

On the Importance of the Orbital Relaxation in Ground-State Coupled Cluster Calculations in Solution with the Polarizable Continuum Model of Solvation

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ABSTRACT: In the description of the electrostatic interaction between a solute treated at coupled cluster (CC) level of theory and a solvent modeled as a continuum dielectric, the solvent response depends on various contributions: the choice of the reference wave function, the correlation density, and the orbital relaxation. In previous work, we examined the first two factors with the coupled cluster singles and doubles (CCSD) method and its variant Brueckner doubles (BD) method. The CC wave function was combined with the polarizable continuum model (PCM) of solvation in an integrated and efficient method able to describe energy and molecular properties through analytic energy gradients. Additionally, we investigated some approximations, and proposed new ones, that reduce the computational cost to nearly that of gas phase CC while keeping most of the complete model description. In this work, we study the contribution of the orbital relaxation and compare it to the other effects. Such contribution is introduced with a self-consistent macroiteration procedure, where the reaction field is updated with a refined density. The results presented here show that the effect of the orbital relaxation is small for CCSD, while for BD the integrated and self-consistent approaches are equivalent. Thus, these results further confirm that the integrated CCSD-PCM and BD-PCM methods, especially with their respective approximations, are an efficient approach to perform high-level electronic structure calculations in solution.

1. INTRODUCTION

The interest in introducing the solvent effect in coupled cluster (CC)^{1,2} calculations is evident by considering the increasing number of publications on the subject, see for example refs 3–17.

We investigated the ability of the polarizable continuum model (PCM)^{18–20} of solvation to provide such effect in a reliable way, while maintaining the computational burden close to that of gas phase CC. We originally followed the approach in ref 11 for coupled cluster singles and doubles (CCSD) called perturbation theory energy and density (PTED) scheme for historical reasons^{21,22} and its approximation called PTE. In CCSD-PCM-PTED, the solvent reaction field is separated in a contribution from the reference wave function [usually the Hartree–Fock (HF) wave function] and a correlation contribution, which nonlinearly depends on the reduced one particle density matrix (1PDM). Such dependence from the 1PDM makes the PTED scheme computationally much more expensive than gas phase CCSD, since it requires the evaluation of the Λ vector.^{23,24} In the PTE scheme, the correlation reaction field is neglected. This reduces the computational cost at the expense of the accuracy of the method.^{13,16,17} However, by considering the part of the 1PDM that does not depend on Λ , i.e., the singles CC amplitudes, 50–80% of the PTE-PTED difference can be recovered while keeping the same computational cost of the PTE scheme. This is called PTES scheme, where the S stands for singles.¹⁷ All these schemes work in the frozen orbital framework, where the reference wave function is decoupled from the correlation calculation, consistently with the most widely used CC methods for isolated molecules. Thus, also the solvent reference and correlation reaction fields are decoupled, and no orbital relaxation is introduced.

One way to take into account such relaxation and to couple the two parts of the reaction field is to use a variant of CCSD called Brueckner doubles (BD).^{25,26} The BD reference function is built such that the amplitudes for the single excitations are all zero. Starting from a guess reference (HF or other), the orbitals are rotated until the above condition is satisfied. BD thus introduces an orbital relaxation that is coupled with the CC expansion (which includes now only double excitations). The numerical tests on the BD-PCM method,¹⁶ for the PTED and PTE schemes, showed that the latter is a much better approximation of the complete model for BD than for CCSD while keeping the computational cost comparable to the gas phase case. Additionally, the larger insensitivity of BD with respect to the choice of the initial reference function (compared to CCSD) makes this method more appealing for cases where the HF wave function may be unstable also in solution.

Another way to introduce the orbital relaxation in a CC-PCM calculation is through an external iteration procedure. This is an old idea, related to the initial implementation of PCM,¹⁹ and has been recently revived by Improta et al. in the context of time-dependent density functional theory.^{27,28} In short, the algorithm:

- (1) computes an initial CC total density;
- (2) computes the reaction field corresponding to this density;
- (3) checks for convergence of the reaction field;
- (4) if not converged, introduces the reaction field in the reference calculation and computes an updated density;
- (5) returns to point 2.

