energies are reported in Table I. No comparison with experiment or basis set effects are reported, as in Ref. 13, since I am only interested in the relative performance of the methods.

The results in Table I show that in the PTED model, the solvent stabilizes each molecule more than the other schemes. PTE is already a very good approximation of PTED, as the largest difference is 0.07 kcal/mol. However, this difference is still significant in that it may become larger for larger systems, as shown by the following examples. The PTE(S) model moves the PTE results in the right direction, but the correction is very small, usually around 0.01 kcal/mol. The improvement of PTES is much larger, usually around 50% of the PTE-PTED difference. This result indicates that the $\bar{\mathbf{Q}}_N(T)$ charges recover half of the correlation reaction field effect, while keeping the T and Λ equations decoupled as in gas phase CCSD.

The number of iterations for the convergence of the T equations for these five molecules are shown in Table II. The convergence thresholds are 10^{-6} for the wave function and 10^{-8} a.u. for the energy. Only PTE and PTES are compared, since the two schemes are directly related. PTE(S) only adds an energy correction that scales as $\mathcal{O}(N^2)$ at the end of the PTE calculation (see Eq. (16)) and therefore it is negligible. For a comparison of the convergence of the PTE and PTED schemes, see Ref. 13. As evident from Table II, the same number of iterations are necessary in solution with the two schemes as in the gas phase. The computational time is the same for all the calculations, since the extra work introduced by the PCM terms is negligible in the reference function calculation, and in the CCSD part of the PTES scheme. Similar results can be expected for the other examples.

TABLE II. Number of iterations for the solution of the T equations for five organic molecules in gas phase and water with the PTE and PTES schemes.

		IEF	
	Gas	PTE	PTES
Pyridine	16	16	16
Aniline	16	16	16
Phenol	16	16	16
p-Br-phenol	17	17	17
Cl-benzene	15	15	15

TABLE III. Interaction energies and energy shifts relative to PTED (kcal/mol) for the stacked uracil dimer. The interaction energies include a BSSE correction. PTED is the reference for the relative energies.

	Gas	PTE	PTE(S)	PTES	PTED
		Interaction energy			
6-31G(d)	−2.43	0.30	0.33	0.39	0.42
6-31+G(d,p)	−3.67	−0.41	−0.38	−0.33	−0.31
	Energy shifts relative to PTED				
		Dimer			
6-31G(d)		−0.46	−0.30	−0.09	0.00
6-31+G(d,p)		−0.36	−0.24	−0.08	0.00
		Monomer			
6-31G(d)		−0.29	−0.19	−0.06	0.00
6-31+G(d,p)		−0.23	−0.16	−0.05	0.00

Table III reports the interaction energies for the stacked uracil dimer in water, and the energy shifts relative to PTED for the dimer and the monomer. The relative energies are defined as the PTED energy minus that of the other methods. The geometry of the dimer is taken from Ref. 30. The monomers have the same geometry and are 3.3 Å apart. The single point calculations are performed with two basis sets: 6-31G(d) and 6-31+G(d,p). These basis sets are too small for quantitative results, as outlined by the gas phase interaction energies in Table III, which are too small compared to the reference –7.5 kcal/mol.[30] However, the focus of this paper is the comparison of the methods presented in Sec. II. All the interaction energies are corrected for the basis set superposition error (BSSE) using the counter poise method.[31, 32] The same BSSE correction is used for the gas phase and PCM calculations, since there is not a well defined procedure to compute this quantity with continuum solvation models. The solvent competes with the stacking interaction, which is greatly reduced in water. For the smaller basis set, the dimer is even less stable than the non-interacting monomers. The decrease of interaction energy due to the solvent, ∼2–3 kcal/mol, is consistent with previous results.[33] The difference between PTE and PTED for the interaction energy is already small: ∼0.10−0.12 kcal/mol. However, PTE(S) and PTES reduce it (for PTES the difference with PTED is ∼0.02–0.03 kcal/mol). The potentiality of the corrections introduced in this work are more evident when one looks at the relative energies of the dimer and the monomer separately. For the dimer, the difference between PTE and PTED reaches half a kcal/mol, while for one monomer the difference is of the order of 0.2–0.3 kcal/mol. In both cases, PTES reduces this difference by ∼80% without increasing the computational
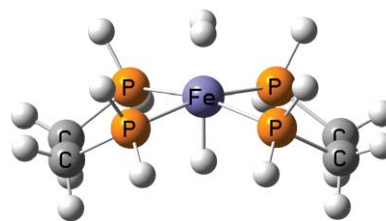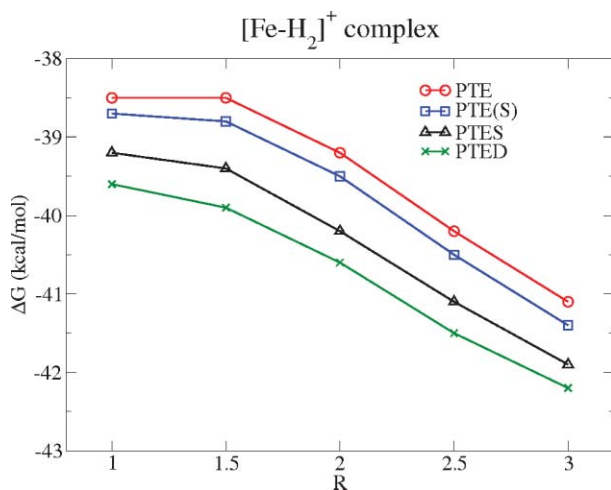