In this procedure, the relaxed CC density is used, including the orbital response. This is a self-consistent method and can be

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applied to any method for which it is possible to compute the 1PDM,²⁹ provided that the appropriate definition of the free energy is used. Indeed, in this work it is applied to CCSD and BD, and the results are compared to the PTED approach described above. The external iteration procedure is also a PTED approach, since the reaction field depends in the correlation density. However, in order to distinguish it from the frozen orbital approach, we will use “SC” for “self-consistent” to indicate the external iteration procedure and will keep “PTED” for the frozen orbital scheme. PCM-SC is not a computationally efficient procedure but is simple to implement and provides useful benchmarking results.

The goal of this work is to compare the PTED and SC schemes, for CCSD and BD, in order to evaluate the effect of the orbital relaxation on the solvent reaction field. Additionally, the approximated PTE and PTES schemes are tested, in search for the best compromise between accuracy and computational cost.

The numerical tests show that the reference reaction field is the major component of the solvent response, as it should be expected. The correlation contribution, however, can be significant and should not be neglected. The orbital relaxation, on the other hand, gives a very small contribution to the reaction field compared to that of correlation. Furthermore, the latter can be very well approximated by using the PTE scheme for BD and the PTES scheme for CCSD, drastically reducing the computational effort. These results indicate that CCSD-PCM-PTES and BD-PCM-PTE are very promising approaches to perform high-level calculations in solution at a cost comparable to the corresponding gas phase methods.

The paper is organized as follows: In Section 2, the free energy expressions for the PTED and SC schemes are presented and compared. The numerical applications are reported in Section 3, while an overall discussion and concluding remarks are the content of Section 4.

2. THEORY

In this section, we compare the free energy³⁰ expressions for the PCM-PTED and PCM-SC schemes when combined with the CCSD and BD methods. For a review of PCM, the interested reader is referred to refs 18–22, and 31–36. for the combination of PCM and CCSD/BD, to refs 11, 13, 16, and 17 and for the PCM-SC scheme to refs 27 and 28.

As outlined in Section 1, the solvent reaction field (i.e., the apparent surface charges) is defined differently in the PTED and SC schemes. In the former, the reaction field is divided into two contributions: one that depends on the reference function and the nuclei, $\bar{\mathbf{Q}}^0$, and one that depends on the CC reduced 1PDM, $\bar{\mathbf{Q}}_N$.^{11,13,16,17} The total reaction field is the sum of the two contributions: $\bar{\mathbf{Q}}^{\text{PTED}} = \bar{\mathbf{Q}}^0 + \bar{\mathbf{Q}}_N$. For CCSD, no orbital response is included in the total reaction field, since the reference wave function is decoupled from the coupled cluster expansion. On the other hand, for BD, the “correlation” reaction field $\bar{\mathbf{Q}}_N$ includes the orbital response, since this is included in the 1PDM through the solution of the Λ equations.²⁶ The interaction of the “reference” reaction field $\bar{\mathbf{Q}}^0$ with the solute wave function is included in the Fock operator, while the interaction of $\bar{\mathbf{Q}}_N$ introduces explicit terms in the CC equations (for BD, also $\bar{\mathbf{Q}}^0$ introduces some explicit term).¹⁶ In the SC scheme, the total reaction field, $\bar{\mathbf{Q}}^{\text{SC}}$, is computed all together from the nuclei and the total 1PDM, which includes the orbital response.^{27,28} This is obtained, for CCSD, by solving the appropriate coupled

perturbed HF (CPHF) equations.^{23,24,35} The interaction of $\bar{\mathbf{Q}}^{\text{SC}}$ with the solute wave function is entirely introduced in the Fock operator, and no explicit PCM term appears in the CC equations.

Keeping in mind the difference between $\bar{\mathbf{Q}}^{\text{PTED}}$ and $\bar{\mathbf{Q}}^{\text{SC}}$ described above, we can now introduce and discuss the expressions for the free energy in the two schemes. For PTED, the free energy is

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

where Φ^0 is the reference function, H_0 is the molecular Hamiltonian, T is the excitation operator, Λ is the \mathbf{Z} vector from gradient theory,^{23,24} and \mathbf{V} is the electrostatic potential on the cavity surface. By using the normal product form of an operator (indicated with the N subscript),² the reference contribution to the free energy can be separated from the correlation contribution, so that eq 1 can be rewritten as

$$\begin{aligned} G^{\text{PTED}} &= G_0^{\text{PTED}} + \langle \Phi^0 | (1 + \Lambda) e^{-T} H_{0N} e^T | \Phi^0 \rangle \\ &+ \langle \Phi^0 | (1 + \Lambda) e^{-T} \mathbf{V}_N e^T | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}^0 \\ &+ \frac{1}{2} \langle \Phi^0 | (1 + \Lambda) e^{-T} \mathbf{V}_N e^T | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}_N \\ &= G_0^{\text{PTED}} + \langle \Phi^0 | (1 + \Lambda) e^{-T} H_{0N}^{\text{PTED}} e^T | \Phi^0 \rangle \\ &+ \frac{1}{2} \langle \Phi^0 | (1 + \Lambda) e^{-T} \mathbf{V}_N e^T | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}_N \end{aligned} \quad (2)$$

where

$$G_0^{\text{PTED}} = \langle \Phi^0 | H_0 | \Phi^0 \rangle + \frac{1}{2} \langle \Phi^0 | \mathbf{V} | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}^0 \quad (3)$$

is the reference free energy and

$$H_{0N}^{\text{PTED}} = H_{0N} + \mathbf{V}_N \cdot \bar{\mathbf{Q}}^0 \quad (4)$$

At convergence, eq 2 reduces to^{11,13,16,17}

$$\begin{aligned} G^{\text{PTED}} &= G_0^{\text{PTED}} + \langle \Phi^0 | e^{-T} H_{0N}^{\text{PTED}} e^T | \Phi^0 \rangle \\ &+ \langle \Phi^0 | e^{-T} \mathbf{V}_N e^T | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}_N \\ &- \frac{1}{2} \langle \Phi^0 | (1 + \Lambda) e^{-T} \mathbf{V}_N e^T | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}_N \\ &= G_0^{\text{PTED}} + \Delta E^{\text{PTED}} - \frac{1}{2} \bar{\mathbf{V}}_N \cdot \bar{\mathbf{Q}}_N \end{aligned} \quad (5)$$

where

$$\begin{aligned} \Delta E^{\text{PTED}} &= \langle \Phi^0 | e^{-T} H_{0N}^{\text{PTED}} e^T | \Phi^0 \rangle \\ &+ \langle \Phi^0 | e^{-T} \mathbf{V}_N e^T | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}_N \end{aligned} \quad (6)$$

Equations 1–6 apply to both CCSD and BD, although for the latter, the last term in eq 6 vanishes since the singles amplitudes are zero.¹⁶

For the PCM-SC scheme, the free energy is

$$\begin{aligned} G^{\text{SC}} &= \langle \Phi^0 | (1 + \Lambda) e^{-T} H_0 e^T | \Phi^0 \rangle \\ &+ \frac{1}{2} \langle \Phi^0 | (1 + \Lambda) e^{-T} \mathbf{V} e^T | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}^{\text{SC}} \end{aligned} \quad (7)$$

Note that, for CCSD, the expression in eq 7 is different from that used in refs 27 and 28, since the orbital response is only explicitly

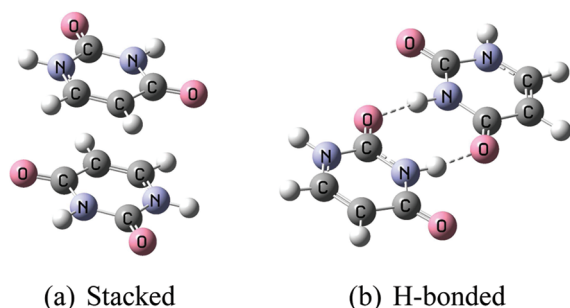
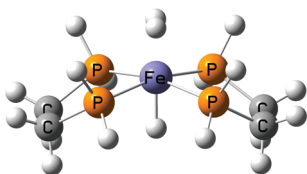


Figure 1. Structure of the uracil dimers.