FIG. 1. Structure of the $H_2[FeH(PP)_2]^+$ complex.

FIG. 2. Solvation free energy (kcal/mol) in the $H_2[FeH(PP)_2]^+$ complex, in gas and in THF, at various H–H bond distances. R is a scaling factor from the equilibrium bond distance.

time compared to the PTE scheme. Also, in this case, the stabilization due to PTED is larger than that of the various approximations.

The last system considered is a trans-hydride complex of Fe^+: $H_2[FeH(PP)_2]^+$ (see Fig. 1). The results in Fig. 2 show the change in solvation free energy at various H–H bond lengths (R is a scaling factor for the equilibrium distance).[20] The calculations are performed using the Stuttgart/Dresden pseudopotential[34] for Fe, the 6-31G(*d,p*) basis set for the dihydrogen and the hydrogen in trans position, and the 6-31G(*d*) basis for the rest of the atoms. The initial geometry was obtained by optimization with the B3LYP (Ref. 35 and 36) hybrid functional and can be found in the supporting material of Ref. 20. An extra sphere is included along the Fe–H_2 bond to avoid "solvent pockets" at longer H–H distances (the sphere diameter being equal to the Fe–H_2 distance: 1.6219 Å). In this case, the PTE-PTED difference is much larger, between 1.1 and 1.4 kcal/mol. PTE(S) again improves upon the PTE approximation, but the magnitude of the improvement is small: 0.2–0.3 kcal/mol. The PTES results, on the other hand, are much closer to those of PTED, with a 65%–70% improvement of the agreement compared to PTE. The iterative PCM contribution to the CCSD equations through the PTES scheme, thus, recovers most of the correlation solvent effect at a computational cost equivalent to the PTE scheme. It is interesting to note that both approximations still suffer from the CCSD sensitivity to the choice of the reference function, and in cases where the HF wave function may be unstable an approach such as the Brueckner doubles method may be preferable.[20] Such effect is the subject of ongoing research.

IV. CONCLUSIONS

In this work, I present two approaches that improve the reference reaction field approximation (PTE) for the CC wave function computed within the framework of the polarizable continuum model. The PCM-PTE approximation is computational equivalent to a gas phase CC calculation, since the solvent effect is folded in the polarized orbitals and orbital energies from the reference wave function calculation. However, the correlation PCM contributions (neglected in the PTE scheme) can be significant and tend to further stabilize the solute. Including such correlation effects, called PTED scheme, requires the CC reduced 1PDM, which is not necessary in gas phase calculations. The PTED scheme is, therefore, much more computationally demanding than gas phase CC.

The schemes proposed in this work, called PTE(S) and PTES, try to recover part of the correlation PCM contribution without evaluating the complete reduced 1PDM. Only the part of the CC 1PDM that depends on the *t* amplitudes is used to compute the correlation PCM effect. In the PTE(S) scheme, such contribution is introduced as an energy correction after that the CC equations for the *t* amplitudes are solved. In the PTES scheme, the PCM terms derived from the *t* part of the 1PDM are included in the iterative solution of the CC equations. The extra work required by these terms is negligible compared to gas phase CC.

The results reported in Sec. III show that both PTE(S) and PTES schemes improve the PTE approximation towards the PTED results. Such improvement is very small for the PTE(S) scheme, while it is significant for PTES. In fact, PTES recovers 50%–80% of the correlation PCM contribution. Therefore, the PTES scheme is an efficient way to perform CC calculations in solution without significantly increasing the computational burden compared to gas phase. Additionally, the CC amplitudes computed with the PTES scheme represent a much better starting point for calculations with the complete PTED scheme.