Figure 2. Structure of the $\text{H}_2[\text{FeH}(\text{PP})_2]^+$ complex.

included in the apparent charges and not in the potential. Using the definition in eq 7, G^{SC} is consistent with the equations for the CC amplitudes. On the other hand, for BD, eq 7 includes the orbital response through the Λ vector and is equivalent to refs 27 and 28. Separating the reference contribution from the correlation one, eq 7 becomes

$$G^{\text{SC}} = G_0^{\text{SC}} + \langle \Phi^0 | (1 + \Lambda) e^{-T} H_{0N} e^T | \Phi^0 \rangle + \frac{1}{2} \langle \Phi^0 | (1 + \Lambda) e^{-T} \mathbf{V}_N e^T | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}^{\text{SC}} \quad (8)$$

where

$$G_0^{\text{SC}} = \langle \Phi^0 | H_0 | \Phi^0 \rangle + \frac{1}{2} \langle \Phi^0 | \mathbf{V} | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}^{\text{SC}} \quad (9)$$

Using the CC amplitudes equation in the presence of the reaction field:

$$\langle \Phi | e^{-T} H_{0N}^{\text{SC}} e^T | \Phi^0 \rangle = 0 \quad (10)$$

where Φ is an excited determinant and

$$H_{0N}^{\text{SC}} = H_{0N} + \mathbf{V}_N \cdot \bar{\mathbf{Q}}^{\text{SC}} \quad (11)$$

eq 8 can be simplified to

$$\begin{aligned} G^{\text{SC}} &= G_0^{\text{SC}} + \langle \Phi^0 | e^{-T} H_{0N}^{\text{SC}} e^T | \Phi^0 \rangle \\ &\quad - \frac{1}{2} \langle \Phi^0 | (1 + \Lambda) e^{-T} \mathbf{V}_N e^T | \Phi^0 \rangle \cdot \bar{\mathbf{Q}}^{\text{SC}} \\ &= G_0^{\text{SC}} + \Delta E^{\text{SC}} - \frac{1}{2} \bar{\mathbf{V}}_N \cdot \bar{\mathbf{Q}}^{\text{SC}} \end{aligned} \quad (12)$$

where

$$\Delta E^{\text{SC}} = \langle \Phi^0 | e^{-T} H_{0N}^{\text{SC}} e^T | \Phi^0 \rangle \quad (13)$$

As mentioned in Section 1, G^{SC} is computed with a self-consistent procedure: several PCM macroiterations are performed where the charges $\bar{\mathbf{Q}}^{\text{SC}}$ are calculated with an updated density and reentered in the reference and CC equations. The iterative procedure is stopped when convergence on the reaction field is achieved.

Table 1. Solvation Free Energy (kcal/mol) for CCSD^a

	exptl ^b	PTE ^c	PTES	PTED ^c	SC
Pyridine					
Cyc	−4.30	−1.76	−1.78	−1.78	−1.79
Dce	−5.53	−4.04	−4.08	−4.11	−4.11
H ₂ O	−4.70	−4.73	−4.77 ^d	−4.80	−4.80
Aniline					
Cyc	−5.52	−1.92	−1.94	−1.94	−1.95
Dce	−7.39	−4.51	−4.54	−4.57	−4.57
H ₂ O	−5.49	−5.32	−5.35 ^d	−5.38	−5.38
Phenol					
Cyc	−5.57	−2.14	−2.16	−2.16	−2.17
Dce	−7.48	−4.94	−4.97	−4.99	−4.99
H ₂ O	−6.62	−5.79	−5.82 ^d	−5.85	−5.85
<i>p</i> -Bromophenol					
Cyc	−7.14	−2.39	−2.42	−2.42	−2.43
Dce	−9.10	−5.40	−5.44	−5.46	−5.46
H ₂ O	−7.13	−6.29	−6.33 ^d	−6.36	−6.35
Chlorobenzene					
Cyc	−5.10	−0.95	−0.97	−0.98	−0.98
Dce		−2.15	−2.18	−2.20	−2.20
H ₂ O	−1.12	−2.50	−2.53 ^d	−2.57	−2.57

^a Cyc: cyclohexane, Dce: dichloroethane, H₂O: water. ^b Ref 39. ^c Ref 13. ^d Ref 17.

Equations 5 and 12 look very similar. For the CCSD method, the difference is that the SC scheme includes the orbital response in the reaction field, and the reference and CC equations are coupled by $\bar{\mathbf{Q}}^{\text{SC}}$. In the PTED scheme, the reference and the post-HF part are decoupled, which is consistent with the gas phase CC method. For the BD method, the PTED and SC schemes are equivalent since in BD the reference and the CC expansion are already coupled, and the orbital response is taken into account in both schemes.

3. RESULTS

A variety of systems is used to compare the PTED and SC schemes. The solvation free energy, defined as the difference between the free energy in solution and the gas phase energy, is computed for five organic molecules: pyridine, aniline, phenol, *p*-bromophenol, and chlorobenzene, in three solvents of increasing polarity: cyclohexane, dichloroethane, and water. Two dimers of uracil in stacked and hydrogen bonded (H-bonded) conformation, see Figure 1, are used to compare the interaction energy in gas phase and water and the solvation free energy. Finally, a dihydrogen complex of Fe⁺ in tetrahydrofuran (THF), see Figure 2, is analyzed by comparing the solvation free energy at different H–H bond lengths. The PCM cavity is built from interlocking spheres centered on each nucleus and using the universal force field (UFF) radii.³⁷ The symmetric version of integral equation formalism PCM (IEF-PCM)³⁶ is used, and Scalmani and Frisch's continuous surface charge (CSC) scheme³⁵ is employed. All the calculations are performed with a development version of the Gaussian suite of programs.³⁸

In this section, results for two approximations of the PTED model are also presented. One approximation is called PTE

Table 2. Solvation Free Energy (kcal/mol) for BD^a

	exptl ^b	PTE ^c	PTED ^c	SC
Pyridine				
Cyc	−4.30	−1.79	−1.80	−1.79
Dce	−5.53	−4.10	−4.11	−4.10
H ₂ O	−4.70	−4.79	−4.80	−4.79
Aniline				
Cyc	−5.52	−1.94	−1.94	−1.94
Dce	−7.39	−4.54	−4.55	−4.55
H ₂ O	−5.49	−5.35	−5.36	−5.36
Phenol				
Cyc	−5.57	−2.17	−2.17	−2.17
Dce	−7.48	−4.98	−4.99	−4.99
H ₂ O	−6.62	−5.83	−5.84	−5.84
<i>p</i> -Bromophenol				
Cyc	−7.14	−2.42	−2.42	−2.42
Dce	−9.10	−5.44	−5.45	−5.45
H ₂ O	−7.13	−6.33	−6.34	−6.34
Chlorobenzene				
Cyc	−5.10	−0.97	−0.98	−0.98
Dce		−2.19	−2.19	−2.19
H ₂ O	−1.12	−2.55	−2.55	−2.55

^a Cyc: cyclohexane, Dce: dichloroethane, H₂O: water. ^b Ref 39. ^c Ref 16.

scheme, for CCSD and BD,^{11,13,16} where the correlation reaction field contribution is neglected. The other is the PTES scheme (where S stands for singles), for CCSD,¹⁷ where only part of the CCSD reduced IPDM is used to compute the correlation reaction field. Both these approximated schemes do not require the calculation of the complete CC reduced IPDM, thus decoupling the *T* and Λ equations. This strongly reduces the computational cost, making the PCM-PTE and -PTES methods similar to gas phase CC.