[1]R. J. Bartlett and M. Musial, Rev. Mod. Phys. **79**, 291 (2007).
[2]I. Shavitt and R. J. Bartlett, *Many-Body Methods in Chemistry and Physics* (Cambridge University Press, Cambridge, England, 2009).
[3]J. Kongsted, A. Osted, T. B. Pedersen, K. V. Mikkelsen, and O. Christiansen, J. Phys. Chem. A **108**, 8624 (2004).
[4]A. Osted, J. Kongsted, K. V. Mikkelsen, and O. Christiansen, J. Phys. Chem. A **108**, 8646 (2004).
[5]K. Aidas, J. Kongsted, A. Osted, K. V. Mikkelsen, and O. Christiansen, J. Phys. Chem. A **109**, 8001 (2005).
[6]K. Sneskov, T. Schwabe, J. Kongsted, and O. Christiansen, J. Chem. Phys. **134**, 104108 (2011).
[7]L. V. Slipchenko, J. Phys. Chem. A **114**, 8824 (2010).
[8]D. Kosenkov and L. V. Slipchenko, J. Phys. Chem. A **115**, 392 (2011).
[9]O. Christiansen and K. V. Mikkelsen, J. Chem. Phys. **110**, 1365 (1999).
[10]O. Christiansen and K. V. Mikkelsen, J. Chem. Phys. **110**, 8348 (1999).
[11]R. Cammi, J. Chem. Phys. **131**, 164104 (2009).
[12]M. Caricato, B. Mennucci, G. Scalmani, G. W. Trucks, and M. J. Frisch, J. Chem. Phys. **132**, 084102 (2010).
[13]M. Caricato, G. Scalmani, G. W. Trucks, and M. J. Frisch, J. Phys. Chem. Lett. **1**, 2369 (2010).
[14]S. Miertus, E. Scrocco, and J. Tomasi, Chem. Phys. **55**, 117 (1981).
[15]J. Tomasi, B. Mennucci, and R. Cammi, Chem. Rev. **105**, 2999 (2005).
[16]F. Olivares del Valle and J. Tomasi, Chem. Phys. **150**, 139 (1991).
[17]M. Aguilar, F. Olivares del Valle, and J. Tomasi, Chem. Phys. **150**, 151 (1991).
[18]E. A. Salter, G. W. Trucks, and R. J. Bartlett, J. Chem. Phys. **90**, 1752 (1989).
[19]J. Gauss, J. F. Stanton, and R. J. Bartlett, J. Chem. Phys. **95**, 2623 (1991).

[20]M. Caricato, G. Scalmani, and M. J. Frisch, J. Chem. Phys. **134**, 244113 (2011)

[21]E. Cances, B. Mennucci, and J. Tomasi, J. Chem. Phys. **107**, 3032 (1997).

[22]B. Mennucci, E. Cances, and J. Tomasi, J. Phys. Chem. B **101**, 10506 (1997).

[23]A. Klamt and G. Schüürmann, J. Chem. Soc., Perkin Trans. **2**, 799 (1993).

[24]M. Cossi, N. Rega, G. Scalmani, and V. Barone, J. Comput. Chem. **24**, 669 (2003).

[25]F. Lipparini, G. Scalmani, B. Mennucci, E. Cancès, M. Caricato, and M. J. Frisch, J. Chem. Phys. **133**, 014106 (2010).

[26]The "free" energy status derives from the work spent to polarize the solvent, (Ref. 15) and does not include any thermal contribution from the solute (Ref. 37).

[27]G. Scalmani and M. J. Frisch, J. Chem. Phys. **132**, 114110 (2010).

[28]M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.* Gaussian Development Version, Revision H.09+, Gaussian, Inc., Wallingford, CT (2010).

[29]A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard, and W. M. Skiff, J. Am. Chem. Soc. **114**, 10024 (1992).

[30]J. Šponer, P. Jurečka, I. Marchan, F. J. Luque, M. Orozco, and P. Hobza, Chem. Eur. J. **12**, 2854 (2006).

[31]S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).

[32]S. Simon, M. Duran, and J. J. Dannenberg, J. Chem. Phys. **105**, 11024 (1996).

[33]F. Lipparini, G. Scalmani, and B. Mennucci, Phys. Chem. Chem. Phys. **11**, 11617 (2009).

[34]M. Dolg, U. Wedig, H. Stoll, and H. Preuss, J. Chem. Phys. **86**, 866 (1987).

[35]A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[36]P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Chem. Phys. **98**, 11623 (1994).

[37]J. Ho, A. Klamt, and M. L. Coote, J. Phys. Chem. A **114**, 13442 (2010).