The results for the solvation free energies of the five molecules are reported in Table 1 for CCSD and Table 2 for BD. The tables also report the experimental data.³⁹ The geometries are taken from ref 13 for CCSD and ref 16 for BD. The 6-31+G(d,p) basis set is used. The calculations in Tables 1 and 2 basically show no difference between PTED and SC, as all of the results are within 0.01 kcal/mol from each other. For CCSD, the difference between PTE and PTED, which is a measure of the correlation reaction field effect, although already small (at most 0.07 kcal/mol), is larger than the orbital response effect. Additionally, such difference can be greatly reduced with the PTES scheme ($\geq 50\%$). For BD, PTE is able to recover most of the correlation solvent effect through the coupling of the reference function and the CC expansion, without introducing the explicit correlation reaction field. The comparison with experiment also shows that nonelectrostatic effects, neglected in the calculations, are far more important for low-polar solvents than other effects. As shown in refs 13 and 16, such contributions can be recovered by adding the proper correction³⁹ to the PCM electrostatic free energy. Therefore, for this first set of molecules, the orbital response is the smallest of all the contributions to the free energy.

Tables 3–6 collect the data computed for the uracil dimers in stacked and H-bonded conformations (see Figure 1). The geometry for the stacked conformation is taken from ref 40,

Table 3. CCSD Interaction and Solvation Free Energies (kcal/mol) for the Stacked Uracil Dimer^a

interaction energy					
	gas	PTE	PTES	PTED	SC
6-31G(d)	−2.43	0.30	0.39	0.42	0.39
6-31+G(d,p)	−3.67	−0.41	−0.33	−0.31	−0.33
solvation free energy					
	PTE	PTES	PTED	SC	
Dimer					
6-31G(d)	−22.63	−23.01	−23.10	−22.97	
6-31+G(d,p)	−25.36	−25.64	−25.71	−25.63	
Monomer 1					
6-31G(d)	−12.68	−12.92	−12.97	−12.90	
6-31+G(d,p)	−14.31	−14.49	−14.54	−14.48	
Monomer 2					
6-31G(d)	−12.68	−12.92	−12.97	−12.90	
6-31+G(d,p)	−14.31	−14.49	−14.54	−14.48	

^a The interaction energies include a BSSE correction.

Table 4. BD Interaction and Solvation Free Energies (kcal/mol) for the Stacked Uracil Dimer^a

interaction energy				
	gas	PTE	PTED	SC
6-31G(d)	−2.44	0.43	0.43	0.43
6-31+G(d,p)	−3.64	−0.29	−0.28	−0.29
solvation free energy				
	PTE	PTED	SC	
Dimer				
6-31G(d)	−23.02	−23.05	−23.05	
6-31+G(d,p)	−25.67	−25.70	−25.69	
Monomer 1				
6-31G(d)	−12.94	−12.96	−12.96	
6-31+G(d,p)	−14.51	−14.52	−14.52	
Monomer 2				
6-31G(d)	−12.94	−12.96	−12.96	
6-31+G(d,p)	−14.51	−14.52	−14.52	

^a The interaction energies include a BSSE correction.

and the monomers are 3.3 Å apart. The geometry for the H-bonded dimer is taken from ref 41 and reoptimized at the B3LYP level^{42,43} with the aug-cc-pVDZ basis set⁴⁴ imposing *C_s* symmetry. The calculations are performed with the 6-31G(d) and 6-31+G(d,p) basis sets. The tables report the interaction energies, in gas and in solution, and the solvation free energies in kcal/mol. The interaction energies include a correction for the basis set superposition error (BSSE) through the counterpoise method.^{45,46} The same BSSE correction is used for the gas phase and PCM calculations, since there is not a well-defined procedure

Table 5. CCSD Interaction and Solvation Free Energies (kcal/mol) for the H-Bonded Uracil Dimer^a

interaction energy					
	gas	PTE	PTES	PTED	SC
6-31G(d)	−10.32	−5.53	−5.48	−5.47	−5.49
6-31+G(d,p)	−10.53	−5.12	−5.08	−5.07	−5.08
solvation free energy					
	PTE	PTES	PTED	SC	
Dimer					
6-31G(d)	−20.90	−21.32	−21.43		−21.29
6-31+G(d,p)	−23.61	−23.93	−24.02		−23.92
Monomer 1					
6-31G(d)	−12.85	−13.09	−13.15		−13.08
6-31+G(d,p)	−14.52	−14.71	−14.76		−14.70
Monomer 2					
6-31G(d)	−12.83	−13.07	−13.13		−13.05
6-31+G(d,p)	−14.50	−14.67	−14.72		−14.67

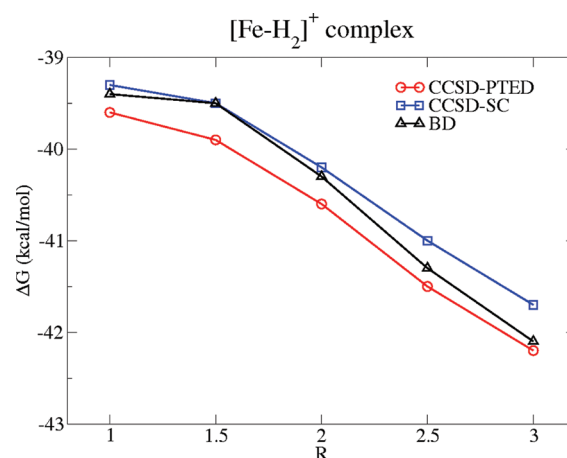
^a The interaction energies include a BSSE correction.

to compute this quantity with continuum solvation models. These basis sets are not large enough for quantitative results, as shown by a comparison of the gas phase interaction energies with the best estimates in the literature:^{29,41,40} −12.4 and −7.5 kcal/mol for the H-bonded and the stacked dimers, respectively. There is a difference of 2–4 kcal/mol with the values in this work (see Tables 3–6). However, here we are only interested in the comparison between the various PCM approaches. The solvent competes with the pair interaction, so that the interaction energy is reduced by ~3 kcal/mol for the stacked conformation and ~5 kcal/mol for the H-bonded one. For CCSD (Tables 3 and 5), the difference in the interaction energies between the PTED and SC schemes is about 0.01–0.03 kcal/mol with both basis sets. This is again smaller than the PTE-PTED difference, which is already small (0.04–0.12 kcal/mol). The solvation free energy difference between the PTE and PTED schemes is larger, around 0.4–0.5 kcal/mol for the dimer and 0.2–0.3 kcal/mol for the monomers. On the other hand, the effect of the orbital relaxation produces a difference of only 0.08–0.14 kcal/mol for the dimer and 0.06–0.07 kcal/mol for the monomers. As in the previous example, the PTES scheme strongly reduced the PTE-PTED difference to 0.01–0.02 kcal/mol for the interaction energy, 0.07–0.11 kcal/mol for the solvation free energy of the dimers, and 0.05–0.06 kcal/mol for the monomers, while keeping the computational cost of the PTE scheme. For BD, there is no difference between the PTED and the SC approaches, as in the previous example. Furthermore, PTE is a very good approximation, since the difference with PTED is at most 0.01 kcal/mol for the interaction energy and 0.03 kcal/mol for the solvation energy, see Tables 4 and 6.

For the $\text{H}_2[\text{FeH}(\text{PP})_2]^+$ complex, the geometry is taken from ref 16. The calculations are performed with the Stuttgart/Dresden pseudopotential⁴⁷ 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. An extra sphere is included along the Fe–H₂ bond to avoid “solvent pockets” at longer H–H distances (the sphere diameter being equal to the Fe–H₂

Table 6. BD Interaction and Solvation Free Energies (kcal/mol) for the H-Bonded Uracil Dimer^a

interaction energy				
	Gas	PTE	PTED	SC
6-31G(d)	−10.34	−5.46	−5.45	−5.45
6-31+G(d,p)	−10.55	−5.08	−5.08	−5.08
solvation free energy				
	PTE	PTED		SC
Dimer				
6-31G(d)	−21.33	−21.36		−21.36
6-31+G(d,p)	−23.96	−23.98		−23.98
Monomer 1				
6-31G(d)	−13.12	−13.13		−13.13
6-31+G(d,p)	−14.73	−14.74		−14.74
Monomer 2				
6-31G(d)	−13.10	−13.11		−13.11
6-31+G(d,p)	−14.70	−14.71		−14.71

^a The interaction energies include a BSSE correction.**Figure 3.** Solvation free energy (kcal/mol) for the $\text{H}_2[\text{FeH}(\text{PP})_2]^+$ complex at various H–H bond distances. R is a scaling factor from the equilibrium bond distance.

distance: 1.6219 Å). Figure 3 shows the change in solvation free energy when scaling the equilibrium H–H distance (0.8105 Å) by a factor R . For BD, only one curve is reported since the results with the SC and PTED schemes are equivalent. The difference between the two schemes for CCSD is at most 0.4–0.5 kcal/mol. This is ~3 times smaller than the correlation effect (1.1–1.4 kcal/mol),¹⁶ and in the opposite direction. In our previous work, we showed that the approximated CCSD-PCM-PTES and BD-PCM-PTE schemes recover most, if not all, of this effect (compare Figure 6 in ref 16 and Figure 2 in ref 17).

4. DISCUSSION AND CONCLUSIONS

The test examples in Section 3 show that, for CCSD, the orbital relaxation is the smallest among all the contributions to

the solvent reaction field. The most important one is the contribution from the reference wave function, as expected. However, the correlation contribution can be significant, as for the uracil dimers, where it reaches 0.5 kcal/mol, and even more the Fe complex, where it is of the order of 1.1–1.4 kcal/mol.¹⁶ In the latter case, the orbital relaxation contribution may amount to a third of the correlation one.

Although this effect may seem significant, it comes at the prize of a computationally less efficient, and somewhat less elegant formulation. Indeed, in the self-consistent macroiteration procedure of the CCSD-PCM-SC scheme,^{27,28} the coupling of the reference wave function and the post-HF part are only provided by the reaction field, and not through a variational optimization of the CC free energy functional. Additionally, the inclusion of the orbital relaxation effect makes the formulation of free energy derivatives complicated (it requires the derivative of the CC density), and expensive, thus limiting its applicability for molecular properties in solution. The advantage of this strategy, however, is the rather straightforward implementation, and the possibility to use it with any method for which the 1PDM is available.

The PTED scheme, on the other hand, is based on the decoupling of the reference function and the correlation contributions to the reaction field. This is consistent with CC for isolated molecules. It also allows for an efficient formulation of the free energy analytic gradients, and therefore, it can be efficiently used to compute molecular properties in solution. As mentioned above, this approach neglects the contribution of the orbital relaxation to the reaction field, but this effect is relatively small.

For the BD variant of CCSD, the SC and PTED schemes are equivalent, since the orbital response is taken into account in both. This is an advantage of this method over CCSD, especially when the HF wave function may be unstable.¹⁶ However, BD is computationally more expensive than CCSD, and the latter can be used in the majority of cases.

Other effects that can be more important than the orbital response are the nonelectrostatic contributions to the free energy, when low-polar solvents are used, see Tables 1 and 2. These can be accounted for in a variety of ways, and we showed an example in refs 13 and 16. In the same papers, we also mentioned that explicit solute–solvent interactions, like strong H-bonds, can play an important role that cannot be accurately reproduced by continuum solvation models.

Computational efficiency can be obtained with careful approximations of the PTED model, for CCSD and BD, through the PTES and PTE schemes, respectively. Both these approximated schemes recover most of the correlation reaction field contribution (50–80% with CCSD-PCM-PTES and ~100% with BD-PCM-PTE), while keeping the computational cost comparable with the correspondent gas phase methods.

In conclusion, although the orbital response can provide a nonnegligible contribution to the free energy, this remains rather small compared to the other contributions (reference and correlation). Additionally, the frozen orbitals CCSD-PCM-PTED scheme is consistent with gas phase CCSD, and analytical free energy gradients can be efficiently formulated with small modification of the gas phase formulas and computer code. Therefore, the latter can be considered more appropriate for CC calculation in solution with PCM. In light of all of these results, the best compromise between accuracy and computational effort is achieved with the PTES approximation for CCSD¹⁷ and the PTE approximation for BD.¹⁶

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